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ABSTRACT

The present work was aimed at investigating the usefulness of 1-(*n*-alkyl)-3-methylimidazolium-derived ionic liquids (ILs) in liquid–liquid separation processes. For this purpose, a series of 1-(*n*-alkyl)-3-methylimidazolium tetrafluoroborates and hexafluorophosphates were prepared by standard synthetic methods and characterized by ^{1}H NMR. Experiments were performed to assess the influence of the alkyl group and the anion on the physical properties of the IL. Equilibrium studies on the extraction of heavy metal ions (copper, zinc, and chromium) and some common pollutant aromatic compounds (phenol, tyrosol, and *p*-hydroxybenzoic acid) from aqueous media then were performed with

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some selected ILs. The effects of temperature and the pH on the distribution ratio of solutes between the IL/aqueous phases also were analyzed. The results suggest that some of the ionic liquids tested are adequate to extract metal ions and organic compounds from aqueous solutions, with a high efficiency in some instances.

Key Words: Ionic liquid (IL); Liquid–liquid extraction; Organic solutes; Metal ions.

INTRODUCTION

Ionic liquids (ILs) represent a new class of solvents with an ionic character that consist entirely of ions. Usually, the term molten salts is associated with very corrosive and viscous high-temperature solvents. In contrast, room temperature ILs can be fluid at temperatures as low as −96°C, are colorless, easily handled, and capable of dissolving a wide range of organic and inorganic compounds to very high concentrations.[1] The *N*-butylpyridinium cation was the first studied IL example, followed by the system 1-ethyl-3-methylimidazolium. The unsymmetrical nature of the cation is crucial, and the nature of the anion is determinant to the chemical and physical properties of the ILs. The substituent bound to the second nitrogen of methylimidazole (mim) usually is an alkyl group, where by increasing the chain length one can change properties such as viscosity, hydrophobicity, and melting point.[1–3] The inclusion of metal ligating groups also is referenced in recent literature.[4] Several anions can be used (e.g., PF_6^-, BF_4^-, Br^-) that influence the properties of the IL (such as the miscibility with water) and the type of compounds that the liquid is capable of dissolving.

Traditional solvent extraction procedures using volatile organic compounds (VOC) are typical in several industrial processes, from chemical synthesis and pharmaceuticals to hydrometallurgy. The use of toxic, flammable, and volatile solvents, together with the problems related to the disposal of spent extractants and diluents and the costs associated with these processes, have boosted research into the development of safe and environment friendly separation processes. The ILs are one of the alternatives to the use of VOCs because they possess several desirable properties, such as a liquid expanse up to 300°C, good solvent properties for a wide range of materials, low vapor pressures, stability up to 200°C, easy preparation, and relatively low cost. Typical syntheses of some ILs have been described in the literature, by using standard nucleophilic substitution reactions.[5] Regarding the use of ILs in separation processes, Visser et al.[6] have described several possible applications. Furthermore, Huddleston et al.[3,5] have studied the partition of several organic solutes in

IL-water systems. In addition, Cull et al.[7] have published studies regarding the use of ILs in antibiotic production, while Dai et al.[8] and Visser et al.[2] have mentioned the extraction of alkaline and alkaline-earth cations by crown ethers in ILs. The use of ILs in metal catalysis also is referred in the literature.[1] The extraction of Cd and Hg with ILs, where the cation contains components, such as sulfur atoms, that can bind to the metal ions, also has been described by Visser et al.[4] The same group[6,9] has observed that the extraction of metal ions by the IL phase can be improved by changing the hydration environment of the metal, using either organic ligands or inorganic anions. In line with this strategy, Wei et al.[10] have recently reported the use of dithizone as a metal chelator to form neutral metal–dithizone complexes that have high distribution ratios of copper, zinc, lead, and cadmium between the selected IL phase ([C_4-mim][PF_6^-]) and the aqueous phase.

In the present study, we report on the extraction efficiencies of phenolic compounds and some heavy metal ions by 1-(*n*-alkyl)-3-methylimidazolium-derived ILs. For simplicity, the cationic portion of the tested ILs will be designated as [C_n-mim] where *n* represents the length of the *n*-alkyl substituent.

