Analysis of phthalates via HPLC-UV in environmental water samples after concentration by solid-phase extraction using ionic liquid mixed hemimicelles

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Abstract

Ionic liquid mixed hemimicelles-based solid-phase extraction for the preconcentration of five phthalates in environmental water sample was investigated in this paper. A comparative study on the use of room temperature ionic liquids (RTILs) 1-hexyl-3-methylimidazolium bromide ([C₆mim]Br) and 1-dodecyl-3-methylimidazolium bromide ([C₁₂mim]Br)-coated silica as sorbents was presented. Owing to having bigger adsorption amounts for analytes [C₁₂mim], Br-coated silica was selected as SPE material and the five analytes di-ethyl-phthalate (DEP), di-*n*-propyl-phthalate (DnPP), di-*n*-butyl-phthalate (DnBP), di-cyclohexyl-phthalate (DcHP) and di-(2-ethylhexyl)-phthalate (DEHP) can be quantitatively extracted under optimal conditions. The analytes retained on the cartridge were desorbed completely with 3 mL methanol (pH 2). Predominant factors influencing the extraction efficiency, such as RTILs concentration, pH value, ionic strength and breakthrough volume were discussed. The proposed method had been applied to determining the five phthalates in four environmental water samples and concentration factor of 600 was achieved easily. Detection limits obtained ranged between 0.12 and 0.17 µg/L. The accuracy of this method was evaluated by recovery measurement on spiked samples, and good recovery results (85–107%) with relative standard deviation (R.S.D.) of below 6% were achieved.

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1. Introduction

Phthalic acid esters (phthalates, PAEs) are widely used as polymer additives in the manufacture of plastics (primarily polyvinyl chloride), rubber and styrene to make them flexible. Globally, over 18 billion pounds of PAEs are used each year. They can be leached from the above-mentioned products and find a way to various environmental matrices such as environmental water, soil and plants [1–3]. Nowadays, due to its massive use and persistent character, PAEs are considered as ubiquitous environmental pollutants. A number of researches proved that PAEs exerted a pernicious impact on human health; furthermore,

some PAEs can cause endocrine system disorders [4,5], produce carcinogenic effects and afflict the development of reproductive system [6].

The very low concentration level of PAEs and the complex matrix of many environmental samples make sample preconcentration necessary for a reliable determination of these compounds. Several analytical methods have been developed for determining PAEs by gas chromatography (GC) [7,8], high performance liquid chromatography (HPLC) [9,10] using different preconcentration techniques such as liquid–liquid extraction (LLE) [11], solid-phase microextraction (SPME) [12,13] and solid-phase extraction (SPE) [14–17] in several types of matrices. Among above-mentioned sample pretreatment procedures, solid-phase extraction based on different types of sorbents such as C₈ [15], organic polymers [16] was widely used.

Recently, a new SPE method based on hemimicelles and admicelles (mixed hemimicelles) has been proposed for the preconcentration of a variety of organic pollutants from complex

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environmental matrices [9,18–20]. The sorbents used are produced by adsorbing ionic surfactants (such as sodium dodecyl sulfate or cetyltrimethylammonium bromide) on the metal oxides (such as alumina or silica) surface. Mixed hemimicelles used in SPE have many advantages, such as high extraction efficiency, high breakthrough volume, easy elution of analytes and high flow rate for sample loading; furthermore, this kind of SPE technique requires no clean-up steps and the sorbents is easy to regenerate, and is thus able to meet the needs of rapid analysis.

Room temperature ionic liquids (RTILs) are ionic compounds that are liquids at ambient temperature and consist of ionic species [21]. RTILs belong to a relatively new class of solvents which are amphiphilic molecules with a hydrophilic polar headgroup (ionic in nature) and a hydrophobic hydrocarbon chain (the tail). In recent years, RTILs have attracted great attentions due to their unique chemical and physical properties such as nonvolatile (environmentally benign), excellent solvation qualities, non-flammable and high thermal stability [22,23]. As a result, RTILs are widely used in liquid–liquid extraction [24,25], synthesis [26,27], separation [28,29] and electrochemistry [30,31]. Some research groups have also studied the aggregation and micelles formation of ionic liquids in aqueous solution [32]. As RTILs can dissolve many kinds of organic, organometallic and inorganic compounds [33,34], their applications in analytical chemistry have also received attentions recently [35–39]. He et al. determined the testosterone and epitestosterone in human urine using cloud extraction method based on aqueous two-phase systems consisting of ionic liquid 1-butyl-3-methylimidazolium chloride, coupled with HPLC/spectrophotometry detection, the detection limit of 1 ng/mL was obtained [38]. Generally, cloud extraction method was a simple, rapid and effective sample pretreatment technique; however, some limitations still existed, such as the RTILs-rich phase was dense and it was not easy to be injected into HPLC for analysis; high concentration of ionic liquid in sampling solution may produce large interferential peaks.

