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ARTICLE TYPE

Functionalized phosphonium based ionic liquids: properties and application in metal extraction

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The extraction of Cu(II), Zn(II), Co(II), Ni(II) and Pb(II) from model aqueous solutions using phosphonium based ionic liquids as sole extraction agents has been explored. The hydrophobic trioctyl(4-vinylbenzyl) phosphonium chloride, $[P_{888(4\text{-}VB)}]Cl$, allows almost complete removal of Pb(II), Cu(II), Zn(II) without addition of HCl, while the extraction of Co(II) and Ni(II) was almost null. An efficient extraction (*ca.*100%) of Pb(II), Cu(II) and Zn(II) was obtained using $[P_{888(4\text{-}VB)}][NO_2]$.

Introduction

Phosphonium salts constitute an important sub-class of ionic liquids (ILs) which are known to have important properties, sometimes superior in comparison with those of the widely investigated nitrogen-based ILs, in particular dialkylimidazolium salts. Tetraalkylphosphonium ILs generally present greater inertness under basic conditions[1] and increased thermal and electrochemical stabilities.[2] Their potential applications include the use as electrolytes for batteries and dye-sensitized solar cells, as corrosion inhibitors, lubricants, reaction media and extraction agents. However, this class of ILs has been less systematically studied than nitrogen-based ILs and some detailed studies about the physicochemical and thermal properties of tetralkylphosphonium chlorides have been only recently published.[3]

The principal drawbacks limiting their use are the high viscosity and the physical state (solid) at room temperature. However, analogously with nitrogen based ILs, a careful selection of anion and substituents on cation can minimize these problems. For example, it has been shown[4] that trialkyl benzyl phosphonium cations combined with bis(trifluoromethanesulfonyl)imide anion can effort low-melting salts with high thermal stability and conductivity. On the other hand, hydrophobic and polar ILs, exhibiting stable phase separation and high hydrogen bonding ability after mixing with water, have been obtained coupling tetraalkylphosphonium cations (in particular, tetra-*n*-hexylphosphonium and tri-*n*-hexyl-*n*-octylphosphonium) with ethylphosphonate anion.[5] It is noteworthy that phosphonium cations can give hydrophobic ILs also when two hydroxyl groups are introduced on the alkyl chains: trioctyl(2,3-dihydroxypropyl)phosphonium chloride is only partially soluble in water and the analogous bis(trifluoromethanesulfonyl)imide salt is completely insoluble.[6]

It has been previously suggested[6] that the ability of these hydrophobic dihydroxyl functionalized ILs to complex metals might be exploited not only in catalysis but also for other peculiar applications, such as extraction of metals and water remediation from industrial wastes and effluents. Liquid-liquid extraction is one of the most important techniques employed for metal ion separation. The possibility to operate in continuous mode, using relatively simple equipment and employing only small amounts of the reagents are surely some of the advantages.[7] The principal drawback of classical liquid-liquid extraction[8] is however the use of flammable, volatile or toxic water-immiscible solvents. The employ of ILs as water-immiscible extractants has been considered as an important alternative approach to improve the sustainability of the process.[9] However, as stated by Binnemans *et al.*,[7] the application of ILs as solvents for the extraction of metal ions has only partially met the high expectations. Due to the high hydrophilicity of hydrated metal ions often other extractants have to be added. Moreover, extraction of metal ions from water solution to IL generally occur *via* an ion exchange mechanism: thus, IL cations are lost during extraction of a metal ion with a neutral extractant, whereas ILs anions are lost when anionic metal complexes are extracted.[10] Finally, problems can arise for the application of ILs in water recovery if a significant dissolution of the IL in the aqueous phase occurs during the extraction process. Although these losses can be reduced modifying the IL's structure through the introduction of long alkyl or fluorinated chains, thus increasing IL hydrophobicity, the same structural alterations often have negative effects on extraction efficiency. Unfortunately, hydrophobic ILs generally contain fluorinated anions which can release HF after prolonged contact with water (in particular, $[BF_4]^-$ and $[PF_6]^-$) or are quite expensive. Phosphonium salts are actually an exception: they give hydrophobic salts also with the hydrophilic, not expensive and ecofriendly chloride as counteranion. Tetralkylphosphonium chlorides in toluene or kerosene have been used in extraction of metal ions (from aqueous solutions).[11] More recently, they are been used as undiluted solvents for separation of nickel by cobalt from 8M HCl aqueous solutions.[7]

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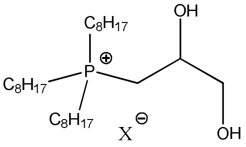
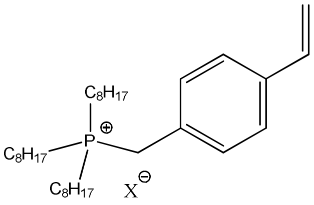
Considering the potential binding ability of the *vic*-diol moiety towards metal cations, we decided to investigate the possibility to apply trioctyl(2,3-dihydroxypropyl)phosphonium salts with chloride, hexafluorophosphate, bis(trifluoromethanesulfonyl)imide and nitrite counteranion (**1**) in the extraction of several common heavy metal pollutants (Cu(II), Zn(II), Ni(II) and Pb(II)) and Co(II) from water, avoiding the addition of HCl to the aqueous phase.

