Available online at www.sciencedirect.com

Separation and Purification Technology 61 (2008) 324–331

Separation and Purification Technology

www.elsevier.com/locate/seppur

Solvent extraction of selected endocrine-disrupting phenols using ionic liquids

Jing Fan[a], Yunchang Fan[a], Yuanchao Pei[a], Kun Wu[a], Jianji Wang[a,*], Maohong Fan[b]

[a] *School of Chemistry and Environmental Science, Henan Key Laboratory for Environmental Pollution Control, Henan Normal University, Xinxiang, Henan 453007, PR China*

[b] *School of Materials Science and Technology, Georgia Institute of Technology, Atlanta, GA 30332, USA*

Received 26 August 2007; received in revised form 10 November 2007; accepted 12 November 2007

Abstract

In this paper, investigations have been carried out to determine the suitability of imidazolium-based ionic liquids (ILs), 1-methyl-3-alkylimidazolium hexafluorophosphate [$C_n$mim][PF_6] (n = 4, 6, 8) and 1-methy-3-alkylimidazolium tetrafluoroborate [$C_n$mim][BF_4] (n = 6, 8), in replacing volatile organic solvents for liquid–liquid extraction of selected endocrine-disrupting phenols from aqueous solutions. New experimental data have been reported for the extraction of phenol, bisphenol A, pentachlorophenol, 4-octylphenol and 4-nonylphenol by the ILs. The results showed that distribution ratios of the endocrine-disrupting phenols were influenced significantly by pH of the aqueous phase, nature of the ILs, chemical structure of the phenols, and the presence of some salts in aqueous solutions. It was found that in the range of pH <7, most of the phenols were extracted quantitatively from aqueous solution into the ILs. The selective separation of some of the phenols from their binary mixtures was also investigated, and the possible driven forces for the extraction were discussed based on the hydrogen-bonding and hydrophobic interactions between the ILs and the phenols. It is expected that these results are promising for the liquid–liquid extraction, separation and preconcentration of endocrine-disrupting phenols in analytical science and related industrial process.

Keywords: Ionic liquid; Liquid–liquid extraction; Endocrine-disrupting phenol; Greener solvent

1. Introduction

Liquid–liquid extraction is an effective separation method in analytical science and in chemical industry. Generally speaking, traditional solvent extraction employed partitioning of a solute between two immiscible phases, typically an organic solvent and an aqueous solution. The organic solvents used are usually volatile, toxic and flammable. Therefore, to establish more effective and cleaner extraction methods are desired for the development of new separation processes.

Endocrine-disrupting chemicals (EDCs), also called environmental hormone, have already become a threat to the global eco-system. They are stimulants in our living environments, which function as hormones, interfered with the normal secretory process in human body, leading to various negative biological effects and a threat to the health of human beings and animals [1,2]. The alkylphenol, pentachlorophenol, and bisphenol A are common endocrine-disruptors. These compounds are of human health concern due to their potential hazards to human reproductive health [3]. Alkyl phenols have been used to make non-ionic surfactant of alkyl phenol polyethyleneoxide ether in auxiliary ingredient industry. Bisphenol A and pentachlorophenol were applied to produce epoxyresin and phenolics, insecticide and herbicide, respectively. These phenols widely exist in environment.

Ionic liquids (ILs) are, as their name implied, liquid ionic media composed of organic cations and inorganic or organic anions, which remain liquid at the temperatures below 100 °C. They have no-detectable vapor pressure, and are non-flammable at ambient conditions. Their properties could be modified by suitable combination of different cations and anions. Therefore, ILs are regarded to be novel environmentally benign solvents for chemical synthesis and catalysis [4–6], chromatographic methods [7], and electrochemical applications [8,9]. In recent years, application of ILs in separation and extraction of organic compounds, for example, substituted benzene derivatives [10], biofuels [11], antibiotics [12], organic acids [13], polycyclic aromatic hydrocarbons [14], amino acids [15,16], azo dyes

---

* Corresponding author. Tel.: +86 373 3325805; fax: +86 373 3326445.
E-mail address: jwang@henannu.edu.cn (J. Wang).

1383-5866/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2007.11.005

[17], S-compounds in diesel oil [18,19], anabolic androgenic steroids [20], some phenolic compounds [21], and some organic compounds bearing different functionalities [22], has received increasing attention, and several excellent reviews have been published [23–27].

In this work, experimental measurements have been performed to determine distribution ratios of endocrine-disrupting phenols between ILs and aqueous solution at different pH values. Five phenols with different chemical structures were chosen: phenol, pentachlorophenol, bisphenol A, 4-octylphenol and 4-nonylphenol. At the same time, [C_4mim][PF_6], [C_6mim][PF_6], [C_8mim][PF_6], [C_6mim][BF_4] and [C_8mim][BF_4] ionic liquids (see Fig. 1 for their chemical structure) were selected. This selection makes it possible to investigate how the nature of anions, length of the alkyl chains on the imidazolium ring and chemical structure of the molecular compounds affect extraction of endocrine-disrupting phenols from aqueous solutions.

