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Mercury extraction by ionic liquids: temperature and alkyl chain length effect

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Abstract—The preliminary results described here show the complete transfer of Hg(II) ions, in the absence of a chelating agent in 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids; the lag time required to gain the quantitative metal ion partition turned out to be strongly dependent both on alkyl chain length on the imidazolium ring and on the working temperature.

Liquid/liquid extraction is a very effective analytical method for the recovery and separation of both metal species and organic compounds. The organic phases employed in these biphasic systems are usually toxic, volatile and flammable organic solvents (VOCs) and their use involves environmental and safety concerns of emission loss and fire hazard.

Room temperature ionic liquids (RTILs) are being recently considered as replacement solvents in a wide range of applications,[1] due to their unique chemical and physical properties. Among these, negligible vapour pressure, good thermal stability and tuneable water miscibility make their use particularly attractive in separation processes.[2]

In the last few years, extraction of a wide range of metal ions by using RTILs containing proper complexing agents such as crown ethers, calixarenes and various organic ligands has been reviewed by Zhao et al.[2] It is noteworthy that, if compared with conventional (molecular) organic solvents, significant differences both in efficiency and in chemical equilibria can be found in RTILs when employed in such biphasic systems.[3]

A new approach for metal ion extraction, based on the so-called Task Specific Ionic Liquids (TSILs), has been also recently proposed, as widely reviewed by Lee.[4] TSILs contain specific chelating groups covalently incorporated within one of the ionic liquid components, typically within the cation. This method can be used to develop new functionalized ILs with a number of advantages: they can not only increase the affinity of a target species for the IL over a second phase, but also greatly diminish the chance for loss of the chelating agent to the aqueous phase.

The removal of toxic heavy metal ions from wastewater is of great concern in the environmental field of waste and pollution reduction, and Hg(II) ion extraction from aqueous solutions was efficiently achieved using dithizone solubilized in 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$)[5] and various TSILs, incorporating thiourea, thioether and urea,[6] ethylene glycol[7] or alcoholic and ethereal functionalities.[8]

In this Letter, preliminary results about the partitioning properties of $[C_nMIM][PF_6]$ ionic liquids, with $n = 4, 6, 8$, towards Hg(II) ions are shown. A spontaneous partition of Hg(II) ions in $[C_4MIM][PF_6]$ was already reported[6] and a distribution ratio of 0.84 was found. Experiments were performed by mixing equal volumes of ionic liquid and an aqueous solution of metal ion at $pH = 7$, shaking for few minutes and then centrifuging to separate the two phases. In our experimental procedure, liquid/liquid extraction was carried

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Keywords: Ionic liquids; Mercury ions extraction; Biphasic system; Temperature effect.

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Table 1. Hg(II) Ion percentages in ionic liquid at 60 °C as a function of time

Time (h)	% Hg(II) in IL		
	[C_4MIM][PF_6]	[C_6MIM][PF_6]	[C_8MIM][PF_6]
4	70	62	90
6	79	76	94
8	86	82	97
12	97	97	100
24	98	100	—
30	100	—	—

out by contacting equal volumes of ionic liquid and a $HgCl_2$ buffered aqueous solution at pH = 4.68, kept under stirring at constant temperature.[†] This method offered several advantages, including the possibility to control the working temperature and to evaluate any effect of temperature on metal ion partitioning. Unexpectedly, in all three 'classical' imidazolium-based ionic liquids, a nearly quantitative transfer of Hg(II) ions was gained, in the absence of a chelating agent in the ionic liquid phases; this transfer did not occur instantaneously, but a lag time was needed to reach it (Table 1).

Except for the first hours, the trends of Hg(II) partition in [C_4MIM][PF_6] and [C_6MIM][PF_6] were quite similar and in 24–30 h the whole amount of metal ion was transferred into the organic phase. On the other hand, Hg(II) ion extraction in [C_8MIM][PF_6] was very fast: after only 4 h, ca. 90% of metal ion was in ionic liquid phase and the complete removal from the aqueous compartment was gained in 12 h. Therefore, significant different patterns of Hg(II) ions transfer could be obtained simply by increasing the alkyl chain length on the imidazolium ring.

It is the first time that 'classical' ionic liquids show marked partitioning properties towards Hg(II) ions and our results highlighted the key role of the hydrocarburic moiety on metal ion association. Quantitative studies to evaluate the importance of hydrophobic/hydrophilic balance of the imidazolium cation are now in progress. Moreover, preliminary experiments performed in the absence of or with different buffers from acetate seemed to show that the nature and the presence of the anion derived from buffer systems play a significant role in the Hg(II) extraction. Anyhow, no similar spontaneous partitioning examples were reported in the literature, except for TSILs, and all proposed or proved mechanisms dealt with mediated-ligand processes, for example, ion pairing extraction and cation (or anion) exchange.[9]

To further investigate the partitioning behaviour of Hg(II) ions in ionic liquids, the temperature was varied in the range 25–60 °C. In Figure 1, the temperature effect on the Hg(II) partition in [C_8MIM][PF_6] is reported. Independently of the working temperature, a complete Hg(II) ion transfer in RTIL was achieved and the higher temperature was used, the faster metal ion transfer in ionic liquid carried on. The high viscosity of most 1,3-dialkylimidazolium ionic liquids can significantly reduce the rates of mass transfer between the two phases in a liquid/liquid extraction process. In the literature, the temperature effect on the viscosity of [C_nMIM][PF_6] is reported:[10] viscosity markedly decreased as the temperature is increased in the range 25–100 °C and such behaviour could then provide a rationale for our results.