The extraction efficiency of these ILs was furthermore compared with that of another class of hydrophobic phosphonium salts based on trioctyl(4-vinylbenzyl) phosphonium cation (**2**). The polymerizable nature of the vinyl group might be useful to develop immobilized ILs for metal separation from water.



1, $[P_{8,8,8(gly)}]X$



2, $[P_{8,8,8(4\text{-}VB)}]X$

$X^- = Cl^-, PF_6^-, BF_4^-, NO_2^-, Tf_2N^-$

The main physicochemical (viscosity, conductivity and polarity) properties of these phosphonium salts were determined. The effect of IL structure on metal extraction was evaluated determining extraction percentages by ICP-MS.

Experimental

NMR spectra were recorded at room temperature using a Bruker instrument at 250 MHz (^1H) and 75.7 MHz (^{13}C), in DMSO-d$_6$, $CDCl_3$ or D_2O. ICP-MS analyses were carried out using Agilent 7500 ce instrument.

Trioctyl(2,3-dihydroxypropyl)phosphonium chloride, $[P_{8,8,8(gly)}]Cl$, hexafluorophosphate, $[P_{8,8,8(gly)}][PF_6]$ and bis(trifluromethanesulfonyl)imide, $[P_{8,8,8(gly)}][Tf_2N]$ were prepared as previously reported.[6] $CuCl_2{\cdot}2H_2O$ (>99.0%), $ZnCl_2$ (>98%), $NiCl_2{\cdot}6H_2O$ (> 99.9 %), $CoCl_2{\cdot}6H_2O$ (>98%), $ZnCl_2$ (>98%) were purchased from Aldrich.

Trioctyl(2,3-dihydroxypropyl)phosphonium nitrite, $[P_{8,8,8(gly)}][NO_2]$

To a solution of trioctyl(2,3-dihydroxypropyl)phosphonium chloride, $[P_{8,8,8(gly)}]Cl$, (16 g, 33 mmol) in acetonitrile (10 ml) an equimolar amount of $AgNO_2$ (yellow solid, freshly prepared from $AgNO_3$ and $NaNO_2$ in water) was added. The mixture was stirred at room temperature for 24h, then the precipitate was filtered off and the resulting aqueous solution was evaporated at reduced pressure. The residue liquid was dissolved in anhydrous acetone and the solution was cooled at -40°C for 48 h. After filtration on glass septa (porosity 4) containing two different powdered layers of 1 cm each of celite (lower layer) and decolorizing carbon (upper layer), the solvent was removed at reduced pressure. The isolated IL was dried under vacuum (2x10^{-3} mm Hg, 80°C, 6h) and analyzed by NMR.

^1H NMR (DMSO-d$_6$, δ ppm): 6.00 (s, 1H, OH), 5.23 (s, 1H, OH), 3.90 (m, 1H, $C\underline{H}OH$), 3.38 (m, 2H, $C\underline{H_2}OH$), 2.41 (m, 8H, P^+CH_2), 1.25 (m, 36H, CH_2), 0.86 (m, 9H, CH_3); ^{13}C NMR (DMSO-d$_6$, δ ppm): 66.6 (m, CH_2OH, CHOH), 31.3, 30.2 (d, J = 15 Hz), 28.4, 28.2, 23.3 (d, J = 47 Hz, $P^+\underline{C}H_2CH(OH)CH_2OH$), 22.5, 21.2 (d, J = 4.5 Hz), 19.1 (d, 47Hz $P^+\underline{C}H_2CH_2CH_2CH_2$–), 14.2.

Trioctyl(4-vinylbenzyl)phosphonium chloride, $[P_{8,8,8(4\text{-}VB)}]Cl$

Under an argon atmosphere, trioctylphosphine (16,7 g, 45 mmol) was added to a solution of 1-(chloromethyl)-4-vinylbenzene (6,87 g, 45 mmol) in toluene (20 ml), previously accurately deareated and containing a small amount of 2,6-di-*tert*-butyl-4-methylphenol as radical inhibitor. The resulting mixture was stirred for 48 h at room temperature, then the solvent was removed at reduced pressure and the resulting white solid (99% yield) was washed with ethyl acetate, dried under vacuum and analyzed by NMR. The ^1H NMR spectrum exactly matched literature data.[12]