2. Experimental

2.1. Reagents

1-Bromobutane, 1-bromohexane, 1-bromooctane and 1-methylimidazole (Shanghai Chem. Co., C. P.) were distilled twice at reduced pressure. The middle fraction of the distillate was collected. Sodium hexafluorophosphate $NaPF_6$ (Shanghai Chem. Co., C. P.) was purified by recrystallization twice from deionized water. Sodium tetrafluoroborate $NaBF_4$ (Tianjin Kemio Chem. Co., A. R.), pentachlorophenol (Shanghai Chem. Co., A. R.), phenol (Beijing Chem. Co., A. R.), bisphenol A (Tianjin Guangfu Chem. Co., A. R.), 4-octylphenol (Aldrich, A.R.) and 4-nonylphenol (Alfa Aesar, A.R.) were used without further purification. The pH values of aqueous solutions were adjusted by using aqueous HCl or NaOH and measured by using a digital pH meter (Hangzhou, pHs-2).

2.2. Preparation of ionic liquids

[C_4mim][PF_6], [C_6mim][PF_6], [C_8mim][PF_6], [C_6mim][BF_4] and [C_8mim][BF_4] were synthesized according to the procedure described in literature [28,29]. Sodium bromide and any residual reactant were removed from the ionic liquids by washing with water until no precipitation was formed with addition of aqueous silver nitrate solution ($1.0\,mol\,L^{-1}$). The washed ILs were dried under vacuum at 75 °C for 2–3 days to remove small amount of water. All ionic liquids were stored in a desiccator under vacuum prior to use, in order to protect ionic liquids from wetting. The content of water, bromide and sodium in the ILs was, respectively, determined by Karl–Fisher titration, bromide-selective electrode and atomic absorption spectrometry. It was found that less than 0.02 wt.% of water, $0.008\,mol\,kg^{-1}$ of Br^- and $0.021\,mol\,kg^{-1}$ of Na^+ were remained in the ILs. The ionic liquids were also characterized with ^{1}H NMR (Bruker, AV-400), and the results were accordance with those reported in literature [30,31].

2.3. Distribution ratio measurements

Extraction was performed at room temperature (24 ± 1 °C). Because of the limited solubility of the phenols in water, a known amount of phenols was dissolved in deionized water to prepare aqueous phenol solutions in the concentration range of 1×10^{-5} to $4 \times 10^{-3}\,mol\,L^{-1}$. 5.0 mL of such a solution was contacted with 1.0 mL of pure IL. The phase-contacting experiments were carried out in carefully stoppered glass vessels. The system was vigorously stirred with magnetic stirrer. After stirring for 30 min,

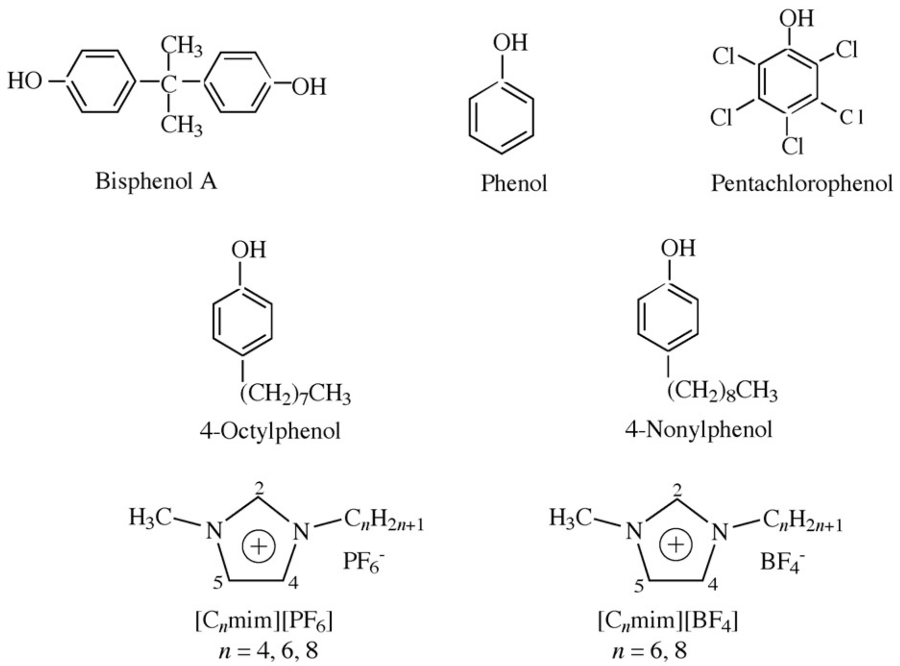

Fig. 1. Chemical structures of the ILs and the phenols.

the two phases were carefully separated using a centrifugal machine. Before and after extraction, concentrations of a given phenolic compound in aqueous solutions were determined with a UV spectrophotometer (Shanghai, model 752) at 272 nm. Its concentration in ionic liquid phases was calculated by material conservation. Distribution ratios of the phenols between a given IL and aqueous solution were calculated by

$$D = \frac{C_{\mathrm{IL}}}{C_{\mathrm{W}}} \tag{1}$$

These also allow the extraction percentage (E) to be calculated by

$$E = \frac{C_{\mathrm{IL}}}{C_{\mathrm{IL}} + C_{\mathrm{W}}} \times 100\% \tag{2}$$

where C_{IL} and C_{W} refer to equilibrium concentration of the phenols in ionic liquids and in aqueous phases, respectively. It should be noted that although ionic liquids employed in this work are immiscible with aqueous phase, they do have very low solubilities in water. Since the ionic liquids solubilized in the aqueous phases also absorb at the selected wavelength, additional measurements were performed in order to subtract the ionic liquids contribution from the total absorbance measured. Therefore, an ionic liquid saturated aqueous solution was used as a reference solution for the spectrometric determination of the phenols concentrations.

