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Dongli Zhang[a][b]; Yuefeng Deng[a]; Ji Chen[a]
[a] State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, P.R. China [b] Graduate School of the Chinese Academy of Sciences, Beijing, P.R. China

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Enrichment of Aromatic Compounds Using Ionic Liquid and Ionic Liquid-Based Aqueous Biphasic Systems

Dongli Zhang,[1,2] Yuefeng Deng,[1] and Ji Chen[1]
[1]*State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, P.R. China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing, P.R. China*

Both hydrophibic [C$_8$mim][PF$_6$] and [C$_4$mim]Cl/(K$_2$CO$_3$, K$_2$HPO$_4$ or K$_3$PO$_4$) aqueous biphasic system (ABS) were employed for the enrichment of aromatic compounds including nitrobenzene, 4-nitrophenol, phenol and aniline from aqueous solutions. In [C$_8$mim][PF$_6$] enrichment system, the distribution ratio (*D*) of nitrobenzene and aniline increase with the increasing of pH values of aqueous phase from 2 to 8, but there is no obvious change for 4-nitrophenol and phenol. And the *D* values of the aromatic compounds decrease with the phase ratio change from 1/5 to 1/30 (IL phase volume/aqueous phase volume). In [C$_4$mim]Cl/(K$_2$CO$_3$, K$_2$HPO$_4$ or K$_3$PO$_4$), the distribution ratio increase with the increasing of the salts concentrations. The distribution ratio order in [C$_8$mim][PF$_6$] and [C$_4$mim]Cl/kosmotropic salt ABS is nitrobenzene $>$ phenol $>$ aniline $>$ 4-nitrophenol. It is expected that these results are promising for the removal of the aromatic compounds from water, especially for sample enrichment in analytical science.

Keywords aqueous biphasic system; aromatic compounds; enrichment; ionic liquids

INTRODUCTION

The preventation of the pollution from aromatic compounds in water is widely studied in the environmental field. There are many investigations dealing with the aromatic compounds in contaminated water, such as adsorption (1–3), reduction-oxidation (4), membrane separation (5,6), biodegradation (7,8), and solvent extraction (9). Although these techniques have potential application value, some disadvantages also should be paid attention to. The adsorption processes are effective but regeneration of spent adsorbents lead to highly expense. Low efficiency and complicated operation processes in the reduction–oxidation and biodegradation cannot be neglected. Volatile organic compounds (VOCs) used in solvent extraction usually lead to environmental pollution. All of these described above are handicaps for practical application. Therefore, it is important and valuable to develop simple and new methods to dispose of the aromatic compounds in water.

Ionic liquids (ILs) are widely recognized as green and potential benign environmental solvents or replacement for conventional VOCs (10–13) for chemical synthesis (14–16), catalysis and extraction processes (17–20), chromatography methods (21), controlled processing of polymer materials (22), and electrochemical applications (23,24). Nowadays, several investigations have been reported to separate and extract organic compounds such as dyes (25,26), organic acids (27), organic contaminants from soils (28), aromatic hydrocarbons from aromatic mixtures (29), small organic molecules (30), opium alkaloids (31), phenols (32) and aromatic amines (33), using ILs or ILs-based aqueous biphasic systems (ABS).

Wang et al. (32) have reported the extraction of phenols using hydrophobic ILs [C$_n$mim][PF$_6$] ($n = 4, 6, 8$), and the results showed that [C$_8$mim][PF$_6$] had the highest distribution ratio. On the basis of this investigation, we employed [C$_8$mim][PF$_6$] to investigate the enrichment of nitrobenzene, 4-nitrophenol, and phenol (Fig. 1). On the other hand, some new extraction systems using ABS by inexpensive hydrophilic ILs with kosmotropic salt-salt were also attractive. We have reported the phase diagram data for several ILs/salt ABS and the results showed that the biphasic regions order of ABS was as follows: [C$_4$mim]Cl $>$ [C$_6$mim]Cl $>$ [C$_8$mim]Cl (34). On the basis of this investigation, [C$_4$mim]Cl/(K$_2$CO$_3$, K$_2$HPO$_4$ or K$_3$PO$_4$) ABS was used in this study for the enrichment of these aromatic compounds. The aim of this study was to develop simple and new enrichment methods based on hydrophobic ILs and hydrophilic ILs-based ABS as new strategies for the enrichment of aromatic compound, which are simple, and environmentally friendly and highly efficient.