^1H NMR ($CDCl_3$, δ ppm): 7.32 (m, 2H, aromatic CH), 7.18 (m, 2H, aromatic CH), 6.65 (dd, J = 17, 11 Hz, 1H, CH=), 5.70 (d, J = 17 Hz, 1H, =CH_2), 5.25 (d, J = 11 Hz, 1H, =CH_2), 4.30 (d, J = 15 Hz, 2H, P^+CH_2Ph), 2.33 (m, 6H, P^+CH_2Ph), 1.18 (m, 36H, CH_2), 0.83 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 137.6, 135.9, 130.4, 129.0, 128.2, 127.1, 114.9, 31.7, 30.9 (d, J = 15 Hz), 28.4, 28.2, 26.5 (d, J = 47.5 Hz, $P^+\underline{C}H_2Ph$), 22.6, (d, J = 4.5 Hz), 19.1 (d, 47 Hz, $P^+\underline{C}H_2CH_2CH_2CH_2$), 14.2.

Trioctyl(4-vinylbenzyl)phosphonium hexafluorophosphate, $[P_{8,8,8(4\text{-}VB)}][PF_6]$

To a solution of $[P_{8,8,8(4\text{-}VB)}]Cl$ (12 g, 23 mmol) in water-ethanol (2:1, 20 ml) HPF_6 (2.23 ml, 25 mmol) was added and the resulting reaction mixture was stirred at room temperature for 24 h. The resulting biphasic system was separated and the non-aqueous phase was diluted with dichloromethane and repeatedly washed with water (3 x 10 ml). The organic phase was dried ($MgSO_4$) and concentrated at reduced pressure to give 13.8 g of $[P_{8,8,8(4\text{-}VB)}][PF_6]$ as a colourless liquid.

^1H NMR ($CDCl_3$, δ ppm): 7.38 (m, 2H, aromatic CH), 7.26 (m, 2H, aromatic CH), 6.65 (dd, J = 17, 11 Hz, 1H, CH=), 5.70 (d, J = 17 Hz, 1H, =CH_2), 5.30 (d, J = 11 Hz, 1H, =CH_2), 3.80 (d, J = 15 Hz, 2H, P^+CH_2Ph), 2.13 (m, 6H, P^+CH_2Ph), 1.23 (m, 36H, CH_2), 0.87 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 137.6, 135.9, 130.4, 129.0, 128.2, 127.1, 114.9, 31.7, 30.9 (d, J = 15 Hz), 28.4, 28.2, 26.5 (d, J = 47.5 Hz, $P^+\underline{C}H_2Ph$), 22.6, (d, J = 4.5 Hz), 19.1 (d, 47 Hz, $P^+\underline{C}H_2CH_2CH_2CH_2$), 14.2.

Trioctyl(4-vinylbenzyl)phosphonium bis(trifluoromethane)sulfonimide, $[P_{8,8,8(4\text{-}VB)}][Tf_2N]$

A round bottom flask was charged with $[P_{8,8,8(4\text{-}VB)}]Cl$ (12.00 g, 23 mmol) and a mixture of ethanol and water (2 : 1) (20.0 mL) then $Li(Tf_2N)$ (7.1 g, 25.2 mmol) was added in one portion under stirring. The resulting reaction mixture was stirred at 60 °C

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for18h and diluted with CH_2Cl_2 and water. The organic phase was repeatedly washed with water (3 x10 ml), concentrated at reduced pressure and dried at 70 °C for 18 h under high vacuum to give 16.7 g (95%) of $[P_{8,8,8(4\text{-}VB)}][Tf_2N]$ as a colorless liquid. The ^1H NMR spectrum exactly matched literature data.[11]

^1H NMR ($CDCl_3$, δ ppm): 7.41 (m, 2H, aromatic CH), 7.21 (m, 2H, aromatic CH), 6.65 (dd, J = 17, 12 Hz, 1H, CH=), 5.70 (d, J = 17 Hz, 1H, =CH_2), 5.30 (d, J = 12 Hz, 1H, =CH_2), 3.60 (d, J = 14 Hz, 2H, P^+CH_2Ph), 2.06 (m, 6H, P^+CH_2Ph), 1.23 (m, 36H, CH_2), 0.87 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 137.6, 135.9, 129.2, 129.0, 128.2, 127.1, 114.9, 31.7, 30.9 (d, *J* = 15 Hz), 28.9, 28.7, 26.5 (d, *J* = 47.5 Hz, $P^+\underline{C}H_2Ph$), 22.6, (d, *J* = 4.5 Hz), 19.1 (d, 47 Hz, $P^+\underline{C}H_2CH_2CH_2CH_2$), 14.2.