For the selective extraction, concentrations of the components in ionic liquids and aqueous phases were determined at 270 nm by using an Agilent liquid chromatograph (HP1100) equipped with a diode array detector. In the selective extraction from environmental samples, tap water and lake water were collected, kept for some time, filtrated, and then used for the extraction experiments. The values of distribution ratio were measured in triplicate with uncertainties less than 5%.

3. Results and discussion

3.1. Effect of phase volume ratio and temperature

Preliminary experiments showed that the extraction equilibrium was achieved within 10 min or less. Therefore, phase contact time of 30 min was employed throughout the extraction experiments in order to guarantee the distribution equilibrium between two phases.

Table 1 shows, as example, the effect of phase volume ratios on values of distribution ratio of bisphenol A and phenol between [C_6mim][PF_6] and aqueous solution. It can be seen that values of distribution ratio decrease slightly with increasing phase volume ratios. The distribution ratios remain rather high at high phase volume ratio, say 50, of aqueous to IL. Therefore, in order to decrease the quantity of IL used in the extraction and the loss of IL in aqueous solution, 1 mL of IL and 5 mL of aqueous solution, i.e., V_{W}:V_{IL} = 5:1 were typically used in the extraction.

Table 1
Distribution ratios between [C_6mim][PF_6] and aqueous phase for bisphenol A (pH 7.03) and phenol (pH 7.16) at different phase volume ratios

Phenols	$V_{\mathrm{W}}/V_{\mathrm{IL}}$					
	1	5	10	12	25	50
Bisphenol A	490.5	473.1	455.7	445.1	432.3	414.1
Phenol	21.6	18.3	18.0	17.1	16.5	15.9

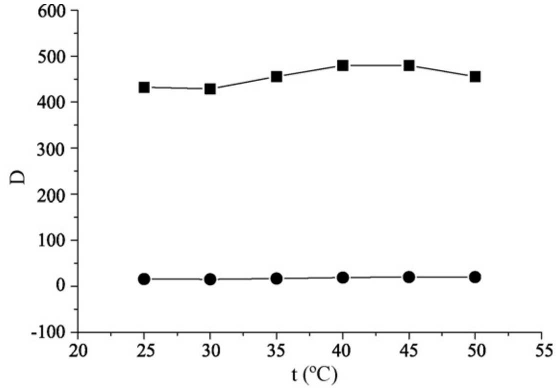

Fig. 2. Effect of temperature on the distribution ratios of phenol and bisphenol A between [C_6mim][PF_6] and aqueous solution: (■), bisphenol A and (●), phenol.

To examine the effect of temperature on the extraction of the phenols, the extraction experiments of phenol and bisphenol A by [C_6mim][PF_6] were carried out at 25, 30, 35, 40, 45 and 50 °C. Fig. 2 shows the temperature dependence of the distribution ratios. Obviously, temperature has little influence on the distribution ratios within the experimental error. Therefore, the extraction experiments were performed at room temperature (24 ± 1 °C).

3.2. pH dependence of the distribution ratios

Experimental data of distribution ratios for the phenols between ILs and aqueous solutions are collected in Table 2 as a function of aqueous phase pH. As an example, the pH dependence of distribution ratios of the phenols between [C_6mim][PF_6] and aqueous solution is shown in Fig. 3. As can be seen, D values of the endocrine-disrupting phenols except phenol are quite high, and they remain an almost plateau under the condition of pH <7, and then they decrease steeply in the range of pH >7. Similar results have been found in other ionic liquids studied. This behavior can be related to the charged characteristics of the phenols at different pHs. It is known that the ionization constants (pK_a) of phenol, pentachlorophenol, bisphenol A and 4-nonylphenol in water are 9.96, 4.74, 10.3 and 10.28, respectively [32–35]. Although we found no pK_a value available for 4-octylphenol in literature, it can be deduced that pK_a value of 4-octylphenol should be similar to that of 4-nonylphenol based on the Hammett–Taft equation [32]. For phenol, 4-nonylphenol, 4-octylphenol and bisphenol A, calculation of the fractions of the species in aqueous solutions [36] indicated that they existed in molecular form in the range of pH ≤ 7. Then, their anionic fraction increases with increasing aqueous phase pH, and reaches 50% at pH = pK_a. Therefore, it seems appropriate to state that the interactions between ionic liquid and molecular form of the

Table 2
Distribution ratios of the phenols between ILs and aqueous solution as a function of pH of aqueous phase (24 ± 1 °C)

