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Removal and Analysis of Mercury (II) From Aqueous Solution by Ionic Liquids

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Abstract

In this work, a novel room temperature ionic liquids 1-butyl-imidazolium di(2-ethylhexyl) phosphate [BIm$^+$][D2EHP$^-$] and 1-methyl-imidazolium di(2-ethylhexyl) phosphate [MIm$^+$][D2EHP$^-$] were synthesized and tested as extractants in the batch removal of mercury (II) from aqueous solution. The influence of contact time, aqueous to organic phase's volume ratio, initial concentration of Hg (II), IL concentration, pH levels, ionic strength, and temperature was evaluated. The extraction equilibrium was established in 30 min for [MIm$^+$][D2EHP$^-$] and in 15 min for [BIm$^+$][D2EHP$^-$]. The maximum mercury extraction was obtained at pH 5.81. For the extraction of mercury, [([MIm$^+$][D2EHP$^-$])$_5$ (HgCl$_2$)]$_{org}$, [([MIm$^+$][D2EHP$^-$])$_5$ (HgClOH)]$_{org}$, [([BIm$^+$][D2EHP$^-$])$_{3/2}$ (HgCl$_2$)]$_{org}$ and [([BIm$^+$][D2EHP$^-$])$_{3/2}$ (HgClOH)]$_{org}$ species were formed.

Regarding the ionic strength for [MIm$^+$][D2EHP$^-$], the results show a significant improvement of the mercury extraction yield (100%) upon the addition of sodium acetate to the aqueous phase in a Na$^+$/Hg^{2+} mass ratio ranging from 0.1 to 2.0. The relationship between the percentages of the extracted species and the extraction yield was established by calculations using CHEAQS V. L20.1 software. The results revealed a decrease in the extraction yield of Hg (II) with decreasing proportions of HgCl$_{2aq}$ from 65.15 to 40.31% and of HgClOH$_{aq}$ from 31.31 to 0.1%, when NaCl was added.

The very important optimal sorption capacities for ([BIm$^+$][D2EHP$^-$]) and ([MIm$^+$][D2EHP]) were 58.39 mg/g and 93.23 mg/g respectively. With a longer alkyl chain on the imidazolinic ring, the decreasing of extraction yield was observed.

Keywords: Mercury; Ionic liquid; Solvent extraction; Speciation

Introduction

Removal of heavy metals and more particularly of mercury from wastewater has become a major environmental issue to be addressed [1]. Mercury (Hg) is one of the most toxic heavy metals commonly found in nature. Its toxicity is related to the bio concentration capacity of its derivatives in living organisms through food chain. Mercury and derivatives are considered as being hazardous contaminants with negative impact on human health and biodiversity [2-5]. Bio-accumulation in living organisms is accentuated by increasing emission sources, which has stimulated worldwide efforts aiming regulation and reduction of these emissions, especially in water sources.

Large-scale uses of mercury in industrial processes impose its recovery from secondary industrial resources. In this regard, several techniques for mercury (II) removal from aqueous solutions such as reduction process [6], chemical precipitation [7], membrane separation [8], ion-exchange [9], solvent extraction [10], coagulation [11], adsorption [12,13] and magnetic ferrites treatment [14] have been developed so far. Most of them turned out to be quite unsatisfactory in total elimination of heavy metals. The use of ionic liquids for mercury elimination (ILs) would be an interesting route to explore. ILs have recently received increased attention from both industrial and academic communities because of their unusual properties and great potential as "green" solvents for industrial processes [15]. They show unique properties such as non-volatility (negligible vapor pressure), thermal stability, nonflammable nature, lower reactivity, strong ability to dissolve a large variety of organic and inorganic compounds, along with a potential to extract rare earth (lanthanides plus Sc and Y) and heavy metals.

Ionic liquids, also called room temperature ionic liquids (RILS) and ambient temperature molten salts, which are liquids at ambient temperature [16], are totally composed of organic cations and inorganic/organic anions. ILs are environmentally harmless, nonvolatile, nonflammable, and display many properties of conventional organic solvents such as excellent solvation qualities, low viscosity, low vapor pressure, high ionic conductivity, appreciable thermal and electrochemical stability in a wide temperature range [17-20]. They are considered as alternatives to classical organic solvents and, as such, have been applied for many purposes such as organic synthesis, electrochemistry, and liquid phase extraction, catalysis for clean technology and polymerization processes [21-25]. A number of papers have been devoted to the description of synthesis and properties of various ILs, including imidazolium and phosphonium-based ILs and their capacity in the extraction of organic and inorganic compounds [26-28]. The aim of this work is to investigate the ability of newly synthesized ionic liquids, namely 1-butyl-imidazolium di(2-ethylhexyl) phosphate [BIm$^+$][D2EHP$^-$] and 1-methyl-imidazolium di(2-ethylhexyl) phosphate [MIm$^+$][D2EHP$^-$], to extract Mercury (II) from aqueous chloride solutions. The effects of various parameters such as the initial mercury (II) concentration, IL concentration, initial pH

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ion, ionic strength and temperature on the mercury extraction yield were studied. The species extracted into the organic phase were also investigated using slope analysis method. Calculations using CHEAQS V. L20.1 software allowed determining the nature and the amounts of the species present in organic medium and establishing the relation between the nature of the extracted species and the extraction yield [29].