Trioctyl(4-vinylbenzyl)phosphonium nitrite, $[P_{8,8,8(4\text{-}VB)}][NO_2]$

To a solution of trioctyl(4-vinylbenzyl)phosphonium chloride, $[P_{8,8,8(4\text{-}VB)}]Cl$, (16 g, 30.6 mmol) in acetonitrile (10 ml) an equimolar amount of $AgNO_2$ (yellow solid, freshly prepared from $AgNO_3$ and $NaNO_2$ in water) was added. The mixture was stirred at room temperature for 24h, then the precipitate was filtered off and the resulting aqueous solution was evaporated at reduced pressure. The residue liquid was dissolved in anhydrous acetone and the solution was cooled at -40°C for 48 h. After filtration on glass septa (porosity 4) containing two different powdered layers of 1 cm each of celite (lower layer) and decolorizing carbon (upper layer), the solvent was removed at reduced pressure. The isolated IL was dried under vacuum ($2x10^{-3}$ mm Hg, 80°C, 6h) and analyzed by NMR.

^1H NMR ($CDCl_3$, δ ppm): 7.35 (m, 2H, aromatic CH), 7.26 (m, 2H, aromatic CH), 6.65 (dd, J = 17, 11 Hz, 1H, CH=), 5.74 (d, J = 17 Hz, 1H, =CH_2), 5.27 (d, J = 11 Hz, 1H, =CH_2), 4.07 (d, J = 15 Hz, 2H, P^+CH_2Ph), 2.27 (m, 6H, P^+CH_2Ph), 1.21 (m, 36H, CH_2), 0.85 (m, 9H, CH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 137.6, 135.9, 129.2, 129.0, 128.2, 127.1, 114.9, 31.7, 30.9 (d, *J* = 15 Hz), 28.4, 28.2, 26.5 (d, *J* = 47.5 Hz, $P^+\underline{C}H_2Ph$); 22.6, (d, *J* = 4.5), 19.1 (d, 47 Hz, $P^+\underline{C}H_2CH_2CH_2CH_2$), 14.2.

Measurements of Physical Properties

The viscosity of each liquid compound was measured using Brookfield DV-II + Pro instrument equipped with a Brookfield TC-502 water bath. The viscometer was calibrated over the temperature range 20 – 100 °C using reference oils and ionic liquids. Conductance measurements were performed using a CON 510 bench meter supplied with conductivity/TDS electrode. This electrode has a stainless steel ring and a cell constant of K=1.0. It also has an inbuilt temperature sensor for automatic temperature compensation. UV–vis absorption spectra of solvatochromic dyes (Reichardt's betaine dye, *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline) dissolved in ILs recorded with a Cary 2200 spectrophotometer employing 1 mm path length quartz cell. Individual stock solutions of Reichardt's betaine dye, *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline were prepared in dichloromethane. In order to prepare a given dye/IL solution, the appropriate amount of the dye stock solution was transferred into a quartz cuvette. Residual dichloromethane was evaporated under gentle stream of argon gas in dry box. The IL was then added to the cuvette. The cuvette was sealed and the sample was hand mixed for several times before the measurements. To prevent dye aggregation, the dye concentration was chosen low enough but sufficient to allow an absorbance value of about 0.2.

Extraction experiments

Extraction of metal ions from water was performed as follows. Aqueous stock solutions of metal salts were prepared by addition of the proper metal chloride to 1 L of highly purified water (Milli-Q). Each solution was diluted 1:10 to obtain a concentration of metal ions of 100 ppm.

Procedure 1: 0.5 g of dried IL were added to 1.5 g of the proper aqueous metal stock solution (metal concentration 100 ppm). The resulting two phases were mixed using an ultra high vibration shaker (Vortex 3) for 10 min, then the mixture was centrifuged at 3000 rpm for 10 min to favour phases separation. After that, the metal concentration in the aqueous phase was determined by ICP-MS.

Procedure 2: 0.5 g of dried IL were added to 1.5 g of the proper aqueous metal stock solution (metal concentration 100 ppm). The resulting two phases were mixed using an ultra high vibration shaker (Vortex 3) for 10 min, then the resulting mixture was centrifuged at 3000 rpm for 10 min. After that, the organic phase was reused and another extraction was performed, as described in procedure 1 (see above). Subsequently, the metal concentration in the two aqueous phases were determined by ICP-MS.

Procedure 3: 0.5 g of dried IL were added to 1.5 g of the proper aqueous metal stock solution (metal concentration 100 ppm). The resulting two phases were mixed using an ultra high vibration shaker (Vortex 3) for 10 min, then the resulting mixture was centrifuged at 3000 rpm for 10 min. After that, the aqueous phase was re-extracted with fresh IL. The procedure was repeated two times. Finally, after three subsequent extractions, the metal concentration in the aqueous phase was determined by ICP-MS.

Experimental results, collected at least in duplicate, agree within 5%.