pH	$[C_4mim][PF_6]$	$[C_6mim][PF_6]$	$[C_8mim][PF_6]$	$[C_6mim][BF_4]$	$[C_8mim][BF_4]$
Bisphenol A					
1.86	389.0	412.0	447.1	759.1	1043.3
3.26	389.0	412.0	447.0	747.7	1882.6
4.95	382.3	414.8	503.6	808.1	1882.6
7.03	416.1	432.3	492.4	962.1	2465.1
9.17	225.0	233.6	432.0	562.5	802.9
11.61	0.60	0.76	20.8	21.2	40.3
12.01	0.18	0.22	0.45	2.07	31.8
4-Nonylphenol					
3.23[a]	200.0	350.0	550.0	ND[b]	ND
5.19	210.0	347.2	527.8	ND	ND
7.09	200.0	338.9	450.0	ND	ND
8.43	156.3	283.3	316.7	375.0	725.0
10.20	93.2	212.5	235.7	368.8	700.0
11.03	38.6	192.0	227.1	327.8	595.0
12.61	0.49	156.7	163.8	162.7	233.3
4-Octylphenol					
3.23[a]	124.2	211.9	243.3	362.5	656.3
5.27	123.3	231.7	275.0	383.4	645.8
7.04	160.8	237.5	278.6	397.2	687.5
10.22	35.5	111.5	125.0	118.8	132.8
12.07	0.81	53.3	62.5	62.4	75.8
Pentachlorophenol					
3.16[a]	58.9	176.5	541.1	430.0	1175.0
5.12	54.6	171.4	537.5	424.9	1141.7
7.03	27.4	162.5	505.6	408.0	1096.7
10.25	21.5	153.2	496.5	387.8	922.4
12.73	14.3	120.3	462.8	121.0	544.9
Phenol					
3.23	11.4	17.4	23.3	20.2	37.5
5.25	11.3	16.7	23.4	20.8	37.4
7.16	11.2	15.9	22.8	20.1	36.0
9.52	7.8	10.6	11.8	14.1	32.7
11.68	1.9	2.1	3.8	4.1	7.5

[a] $V_W:V_{IL} = 25:1$ was used at these pHs because of the low solubility of 4-nonylphenol, 4-octylphenol and pentachlorophenol in water and their very low concentrations in aqueous phase after extraction.

[b] Not detectable because of low concentration of the compound in aqueous phase after extraction.

phenols are responsible for the high distribution ratios under acidic conditions.

It is found from molecular dynamic simulations that ILs are strongly solvated by the hydrogen-bonding solvents, principally by forming hydrogen bonds with the anions [37]. Based on this result, the hydrogen-bonding interactions of $[PF_6]^-$ or $[BF_4]^-$ with hydroxyl H of the phenols will be expected. On the other hands, hydrophobic interactions between imidazolium cation of the ILs and the phenols are also very important as far as the interactions of the IL with the phenols are concerned. This suggests that hydrogen-bonding and hydrophobic interactions between ILs and the phenols make it easy for the transfer of phenols from aqueous solutions to the ionic liquid phases, leading to high distribution ratios observed experimentally. In basic solutions, part of the hydrogen-bonding interactions vanished because of the decreased fraction of molecular form of the phenols. This may be a possible reason for the decreased distribution ratios observed in the range of pH >7.

3.3. *Effect of chemical structure of both the ionic liquids and the phenols*

As can be seen from Table 2, extraction efficiency of the ILs for a given phenol in the acidic range follows the order: $[C_8mim][PF_6] > [C_6mim][PF_6] > [C_4mim][PF_6]$; $[C_8mim][BF_4] > [C_6mim][BF_4]$; $[C_8mim][BF_4] > [C_8mim][PF_6]$, and $[C_6mim][BF_4] > [C_6mim][PF_6]$ under the same conditions. Fig. 4 is a representative graph showing this trend for the partitioning of phenol into the five ILs. These results imply that, for a given phenolic compound, its distribution ratios increase with increasing length of alkyl chain on the cation of the ILs, and their values are much higher into a IL with $[BF_4]^-$ anion than that with $[PF_6]^-$ anion at given pHs. Clearly, the former can be interpreted by an increase of hydrophobic interactions between a phenolic compound and the ILs, and the latter is ascribed to the different in hydrogen-bonding strength between $[BF_4]^-$ or $[PF_6]^-$ and the given phenolic compound. Quantum