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Address correspondence to Ji Chen, State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. Tel.: +86-431-85262646; Fax: +86-431-85262646. E-mail: jchen@ciac.jl.cn

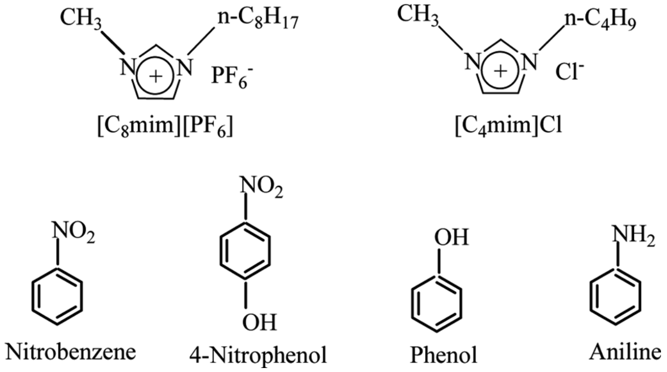


FIG. 1. Chemical structures of ILs and the aromatic compounds.

EXPERIMENTAL

Experimental Material and Apparatus

ILs [C_4mim]Cl and [C_8mim][PF_6] were synthesized, purified and dried in vacuum by previously published methods and characterized by $^1H/^{13}C$ NMR (20,35).

K_2CO_3, K_2HPO_4, K_3PO_4, nitrobenzene, 4-nitrophenol, phenol, and aniline were analytical grade reagents (Beijing Chemical, Beijing, China), and all the solutions were prepared from deionized water.

HPLC system (Waters) equipped with a pump (515 HPLC Pump, Waters), a Duel λ Absorbance Detector (Waters 2487) and a column (SunFire C_{18} analytical column, 250 mm length × 4.6 mm ID: 5 μm particle size) was used for the detection of the target analytes.

Enrichment Procedure

In the hydrophobic enrichment systems of [C_8mim][PF_6], pH effect experiments were carried out by adjusting the pH values of aqueous using HCl and NaOH, and measurement was conducted using a digital pH meter (Shanghai, pHS-3C). Phase ratio experiments were carried out as follows: 1 mL pure [C_8mim][PF_6] was contacted with different volumes aqueous solutions of aromatic compounds from 5 to 30 mL, respectively. The mixtures were vortexed for 10 min and stand for 30 min to reach the equilibrium. The top phase is aqueous phase and the bottom phase is [C_8mim][PF_6] phase. After each extraction, the concentration of the aromatic compounds in the aqueous phase was determined by HPLC-UV at their maximum absorption wavelengths (nitrobenzene, 267.0 nm; 4-nitrophenol, 316.0 nm; phenol, 269.0 nm; aniline, 279.0 nm).

All hydrophilic enrichment systems ABS were made by adding equal volumes of various aqueous solutions of kosmotropic salt (K_3PO_4, K_2HPO_4, or K_2CO_3) to [C_4mim]Cl aqueous solutions (70% w/w) containing nitrobenzene, 4-nitrophenol, phenol, or aniline (1000 μg/mL). The mixtures were vortexed for 10 min and allowed to stand for 30 min to reach the equilibrium. The top phase is [C_4mim]Cl-rich phase and the bottom phase is salt-rich phase. Then the top phases were removed for measurement.

All samples were filtered through a 0.45 μm membrane filter. The analysis was performed using methanol/water solution (60/40, V/V) as mobile phase. The flow rate was 1 mL/min and the volume injected was 5 μL. The relative composition ratio of the aromatic compounds was determined by measuring the relative peak areas of the detector signals.