Extraction percentage is calculated as follows:

$$E\% = \left(\frac{[M]_{aq,i} - [M]_{aq}}{[M]_{aq,i}}\right) \times 100$$

Where $[M]_{aq,i}$ is the initial metal concentration in the aqueous phase before extraction, $[M]_{aq}$ is the metal concentration in the aqueous phase after extraction.

Results and Discussion

The synthesis of phosphonium salts was performed by reacting commercial trioctylphosphine with 3-chloropropane-1,2-diol or 1-(chloromethyl)-4-vinylbenzene under an inert atmosphere (see experimental) to prevent oxidation of trialkylphosphine. Phosphonium chlorides were then converted into the corresponding hexafluorophosphates, tetrafluoroborates, bis(trifluoromethane)sulfonylamides and nitrites through metathesis reactions. As expected, ILs **1-2** appeared as viscous liquids and although the factors that determine ILs viscosity are still not fully understood, a dependence on ionic structure could be immediately evidenced. Table 1 reports some fundamental properties (viscosity, conductivity) of ILs **1** and **2** at 20 °C.

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Viscosities and conductivities were measured at several temperatures between 20 and 80 °C.

Table 1. Physico-chemical properties of phosphonium based ILs at 20 °C.

IL	status	σ μS/cm	η Pa·s
$[P_{888(gly)}]Cl$	Waxy	18.5^a	1.24^a
$[P_{888(gly)}]$ $[PF_6]$	Liquid	5.0	11.62
$[P_{888(gly)}]$ $[BF_4]$	Liquid	11.5	4.95
$[P_{888(gly)}][Tf_2N]$	Liquid	29.0	1.53
$[P_{888(gly)}][NO_2]$	Waxy	24.8^a	0.91^a
$[P_{888(4\text{-}VB)}][PF_6]$	Liquid	1.6	35.20
$[P_{888(4\text{-}VB)}][BF_4]$	Liquid	2.9	15.26
$[P_{888(4\text{-}VB)}]$ $[Tf_2N]$	Liquid	18.5	1.61
$[P_{888(4\text{-}VB)}]$ $[NO_2]$	Waxy	11.6^a	2.87^a

[a] Measured at 40 °C

For these salts, a striking decrease of viscosity on increasing temperature was generally observed and, in agreement with the behaviour characterizing most ILs, the temperature dependency only approximately follows the Arrhenius equation 1, where E_η is the activation energy for viscous flows, and $\ln\eta_\infty$ is the viscosity at infinite temperature, over the examined temperature range (20-80 °C).

$$\ln\eta = \ln\eta_\infty + E_\eta / RT \qquad (1)$$

The Arrhenius plots (here not reported) show indeed a slight upward curvature. In contrast, the Vogel-Fulcher-Tammann (VFT) equation 2 (where η_0 (cP), B (K), and T_0 (K) are fitting parameters) with few exceptions is able to model the temperature effect:

$$\eta = \eta_0\, e^{B/(T-T_0)} \qquad (2)$$

The optimized parameters and related correlation coefficients are reported in Table 2 together with the Arrhenius parameters. The calculated viscosities of the investigated ILs display a good agreement with the corresponding experimental viscosity.

It is quite surprising that glyceryl substituted phosphonium salts **1** are generally characterized by a lower viscosity and higher conductivity than the corresponding styryl substituted salts **2**, despite the presence of two hydroxyl groups.

As expected, the anion chemical structure exerts a significant effect also on conductivity and the less viscous ILs, with $[Tf_2N]^-$ as anion, show the highest conductivities. Conductivity increases on increasing temperature but, in agreement with viscosity, the temperature dependence follows only “approximately” the Arrhenius equation 3:

$$\ln\sigma = \ln\sigma_\infty - E_\sigma / RT \qquad (3)$$

where Eσ is the activation energy for conductivity.

Table 2. Arrhenius and VFT viscosity parameters

IL	Eη KJ mol^{-1}	lnη∞ mPa s	R	η_0 mPa ·s	B K	T_0 K	R^2
$[P_{888(gly)}]Cl$	27.2	-13.4	0.985	21.0	209	262	0.999
$[P_{888(gly)}][PF_6]$	50.0	-16.1	0.995	6.4	476	239	0.999
$[P_{888(gly)}][BF_4]$	35.4	-14.3	0.981	11.0	312	242	0.999
$[P_{888(gly)}][Tf_2N]$	38.0	-12.1	0.989	0.3	933	184	0.999
$[P_{888(gly)}][NO_2]$	28.8	-9.2	0.994	22.0	216	254	0.999
$[P_{888(4\text{-}VB)}][PF_6]$	81.4	-47.8	0.975				
$[P_{888(4\text{-}VB)}][BF_4]$	47.9	-17.8	0.988	1.1	729	216	0.999
$[P_{888(4\text{-}VB)}]$ $[Tf_2N]$	32.7	-12.2	0.986	4.3	369	230	0.999
$[P_{888(4\text{-}VB)}]$ $[NO_2]$	39.0	-18.2	0.972	29.9	175	274	0.999

Data have been therefore fitted using the more appropriate VTF equation 4, where A (μS cm^{-1}), B (K) and T_0 (K) are fitting parameters.

$$\sigma = A\, e^{-B/(T-T_0)} \qquad (4)$$

The optimized parameters and related correlation coefficients are reported in Table 3, together with the Arrhenius parameters.