METHODOLOGY

All chemicals used were of analytical grade. The aqueous solutions were prepared with deionized water. The aqueous media consisted of solutions (300 mg dm^{-3}) of phenol, tyrosol, and *p*-hydroxybenzoic acid (PHBA), or salt solutions of copper and zinc (300 mg dm^{-3} as chlorides), with or without sodium chloride or potassium iodide, and hexavalent chromium (300 mg dm^{-3}, added as the oxide). Sodium hydroxide and hydrochloric acid were used for pH adjustments.

1-(*n*-Alkyl)-3-methylimidazolium ILs were synthesized, where the primary alkyl chain length varied from C_6 to C_{10} to modulate the physical properties of ILs. The synthesis methodology was based on standard nucleophilic substitutions, using alkyl chlorides and commercially available 1-methylimidazole.[5] The counter-ions tested were PF_6^- and BF_4^-. Briefly, equimolar amounts of 1-methylimidazole and the appropriate alkyl chloride were allowed to react at 70°C for 48–72 hr. After extraction of unreacted materials with ethyl acetate, the resulting viscous liquid was stirred overnight with an aqueous solution (1–2 mol dm^{-3}) containing an equimolar amount of either sodium tetrafluoroborate or sodium hexafluorophosphate. After addition of methylene chloride to the IL phase, the aqueous phase was decanted and further extracted with methylene chloride (2 × 1 vol). The organic fractions were combined, washed with water to remove residual inorganic materials, and dried over anhydrous sodium sulfate. The resulting ILs were isolated following solvent removal under vacuum. Analyses by using ^{1}H NMR in deuterated acetone were used to characterize the synthesized ILs. In each instance, the number and multiplicity of signals were fully consistent with the expected structures. Furthermore, the chemical shifts of the imidazolium protons, particularly H2, were consistently upfield from the corresponding protons in the 1-(*n*-alkyl)-3-methylimidazolium chloride precursors, which allowed for unequivocal assessment of purity for each of the ILs used in the subsequent studies. Measurements of the density and viscosity of the synthesized ILs were performed at 25°C, after equilibration with water, by using an Anton Paar DMA 5000 density meter and a Brookfield DV-II+ programmable viscometer, respectively. Similarly, the solubilities of the ILs in water were measured after equilibration with water. Karl-Fisher titration and turbidity measurements were used for determination of the solubilities of water in the ILs and of the ILs in water, respectively.

Distribution ratios of solutes were determined by mixing 2 mL of the water-equilibrated IL and 4 mL of the aqueous phase, containing the solute, in an orbital shaker, with temperature control, for at least 12 hr at 22°C. The phases were separated by settling and aqueous phases were analyzed. The organic compounds were analyzed in a Hitachi U2000 double beam ultraviolet/visible spectrophotometer, while heavy metal ions were analyzed by atomic absorption spectroscopy (Perkin Elmer 3100 spectrophotometer). The concentrations of the organic solutes in the aqueous phase were determined by using Beer's law, after testing the analytical method for each compound, namely for potential interference by the IL. Each experiment was carried out, at least in duplicate, and the results agreed to within 5%.

The solute concentrations in the ILs were obtained by mass balance, and the distribution ratios were calculated according to the equation:

$$D = \frac{\text{Solute concentration in the IL}}{\text{Solute concentration in the aqueous phase}} \tag{1}$$

Concerning the stripping experiments, a similar procedure was followed. Thus, 2 mL of the loaded IL was contacted with 4 mL of the stripping solution (NaOH—0.1 or 0.5 mol dm^{-3}; H_2O; HCl—0.5 mol dm^{-3}). The aqueous phases then were analyzed after reextraction.

The loading capacities of the ILs were measured by contacting 2 mL of the IL phase with 4 mL of fresh aqueous phase, consecutively, stage after stage, until equilibrium was attained. After each contact (12 hr in the orbital shaker), the phases were separated, and the aqueous phases were analyzed.