Experimental

Reagents

The reagents used in this study were 1-methylimidazole (98%, Aldrich), 1-butyl-imidazole (98%, Aldrich), Di(2-ethylhexyl) phosphate (97%, Fluka), Chloride of mercury(II) (99.5%, Aldrich), Chloride of sodium (99.5%, Aldrich), sodium acetate (99%, Aldrich), 4-(2-pyridylazo)-resorcinol (PAR) (97%, Aldrich), chloroform (99%, Fluka), hydrochloric acid (37%, Fluka) and buffer solution at pH=13.0 (Riedel-Dehaen AG).
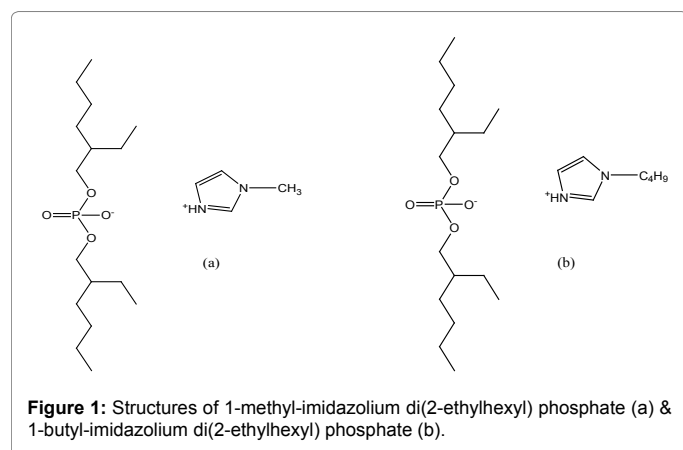
Apparatus

Analytik Jena SPECORD 210 Double Beam UV-VIS was used for spectra recording and absorbance measurements. Spectra were recorded in the range from 400 to 800 nm with 0.2 nm resolution in 10 mm quartz cells. Data were processed with WinLab software.

Sodium was analyzed in aqueous solutions before and after extraction on JENWAY PFP7 Flame Photometer. pH measurements for all solutions were taken on a potentiometer Consort C831, with combined glass electrode, that was calibrated with pH 4.00, 7.00 and 10.00 buffer standards. The logarithmic n-octanol = water partition coefficients (log P) were calculated with Clog P program of the commercial available software ChemDraw® ultra (Cambridge Soft).

Ionic liquids synthesis

A mixture of D2EHPA (6.448 g, 20 mmol) and 1-methylimidazole (1.640 g, 20 mmol) or 1-butylimidazole (2.483 g, 20 mmol) to a 250 mL round-bottom flask fitted for 24 h at room temperature till the formation of a yellow and viscous liquids.

The viscous liquids were washed three times with 50 mL portion of ethyl acetate in a separation funnel. The washed ILs were dried with anhydrous magnesium sulfate and heated under vacuum at 70°C to remove the solvent. The purity of final products was characterized with ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and FTIR (Figure 1). The yields were about 98%.

Figure 1: Structures of 1-methyl-imidazolium di(2-ethylhexyl) phosphate (a) & 1-butyl-imidazolium di(2-ethylhexyl) phosphate (b).

For [MIm$^+$][D2EHP$^-$] the attributions were:

^{1}H NMR: δ/TMS (ppm) = 0.96 (m, 15H, CH$_3$), 1.33 (m, 16H, CH$_2$), 1.56 (m, 4H, CH), 3.93 m, 4H, CH$_2$O P), 5.0 (t, 1H, NH), 5.72 (q; 1H, CH$_{ar}$), 5.89 (q; 1H, CH$_{ar}$), 6.36 (q; 1H, CH$_{ar}$). ^{13}C NMR: δ/TMS (ppm)= 11.6; 14.1; 68.8; 117.8; 119.1; 142.5, 21.7; 23.0; 23.3; 29.3; 30.4; 30.6; 32.6; 34.2; 22.4; 40.3; 108.1; 108.5; 118.0; 141.5. ^{31}P NMR: δ/H$_3$PO$_4$ (ppm) = 0.02. IR: ν (cm^{-1}) = 895 (w), 1045 (P OC, vS, L), 1240 (P=O, S, L), 1380 (w), 1470 (m), 1685 (w, L), 2855 (S), 2955 (vS).

For [BIm$^+$][D2EHP$^-$] the attributions were:

^{1}H NMR: δ/TMS (ppm) = 0.95 (m, 15H, CH$_3$), 1.33 (m, 20H, CH$_2$), 1.55 (m, 4H, CH), 3.93 (m, 4H, CH$_2$O P), 5.1 (t, 1H, NH), 5.72 (q; 1H, CH$_{ar}$), 5.89 (q; 1H, CH$_{ar}$), 6.36 (q; 1H, CH$_{ar}$). ^{13}C NMR: δ/TMS (ppm)= 11.6; 14.1; 68.8; 117.8; 119.1; 142.5, 21.7; 23.0; 23.3; 29.3; 30.4; 30.6; 32.6; 34.2; 22.4; 40.3; 108.1; 108.5; 118.0; 141.0. ^{31}P NMR: δ/H$_3$PO$_4$ (ppm) = 0.021. IR: ν (cm^{-1}) = 895 (w), 1045 (P OC, vS, L), 1240 (P=O, S, L), 1380 (w), 1470 (m), 1685 (w, L), 2855 (S), 2955 (vS).

δ, chemical shift; ν, wave number; s, singulet; d, doublet; t, triplet; q, quadruplet; quint, quintuplet; sext, sextuplet; m, multiplet; J, coupling constante; S, strong; L, large; w, weak.