Table 3. Arrhenius and VFT conductivity parameters

Anion	Eσ KJ mol^{-1}	lnσ∞ (μs/cm)	R	A (μs/cm)	B K	T_0 (K)	R^2
$[P_{888(gly)}]Cl$	34.2	13.5	0.997	1701	429	218	0.999
$[P_{888(gly)}][PF_6]$	42.8	17.0	0.998	3981	548	213	0.999
$[P_{888(gly)}][BF_4]$	35.6	15.8	0.998	101278	1544	123	0.999
$[P_{888(gly)}][Tf_2N]$	35.2	15.2	0.989	4033	360	221	0.999
$[P_{888(gly)}][NO_2]$	31.7	13.3	0.988	6138	678	182	0.998
$[P_{888(4\text{-}VB)}][PF_6]$	51.5	18.2	0.996	1016	352	243	0.995
$[P_{888(4\text{-}VB)}][BF_4]$	47.1	17.8	0.998	6098	680	206	0.999
$[P_{888(4\text{-}VB)}]$ $[Tf_2N]$	38.2	15.8	0.989	2913	332	230	0.996
$[P_{888(4\text{-}VB)}]$ $[NO_2]$	34.1	15.9	0.999	1291	1018	169	0.999

Subsequently, we examined the solvent properties of these ILs determining the solvatochromic Kamlet-Taft parameters, π* (dipolarity/polarizability), β (hydrogen bonding basicity), α (hydrogen bonding acidity) and the Reichardt parameter $E_{T(30)}$. The solvatochromic parameters have been determined exclusively for phosphonium salts **1**, since the salts **2** have an exceedingly high absorption in the UV region of interest. Table 4 reports the Kamlet-Taft parameters of the investigated ILs. Values related to two unfunctionalized tetraalkylphosphonium salts have been added for comparison.

As expected, ILs **1** are generally characterized by a significantly higher hydrogen bonding acidity when compared with the unfunctionalized tetraalkylphosphonium salts: as previously observed[13] for other classes of ILs, the introduction of two hydroxyl groups on cation gives ILs with α values comparable to that of water (1.13), with the exception of chloride salts.

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Table 4. $E_{T(30)}$ and Kamlet-Taft parameters determined at 20 °C.

IL	$E_{T(30)}$	π^*	α	β
$[P_{888(gly)}]Cl^{a}$	48.93	0.84	0.54	1.00
$[P_{888(gly)}]$ $[PF_6]$	54.88	0.93	0.86	0.55
$[P_{888(gly)}]$ $[BF_4]$	55.65	0.88	0.95	0.61
$[P_{888(gly)}][Tf_2N]$	56.97	0.96	0.97	0.35
$[P_{666(14)}][Tf_2N]^{b}$		0.83	0.37	0.27
$[P_{8888}][(EtO)HPO_2]^{c}$		0.85	0.25	1.38

[a]Determined at 50 °C. [b]From ref. 14. [c]From ref. 5.

Furthermore, also for these ILs the hydrogen bonding basicity (β) depends mainly on the anion although an inverse relationship between α and β parameters can be envisaged: basic anions (such as chloride) reduce the cation hydrogen bond donor ability (α decreases from 0.97 to 0.54 going from $[Tf_2N]^-$ to Cl^-, Table 4). The strong proton accepting nature of chloride anion, probably through the formation of hydrogen bonds with the hydroxyl groups of the glyceryl moiety,[6] increases the networking inside the IL and reduces the ability of IL cation to interact with the probe dyes.

$[P_{888(gly)}]Cl$ and $[P_{888(gly)}]$ $[BF_4]$ have been not employed for metal extraction. Preliminary experiments showed indeed a clean-cut decrease in the volume of the organic phase, attributable to a partial dissolution in water, when exactly measured amounts of these ILs were added to water and the phases were vigorously mixed and subsequently separated by centrifugation. Moreover, we avoided the use of $[P_{888(4\text{-}VB)}][PF_6]$ owing to its surfactant properties that drastically reduced the phase separation efficiency after mixing of organic and aqueous phase.

The selected ILs **1** and **2** have been therefore tested as metal ions extractants from water in biphasic separations. The extraction of the individual metal ions Cu(II), Zn(II), Co(II), Ni(II) and Pb(II) was performed by mixing 0.5 g of IL with 1.5 g of water containing a metal ion concentration of 100 ppm. Chloride salts were used as Cu(II), Zn(II), Co(II), Ni(II) and Pb(II) sources.