In this paper, we investigated the applications of RTILs [C₆mim] Br and [C₁₂mim] Br mixed hemimicelles for the pre-concentration of five phthalates DEP, DnPP, DnBP, DcHP and DEHP in environmental water sample. Mixed hemimicelles were prepared by adsorbing [C₆mim] Br and [C₁₂mim] Br on

silica surface and predominant experimental factors affecting the extraction efficiency were studied. To the best of our knowledge, this was the first time that RTILs mixed hemimicelles-based SPE was applied for the pretreatment of PAEs in environmental water samples.

2. Experimental

2.1. Chemicals and materials

All reagents were of analytical grade and used as supplied. Five PAEs were obtained from Beijing Chemicals Corporation (Beijing, China). A stock solution containing 200 mg/L each phthalate was prepared in methanol and stored under dark conditions at 4 °C. The RTILs [C₆mim] Br and [C₁₂mim] Br were supplied by Kemo Reagent Corporation (Hangzhou, China) and their structures were listed in Table 1. Silica was purchased from Sigma Corporation (Steinheim, Germany) and the physical properties were as follows: surface area (300 m²/g); point of zero charge (PZC, 2.9); particle diameter range (70–150 μm), mean pore size (150 Å) and density (1.15 cm³/g). HPLC-grade acetonitrile and methanol were supplied by Merck Corporation (Germany). Water (18.3 MΩ) used in all experiments was prepared using a compact ultrapure water system from Barnstead Corporation (Iowa, USA).

2.2. Sample collection and preservation

Effluent wastewater sample was collected from the Gaobeidian sewage treatment plant (Chaoyang District), the largest sewage treatment plants in Beijing. It is located in the east of Beijing and it receives about the same level of domestic and industrial wastewater. River water samples were taken from the Xiaoqing River (Haidian District, Beijing) and Jingmi Canal (Haidian District) in November 2006. Tap water sample was taken from our lab in Haidian District. All water samples were collected randomly. Samples were collected into pre-cleaned, light-preserved glass bottles and 5000 mL each sample was filtered immediately through 0.22 μm nylon membranes in order to remove suspended solids. We realized that these filters maybe contain a considerable amount of phthalate such as DnBP, so their cleaning with acetone was carried out prior filtration. The

Table 1
Chemical structure of RTILs [C₆mim] Br and [C₁₂mim] Br

Name	Molecular formula	Structure	Abbreviation
1-Hexyl-3-methylimidazolium bromide	C ₁₀ H ₁₉ N ₂ Br		[C ₆ mim] Br
1-Dodecyl-3-methylimidazolium bromide	C ₁₆ H ₃₁ N ₂ Br		[C ₁₂ mim] Br

filtered samples were adjusted to pH 2 with 1 M HNO₃ and stored at dark conditions at 4 °C until analysis.

2.3. SPE based on mixed hemimicelles

An extraction cartridge was prepared by using a SPE plastic tube (6 mL, polypropylene) and 0.5 g silica was packed into it. To prepare mixed hemimicelles column, 25 mL solution containing 25 mg [C₁₂mim] Br was passed through the cartridge column, then the water samples was adjusted to pH 6.5 and passed through the column. Sample loading was performed by using a DOA-PIOU-BN vacuum pump (Michigan, USA) at a flow rate of 5 mL/min. Target analytes were eluted with 3.0 mL methanol (pH 2) and dried with a stream of nitrogen at 60 °C, followed by dissolved in 0.5 mL methanol. The methanol solution was vibrated in an ultrasonic bath for 5 min in order to insure that the phthalates can be dissolved into methanol completely. Finally, a 20 µL of the solution was injected into the HPLC system for analysis.