For the [C_8mim][PF_6] system, D is the concentration ratio of the aromatic compounds between bottom [C_8mim][PF_6] phase to top aqueous phase, and D of the aromatic compounds between [C_8mim][PF_6] phase and aqueous phase is calculated as the following expression

$$D = \frac{(C_{aq,0} - C_{aq}) \times V_{aq}}{C_{aq} \times V_0} \tag{1}$$

where $C_{aq,o}$ and C_{aq} are the concentration of aromatic compounds before and after extraction; and V_{aq} and V_0 are the aqueous and [C_8mim][PF_6] phase volumes, respectively.

While for [C_4mim]Cl/(K_2CO_3, K_2HPO_4 or K_3PO_4) ABS, D is the concentration ratio of aromatic compounds between the top [C_4mim]Cl-rich phase to the bottom salt-rich phase, and D of the aromatic compounds is calculated as the following expression

$$D = \frac{C_{IL} \times V_s}{(C_{IL,0} - C_{IL}) \times V_{IL}} \tag{2}$$

where $C_{IL,0}$ and C_{IL} are the concentration of aromatic compounds before and after extraction; and V_{IL} and V_s are the [C_4mim]Cl-rich phase and salt-rich phase volumes, respectively.

RESULTS AND DISCUSSION

Effect of Phase Volume Ratio

The optimum enrichment phase volume ratio was tested with a series of experiments. Fig. 2 showed the effect of phase ratio values on the distribution ratio of nitrobenzene, phenol, aniline and 4-nitrophenol between [C_8mim][PF_6] and aqueous solutions. The results showed that the phase ratio values had no significant effect on the distribution ratio of the aromatic compounds. The distribution ratio order of the aromatic compounds is as follows: nitrobenzene > 4-nitrophenol > phenol > aniline. To obtain the best extraction efficiency, the phase ratio 1/5 (IL phase/aqueous phase) was selected in all the [C_8mim][PF_6] enrichment experiments.

pH Dependence of the Distribution Ratio D

The pH dependence of the distribution ratio of nitrobenzene, 4-nitrophenol, phenol, and aniline in the

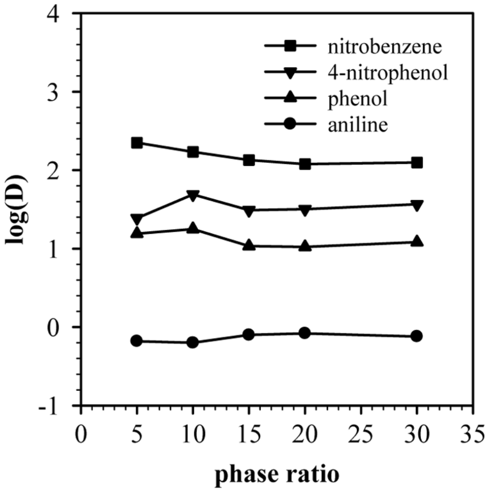


FIG. 2. Effect of phase ratio on the distribution ratios of nitrobenzene, phenol, aniline and 4-nitrophenol between [C_8mim][PF_6] and aqueous solution.

[C_8mim][PF_6] enrichment system is shown in Fig. 3. It shows that the *D* values of nitrobenzene and aniline increase with the increasing of the pH values. But there is no obvious change for 4-nitrophenol and phenol, which is consistent with Wang's results (32). It is known that the p*K*a value of 4-nitrophenol and phenol is 7.15 and 9.95, respectively. Phenol exists in molecular form when pH < p*K*a, then its anionic fraction increases with the increasing of the pH values. Therefore, it seems reasonable to claim that the interactions between [C_8mim][PF_6] and the molecular form of phenols are responsible for the less change of *D* values. In order to simplify the enrichment system, no buffer solution was added to control the pH.