RESULTS AND DISCUSSION

Physical Properties of ILs

The use of a solvent in industrial processes depends on its price and on its physical properties, such as viscosity and density. In fact, it is convenient to have solvents with low viscosities to facilitate mixing and with a large density difference in comparison with the other fluids used in the process to facilitate the phase separation.[3] In view of these considerations, experiments were performed to assess the influence of the alkyl group and the anion on the viscosity, density, solubility of water in the ILs, and solubility of the ILs in water. The results are presented in Table 1.

Table 1 shows that the anion affects the properties of the IL, namely its hydrophobicity. In fact, the BF_4^- salts have lower densities, lower viscosities, and higher water solubility compared with the corresponding PF_6^- salts and, for example, while [C_{10}-mim][BF_4^-] is a liquid, the corresponding PF_6^- salt is a solid at room temperature. Furthermore, increasing the length of the alkyl chain also increases the viscosity and hydrophobicity of the IL. Due to their high miscibility with water, the [C_4–C_6-mim][BF_4^-] liquids were excluded from the subsequent extraction tests.

The tests conducted by using a Brookfield rheometer gave no indication of non-Newtonian behavior of these ILs. As expected, it was noticed that the water content of the IL samples has a strong influence on the viscosity. For instance, in contrast with the value (290 mPa sec) displayed in Table 1, the viscosity of [C_8-mim][PF_6^-] was found to be approximately 2 Pa sec when the measurement was performed soon after the synthesis and the isolation steps. Huddleston et al.[3] have reported higher viscosity values for some of the

Table 1. Physical properties of the tested 1-(*n*-alkyl)-3-methylimidazolium ionic liquids at room temperature.

	n-Alkyl cation	Solubility of H_2O (%)	Solubility in H_2O (%)	$10^{-3}\ \rho^a$ (kg m^{-3})	μ^a (mPa sec)
BF_4^-	C_4–C_5	Soluble	Soluble	—	—
	C_6	High	6.7	—	—
	C_8	5	<0.5	1.084	26.5
	C_{10}	3	<0.5	1.057	59.5
PF_6^-	C_6	0.9	<0.5	1.285	164
	C_8	0.8	<0.5	1.232	290
	C_{10}		Solid		

[a] After equilibration with water at 25°C.

ILs analyzed in the present study, probably due to the different water content of the ILs. Nonetheless, the general variation trend as a function of the alkyl chain length was similar to that shown on Table 1.

The measurement of other properties, such as the surface tension, is currently underway and will be reported elsewhere.

Extraction of Metal Ions from Aqueous Solutions

As expected, due to the hydrated nature of metal ions in aqueous solutions, the results on the extraction of copper and zinc cations from an aqueous phase by the tested ILs were characterized by rather low efficiencies. In fact, the observed distribution ratios between the ILs, [C_8-mim][BF_4^-] and [C_6-mim][PF_6^-], and the aqueous phases varied between 0.11 and 0.15, indicating a large retention of the metal ion in the aqueous phase. The final pH of the aqueous solutions after equilibration with the BF_4^- salt was quite acidic (approximately 3), while extraction with [C_6-mim][PF_6^-] resulted in a slightly acidic aqueous medium (pH $\cong$ 5).

It was anticipated that the partition of anionic species from water to the IL phase would be higher than that of metal cations. Thus, both the effect of the addition of inorganic anions such as chloride and iodide to the solution, to favor the formation of negative complexes of the metal ions, and the extraction of hexavalent chromium were tested. In fact, the dominant Cr(VI) species in aqueous solution at a total chromium concentration below $500\,\mathrm{mg\,dm^{-3}}$ are the oxyanions $HCrO_4^-$ and CrO_4^{2-}. At low pH (pH < 6), $HCrO_4^-$ is the dominant species, while CrO_4^{2-} predominates at higher pH. The dichromate ion, $Cr_2O_7^{2-}$, is the dominant species in acidic environments at Cr(VI) concentrations higher than $500\,\mathrm{mg\,dm^{-3}}$.[11,12]