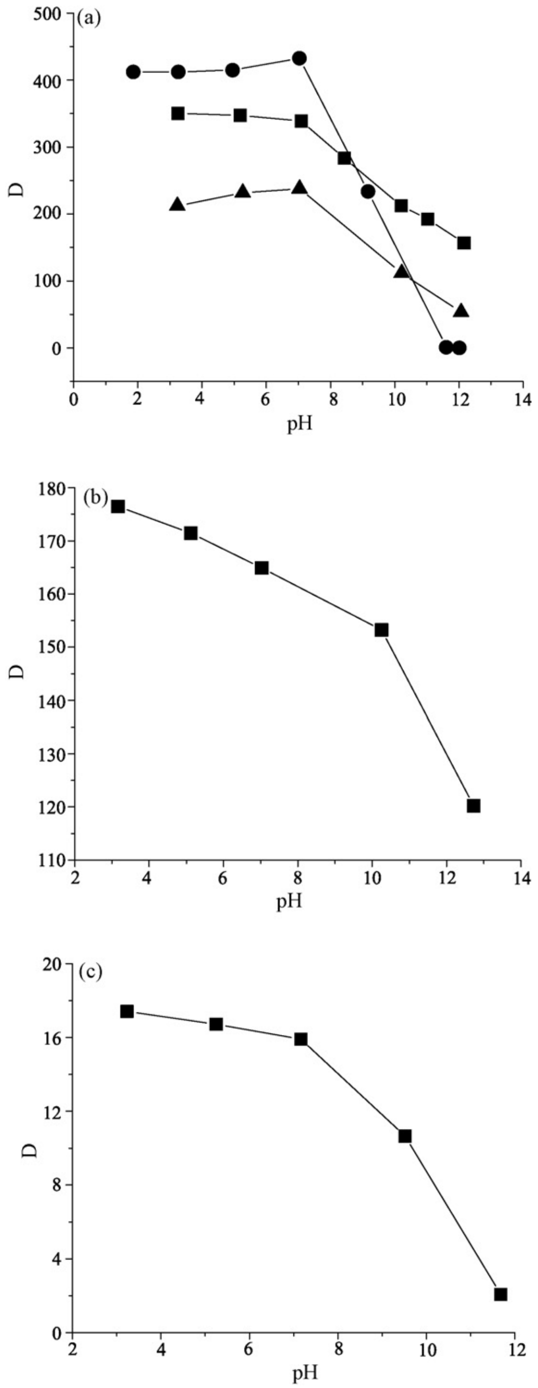

Fig. 3. The pH dependence of distribution ratios of the phenols between $[C_6mim][PF_6]$ and aqueous solutions: (a): (●), bisphenol A; (■), 4-nonylphenol and (▲), 4-octylphenol; (b) pentachlorophenol and (c) phenol.

chemical calculations [38] indicated that effective negative charge of $[BF_4]^-$ is much stronger than $[PF_6]^-$. So, compared with $[PF_6]^-$ anion, strength of hydrogen-bonding between $[BF_4]^-$ and the phenols should be much stronger, suggesting a higher distribution ratio accordingly.

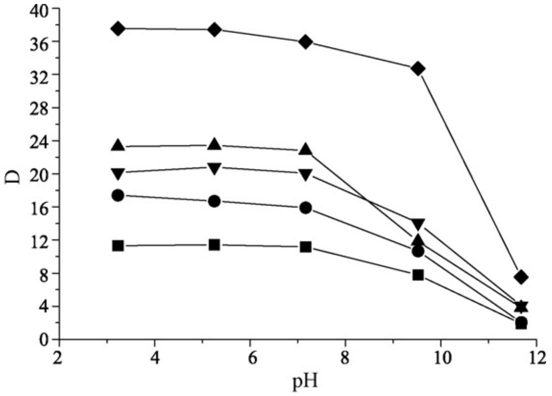

Fig. 4. The pH dependence of distribution ratios of phenol between ionic liquids and water: (♦), $[C_8mim][BF_4]$; (▲), $[C_8mim][PF_6]$; (▼) $[C_6mim][BF_4]$; (●), $[C_6mim][PF_6]$ and (■) $[C_4mim][PF_6]$.

Another interesting result revealed from Table 2 is that, in the acidic range, extraction efficiency of the phenols by a given IL decreases in the order: 4-nonylphenol > 4-octylphenol > phenol; and pentachlorophenol > phenol. Considering the fact that 4-nonylphenol, 4-octylphenol and phenol have similar pK_a values and, therefore, similar acidic strength in water, the decreased extraction efficiency of these phenols is possibly attributed to their decreased hydrophobic interactions with the ILs. However, there is a great difference in pK_a value for pentachlorophenol (4.74) and phenol (9.96). This suggests that the decreased hydrogen-bonding interactions are probably the main reason for the decreased extraction efficiency of phenol relative to pentachlorophenol. Because there are two phenolic hydroxyls and two aromatic rings in bisphenol A molecules, the stronger interactions with ILs and the higher extraction efficiency of this compound will be expected.

3.4. Effect of salts

In order to investigate the effect of salts, present in aqueous phase, on extraction of the phenols, seven kinds of salts including NaCl, $NaNO_3$, Na_2SO_4, NaI, $NaClO_4$, Zn_2SO_4 and $Al_2(SO_4)_3$ were used in this study. As example, the effect of these salts on the distribution ratios of phenol (pH 7.16) and bisphenol A (pH 7.03) between $[C_6mim][PF_6]$ and aqueous solution were determined and shown in Figs. 5 and 6, respectively. It is clear that,

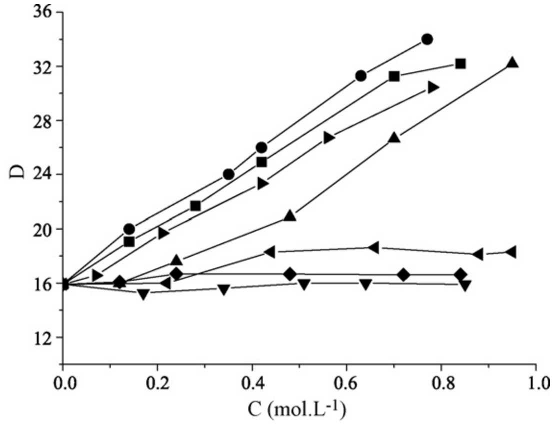

Fig. 5. Effect of type and concentration of salt on the distribution ratios of phenol into $[C_6mim][PF_6]$: (●), $ZnSO_4$; (■), Na_2SO_4; (►), $Al_2(SO_4)_3$; (▲), $NaClO_4$; (◄), NaI; (♦), $NaNO_3$ and (▼), NaCl.