2.4. HPLC analysis

The five phthalates were separated and quantified by using a liquid chromatography–spectrophotometry system (P680 HPLC Pump with a PDA100 Photodiode Array Detector, Dionex, USA) with an automatic sample injector (ASI-100, Dionex, USA). The analytical column was a 250 mm Diamonsil-C₁₈ column (4 µm particle diameter and 4.6 mm i.d.) supplied by Dikma Technologies Corporation (Beijing, China). The mobile phase consisted of acetonitrile and water (acetonitrile: water, 75:25, v/v) and the flow-rate was set at 1 mL/min. Spectrophotometry detection of analytes was performed at 226 nm wavelengths.

2.5. Adsorption studies

The adsorption studies were carried out in batch mode and all experiments were carried out at 25 ± 1 °C in a water bath. Both the adsorption isotherms of [C₆mim]Br and [C₁₂mim]Br on silica were obtained by adding 0.5 g silica to 25 mL aqueous solution containing [C₆mim]Br or [C₁₂mim]Br (0–50 mg), and the initial pH of solutions was adjusted to 6.5. After vigorous stirring of the solutions for 5 min, partial solution of every glass vial was centrifuged at 4000 rpm for 10 min. The concentration of [C₆mim] Br and [C₁₂mim] Br in the supernatants was determined by ESI-MS (ABI, USA) at *m/z* 251 and 167 through different factors of diluting, respectively. The analysis was carried out in the “ESI (+) mode” and the operational parameters used were as follows: Declustering potential, –30 V; entrance potential, –2.8 V; collision cell entrance potential, –11 V; collision energy, –13 V; collision cell exit potential, –4.5 V; source temperature, 300 °C and maximal accumulation time, 50 ms. The zeta-potentials of solutions (after centrifuged) were determined with a zetasizer 2000 apparatus (Malvern, United Kingdom).

The effects of RTILs concentration, pH value and ionic strength on the adsorption were studied by mixing 25 mL aqueous solution containing 1.0 mg/L of DEP, DnPP and DnBP

each with 0.5 g silica. Adsorption studies did not involve DcHP and DEHP owing to their low solubility in water. Both the added amounts of [C₆mim] Br and [C₁₂mim] Br were varied in the range of 0–50 mg. The solution was vigorously stirred for 5 min, and then it was centrifuged at 4000 rpm for 10 min. The concentration of PAEs in the supernatants was determined by LC–spectrophotometry.

3. Results and discussion

3.1. Adsorption isotherms of RTILs on silica particles

The adsorption isotherms of RTILs on silica were useful for understanding the theory of extraction process and optimizing the SPE conditions. As can be seen from Fig. 1 that, before a certain loading point reached (approximately 0.6 and 0.4 mg/g for [C₁₂mim] Br and [C₆mim] Br, respectively), nearly no RTILs were left in the aqueous phase. With the increase of RTILs concentration, both the adsorption amounts of RTILs on silica increased gradually. Maximum adsorption approximately 8 and 14 mg/g for [C₆mim] Br and [C₁₂mim] Br were obtained respectively when the concentration of [C₆mim] Br and [C₁₂mim] Br was about 65 and 80 mg/L, respectively. The amounts of RTILs adsorbed onto silica were clearly a function of the alkyl

Fig. 1. Adsorption isotherms of RTILs on silica at pH 6.5: (A) [C₁₂mim] Br and (B) [C₆mim] Br.

chain length. These adsorption isotherms did not fit conventional adsorption models (e.g. Langmuir) very well, which was probably because adsorbing RTILs onto silica surface was not a simple surface phenomenon but a multistep process involving different kinds of interactions. Generally, ionic surfactant adsorption isotherms on metal oxides can be divided into three regions [40,41]. In the first region the adsorbed ionic surfactant molecules spread themselves on the surface to form single-layer coverage (hemimicelles), probably through coulombic attractive interactions between charged metal oxides surface and the oppositely charged surfactants head group. The second region involves hydrophobic and electrostatic interactions, which result in the formation of bilayers (admicelles). The process of solubilizing analytes in hemimicelles and admicelles (mixed hemimicelles) is termed as “adsolubilization”. Both the above-mentioned regions were suitable for SPE method. At the end of isotherm region the overall surface of metal oxide is compensated and surfactants begin to form micelles in solution, which may result in the solubilization of analytes into micelles in bulk solution again and this isotherm span is unsuitable for SPE.