The distribution ratio of hexavalent chromium between [C_6-mim][PF_6^-] and an acidic aqueous solution (pH $= 2.3 \pm 0.3$) was found to be 0.45, while a ratio of 19 was achieved with [C_8-mim][BF_4^-]. It is known that the transfer of an ion to a hydrophobic phase first involves the release from its hydration shell, which requires the investment of work corresponding to $-\Delta G_{\mathrm{hyd}}$. Thus, ions with low values of $-\Delta G_{\mathrm{hyd}}$ are more hydrophobic and more easily extracted to the IL phase. Since, for ions with the same charge, the values of $-\Delta G_{\mathrm{hyd}}$ vary with the reciprocal of the ionic radius,[13] PF_6^- should have a value of $-\Delta G_{\mathrm{hyd}}$ lower than that of BF_4^-. If the extraction occurs via an ion exchange process with the IL anion, it is expected that the partitioning of any of the negative chromium complexes to the IL phase should be higher with BF_4 than with PF_6 ILs, a prediction consistent with our observations.

On the other hand, the results from the extraction of Cr(VI) with the ILs containing BF_4^- were not affected by an increase in the pH of the initial aqueous solution from 2.3 to 9, while the PF_6^- liquids did not extract hexavalent chromium at pH 9. As reported below for the extraction of organic solutes, the equilibrium pH reached upon extraction is one of the major differences found between the behavior of BF_4^- and PF_6^- salts. Thus, while the equilibrium pH was lower than 3.3 when using the BF_4^- ILs, even for an initial pH of 9, with the PF_6^- ILs the equilibrium pH increased from 2.5 to 7.3 when the initial pH of the aqueous solution augmented from 2 to 9. As previously mentioned, at pH 7, the main Cr(VI) species is CrO_4^{2-}, which may be less extractable by the ILs than $HCrO_4^-$. This IL behavior is similar to that reported for quaternary ammonium salts, which only exhibit extraction abilities toward monovalent oxyanions.[14]

It should be emphasized that the extraction ratios obtained for hexavalent chromium ions with PF_6^- salts appear to be one order of magnitude higher than those published by Visser et al.[9] for Cd^{2+}, Na^+, Co^{2+}, and Fe^{3+}, and similar to those reported for the bulkier mercury ion.

Table 2 presents the results on the extraction of copper and zinc ions from solutions with added sodium chloride or potassium iodide. It is known that zinc is a stronger chloride acceptor than copper. As an example, in chloride rich solutions (3 mol dm^{-3} NaCl) zinc is mainly found as $ZnCl_4^{2-}$, while copper is distributed between the species Cu^{2+}, $CuCl^+$, and $CuCl_2$.[15,16] This difference explains why zinc extraction by [C_6-mim][PF_6^-] is highly affected by the addition of sodium chloride to the initial solution, whereas, the effect on copper extraction is marginal (Table 2). In fact, even in a solution of 4.5 mol dm^{-3}

Table 2. Effect of halide ions on copper and zinc extraction.

Metal	Ionic liquid	[NaCl] (mol dm^{-3})	Extraction (%)	[KI] (mol dm^{-3})	Extraction (%)
Zn	[C_8-mim][BF_4^-]	0.5	37.3	0.5	*
		1	83.0	—	—
		3	99.0	—	—
		4.5	98.8	—	—
	[C_6-mim][PF_6^-]	0	3.5	—	—
		0.5	8.0	0.5	10.0
		1	8.5	1	65.3
		3	47.7	3	—
		4.5	64.7	4.5	*
Cu	[C_6-mim][PF_6^-]	0	0.5	—	—
		3	2.1	—	—
		4.5	5.8	—	—

Note: "*" indicates presence of a third phase.

NaCl, only a small fraction of the total copper is in the extractable anionic form. Thus, copper extraction only increased from 0.5% to 6% when the sodium chloride concentration augmented from 0 to 4.5 mol dm^{-3}. On the contrary, the same increase in the sodium chloride concentration induced an increase in the efficiency of zinc extraction from a vestigial value to 65%, when using the same IL (Table 2). These results corroborate the previous statement that anionic species should be easily extracted by the IL phase.