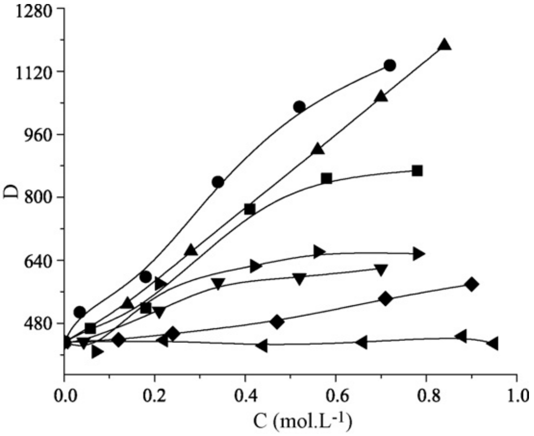

Fig. 6. Effect of type and concentration of salt on the distribution ratios of bisphenol A into $[C_6mim][PF_6]$: (●), $ZnSO_4$; (▲), Na_2SO_4; (■), $Al_2(SO_4)_3$; (►), $NaClO_4$; (▼), NaCl; (♦), $NaNO_3$ and (◄), NaI.

in the presence of salts, the distribution ratios of these phenols increase with increasing concentration of salt present in aqueous phase except for the extraction of phenol in the presence of $NaNO_3$ or NaCl, and that of bisphenol A in the presence of NaI. This can be explained by salting-out effect. Generally, salts dissolved in aqueous solution could combine with water molecules, which reduced the concentration of free water molecules, increased the relative concentration of the phenols, and made the organic molecules be preferably extracted into the IL phase. Therefore, the stronger the hydration ability of salt, the stronger its salting-out effect. It is known that [39] the Gibbs energy of hydration are −4525, −1955, −365 kJ mol^{-1} for Al^{3+}, Zn^{2+}, Na^+, and −1080, −430, −340, −300, −275 kJ mol^{-1} for $SO_4{}^{2-}$, $ClO_4{}^-$, Cl^-, $NO_3{}^-$ and I^-, respectively. This suggests that the salts NaCl, $NaNO_3$ and NaI have the weak hydration ability. Therefore, the change of the distribution ratios of phenol and bisphenol A was not significant in the presence of these salts. The results shown in Figs. 5 and 6 are generally in agreement with this knowledge.

3.5. Selective separation and determination of the endocrine-disrupting phenols

It can be seen from Table 2 that the values of distribution ratios of the phenols are greatly different under the same conditions. This makes it possible to separate some of endocrine-disrupting phenols selectively. As example, Table 3 shows the selective separation results, as determined by HPLC, for phenol + 4-octylphenol, phenol + 4-nonylphenol, bisphenol A + 4-octylphenol and bisphenol A + 4-nonylphenol mixtures by $[C_6mim][PF_6]$ or $[C_8mim][PF_6]$ ionic liquids. These findings indicate that, in a single step, these phenols can be effectively separated from their binary mixtures by using $[C_6mim][PF_6]$ or $[C_8mim][PF_6]$ as extractants. Therefore, quantitative separation is expected to be achieved by a multiple step process.

In order to test the applications of this approach $[C_8mim][PF_6]$ has been used to separate phenol from 4-nonylphenol in tap water and in lake water, respectively. The result shown that phenol and 4-nonylphenol were not detected in these environmental waters. Next, further experiment was carried out to determine the recovery of known amounts of phenol and 4-nonylphenol added to the samples. It is shown that, in a single extraction, 98.3 and 92.5% of 4-nonylphenol was extracted selectively by the ionic liquid, and 82.3 and 94.8% of phenol was remained in the lake water and tap water, respectively. This demonstrates that ionic liquids can be used for the selective separation and determination of some endocrine-disrupting phenols in environmental waters.

3.6. Recovery and reuse of the ILs

Experiments were also carried out for the recovery and reuse of the ILs. For this purpose, the phenolic compound in the final IL phase was separated by back extraction with 0.1 mol L^{-1} NaOH aqueous solution. Usually, most of the phenols can be removed from IL phase by three times of back extraction. For example, after back extraction three times, about 99% of phenol, bisphenol A, 4-octylphenol and 4-nonylphenol, and more than 90% of pentachlorophenol could be removed from $[C_4mim][PF_6]$ and $[C_6mim][PF_6]$ ionic liquids. The recoveried ionic liquids were washed with water to be neutral, dried under vacuum at 75 °C for several days, and then can be reused for the next extraction of the phenols. However, it should be mentioned that the $[C_8mim][PF_6]$ phase containing pentachlorophenol is difficult to recovery because of the less pH dependence of the partitioning of pentachlorophenol in $[C_8mim][PF_6]$.

3.7. Compared with other extracting solvents

In this work, the ILs exhibited high extraction efficiency for the endocrine-disrupting phenols. For example, most of the extraction percentage of bisphenol A, 4-nonylphenol, 4-octylphenol and pentachlorophenol was more than 98% under the acidic conditions. In fact, the five kinds of endocrine-disrupting phenols were extracted nearly quantitatively from aqueous solution into the ILs at pH ≤ 7. In Table 4, the distribution ratios of the phenols into $[C_4mim][PF_6]$, $[C_8mim][PF_6]$ and $[C_8mim][BF_4]$ are compared with those into benzene and dichloromethane [40] at pH ≈ 7. As can be seen, distribution ratios of the phenols between benzene or dichloromethane and

Table 3
Selective extraction of the representative phenols by ionic liquids at pH 12 and $V_w/V_{IL} = 5/1$

E	Phenol (1) + 4-octylphenol (2) $[C_6mim][PF_6]$	Phenol (1) + 4-nonylphenol (2) $[C_8mim][PF_6]$	Bisphenol A(1) + 4-octylphenol (2) $[C_8mim][PF_6]$	Bisphenol A(1) + 4-nonylphenol (2) $[C_8mim][PF_6]$
1	10.6%	17.5%	10.4%	18.0%
2	96.5%	92.0%	79.6%	95.1%