Procedure

The liquid/liquid extraction was carried out by contacting volumes of ionic liquid in chloroform and mercury solution (with known concentration and fixed pH (2.2-6.4), under stirring at constant temperature (20°C). The biphasic system was stirred for homogenization for few minutes, and then both phases were separated by centrifugation. The upper aqueous phase was analyzed through spectrophotometry UV-Visible to determine the concentration of the residual unremoved metal cation.

The mercury concentrations in the aqueous phase were determined, before and after extraction by UV-Visible with PAR as ligand for Mercury with buffer solution at pH=13.0 [28,30]. The absorbance of PAR-Hg(II) complex was measured at 580 nm.

Extraction efficiencies of mercury with ILs

The biphasic system was shaken to ensure it was fully mixed and then centrifuged to separate the two phases after extraction. The upper aqueous phase was taken out and measured with spectrophotometer UV-Visible to determine the concentration of metal that was left in the aqueous phase. The extraction experiments results are discussed in term of extraction yield (Y) defined as follows:

$$(\%) = \frac{(m_i) - (m_f)}{(m_i)} \times 10 \tag{1}$$

where (m_i) and (m_f) are the mass of Hg (II) ions in aqueous phase before and after extraction, respectively [31].

Optimization experiments

Different extraction tests were run to optimize the effect of the operating parameters for maximum extraction efficiency, namely the phase volume ratio, Hg (II) initial concentration, IL concentration, initial pH of the aqueous solution, ionic strength (salt concentration) and temperature. This allowed assessing the role of the ionic liquid as a simple medium or as an active factor in a molecular interaction. In the absence of [BIm$^+$][D2EHP$^-$] and [MIm$^+$][D2EHP$^-$], no extraction of Hg(II) was observed.

Results and Discussion

Effect of volume ratio

The effect of the aqueous organic volume ratio (V_{aq}/V_{org}) was investigated by varying the Aq/Org ratio from 1 to 6 keeping the total volume of phase's constant and initial pH of 5.81. The results are presented in Figure 2.

The best extraction yields was obtained to V_{aq}/V_{org} = 1. The curves were decreasing and the extraction yields stabilized around V_{aq}/V_{org} = 6. We have noticed that for V_{aq}/V_{org} = 1, the difference of the extraction yields was 29% between IL [BIm$^+$][D2EHP$^-$] (63%) and IL [MIm$^+$][D2EHP$^-$] (92%). Whereas, for the others volume ratio, the difference was only 11%. The hydrophobic character was decreased with increasing of water volume, when the both phases were in contact. In conclusion, the volume ratio V_{aq}/V_{org} = 1 will be retained for the continuation of our study.
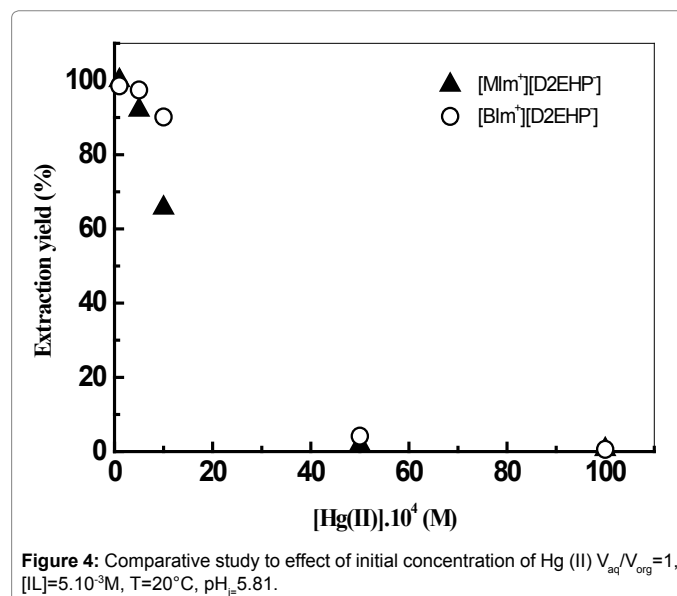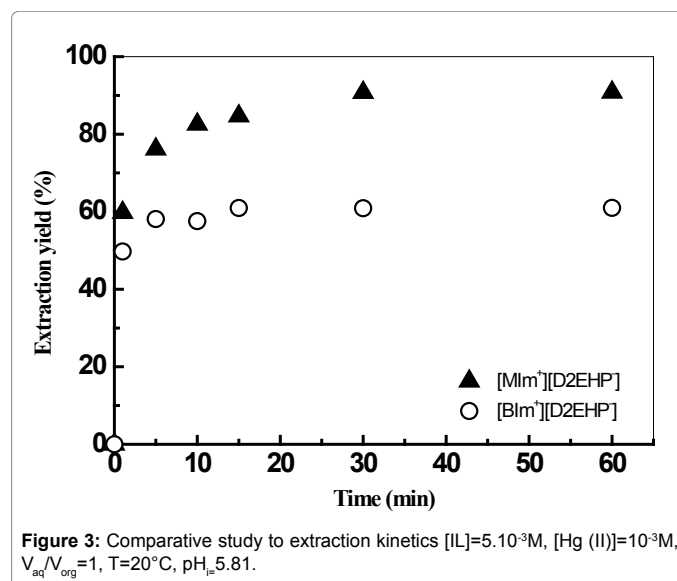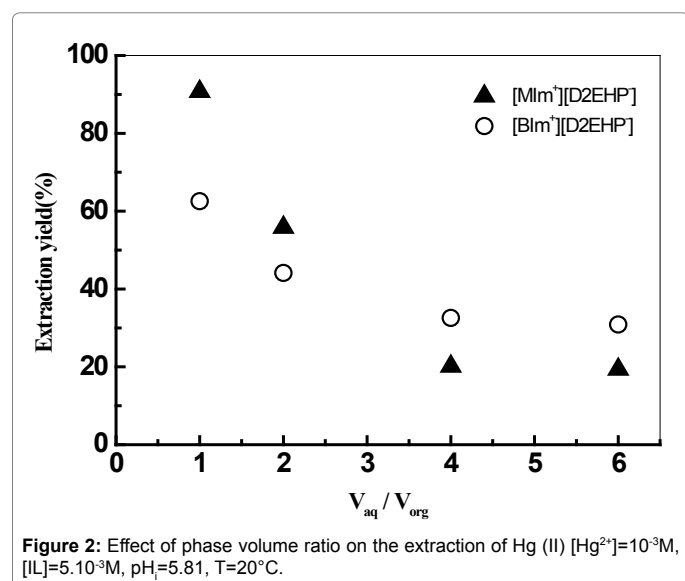
Effect of contact time