To test the effect of the size of the halide anion on zinc extraction, several tests were carried out in the presence of iodide. As the size of the complex anions increases and $-\Delta G_{\mathrm{hyd}}$ decreases [347 and 283 kJ mol^{-1} for Cl$^-$ and I$^-$, respectively[13]], their extraction to a hydrophobic phase is expected to increase.[9] In fact, Table 2 shows that the presence of 1 mol dm^{-3} of iodide ion greatly increased the extraction of zinc with [C_6-mim][PF_6^-]. Thus, whereas zinc extraction from solutions containing a chloride concentration in the range of 0.5–1 mol dm^{-3} was lower than 10%, it rose up to 65% for a 1 mol dm^{-3} iodide ion solution. For a 4.5 mol dm^{-3} iodide solution, the presence of a third phase was detected after extraction with [C_6-mim][PF_6^-], which prevented reliable measurements. This problem also occurred with [C_8-mim][BF_4^-], even with a 0.5 mol dm^{-3} iodide solution.

Similar to what is presented below for the organic compounds tested, the results in Table 2 suggest that ILs containing the BF_4^- anion may be more efficient in the removal of zinc from aqueous solutions than those containing PF_6^-. In this context, the removal of zinc from an aqueous solution containing 3 mol dm^{-3} of NaCl was almost complete (99%, Table 2) when the IL was [C_8-mim][BF_4^-], which is a remarkable result. Binary solute extractions of zinc and copper also were tested. The extraction efficiency was approximately the same for each metal regardless of the solute being fed as a mixture or as a single component.

Extraction of Phenolic Compounds

Loading Capacity

To assess the loading capacity of the ILs for phenolic compounds, the IL phases were contacted with an aqueous solution containing 5 g dm^{-3} of PHBA, following the procedure described in the experimental section. Figure 1 shows the results obtained for several ILs. The results show that PF_6^- salts have a maximum capacity of 10 g dm^{-3} of PHBA after four contacts, while the BF_4^- salts did not attain their maximum capacity after six contacts. In fact, an extraction of 69% of PHBA from a 5 g dm^{-3} solution was obtained after six contacts with the [C_8-mim] [BF_4^-] ILs (not shown).