Table 5. Extraction efficiency for metal extraction (procedure 3) using $[P_{888(gly)}]^+$ based ILs.

M^{2+}	$[P_{888(gly)}][PF_6]$	$[P_{888(gly)}][Tf_2N]$	$[P_{888(gly)}][NO_2]$
	E%	E%	E%
Pb^{2+}	40.1	24.1	99.9
Cu^{2+}	40.2	14.8	99.6
Zn^{2+}	-	8.2	37.6
Co^{2+}	-	-	27.2
Ni^{2+}	-	-	25.2

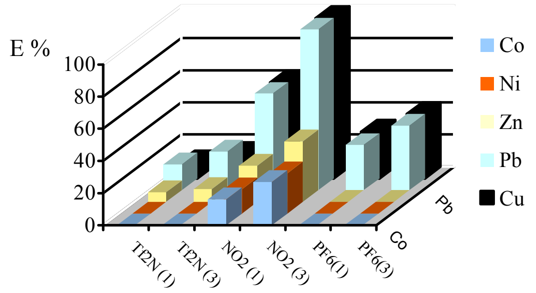

Figure 1. Effect of IL anion on extraction percentage (E%) of metals cations from aqueous solutions (procedure 1 and 3) using $[P_{888(gly)}]^+$ based ILs.

To be sure that the equilibrium conditions were reached, the extraction efficiencies obtained after 10 min stirring were compared with the efficiencies obtained after stirring for 30 min. Since the values were practically identical, a stirring time of 10 min was selected for all experiments. It is noteworthy that the reuse of the organic phase for extraction of fresh metal ion solutions gave only a no-significative increase in extraction efficiency: for these ILs the pre-conditioning phase appears not important.

For each metal, the extraction efficiency was therefore evaluated after one or three consecutive extractions using fresh IL (3 x 0.5 gr), values are depicted in Figure 1. As expected an increase in E (extraction efficiency) was always observed on increased the number of extractions (Figure 1): in particular, three extractions assured a practically complete recover of Pb(II) and Cu(II).

Unfortunately, despite the well-known chelation ability of two vicinal hydroxyl groups, the association of the dihydroxyl functionalized phosphonium cation $[P_{888(gly)}]^+$ to hydrophobic anions (such as $[PF_6]^-$ or $[Tf_2N]^-$) gave ILs having only a moderate metal extraction ability. The high extraction efficiency towards Pb(II) and Cu(II), observed in $[P_{888(gly)}][NO_2]$, is most likely attributable to the anion properties, *i.e.* its coordinating ability or reducing power. The formation of metallic particles in the organic phase was indeed detected in the samples containing Pb(II). The subsequent, ICP-MS analysis of the recovered precipitate after dissolution in HNO_3 (65%) confirmed the formation of Pb(0) in nitrite based ILs.

Since the hydroxyl groups on cation appeared unable to affect significantly extraction efficiency we have decided to test four trioctyl(4-vinylbenzyl)phosphonium salts having as counteranion $[Tf_2N]^-$, $[NO_2]^-$ and Cl^-. It is noteworthy that the highly hydrophobic nature of this aryl substituted phosphonium cation makes it possible the association with the coordinating chloride anion: the corresponding IL is indeed water insoluble.

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Table 6. Extraction efficiency for metal extraction (procedure 3) using $[P_{888(4\text{-}VB)}]^+$ based ILs.

M^{2+}	$[P_{888(4\text{-}VB)}]Cl^a$	$[P_{888(4\text{-}VB)}]Cl$	$[P_{888(4\text{-}VB)}][Tf_2N]$	$[P_{888(4\text{-}VB)}][NO_2]$
	E%	E%	E%	E%
Pb^{2+}	92.1	99.9	28.9	99.9
Cu^{2+}	25.1	99.4	36.3	99.7
Zn^{2+}	84.2	99.9	75.6	97.8
Co^{2+}	-	-	-	39.3
Ni^{2+}	-	-	-	36.5

[a] Procedure 1.

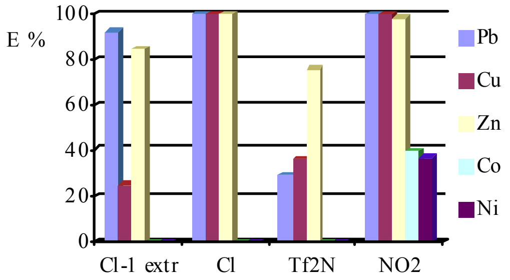

Figure 2. Effect of IL anion on extraction percentage (E%) of metals cations from aqueous solutions using $[P_{888(4\text{-}VB)}]^+$ based ILs.