Table 4
Values of distribution ratios for the phenols between [C$_4$mim][PF$_6$], [C$_8$mim][PF$_6$], [C$_8$mim][BF$_4$] dichloromethane or benzene and water (pH ≈ 7, 24 ± 1 °C)

Phenols	D				
	Dichloromethane[a]	Benzene[a]	[C$_4$mim][PF$_6$]	[C$_8$mim][PF$_6$]	[C$_8$mim][BF$_4$]
Bisphenol A	20.51	17.80	416.1	492.4	2465.1
Phenol	0.24	2.08	11.2	22.8	36.0
Pentachlorophenol	2.21	3.77	27.4	505.6	1096.7
4-Octylphenol	9.64	17.78	160.8	278.6	687.5
4-nonylphenol	10.76	25.71	200.0	450.0	–

[a] Ref. [39].

aqueous phase are significantly lower than those between the ionic liquids and water. For example, the value of distribution ratio for pentachlorophenol into [C$_8$mim][BF$_4$] is about 496 times as high as that into dichloromethane under the same conditions. Even if the [C$_4$mim][PF$_6$] ionic liquid was used for the extraction, which has the lowest extraction efficiency for the phenols investigated in the present work, the average value of distribution ratio for the five phenols is about 23 and 11 times as high as those into dichloromethane and benzene, respectively. Therefore, those ionic liquids have potential application in practical liquid–liquid extraction process of the endocrine-disrupting phenols from aqueous solution.

4. Conclusions

Experimental data for the distribution ratios of selected endocrine-disrupting phenols, including phenol, bisphenol A, pentachlorophenol, 4-octylphenol and 4-nonylphenol, between ionic liquids and aqueous solution have been reported at different pHs. The results shown that nearly quantitative extraction of the phenols was achieved in a single step, and distribution ratios of these endocrine-disrupting phenols were highly influenced by pH of aqueous phase, nature of ionic liquids, and chemical structure of the phenols.

It was found that values of distribution ratio for the phenols increased with increasing length of alkyl chain on the cation of the ILs, extraction efficiency of the ILs with [BF$_4$]$^-$ anion was much higher than those with [PF$_6$]$^-$ anion, and the hydrogen-bonding and hydrophobic interactions between ILs and the phenols play an important role in the partitioning of these phenols into ILs from aqueous solution.

Furthermore, it is shown that some phenols can be separated selectively from their mixtures in environmental waters. From these findings, we conclude that ionic liquids can be used as a potential Greener and high effective solvent to replace traditional volatile organic compounds in liquid–liquid extraction, separation and preconcentration of endocrine-disrupting phenols.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (Grant no. 20573034) and the Natural Science Foundation of Henan province (Grant no. 0511021200).

References

[1] T. Colborn, F.S. Vom Saal, A.M. Soto, Developmental effects of endocrine-disrupting chemicals in wildlife and humans, Environ. Health Perspect. 101 (1993) 378–384.

[2] J. Toppari, J.C. Larsen, P. Christiansen, A. Giwercman, P. Grandjean, L.J. Guillette Jr, B. Jégou, T.K. Jensen, P. Jouannet, N. Keiding, H. Leffers, J.A. McLachlan, O. Meyer, J. Müller, E.R. Meyts, T. Scheike, R. Sharpe, J. Sumpter, N.E. Skakkebæk, Male reproductive health and environmental xenoestrogens, Environ. Health Perspect. 104 (S4) (1996) 741–803.

[3] F. Paris, P. Balaguer, B. Terouanne, N. Servant, C. Lacoste, J. Cravedi, J. Nicolas, C. Sultan, Phenylphenols, biphenols, bisphenol-A and 4-tert-octylphenol exhibit α and β estrogen activities and antiandrogen activity in reporter cell lines, Mol. Cell. Endocrinol. S4 (193) (2002) 43–49.

[4] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (1999) 2071–2083.

[5] J. Dupont, R.F. De Souza, P.A.Z. Suarez, Ionic liquid (molten salt) phase organometallic catalysis, Chem. Rev. 102 (2002) 3667–3692.

[6] P. Wasserscheid, W. Keim, Ionic liquids—new "solutions" for transition metal catalysis, Angew. Chem. Int. Ed. 39 (2000) 3772–3789.

[7] A.M. Stalcup, B. Cabovska, Ionic liquids in chromatography and capillary. Electrophoresis, J. Liq. Chromatogr. Rel. Tech. 27 (2004) 1443–1459.

[8] M.C. Buzzeo, R.G. Evans, R.G. Compton, Non-haloaluminate room-temperature ionic liquids in electrochemistry—a review, Chem. Phys. Chem. 5 (2004) 1106–1120.

[9] F. Endres, Ionic liquids: promising solvents for electrochemistry, Z. Phys. Chem. 218 (2004) 255–283.

[10] J.G. Huddleston, H.D. Willauer, R.P. Swatlosk, A.E. Visser, R.D. Rogers, Room temperature ionic liquids as novel media for 'Clean' liquid–liquid extraction, Chem. Commun. (1998) 1765–1766.

[11] A.G. Fadeev, M.M. Meagher, Opportunities for ionic liquids in recovery of biofuels, Chem. Commun. (2001) 295–296.