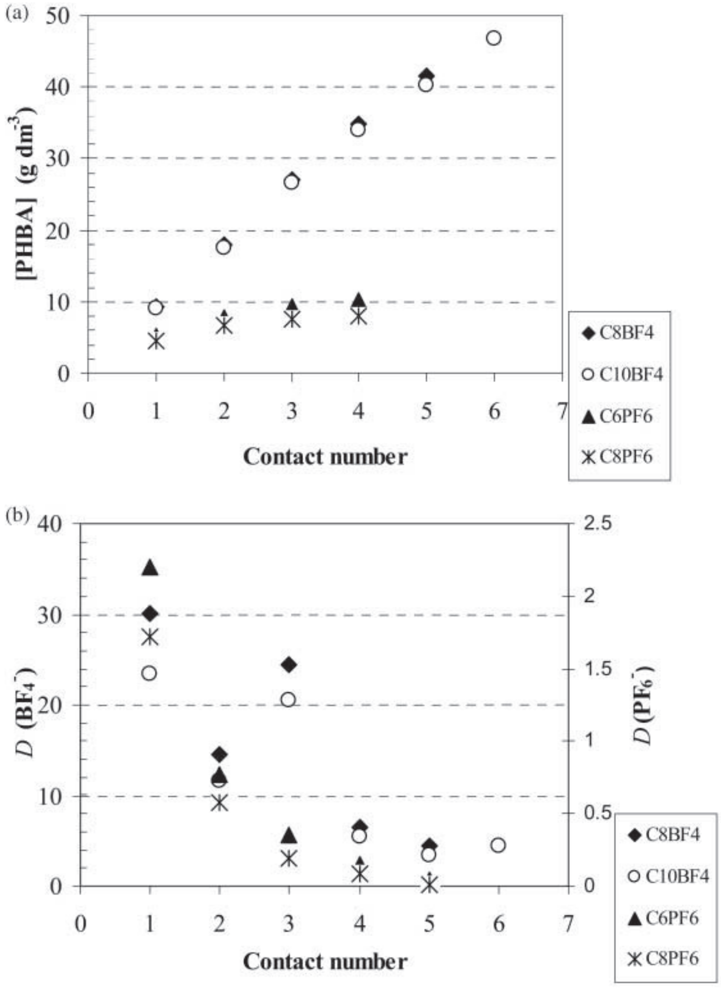

Figure 1. Cumulative concentration and distribution ratios of PHBA in [C_8-mim][BF_4^-], [C_{10}-mim][BF_4^-], [C_6-mim][PF_6^-], and [C_8-mim][PF_6^-].

Effect of Temperature

The effect of temperature on the extraction efficiency of phenolic compounds by ILs was tested within the range of 15–40°C, by using both [C_8-mim][BF_4^-] and [C_8-mim][PF_6^-]. No significant effects were observed with any of the phenolic compounds tested.

Effect of pH

Table 3 shows the initial and final pH of the aqueous solutions, and the percentage of extraction of several phenolic compounds with 1-octanol, [C_8-mim][BF_4^-], [C_{10}-mim][BF_4^-], [C_6-mim][PF_6^-], and [C_8-mim][PF_6^-], while Figs. 2 and 3 show the distribution data.

As follows from Table 3 and Fig. 2, the extraction values and the distribution ratios in the 1-octanol–water system are similar to the corresponding values for the BF_4 IL–water system. Thus, there is a close relationship between the two systems concerning their solubility parameters. The distribution ratios of the PF_6 IL–water system are about one order of magnitude lower than the corresponding 1-octanol–water system (Figs. 2 and 3) as found by Huddleston et al.[3,5] for other organic solutes. Since the PF_6 ILs might be expected to have higher hydrophobicity than their BF_4 counterparts

Table 3. Effect of the pH on the extraction of phenolic compounds.

Phase	Organic compound	Initial pH	Final pH[a]	Extraction[a] (%)
1-Octanol	PHBA	3.7	4.4	91
	Tyrosol	6.2	5.4	68
	Phenol	6.6	6.2	95
BF_4^-	PHBA	2.5	2.3/2.2	93/91
		3.7	3.3/3.8	92/92
		9.2	3.0/3.0	94/92
C_8/C_{10}	Tyrosol	2.3	1.9/2.0	79/81
		6.2	3.1/3.6	76/74
		9.1	2.2/2.2	78/80
	Phenol	2.7	2.3/—	95/—
		6.6	2.1/2.1	95/96
		9.1	2.4/2.6	95/91
PF_6^-	PHBA	2.5	2.5/2.4	51/45
		3.7	3.9/4.2	51/43
		9.2	7.5/8.7	7.4/1.0
C_6/C_8	Tyrosol	2.3	2.4/2.4	46/40
		6.2	4.8/6.0	40/42
		9.1	5.3/7.3	45/52
	Phenol	2.7	2.5/2.8	99/87
		6.6	3.7/6.0	90/85
		9.1	5.8/9.2	89/69

[a] The first figure in these columns corresponds to the first IL presented in the phase column and the second figure corresponds to the second IL.