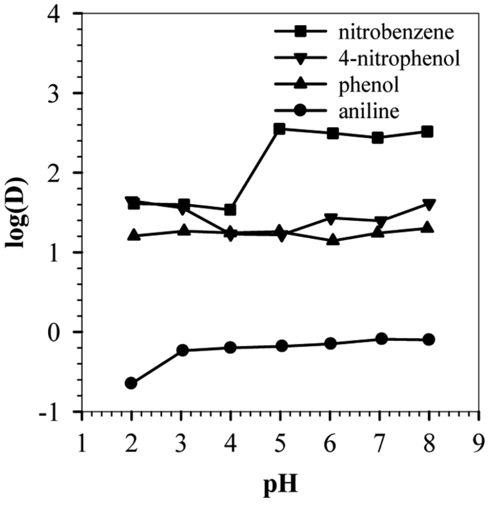


FIG. 3. Effect of pH dependencies of the distribution ratios of nitrobenzene, phenol, aniline and 4-nitrophenol between [C_8mim][PF_6] and aqueous solutions.

The distribution ratio order of the aromatic compounds is also as follows: nitrobenzene > 4-nitrophenol > phenol > aniline.

Effect of Temperature on LogD

The effect of temperature on the distribution ratio *D* was performed at 10, 25, 35, and 45°C under the selected phase ratio 1/5 (IL phase/aqueous phase). The log*D* values of the aromatic compounds decrease with the increasing of the temperature except 4-nitrophenol (shown in Table 1).

The relationships between log*D* and 1/T are shown in Fig. 4.

Then the enthalpy change of reaction, ΔH, could be calculated from the slope of log *D* versus 1/T using Van't Hoff equation given as below:

$$\log D = -\frac{\Delta H}{2.303RT} + C \tag{3}$$

Where *R* is the gas constant and *C* is a constant.

ΔG and ΔS could be calculated by the equations as below:

$$\Delta G = -RT\ln K \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \tag{5}$$

The values of ΔH, ΔG and ΔS are shown in Table 1. It can be seen that all the ΔH values of nitrobenzene, phenol, and aniline are negative. However, the ΔH values of 4-nitrophenol are positive. $\Delta H > 0$ means that the enrichment of nitrobenzene, phenol, and aniline using [C_8mim][PF_6] are exothermic reactions, but of 4-nitrophenol is endothermic reactions. $\Delta G < 0$ indicates the enrichment processes are spontaneous.

Effect of Salts Concentration on ABS

The effect of the amount of salts on the *D* values of nitrobenzene, 4-nitrophenol, phenol, and aniline in ABS was shown in Fig. 5. The D values of the aromatic compounds increased with the increasing of the concentrations of the kosmotropic salts until a single-phase formed when the concentrations of K_2HPO_4, K_2CO_3, and K_3PO_4 exceeded 4.5 mol/L, 4.5 mol/L and 3.5 mol/L, respectively. As reported in our previous paper (34), the biphasic region order of [$C_n$mim]Cl (n = 4, 6, 8)/kosmotropic salt (K_3PO_4, K_2HPO_4, or K_2CO_3) is as follows: [C_4mim]Cl > [C_6mim]Cl > [C_8mim]Cl under the condition of the same given salt and $K_3PO_4 > K_2HPO_4 > K_2CO_3$ under the condition of the same given IL. The stronger the hydration ability of the salt is, the stronger the salting-out effect is (32). The results also showed that the enrichment efficiency of the ABS to the aromatic compounds in the order

TABLE 1
The thermodynamic properties for the aromatic compounds from aqueous to [C_8mim][PF_6]