Finally, to evaluate the ionic liquid role as a simple medium or as an active partner in a molecular interaction, a set of partitioning experiments in chloroform/water biphasic systems was performed. In the absence of [C_nMIM][PF_6], no partition of Hg(II) was observed;[11] extraction properties towards Hg(II) ions could be therefore evaluated by solubilizing little amounts of ionic liquid in the organic solvent.

Firstly, no extraction of Hg(II) ions was observed when [C_4MIM][PF_6] was added to the organic solvent and this result could be explained both with the low solubility of this ionic liquid in chloroform and with its even low solubility in water.[12]

Experiments with different ionic liquid/Hg(II) molar ratios were then carried out and, besides [C_6MIM] and [C_8MIM][PF_6], another imidazolium salt was used, with a longer alkyl chain on the imidazolinic ring, that is

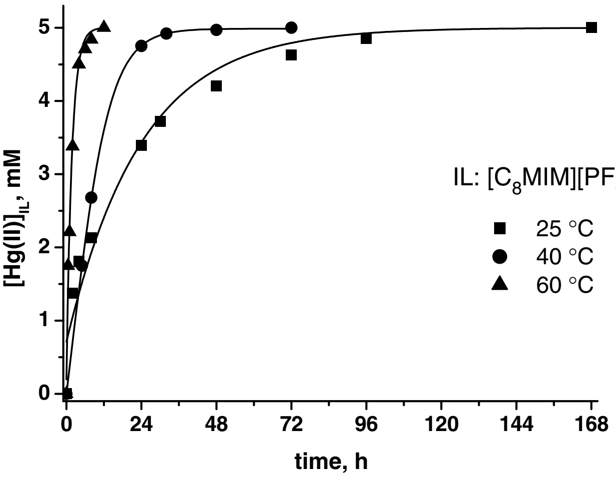

Figure 1. [Hg(II)] in ionic liquid versus time at 25 (■), 40 (●) and 60 °C (▲) with [C_8MIM][PF_6] as extracting phase; aqueous phase: 5×10^{-3} M $HgCl_2$ in 0.15 M acetate buffer, pH 4.68.

[†] Extraction experiments were performed by contacting 1 mL of ionic liquid and 1 mL of a 5×10^{-3} M $HgCl_2$ solution in 0.15 M acetate buffer, pH 4.68; they were kept under stirring in a glycerine/water bath at constant temperature and the metal ion concentration in the upper aqueous phase was monitored following a sensitive spectrophotometric method previously described.[13] Then, Hg(II) ion concentration in ionic liquid was calculated as the difference. Each experiment was done in at least triplicate and result agreed to within 5%. All chemicals were obtained from Sigma–Aldrich and used without further purification.

Ionic liquids were synthesized by following a slightly modified reported procedure.[14] Alkyl bromide was used instead of the corresponding chloride to prepare alkylmethylimidazolium salts; in this way reactions proceeded more rapidly and quantitative yields and nearly colourless final products were obtained.

Table 2. Hg(II) Percentages in chloroform at 25 °C as a function of time

	% Hg(II) in chloroform		
	8 h	24 h	48 h
[C_6MIM][PF_6]/Hg(II)			
1:1	38	63	67
2:1	51	80	85
10:1	68	86	90
[C_8MIM][PF_6]/Hg(II)			
1:1	76	87	93
2:1	94	100	—
[C_{12}MIM][PF_6]/Hg(II)			
1:1	80	83	83
2:1	91	100	—

[C_{12}MIM][PF_6]. At room temperature it is a white solid with mp = 56 °C and so it could be readily employed in such partitioning tests to evaluate the effect of a further increase in the system hydrophobicity on the metal ion extraction. In Table 2, Hg(II) percentages in organic phases as a function of time are reported.

All ionic liquids showed a remarkable ability to extract Hg(II) ions from the aqueous phase and different trends depending on the ionic liquid itself and on the molar ratio used were observed. In particular, the addition of growing amounts of [C_6MIM][PF_6] to the chloroform produced a corresponding increase of Hg(II) ion percentage partitioned in the organic phase, but even with a 10:1 molar ratio, after 48 h ca. 10% of metal ion still remained in the aqueous phase.

On the contrary, in the case of [C_8MIM][PF_6], a 2:1 molar ratio is high enough to achieve the complete transfer of Hg(II) in the organic phase at 25 °C, with a similar trend to that observed in the pure ionic liquid at 60 °C. Furthermore, comparable results were gained with [C_{12}MIM][PF_6], pointing out that further modifications in the hydrocarburic moiety of imidazolium salt did not significantly affect the efficiency of Hg(II) ion extraction.

Thus, the results seemed to show that specific molecular interactions between Hg(II) ions and the ionic liquids established and the hydrophobic/hydrophilic features of the whole system affect the metal ion association and extraction processes. The observed properties may be then related, at least for a hydrophobic ion as Hg(II), to the structural characteristics of ionic liquids.

In conclusion, it is reported here the first example of the complete partition of Hg(II) ions in a 'classical' imidazolium-based ionic liquid, where the only 'functionalization' is related to the hydrophobic moiety. Interestingly, binding and transport properties of metal ions in such environmentally friend media could be controlled.

Clearly, an understanding of the transfer mechanism of metal ions in [C_nMIM][PF_6] ionic liquids is of primary importance in view to develop a back-extraction system or, alternatively, electrochemical recovery of Hg(II) ions should be attempted. Metal ion stripping is indeed at the basis of a future employment of ionic liquids as a bulk liquid membrane or as a chelating agent in an *in continuum* separation process and several studies addressing this issue are now underway in our laboratories.

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