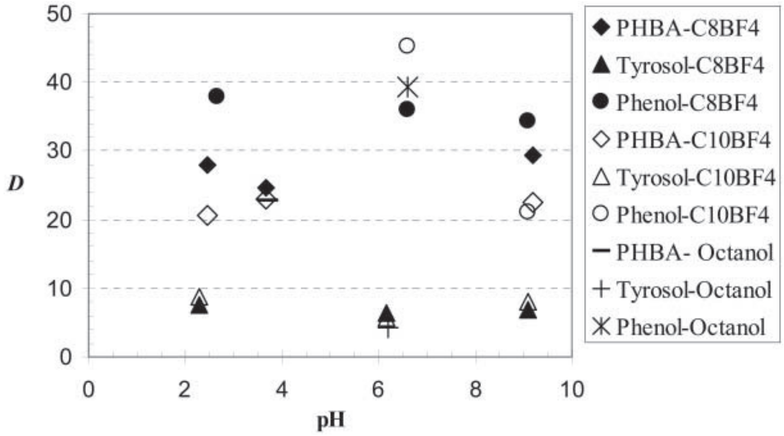

Figure 2. Effect of the initial pH on the distribution ratios in 1-octanol, [C_8-mim][BF_4^-], and [C_{10}-mim][BF_4^-].

because of the relative anion dimensions and polarizabilities, further studies are needed to rationalize the lower extraction efficiencies of the PF_6 ILs.

The results indicate that ILs containing the BF_4^- anion are very efficient in removing phenolic compounds from an aqueous phase, as evidenced by the high distribution ratios generally obtained. In fact, more than 90% of PHBA and phenol are removed from 300 mg dm^{-3} solutions, while this value

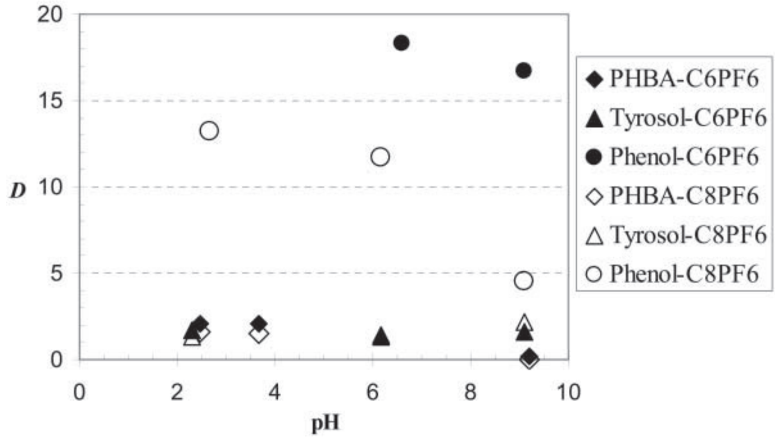

Figure 3. Effect of the initial pH on the distribution ratios in [C_6-mim][PF_6^-] and [C_8-mim][PF_6^-].

decreases to slightly less than 80% for tyrosol. It is to be noticed that the pH of the initial aqueous solution generally does not appear to have any significant influence on the extraction results. The efficiencies of the corresponding extractions of PHBA and tyrosol with PF_6^- ILs are significantly lower than those of the corresponding BF_4^- ILs. Furthermore, a very marked reduction of the efficiency of removal of PHBA by PF_6^- ILs was observed for the most alkaline initial aqueous solutions used. The fact that the extraction of PHBA is pH-dependent presumably reflects the contribution of the ionized form ($pK_{a1} = 4.5$; $pK_{a2} = 9.3$) in basic media. By contrast, both tyrosol and phenol ($pK_a = 10$) are weaker acids, and their ionization states should not be changed within the tested pH range.

Another interesting difference between the behavior of BF_4^- and PF_6^- ILs is the equilibrium pH obtained (Table 3). Thus, while with the BF_4^- ILs the equilibrium pH was consistently between 2 and 3, even for an initial pH of 9, with the PF_6^- ILs, the corresponding equilibrium pH was higher, particularly when starting from pH 9. To investigate if this decrease in pH is due to the extraction procedure, a test was conducted by contacting deionized water, as well as deionized water containing sodium hydroxide (pH 8–9) with two representative BF_4^- and PF_6^- ILs. The results presented in Table 4 show that, even without any extractable solute in the aqueous phase, there is an increase in the H^+ concentration in the aqueous phase during the contact. This decrease in pH may be due to partial hydrolysis of the anion within the IL solubilized in the aqueous phase upon contact. Due to the solubilization of the IL, it must be possible to detect the PF_6^- and BF_4^- anions in the aqueous phase after extraction. To investigate this possibility, some of the aqueous phases were analyzed by ion chromatography against standards of $NaPF_6$ and $NaBF_4$. The results of these qualitative analyses show that the chromatograms of the standards display a single peak coeluting with the fluoride anion. This peak also is present in the ion chromatograms of aqueous solutions after extraction with $[C_8\text{-mim}][BF_4^-]$. Furthermore, the analysis of phosphorus and boron in solution by inductively coupled plasma showed the presence of these species both in the washing waters of the ILs and in the aqueous phases after

Table 4. Initial and final pH after equilibration with water.