[12] A. Soto, A. Arce, M.K. Khoshkbarchi, Partitioning of antibiotics in a two-liquid phase system formed by water and a room temperature ionic liquid, Sep. Purif. Technol. 44 (2005) 242–246.

[13] M. Matsumoto, K.J. Mochiduki, K. Fukunishi, K. Kondo, Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to *Lactobacillus rhamnosus*, Sep. Purif. Technol. 40 (2004) 97–101.

[14] W. Zhao, M. Han, S. Dai, The extraction of polycyclic aromatic hydrocarbons in water using ionic liquid 1-methyl-3-hexylimidazolium hexafluorophosphate, Environ. Chem. (in Chinese) 24 (2005) 467–470.

[15] S.V. Smirnova, I.I. Torocheshnikova, A.A. Formanovsky, I.V. Pletnev, Solvent extraction of amino acids into a room temperature ionic liquid with dicyclohexano-18-crown-6, Anal. Bioanal. Chem. 378 (2004) 1369–1375.

[16] J.J. Wang, Y.C. Pei, Y. Zhao, Z.G. Hu, Recovery of amino acids by imidazolium based ionic liquids from aqueous media, Green. Chem. 7 (2005) 196–202.

[17] R. Vijayaraghavan, N. Vedaraman, M. Surianarayanan, D.R. MacFarlane, Extraction and recovery of azo dyes into an ionic liquid, Talanta 69 (2006) 1059–1062.

[18] A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, P. Wasserscheid, Deep desulfurization of diesel fuel by extraction with ionic liquids, Chem. Commun. (2001) 2494–2495.

[19] S.G. Zhang, Z.C. Zhang, Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature, Green. Chem. 4 (2002) 376–379.

[20] C.Y. He, S.H. Li, H.W. Liu, K. Li, F. Liu, Extraction of testosterone and epitestosterone in human urine using aqueous two-phase systems of ionic liquid and salt, J. Chromatogr. A 1082 (2005) 143–149.

[21] K.S. Khachatryan, S.V. Smirnova, I.I. Torocheshnikova, N.V. Shvedene, A.A. Formanovsky, I.V. Pletnev, Solvent extraction and extraction-voltammetric determination of phenols using room temperature ionic liquid, Anal. Bioanal. Chem. 381 (2005) 464–470.

[22] S. Carda-Broch, A. Berthod, D.W. Armstrong, Solvent properties of the 1-butyI-3-methyiimidazoIium hexafluorophosphate ionic liquid, Anal. Bioanal. Chem. 375 (2003) 191–199.

[23] S. Pandey, Analytical applications of room-temperature ionic liquids: a review of recent efforts, Anal. Chim. Acta 556 (2006) 38–45.

[24] J.L. Anderson, D.W. Armstrong, G. Wei, Ionic liquids in analytical chemistry, Anal. Chem. 78 (2006) 2892–2902.

[25] J.F. Liu, J.Å. Jönsson, G.B. Jiang, Application of ionic liquids in analytical chemistry, Trends Anal. Chem. 24 (2005) 20–26.

[26] G.A. Baker, S.N. Baker, S. Pandey, F.V. Bright, An analytical view of ionic liquids, Analyst 130 (2005) 800–808.

[27] H. Zhao, S.Q. Xia, P.S. Ma, Use of ionic liquids as 'Green' solvents for extractions, J. Chem. Technol. Biotechnol. 80 (2005) 1089–1096.

[28] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, Green. Chem. 3 (2001) 156–164.

[29] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Hydrophobic, highly conductive ambient-temperature molten salts, Inorg. Chem. 35 (1996) 1168–1178.

[30] K. Shimojo, M. Goto, Solvent extraction and stripping of silver Ions in room-temperature ionic liquids containing calixarenes, Anal. Chem. 76 (2004) 5039–5044.

[31] J.D. Holbrey, K.R. Seddon, The phase behavior of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals, J. Chem. Soc. Dalton Trans. (1999) 2133–2140.

[32] J.A. Dean, Lange's Handbook of Chemistry, 14th ed., McGraw-Hill, New York, 1992.

[33] National primary drinking water regulations, U.S. Environmental Protection Agency.

[34] P. Ivashechkin, P.F. Corvini, M. Dohmann, Behavior of endocrine-disrupting chemicals during the treatment of municipal sewage sludge, Water Sci. Technol. 50 (2004) 133–140.

[35] http://ecb.jrc.it/classlab/4899a2_DE_nonylphenol.doc.

[36] H.A. Laitimen, W.E. Harris, Chemical Analysis, second ed., McGraw-Hill, New York, 1975, pp. 41.

[37] C.G. Hanke, N.A. Atamas, R.M. Lynden-bell, Solvation of small molecules in imidazolium ionic liquids: a simulation study, Green. Chem. 4 (2002) 107–111.

[38] H. Tsunekawa, A. Narumi, M. Sano, A. Hiwara, M. Fujita, H. Yokoyama, Solvation and ion association studies of LiBF4-propylenecarbonate and LiBF4-propylenecarbonate-trimethyl phosphate solutions, J. Phys. Chem. B 107 (2003) 10962–10966.

[39] Y. Marcus, Thermodynamics of salvation of ions, J. Chem. Soc. Faraday Trans. 87 (1991) 2995–2999.

[40] H.B. Lee, T.E. Peart, Determination of 4-nonylphenol in effluent and sludge from municipal sewage treatment plants, Anal. Chem. 67 (1995) 1976–1980.