The results presented in Figure 3 showed that a minimum of 30 minutes for [MIm$^+$][D2EHP$^-$] and 15 minutes for [BIm$^+$][D2EHP$^-$] of shaking time is needed for extraction of mercury (II). The prolonged shaking had no positive effect on the extraction of Hg (II).

The hydrophobic character of IL was estimated by calculating log P, defined as the partition coefficient between two phases of a substance, generally n-octanol and water. This parameter developed by Hansch [32] is widely used in medicinal chemistry for QSAR studies, but was scarcely used in chemistry to the best of our knowledge. We recently reported the use of this parameter in the correlation between the reagent solubility and reactivity in phase transfer Heck reaction [33]. Log P values can be easily assessed using ChemDraw` ultra (Cambridge Soft) with Ghose's method [34], are respectively Log P=0.81 to [BIm$^+$][D2EHP$^-$] and Log P=-0.43 to [MIm$^+$][D2EHP$^-$]. [BIm$^+$][D2EHP$^-$] is more hydrophobic than [MIm$^+$][D2EHP$^-$]. With a longer alkyl chain on the imidazolinic ring, the decreasing of extraction yield was observed [35].

Effect of Hg (II) initial concentration

Increasing initial concentration of mercury (II) in the range $10^{-4}M$-$10^{-2}M$ was found to induce a decrease of the extraction yield
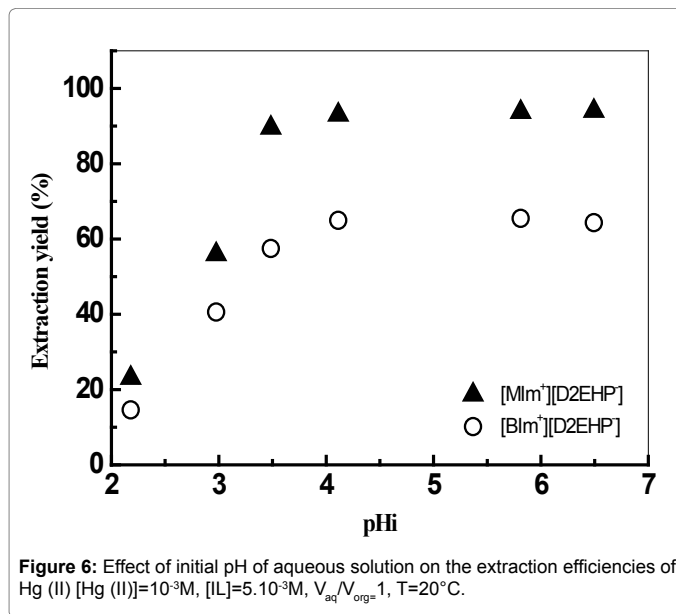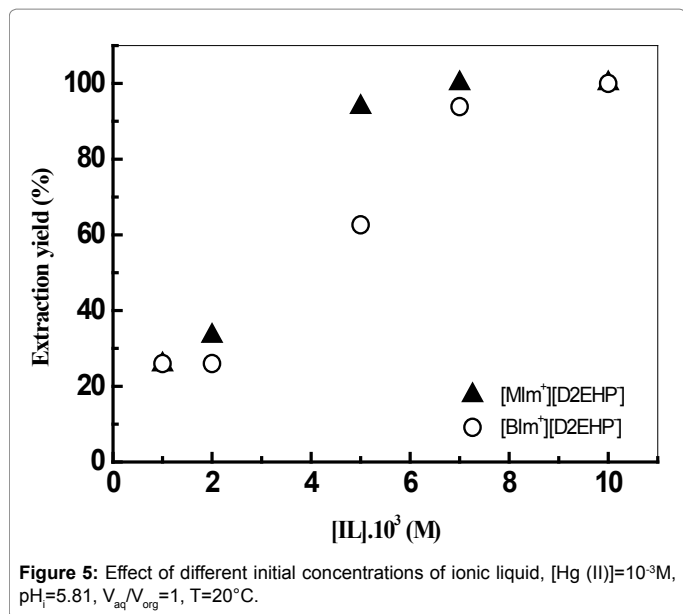

Figure 3: Comparative study to extraction kinetics [IL]=5.10^{-3}M, [Hg (II)]=10^{-3}M, V_{aq}/V_{org}=1, T=20°C, pH$_i$=5.81.

Figure 4: Comparative study to effect of initial concentration of Hg (II) V_{aq}/V_{org}=1, [IL]=5.10^{-3}M, T=20°C, pH$_i$=5.81.

(Figure 4). Further investigations were achieved using a medium value of 10^{-3}M of the initial concentration of Hg (II).