	Nitrobenzene				4-Nitrophenol			
T (°C)	Log(D)	ΔG (kJ/mol)	ΔH (kJ/mol)	TΔS (KJ/mol · K)	Log(D)	ΔG (kJ/mol)	ΔH (kJ/mol)	TΔS (KJ/mol · K)
15	2.60	−5.96	−30.27	−24.04	1.51	−3.62	12.35	15.97
25	2.55	−6.23		−23.95	1.55	−3.84		16.19
35	2.54	−6.46		−23.75	1.64	−4.19		16.55
45	2.50	−6.74		−23.67	1.74	−4.61		16.96
	Phenol				Aniline			
	Log(D)	ΔG (kJ/mol)	ΔH (kJ/mol)	TΔS (KJ/mol · K)	Log(D)	ΔG (kJ/mol)	ΔH (kJ/mol)	TΔS (KJ/mol · K)
15	1.42	−6.15	−3.23	0.18	−0.01	0.03	−7.99	−8.01
25	1.41	−6.37		0.26	−0.09	0.23		−8.22
35	1.38	−6.58		0.31	−0.13	0.35		−8.33
45	1.37	−6.79		0.39	−0.15	0.39		−8.38

of [C_4mim]Cl/K_3PO_4> [C_4mim]Cl/K_2HPO_4 > [C_4mim]Cl/K_2CO_3 on the same concentration of the salts in our investigation. The three kosmotropic salts (K_3PO_4, K_2HPO_4, and K_2CO_3) used to salting-out [C_4mim]Cl follow the Homeister series. In the salting-out processes, the kosmotropic anions play an important role due to the stronger interaction with water, while the cations have a measurable but much smaller effect on the salting-out strength (36, 37). A single-phase formed in the system of [C_4mim]Cl/K_3PO_4 ABS when the concentration of K_3PO_4 exceed 3.5 mol/L. Therefore, the enrichment efficiency of [C_4mim]Cl/K_2HPO_4 is better than [C_4mim]Cl/K_3PO_4 and [C_4mim]Cl/K_2CO_3. Moreover, the *D* values of the aromatic compounds increase with the increasing of the concentration of the salts. The order is also as follows: nitrobenzene > 4-nitrophenol > phenol > aniline.

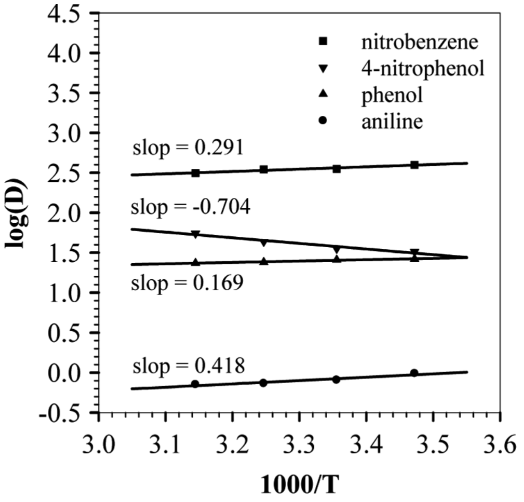
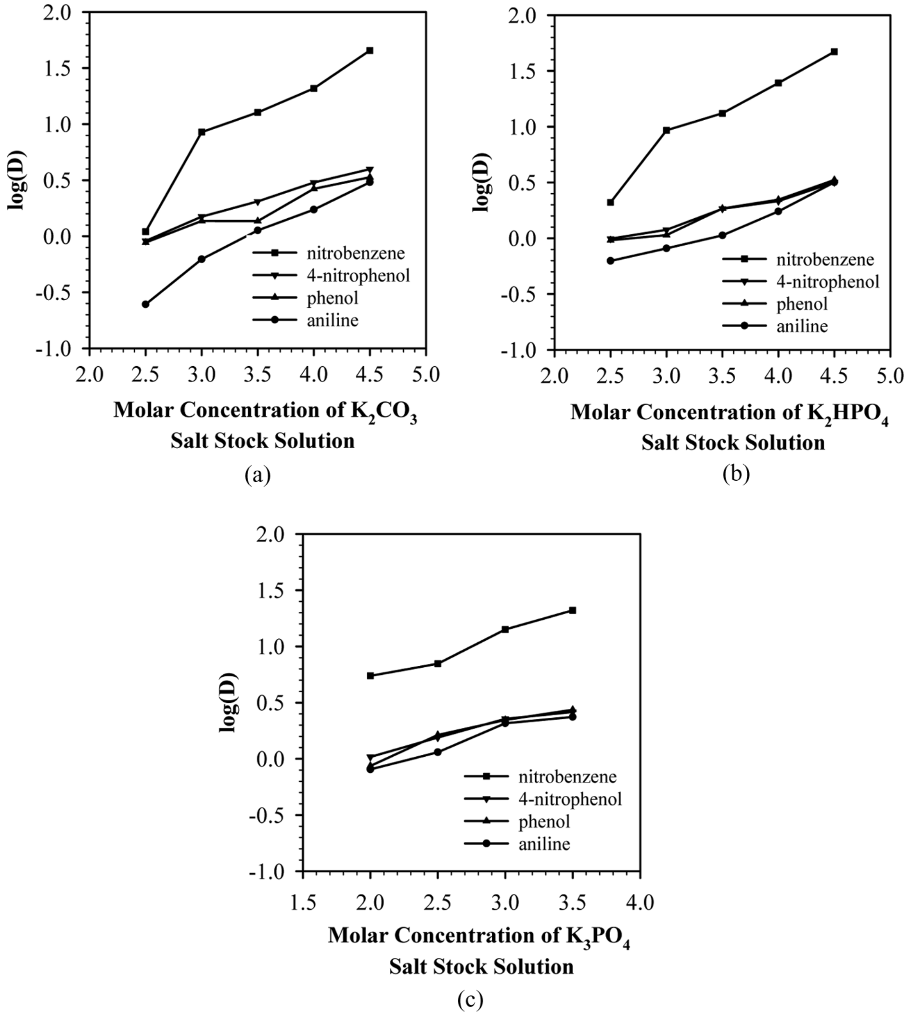