3.2. Effect of RTILs concentration on the zeta-potential of silica particles

Zeta-potential measurements can provide very useful information on adsorption phenomena since changes in the zeta-potential reflect the adsorption on surface directly. In order to study the process of self-aggregated micelles formed on metal oxide surface, many research groups investigated the zeta-potential curves of ionic surfactants adsorbed onto various metal oxides surfaces [42–44]. Fig. 2 showed that the zeta-potential of silica particles was a function of RTILs concentration. It can be observed that both the zeta-potentials of silica increased from negative to zero and converted to positive with increasing RTILs concentration. The zeta-potential changes can be interpreted as follows. At first the silica particles had a negative zeta-potential for the reason that the solution pH was higher than the silica PZC (about 3.0). At low RTILs concentrations (<5 mg added amount) a zeta-potential plateau of two systems about -13 MV was observed, which indicated that the RTILs adsorption amounts were not detectable. With the increase of RTILs concentration, the RTILs molecules began to adsorb on

Fig. 2. The zeta-potential of silica particles as a function of RTILs concentration at pH 6.5: (■) [C₁₂mim] Br; (▲) [C₆mim] Br.

negatively charged silica surface obviously through electrostatic attraction interactions, and the self-assembled surface micelles were formed gradually. The formed micelles screened the partial negative charges of silica surface, which resulted in a less negative zeta-potential. With the sign reversing after passing through a zero zeta-potential, the zeta-potential became positive with further RTILs adsorption, and attained a maximum of 9.8 and 7.2 MV when the added amounts of [C₁₂mim] Br and [C₆mim] Br were about 25 and 20 mg, respectively. The zeta-potential values did not change with a further increase in RTILs concentration, indicating the silica surface was saturated by RTILs adsorption. After compensation of the surface charge, the zeta-potential became almost independent of the RTILs concentration.

3.3. Sorbent selection

Fig. 3 depicted the adsorption percentages of adsorbed PAEs as a function of the RTILs amount added. In the absence of RTILs, the PAEs hardly adsorbed onto the silica surface. In contrast, with increases in RTILs concentration, both the PAEs adsorption amounts of micelles systems increased remarkably. The increase in adsorption amounts can be explained by the gradual formation of mixed hemimicelles (hemimicelles and admicelles) on silica surface, and then the analytes were extracted gradually. Maximum adsorption percentages were obtained when the added amounts were in the range of 15–30 mg for [C₁₂mim] Br and 10–20 mg for [C₆mim] Br, respectively. Both the DnBP maximum adsorption percentages were above 90%; the main difference was the maximum adsorption percentages of DEP and DnPP, which were about 70 and 85% for [C₁₂mim]Br-coated silica system while 60 and 80% for

Fig. 3. Effect of the added amounts of (A) [C₁₂mim] Br and (B) [C₆mim] Br on the PAEs adsorption percentages at pH 6.5: (▲) DnBP; (■) DnPP; (◆) DEP.

Fig. 4. Effect of (A) pH and (B) ionic strength on the extraction percentages: (▲) DnBP; (■) DnPP; (◆) DEP.

[C₆mim]Br-coated silica system, respectively. The experimental results also indicated clearly that the adsorption amounts had a positive relationship with the RTILs alkyl chain length. After a maximum adsorption plateau, the adsorption amounts began to decrease when the added amounts exceeded 30 mg for [C₁₂mim] Br and 20 mg for [C₆mim] Br, which can be explained that with more ionic liquids added the RTILs molecules began to form micelles in the bulk aqueous solution; furthermore, the micelles made the PAEs redistribute into the solution again. Given these findings, the [C₁₂mim] Br adsorption system had higher adsorption amount than [C₆mim] Br and was more suitable for SPE method; therefore, 25 mg [C₁₂mim] Br was adopted in the following studies.