Effect of IL concentration

The role of the ionic liquid was studied by varying the IL amount in the range $10^{-3}M$-$10^{-2}M$ at 293 K under 900 rpm stirring. The results showed that the extraction yield of Hg (II) increases significantly with increasing IL concentration (Figure 5), thereby demonstrating the extraction of Hg (II) ions by a biphasic IL-aqueous chloride system.

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.

Figure 2: Effect of phase volume ratio on the extraction of Hg (II) [Hg^{2+}]=10^{-3}M, [IL]=5.10^{-3}M, pH$_i$=5.81, T=20°C.

Figure 5: Effect of different initial concentrations of ionic liquid, [Hg (II)]=10^{-3}M, pH_i=5.81, V_{aq}/V_{org}=1, T=20°C.

Figure 6: Effect of initial pH of aqueous solution on the extraction efficiencies of Hg (II) [Hg (II)]=10^{-3}M, [IL]=5.10^{-3}M, V_{aq}/V_{org}=1, T=20°C.
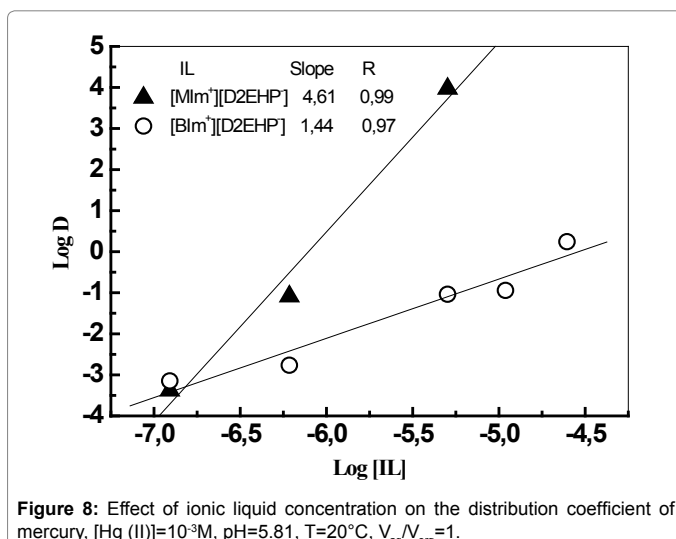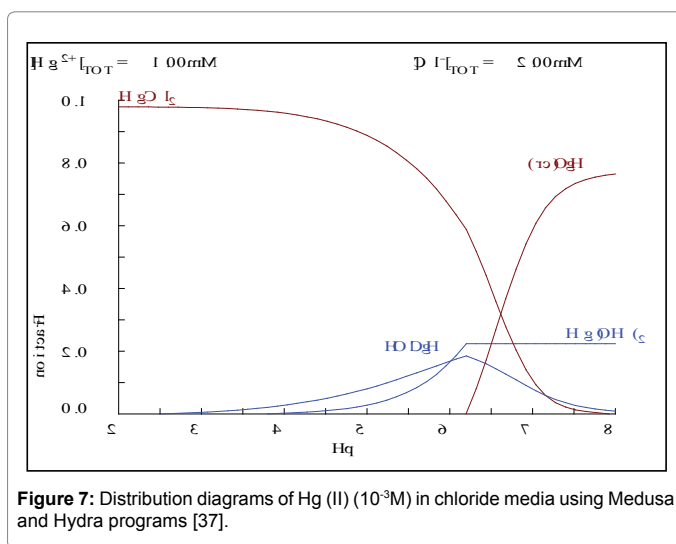
Effect of initial pH

For any extraction process, initial pH of the feed is an important parameter which governs the efficiency of the separation process. Extraction of metal from aqueous solution depends on the strength of the acid/base. Effect of pH in the aqueous phase on extraction of mercury was studied by varying initial pH in the range 2.2-6.4; pHi was adjusted by adding necessary moieties of HCl or NaOH 0.01 mol L^{-1} (Figure 6). Percentage extraction of Hg (II) increased with increase in the initial pH of the aqueous phase. As can be seen, extraction of mercury was optimum at pH_i = 5.81, the extraction yield was (94%) and (65%) for [MIm+][D2EHP-] and [BIm+][D2EHP-] respectively. The optimal sorption capacities for ([BIm+][D2EHP-]) and ([MIm+][D2EHP-]) were 58.39 mg/g and 93.23 mg/g respectively. Other authors showed that the best extraction of Hg (II) by the tetraethyleneglycol-bis(3-methylimidazolium) diiodide Ionic liquid, was obtained at optimal initial pH between 6.0-8.0 [36].
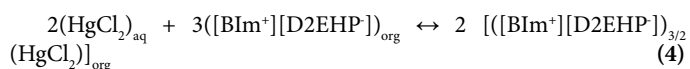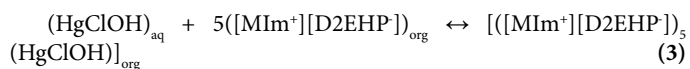
From Figure 7, it can be seen that maximum mercury extraction obtained at the pH_i range 4.1-5.81 could be due to the presence of Hg (II) with a high percentage. The increase of the yield of extraction with an increase of initial pH was related with a relative increase of percentage of $HgClOH_{aq}$ and $Hg(OH)_2$ species, however the $HgCl_{2aq}$ decreases substantially. The uptake of mercury ion beyond pH >8 is attributed to the formation of metal hydroxide species such as insoluble precipitate of $Hg(OH)_2$.