FIG. 4. Relationship between distribution ratio D and temperature in [C_8mim][PF_6] enrichment systems.

Effect of Chemical Structure of Both the Ionic Liquids and the Aromatic Compounds

The structures of both the cation and the anion of the ILs have strong effects on their extractive performances. The hydrophobicities of the ILs increase with the increasing of the length of alkyl chain of the cation. Therefore, the *D* values of a given aromatic compound in [C_8mim][PF_6] enrichment system is relatively higher. Changing the anion from $[PF_6]^-$ to Cl^-, the corresponding imidazole ILs will change from hydrophobic IL to the hydrophilic one. The results show that both of [C_8mim][PF_6] and [C_4mim]Cl/kosmotropic salt ABS could enrich the aromatic compounds efficiently. It is found that hydrogen bonding existed between $[PF_6]^-$ or Cl^- and the functional groups of the aromatic compounds, as well as the C2-H of imidazolium ring forming $H\cdots F$ or $H\cdots Cl$. The specific $\pi-\pi$ interactions existed between imidazolium ring and aromatic ring of the aromatic compounds (38). On the other hand, the ABS formation results in [C_4mim]Cl-rich phase is more lipophilic than the inorganic kosmotropic salt (K_2CO_3, K_2HPO_4 or K_3PO_4)-rich phase, and the aromatic compounds will preferentially partition to the more organic phase.

The structures of the aromatic compounds also have influence on the *D* values. Nitryl is an electron-withdrawing group, which decrease the electron cloud density of benzene ring. However, electrons move from the oxygen atom of –OH to benzene ring due to forming $p-\pi$ conjugated



(a) (b) (c)

FIG. 5. Effect of salts on the distribution ratios of nitrobenzene, phenol, aniline and 4-nitrophenol between [C_4mim]Cl and aqueous solutions. (a) [C_4mim]Cl/K_2CO_3 (b) [C_4mim]Cl/K_2HPO_4 (c) [C_4mim]Cl/K_3PO_4.