3.4. Effect of pH

pH is one of the prime factors influencing the adsorption behavior of a mixed hemimicelles system. In present study the effect of pH was examined by varying pH between 1.5 and 9.0.

As shown in Fig. 4(A), the [C₁₂mim] Br-coated silica system exhibited no obvious adsorption for three PAEs when pH was between 1.5 and 3.5. With the increase of pH, the PAEs adsorption amounts increased dramatically before reaching a maximum above pH 6.0. This can be attributed to the fact that the silica surface was positive charged when the pH was below its PZC (2.9) and the [C₁₂mim]⁺ was hardly adsorbed to the silica surface. With increases in pH value, the silica surface gradually became negative charged such that there was a strong electrostatic attraction interaction between RTILs molecules and the negatively charged silica surface, which was sufficient to produce a great adsorption affinity for PAEs. Therefore, pH 6.5 was selected for the following studies.

3.5. Effect of ionic strength

NaCl concentration ranged between 0.05 and 0.4 M/L. It can be seen from Fig. 4(B) that the adsorption amounts of three PAEs decreased with increasing ionic strength. The experimental results suggest that the role of electrostatic interactions in the adsorption process was significant and the competition of sodium ions for the silica substrate was existed obviously. As we known that in the first adsorption region the adsorbed RTILs ions spread themselves on the silica surface to form a single-layer coverage through coulombic attraction interactions. As a result, the effect of salt concentration was to suppress the thickness of electrical adsorption layer at the silica/solution interface, which led to the decrease of mixed hemimicelles formed on the silica surface.

3.6. Breakthrough volume and desorption

The breakthrough volume for PAEs was determined using a series of different volume aqueous solution (100–500 mL) spiked with 1 µg of each the PAEs at pH 6.5. Insufficient recovery was considered to occur when the recovery was below 90%. With the increase of solution volume, insufficient recoveries occurred when aqueous solution volume was above 300 mL; for instance, the recovery of 78, 82, 85, 86 and 89% for DEP, DnPP, DnBP, DcHP and DEHP were obtained respectively when the passing volume was 400 mL. The sample loading rate experiments (1–10 mL/min) were carried out by passing 300 mL aqueous solution spiked with 1 µg of each the PAEs. The sample loading rate was considered too fast when the recoveries of PAEs in eluate were below 90%. The experimental results indicated that good recoveries were obtained when loading rate was between 1 and 5 mL/min; when loading rate increased to 8 mL/min, insufficient recoveries of 76, 83, 85, 85 and 84% for

Table 2
Analytical parameters of the proposed method

Analytes	Linearity range (µg/L)	Correlation coefficient (r^2)	LOD (µg/L)	Preconcentration factor	R.S.D. (%) ($n=6$)
DEP	0.6–50	0.9912	0.17	600	5.9
DnPP	0.6–50	0.9910	0.15	600	4.8
DnBP	0.6–50	0.9924	0.13	600	5.2
DcHP	0.6–50	0.9921	0.14	600	4.9
DEHP	0.6–50	0.9918	0.12	600	4.1

Table 3
Determination and recoveries of PAEs in real water samples

Samples	Added ($\mu\text{g/L}$)					Founded ^a ($\mu\text{g/L}$)					Recovery ^b (%)				
	DEP	DnPP	DnBP	DcHP	DEHP	DEP	DnPP	DnBP	DcHP	DEHP	DEP	DnPP	DnBP	DcHP	DEHP
Tap water	0	0	0	0	0	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c					
	1.0	1.0	1.0	1.0	1.0	0.85	0.93	1.05	0.92	0.90	85 $\pm$ 3	93 $\pm$ 4	105 $\pm$ 6	92 $\pm$ 4	90 $\pm$ 5
Jingmi Canal	0	0	0	0	0	0.82	n.d. ^c	0.52	n.d. ^c	0.53					
	1.0	1.0	1.0	1.0	1.0	1.78	0.87	1.46	1.02	1.49	96 $\pm$ 5	87 $\pm$ 3	94 $\pm$ 5	102 $\pm$ 5	96 $\pm$ 4
Xiaoqing River	0	0	0	0	0	1.15	n.d. ^c	0.51	0.46	1.36					
	1.0	1.0	1.0	1.0	1.0	2.10	0.96	1.56	1.53	2.26	95 $\pm$ 4	96 $\pm$ 5	105 $\pm$ 5	107 $\pm$ 6	90 $\pm$ 3
Gaobeidian effluent	0	0	0	0	0	n.d. ^c	n.d. ^c	0.67	0.49	0.52					
	1.0	1.0	1.0	1.0	1.0	0.93	0.87	1.58	1.36	1.47	93 $\pm$ 4	87 $\pm$ 5	91 $\pm$ 4	87 $\pm$ 3	95 $\pm$ 5