Determination of the metal-organic complex Species

The stochiometric coefficients for the extraction reaction can be determined from the intercept of the plot of log D vs. log [IL] [37,38]. Figure 8 shows a plot of log D vs. log [IL] at initial pH 5.81. The plots illustrates the slopes of nearly 5 moles of [MIm+][D2EHP-] and 1.5 moles of [BIm+][D2EHP-] for extraction of one mole of Hg(II) into the organic phase.

The extraction mechanism of mercury in chloride medium by ionic liquid diluted in chloroform may be represented as:

$$(HgCl_2)_{aq} + 5([MIm^+][D2EHP^-])_{org} \leftrightarrow [([MIm^+][D2EHP^-])_5 (HgCl_2)]_{org} \quad (2)$$

Figure 7: Distribution diagrams of Hg (II) (10^{-3}M) in chloride media using Medusa and Hydra programs [37].

Figure 8: Effect of ionic liquid concentration on the distribution coefficient of mercury, [Hg (II)]=10^{-3}M, pH=5.81, T=20°C, V_{aq}/V_{org}=1.

$(HgClOH)_{aq} + 5([MIm^+][D2EHP^-])_{org} \leftrightarrow [([MIm^+][D2EHP^-])_5(HgClOH)]_{org}$ **(3)**

$2(HgCl_2)_{aq} + 3([BIm^+][D2EHP^-])_{org} \leftrightarrow 2 [([BIm^+][D2EHP^-])_{3/2}(HgCl_2)]_{org}$ **(4)**

$2(HgClOH)_{aq} + 3([BIm^+][D2EHP^-])_{org} \leftrightarrow 2 [([BIm^+][D2EHP^-])_{3/2}(HgClOH)]_{org}$ **(5)**

Effect of ionic strength

The influence of the ionic strength on the extraction yields of Hg (II) using ionic liquid was studied by adding sodium chloride and sodium acetate to the aqueous phase. The effects of some salts at various mass ratios Na^+/Cd^{2+} on the extraction of Hg (II) were evaluated. The results showed that the addition of amount of the chloride sodium to the aqueous phase has an antagonistic effect on the yield of extraction at different values of initial pH (Figures 9 and 10). The extraction of mercury enters in competition with the sodium. The extractant goes on extracting the Na^+ instead of Hg (II) [39].
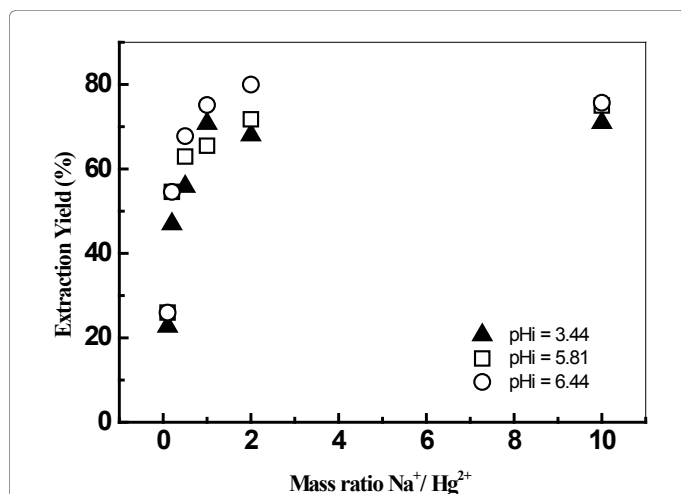

Figure 9: Effect of NaCl on extraction yield [Hg (II)]=10^{-3}M, [[MIm$^+$][D2EHP$^-$]]=5.10^{-3}M, V_{aq}/V_{org}=1, T=20°C.
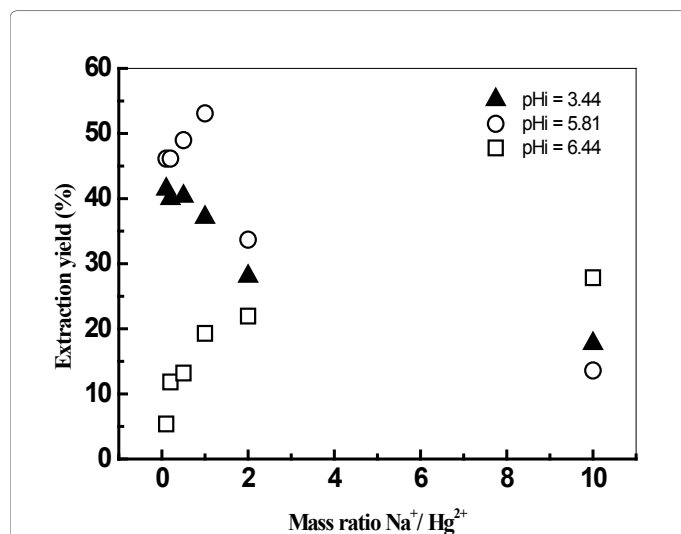
Figure 10: Effect of NaCl on extraction yield [Hg (II)]=10^{-3}M, [[BIm$^+$][D2EHP$^-$]]=5.10^{-3}M, V_{aq}/V_{org}=1, T=20°C.