Extraction efficiency values (Table 6 and Figure 2) show that $[P_{888(4\text{-}VB)}][Tf_2N]$, analogously to the corresponding IL of the other series, has no affinity for Co(II) and Ni(II). However, it shows a fairly good extraction ability towards Zn(II) (E% = 76). On the other hand, $[P_{888(4\text{-}VB)}][NO_2]$ presents an excellent extraction ability for Pb(II), Cu(II) and Zn(II). These metal cations can be however efficiently extracted also by $[P_{888(4\text{-}VB)}]Cl$, which is able to remove 92% of Pb(II) and 84% Zn(II) after a single extraction.

The coordination ability of the IL anion appears therefore fundamental in metal extraction from water. The hydrophobic $[P_{888(4\text{-}VB)}]Cl$ is indeed able to perform an efficient transfer of metal ions from water to organic phase. The formation of polychlorometallate anions, as key species able to positively affect the transfer process, could be hypothesized considering their stability in ILs. Halometallate ILs have been widely applied as Lewis acids and solvents in synthesis or in electrochemistry,[15-16] and their involvement for the cobalt/nickel separation from 8 M HCl solutions has been recently reported.[7]

However, considering the different working conditions (in our experiments the pH of the aqueous medium was in the range 4.5-5) to verify their actual formation, UV-vis measurements have been carried out on the organic phase in the case of Cu(II). Extraction of a blue colored (*ca.* 0.1 M) aqueous solution of $CuCl_2$ (the blue color is indicative for the fully hydrated Cu(II) ion) with $[P_{888(4\text{-}VB)}]Cl$ gave a yellow organic phase attributable to the formation of $[CuCl_4]^{2-}$ ion. This species was identified by UV-vis spectroscopy, on the basis of its typical absorption around 408 nm the other two maxima (at 291 nm and 231 nm, respectively) being completely covered by the strong absorption of the IL below 300 nm.[17]

Therefore, taking into account the coordination number of the different anions, we propose the following pathway (eq 5) for extraction of Cu(II) and Zn(II),

$$\underbrace{2\,[P_{888(4\text{-}VB)}]Cl}_{\text{IL-phase}} + M^{2+} + 2Cl^- \rightleftarrows \underbrace{[P_{888(4\text{-}VB)}]_2[MCl_4]}_{\text{IL-phase}} \quad (5)$$

based on the formation of anionic tetrahedral metal chloride complexes, which become the "new" IL counteranions. A similar pathway can be hypothesized also for Pb(II),[18] even if the very low concentration of the metal salt could favour the formation of an octahedral complex $[PbCl_6]^{4-}$ arising from an analogous process:

$$\underbrace{4\,[P_{888(4\text{-}VB)}]Cl}_{\text{IL-phase}} + Pb^{2+} + 2Cl^- \rightleftarrows \underbrace{[P_{888(4\text{-}VB)}]_4[PbCl_6]}_{\text{IL-phase}} \quad (6)$$

Although the ionic nature of ILs can allow a variety of mechanisms, including solvent ion-pair extraction (eq 5 and 6), ion exchange (metal-IL cation) and simultaneous combination of them,[19] the inability to detect the IL cation ($[P_{888(4\text{-}VB)}]^+$) in water phase after extraction of concentrated metal solutions (0.1M) by NMR suggests a moderate (if any) involvement of the metal-IL cation exchange mechanism, with a very low IL leaching. It is noteworthy that only very small quantities of other tetralkylsubstituted phosphonium based ILs have been measured by Binnemans et al. in the aqueous phase after solvent extraction.[7]

Probably, an analogous mechanism can be hypothesized also for bis(trifluoromethane)sulfonylamide based ILs, although the chelating ability of this anion should give complexes of different speciation and geometry.

Finally, it is to mention the chelating and reducing properties of nitrite anion which favour also in the case of the styryl functionalized cation, $[P_{888(4\text{-}VB)}]^+$, extraction and deposition of reducible metals, such as Pb(II).

Conclusions

In this paper we report the successful use of phosphonium based ILs for the extraction of some common metal cations from water using two series of functionalized phosphonium based ILs. IL anion strongly affects the efficiency of the extraction process which is however affected also by cation functionalization. Differences in extraction are observed between the ILs possessing diol-substituted (hydrogen bond donor) and styryl-substituted (non- hydrogen bond donor) cations. In this context, $[P_{888(4\text{-}VB)}]Cl$ allows a nearly complete extraction of Pb(II), Cu(II), Zn(II), while the extraction of Co(II) and Ni(II) was negligible.

Reduction and possible chelation of metal ion species by nitrite-based ILs distinguish these solvents from the other investigated ILs. On the other hand, the chelation ability of chloride anion appears to be the driving force in the extraction of metal ion species able to give stable polychlorometallate anions. Pb(II), Cu(II), Zn(II) can be extracted avoiding the addition of HCl (8 M) to the aqueous phase.

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Notes and references

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