^a Mean of three determinations.

^b S.D. for three determinations.

^c Not detected.

DEP, DnPP, DnBP, DcHP and DEHP were obtained, respectively. Therefore, 300 mL solution volume and 5 mL/min flow rate was selected for the next studies.

Desorption of PAEs from the $[\text{C}_{12}\text{mim}]$ Br-coated silica mixed hemimicelles column was studied with different organic solvent such as acetonitrile, methanol and methanol (pH 2, adjusted with 1 M HNO_3). Quantitative recoveries (above 90%) of PAEs were obtained using 3 mL methanol (pH 2). When using 3 mL acetonitrile, the recoveries were 76, 70, 83, 82 and 79% for DEP, DnPP, DnBP, DcHP and DEHP were achieved, respectively, and a higher volume acetonitrile (8 mL) was required for desorbing the PAEs completely. When using 3 mL methanol, the recoveries were 81, 76, 85, 82 and 88% for DEP, DnPP, DnBP, DcHP and DEHP, respectively. Thus, 3 mL methanol (pH 2) was recommended for desorption. By drying the desorption solution with a nitrogen flow and redissolving the analytes in 0.5 mL methanol, the preconcentration factor of 600 for each PAEs was obtained.

3.7. Analytical performance

Quantitative parameters of the proposed method such as linear range, correlation coefficients, limits of detection (LODs) and relative standard deviation (R.S.D.), were evaluated by enriching 300 mL standard solutions (Table 2). Calibration curves were run using 300 mL deionized water spiked with 0.6–50 ng/mL each the PAEs. According to the overall SPE procedure and HPLC analysis method above-mentioned, the calibration curves were established. Each analyte exhibited good linearity with correlation coefficient (r^2) > 0.99 in the studied range. The limits of detection, calculated on the basis of signal-to-noise ratio of 3 ($\text{S/N}=3$) [45] ranged between 0.12 and 0.17 $\mu\text{g/L}$. The precision of analytical method was investigated using six replicate experiments with 300 mL standard solution containing each the PAEs 1.0 $\mu\text{g/L}$, and the relative standard deviation (R.S.D.) of below 6.0% was obtained.

3.8. Analysis of real water samples

In order to validate the method, the method was applied to four real environmental water samples with the results shown in

Fig. 5. Solid-phase extraction/LC–spectrophotometry chromatograms: (A) standard solution containing 0.3 mg/L of each the PAEs; (B) Xiaoqing River water sample; (C) Jingmi Canal; (D) Gaobeidian effluent; (E) tap water. (1) DEP; (2) DnPP; (3) DnBP; (4) DcHP; (5) DEHP.

Table 3. No PAEs were found in the tap water; for the case of other three water samples, different PAE contents were found. The accuracy of the method was evaluated by a recovery test carried out with PAEs-spiked water samples. Recoveries ranged between 85 and 108% for the five PAEs. The chromatograms of all the water samples were shown in Fig. 5.

4. Conclusions

A novel SPE method based on [C₁₂mim] Br-coated silica mixed hemimicelles was developed for the analysis of five PAEs in four environmental water samples. The method was effective for the preconcentration of trace PAEs in environmental water prior to HPLC analysis. The strong hydrophobic interactions between the mixed hemimicelles and PAEs resulted in the high retention of analytes; however, the retained PAEs can be desorbed easily with 3 mL methanol (pH 2) and no carryover was observed in the next analysis. Good recovery and precision were obtained, which indicated that [C₁₂mim] Br-coated silica mixed hemimicelles SPE method has high analytical potential for the preconcentration of other trace organic pollutants from water samples.

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