The sodium complexes formed in organic phase, were ([MIm$^+$][D2EHP$^-$]NaCl) and ([BIm$^+$][D2EHP$^-$]NaCl) respectively, and the reactions mechanism may be given by the following equations:

$NaCl_{aq} + ([MIm^+][D2EHP^-])_{org} \leftrightarrow ([MIm^+][D2EHP^- NaCl)_{org}$ **(6)**

$NaCl_{aq} + ([BIm^+][D2EHP^-])_{org} \leftrightarrow ([BIm^+][D2EHP^- NaCl)_{org}$ **(7)**
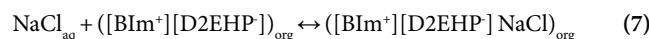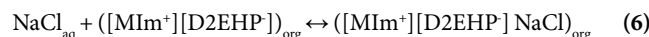
The results found by calculation program using CHEAQS V. L20.1 are summarized in Table 1. From this table it can be seen that the decrease of the extraction yield of Hg (II) is related with the decrease gradually of percentage of HgCl$_{2aq}$, HgClOH$_{aq}$ species from 65.15 to 40.31% and from 31.31 to 0,1%, respectively with the addition of NaCl in the field of mass ratio between 0 and 10. On the other hand, the percentage of HgCl$_3^-$ and HgCl$_4^{2-}$ species continues to increase. These observations suggest that the metal complexes of mercury (HgCl$_3^-$ and HgCl$_4^{2-}$) formed in the aqueous phase, probably plays a role in masking the extraction of mercury (II) by the ionic liquid.

The Figure 11 shows a comparative study on the extraction behavior of mercury (II) with [MIm$^+$][D2EHP$^-$] from different salt medium using (sodium chloride and sodium acetate) at the same initial pH of aqueous solution. From Figure 11 it can be seen that the addition of sodium acetate in aqueous solution of Hg (II) increases the extraction yield to 100% for m$_{Na}$/m$_{Hg}$ = 0.1 to 1, Whereas the decrease from 98.73% to 89.70% is explained by the fact that the cations of salts enters in competition with Hg^{2+} during the extraction with [MIm$^+$][DEHP$^-$].

The experimental data of the extraction yield according to the ionic strength are presented in Table 2.

It can be seen that the increase of the extraction yield is related with the decrease of percentage of HgCl$_{2aq}$, HgClOH$_{aq}$ and Hg(OH)$_{2aq}$ species and the increase of Hg(CH$_3$COO)$_4^{2-}$ species.

Effect of temperature

The effect of temperature on the extraction of the Hg (II) using ionic liquids was examined at 293, 303 and 318 K respectively. The effect of temperature on the extraction of Mercury (II) ions was studied under optimum conditions. Different thermodynamic parameters were computed using Van't Hoff equation in the form [40]:

$$\ln Kc = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$ **(8)**

$$\Delta G = - RT \, Ln \, Kc$$ **(9)**

where ΔH, ΔS, ΔG, and T are the enthalpy, entropy, Gibbs free energy, and temperature in Kelvin, respectively.

The values of equilibrium ratio (Kc), were calculated at each temperature using the relationship.

$$Kc = Fe / (1 - Fe)$$ **(10)**

where Fe is the fraction of Hg (II) extracted at equilibrium.

The plot of Ln Kc vs 1/T is a straight line as shown in Figure 12 with good correlation coefficient. The numerical values of ΔH, ΔS are computed from the slope. The negative value of Gibbs free energy as shown in Table 3 indicates the spontaneous nature of extraction, while negative value of ΔH reflects the exothermic extraction behavior. The negative value of ΔS indicates the complex stability.

Comparative study

In this section our results are compared with those found in the literature.

The comparison between the removal percentage in our work, which

Mass ratio Na^+/ Hg^{2+}	Extraction yield (%) pH_i=5.81		Speciation of Hg (II) (%)				
	$[MIm^+][D2EHP^-]$	$[BIm^+][D2EHP^-]$	$HgCl_{2aq}$	$HgClOH_{aq}$	$Hg(OH)_{2aq}$	$HgCl_3^-$	$HgCl_4^{2-}$
0	93.70	65.47	65.15	31.31	3.26	0.24	0
0.1	25.97	46.14	83.51	15.03	0.59	0.85	0
0.2	54.56	46.14	91.85	4.04	0.04	3.99	0.08
0.5	62.92	48.98	89.88	2.05	0.01	7.74	0.32
1	65.50	53.09	83.38	0.98	0	14.36	1.28
2	71.76	33.68	65.20	0.33	0	27.68	6.78
10	75.00	13.58	40.31	0.1	0	37.38	22.2

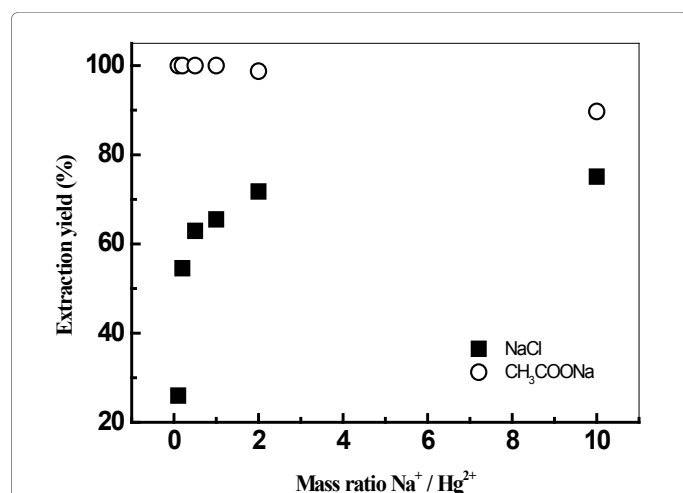**Table 1:** Nature and percentages of extracted species at different concentration of NaCl.