system with the benzene ring in the structure of 4-nitrophenol. Therefore, the distribution ratio order is nitrobenzene >4-nitrophenol. For the phenol, the conjugative effect makes the electron cloud average increasing the electron density of the benzene ring. The oxygen atom of –OH moving to the benzene ring will increase the polarity of O-H. Therefore, the hydrogen atom of phenol hydroxyl is more active than alcoholic hydroxyl, and the acidity of 4-nitrophenol increases exceeding phenol, which is consistent with the pK_a value for phenol (9.95) and 4-nitrophenol (7.15). The order of *D* values is 4-nitrophenol > than phenol. In the structure of aniline, amido is a donor group and the pK_a value of aniline is 9.38. The functional group changed from the electron-attraction group nitryl to donor group amido. Therefore, the distribution ratio order is as follows: nitrobenzene > 4-nitrophenol > phenol > aniline, which is consistent with the order distributed in the octanol/water system.

Comparison of Log *D* in Different Systems

The data on the D values of nitrobenzene, 4-nitrophenol, phenol, and aniline are summarized in Table 2 including the system of octanol/water, [C_8mim][PF_6]/H_2O, and [C_4mim]Cl/kosmotropic salt ABS. When the concentration of K_2HPO_4, K_2CO_3 and K_3PO_4 reach to 4.5 mol/L, 4.5 mol/L and 3.5 mol/L, the composition of the ABS are 35% [C_4mim]Cl/37% K_3PO_4, 35% [C_4mim]Cl/39% K_2HPO_4, and 35% [C_4mim]Cl/31% K_2CO_3, respectively. As can be seen, the maximal D values of the aromatic compounds in these systems are different. Although the distribution ratio of the four aromatic compounds in the system of [C_4mim]Cl/kosmotropic salt ABS are inferior to octanol/water and [C_8mim][PF_6], [C_4mim]Cl is hydrophilic and inexpensive. Therefore, the hydrophilic enrichment systems of [C_4mim]Cl/kosmotropic salt ABS may be promising for removal of the aromatic

TABLE 2
Comparison of log*D* for the aromatic compounds in the octanol/water, $[C_8mim][PF_6]$, 35% $[C_4mim]$ Cl/37% K_3PO_4, 35% $[C_4mim]Cl$/39% K_2HPO_4 and 35% $[C_4mim]Cl$/31% K_2CO_3

Aromatic compounds	Log *D*				log P_{OW} (40,41)
	$[C_8mim][PF_6]$	35% $[C_4mim]Cl$/ 37% K_3PO_4	35% $[C_4mim]Cl$/ 39% K_2HPO_4	35% $[C_4mim]Cl$/ 31% K_2CO_3	
Nitrobenzene	2.51	1.32	1.67	1.66	1.85
4-Nitrophenol	1.61	0.42	0.50	0.60	1.9
Phenol	1.30(1.36)[a]	0.44	0.52	0.53	1.5
Aniline	1.16	0.37	0.50	0.48	0.9

[a] Ref. (32).

compounds from water in analytical science. Furthermore, the ILs used in this paper may be recycled by the method of photodegradation reported by Dionysiou et al. (39). However, a detailed study of recycling the ILs needs further investigation.

CONCLUSIONS

Both of hydrophobic and hydrophilic ILs enrichment systems $[C_8mim][PF_6]$ and $[C_4mim]Cl$/kosmotropic salt ABS (K_3PO_4, K_2HPO_4, and K_2CO_3) have been employed to enrich the aromatic compounds nitrobenzene, 4-nitrophenol, phenol, and aniline from water. The *D* values of the aromatic compounds between ILs and aqueous solutions have been reported at different pH values, phase ratio and salts concentrations. It shows that the *D* values of aniline and nitrobenzene increase with the increasing of the pH values, but there is no obvious change for 4-nitrophenol and phenol in the system of $[C_8mim][PF_6]$. In $[C_4mim]Cl$/kosmotropic salt ABS, the *D* values increased with the increasing of the concentration of salts. Therefore, these results will be further evaluated in order to provide the potential basis for environmental application.

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