Ionic liquid	Initial pH/final pH
$[C_8\text{-mim}][BF_4^-]$	5.7/2.2
	8.3/2.3
$[C_6\text{-mim}][PF_6^-]$	5.7/4.2
	8.3/7.6

extraction. Nonetheless, some of the reasons underlying the different observed behaviors as a function of pH have yet to be clarified.

Stripping of the IL phase

Table 5 displays representative stripping results obtained for PHBA and shows that reextraction of this solute to the aqueous phase is easily performed, although the behavior of the PF_6^- and BF_4^- ILs tested is, once again, quite different. In fact, PHBA is completely removed from the PF_6^- IL phase with 0.1 mol dm^{-3} NaOH and approximately 61% is removed with water. However, complete stripping of the same solute from the BF_4^- IL phases typically requires a higher NaOH concentration (0.5 mol dm^{-3}).

The potential reuse of the PF_6^- and BF_4^- ILs was investigated by performing consecutive contacts (extraction/stripping) using PHBA and [C_8-mim][BF_4^-] or [C_6-mim][PF_6^-]. To increase the sensitivity, these experiments were conducted with the IL phase diluted in dichloromethane (1IL : 3CH_2Cl_2 and 1IL : 10 CH_2Cl_2, vol : vol). The results showed that the capacity of the ILs toward PHBA did not change after three extraction/stripping stages.

CONCLUSIONS

Both the anion and the length of the *n*-alkyl chain of the IL affect its physical properties. The results obtained in this study allowed the selection of the [C_{8-10}-mim][BF_4^-] and [C_{6-8}-mim][PF_6^-] ILs for extraction experiments.

The removal of Cu^{2+} and Zn^{2+} from dilute aqueous solutions was found to be very inefficient. However, both the extraction of zinc from

Table 5. Stripping of *p*-hydroxybenzoic acid from the IL phase.

Ionic liquid	Loaded IL PHBA (g dm^{-3})	Stripping phase	Stripping (%)
[C_8-mim][BF_4^-]	9.23	NaOH—0.5 mol dm^{-3}	99.0
	9.24	NaOH—0.1 mol dm^{-3}	76.2
	9.24	H_2O	6.1
[C_{10}-mim][BF_4^-]	9.07	HCl—0.5 mol dm^{-3}	6.8
[C_6-mim][PF_6^-]	5.16	NaOH—0.5 mol dm^{-3}	100
[C_8-mim][PF_6^-]	4.24	NaOH—0.5 mol dm^{-3}	100
	4.23	NaOH—0.1 mol dm^{-3}	100
	4.50	H_2O	60.7
	4.55	HCl—0.5 mol dm^{-3}	50.2

chloride-containing media and the extraction of Cr(VI) appear very promising, namely with BF_4^- ILs. This is in full agreement with the prediction of higher distribution ratios for metals in anionic forms. Concerning the phenolic compounds studied, high extraction efficiencies were attained with BF_4^- ILs. The corresponding values with PF_6^- ILs were in some instances about 50% lower.

The extractions of tyrosol and phenol were not affected by a change in the initial pH from 2 to 9. Regarding PHBA, however, the extraction efficiency was significantly lower at pH 9, when $[C_{6-8}\text{-mim}][PF_6^-]$ ILs were used. This fact may be due to the pH influence on the extent of PHBA ionization.

Further research is necessary to rationalize the extraction efficiencies of solutes with BF_4^- and PF_6^- ILs.

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