Figure 11: Effect of sodium chloride and sodium acetate on extraction yield, [Hg (II)]=10^{-3}M, [[MIm$^+$][D2EHP$^-$]]=5.10^{-3}M, V_{aq}/V_{org}=1, T=20°C.
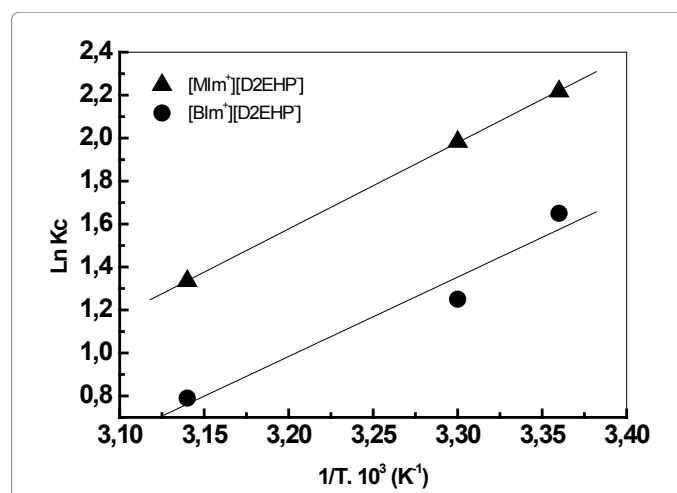

Figure 12: Variation of Ln Kc with 1/T for the extraction of Hg (II) using ionic liquids ([MIm$^+$][D2EHP$^-$]) and ([BIm$^+$][D2EHP$^-$]).

.Mass ratio Na^+/Hg^{2+}	Extraction yield (%) pH_i=5.81	Speciation of Hg (II) (%)				
		$HgCl_{2aq}$	$HgClOH_{aq}$	$Hg(OH)_{2aq}$	$Hg(CH_3COO)_3^-$	$Hg(CH_3COO)_4^{2-}$
0	93.70	65.15	31.31	3.26	0	0
0.1	100	64.79	30.77	3.17	0.27	0.71
0.2	100	53.57	13.09	0.69	2.75	29.46
0.5	100	26.72	3.72	0.11	3.03	66.04
1	100	2.51	0.26	0.01	1.80	95.36
2	98.73	0.04	0	0	0.59	99.37
10	89.70	0	0	0	0.26	99.74

Table 2: Nature and percentages of extracted species of Hg (II) with [MIm$^+$][D2EHP$^-$] at different concentration of CH$_3$COONa.

Thermodynamic parameters	Values ($[MIm^+][D2EHP^-]$)	Values ($[BIm^+][D2EHP^-]$)
ΔH (KJ/mol)	-30.6	-33.1
ΔS (J/mol K)	-89.65	-93.5
ΔG (KJ/mol)	-4.33 (T=293K)	-5.70 (T=293K)

Table 3: Thermodynamic constants of the extraction of mercury ions.

are of 94.0% for ($[MIm^+][D2EHP^-]$) and 65.0% for ($[BIm^+][D2EHP^-]$); with those found in the literature, we notice a strong increase of the quantities which we extracted (Table 4).

Conclusion

The extraction equilibrium was reached after 30 min. This novel extraction system can be employed for separation and preconcentration of metal ions. This work showed that ionic liquid [BIm$^+$][D2EHP$^-$] has

not a stronger extracting power for Hg(II) than [MIm$^+$][D2EHP$^-$]. This fact is related to the more hydrophobic character due at longer alkyl chain on the imidazolinic ring. It is noticeable that the ionic liquid is better when the alkyl chain is a butyl or even longer to reinforce the hydrophobicity.

The extraction yield increased with ionic liquid concentration. The stoichiometry between the metal and the extractant is 5/1 and 3/2 for ([MIm$^+$][D2EHP$^-$]) and ([BIm$^+$][D2EHP$^-$]) respectively. The extraction percentage increases with an increase of initial pH of the aqueous phase and it is better to extract Hg(II) in the pH range of 4.1 to 5.81, or HgCl$_{2aq}$, HgClOH$_{aq}$ and Hg(OH)$_{2aq}$ species exist with larger percentages.

Total Hg(II) removal (100%) was achieved by adding sodium acetate in Na$^+$/Hg^{2+} masse ratio ranging from 0.1 to 2. However, the addition of NaCl induced an antagonistic effect on the yield of extraction at different initial pH. The extraction process turned out to be exothermic, and the

Extractant	Yield (%)	[Ext] (mM)	[Hg (II)] (mM)	pHi	Time (min)	Volume ratio	Reference
[BIm$^+$][D2EHP$^-$]	65.0	5.0	1.0	5.81	15	1	This work
[MIm$^+$][D2EHP$^-$]	94.0	5.0	1.0	5.81	30	1	This work
4-methyl-N-8-quinolinyl-benzene-sulphonamide	95.0	5.0	0.1	1.0	40	1	[41]
LIX 34	75.0	10.0	0.02	1.1	40	1	[41]
[C$_4$MIm$^+$][PF6$^-$]	70.0	-	5.0	4.68	240	1	[35]
[C$_6$MIm$^+$][PF6$^-$]	62.0	-	5.0	4.68	240	1	[35]
Aliquat336	99.9	7.0	2.0	2.0	20	1	[42]
N-octylpyridinium tetrafluoroborate and *N*-octylpyridinium trifluoromethylsulfonate	81%	10.0	0.1	5.0	120	1	[43]

Table 4: Removal percentage of used extractant.

negative value of Gibbs free energy (ΔG) indicates the spontaneous nature of the Hg extraction. Among the two ionic liquids studied in the present work, [MIm$^+$][D2EHP$^-$] seems to be the most interesting candidate for the extraction of Hg(II) from aqueous media.

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