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AuX₄(w) + C⁺A⁻(IL) ⇌ C⁺AuX₄(IL) + A⁻(w)

Tetrahalogenoaurate anions have been successfully removed from water using betaine derivative cations ionic liquids, by precipitation using hydrophilic ionic liquid or by liquid-liquid extraction with hydrophobic ionic liquids.
Efficient extraction of gold from water by liquid-liquid extraction or precipitation using hydrophobic ionic liquids.

Stéphanie Boudesocque, Aminou Mohamadou and Laurent Dupont*

Extraction of tetrachloroaurate or tetrabromoaurate anions has been carried out with several ionic liquids bearing trialkyl(2-ethoxy-2-oxoethyl)ammonium (with alky group = C₃H₇, C₅H₁₁, PrGBOEt⁺ or n-C₄H₉ [BuGBOE!’⁺] cations and halide (Cl⁻ or Br⁻), bis(trifluoromethanesulfonylimide (TF₂N⁻) and dicyanamide (Dca’) anions. The removal of gold anionic moieties from water was first studied by mixing aqueous solutions containing gold complexes and water soluble bromide ionic liquids. This led to the formation of a solid precipitate corresponding to hydrophobic ionic liquid based on a tetrahalogenoaurate anion. Liquid–liquid extraction of anionic gold complexes with hydrophobic ionic liquids was also investigated.

Introduction

Ionic liquids (ILs) are solvents constituted by ion pairs. These organic salts, with a low melting point, are considered as green solvents because of their specific physicochemical properties (non-flammability, low vapour pressure). The replacement of conventional solvents by ionic liquids offers clear advantages, therefore, the scope of ionic liquids gradually has grown up over the last twenty years particularly in the field of electrochemistry and catalysis. In the last decade, significant works have highlighted the potential of hydrophobic room temperature ionic liquids (RTILs) as substitute to traditional solvents, used in liquid-liquid extraction processes, for the separation of metal ions. The liquid-liquid extraction is one of the efficient techniques to separate and concentrate metal ions from industrial wastewater. The major drawback of this technique is the loss of organic diluent via volatilisation, which has a detrimental impact on the environment and human health. Consequently, “greener” extraction methods are required and the use of ILs as alternatives to traditional organic solvents could overcome this disadvantage. Since ionic liquids are more expensive than traditional solvents, their use in commercial processes is rather limited particularly in processes where large quantities of solvent are required. However the development of cost-effective ILs should render their use appropriate for industrial applications, in particular for the recovery of high-value metals from ore leaching. Recently, several studies have evidenced the potential of ILs for the treatment of ore leaching and the recovery of precious metal such as Pt(II), Pd(II) and Au(III). Among these metals, gold is an important high value metal. Recently, the application of 1-butyl-3-methylimidazolium hydrogen sulphate or analogue ILs as solvent media to leach of gold-bearing ores have been attempted and some advantages of this methodology, such as the recyclability of ionic liquids have been demonstrated. Other ILs based on some organic cations (pyridinium, pyrrolidinium, and methylimidazolium) have been also developed as carriers for extraction of noble metal ions from aqueous solution, including Au(III) with a good efficiency. These studies open the door to the development of greener methodologies which will in the long term, allow the substitution of the organic solvents and cyanide salts used for the recovery of precious metals.

In this objective, we report the ability of task-specific ionic liquids to extract tetrahalogenoaurate ions (AuCl₄⁻ or AuBr₄⁻) from aqueous effluents. The studied ILs were generated by association between a cationic ester derivative of betaine tri(n-alkyl)(2-ethoxy-2-oxoethyl)ammonium (RGOBOE⁺ with R = C₃H₇, C₅H₁₁, n-C₄H₉ or n-C₆H₁₃) and anions commonly used to generate ionic liquids such as bis(trifluoromethylsulfonylimide (TF₂N⁻) and dicyanamide (N(C₃)N⁻ = Dca’). In a previous study, we showed the ability of such ionic liquids to extract metal ions. In this work, we completed our investigations by evaluating the potential of these ILs as extracting agents for the high value metals such as Au. The choice of the betaine derivative is justified by its accessibility via simple synthetic route, by its availability, the cost of starting materials, and its structural modularity, which allows the control of the cation hydrophobicity by varying the alkyl chain length bound to ammonium group. Two different methods are investigated to remove AuX₄⁻ from water. Firstly, the precipitation of AuX₄⁻ from an aqueous phase, with an organic cation from water soluble ionic liquids [EtGBOE’][Br⁻], [PrGBOE’][Br⁻] and [BuGBOE’][Br⁻] is reported. Secondly, the liquid-liquid extraction of AuX₄⁻ from an aqueous solution using hydrophobic ILs [BuGBOE’][TF₂N⁻], [EtGBOE’][TF₂N⁻] or [BuGBOE’][Dca’] was investigated. In order to develop and better understand the extraction process, we have studied the fundamental aspect of the metal transfer from the aqueous phase to the IL phase taking into account the hydrophobicity of the organic cation and the nature of the IL anions.
The coordination of Au(III) in the IL phase was also investigated by UV-vis spectroscopy.

**Results and discussion**

**Synthesis**

The ILs were synthesized by a two-step procedure described previously. All syntheses were done with the same experimental conditions. The cationic esters derivatives of betaine triethyl[(2-ethoxy-2-oxoethyl)ammonium bromide ([EtGBOEt][Br]), tri(n-propyl)[(2-ethoxy-2-oxoethyl)ammonium bromide ([PrGBOEt][Br]) and tri(n-butyl)[(2-ethoxy-2-oxoethyl)ammonium bromide ([BuGBOEt][Br])] were successfully synthesized by the reaction of ethyl 2-bromooacetate and triethylamine, tri(n-propyl)amine or tri(n-butyl)amine, respectively. The association of [BuGBOEt][Br] and [EtGBOEt][Br] with NaDca or LiTfN generates hydrophilic ILs by anionic metathesis, ([EtGBOEt][Tf2N], [BuGBOEt][Tf2N] or [BuTf2][Dca]) in quantitative yield (figure 1).

The association of [PrGBOEt][Br] with LiTfN generates a solid IL which was used only for precipitation experiments. The associations between [EtGBOEt][Br] and [PrGBOEt][Br] with NaDca generate hydrophilic ILs which were not considered in this study. The various ILs obtained were solubilized in ethyl-acetate and recovered by evaporation under vacuum. The resulting oils were washed with distilled water until no bromide impurities are detected in aqueous phase, with an AgNO3 test, and then freeze-dried. Their purity was checked by nuclear magnetic resonance spectroscopy and C, H, N elemental analysis.

**Precipitation of tetrahalogenate-based ionic liquids**

Precipitation experiments are similar to a metathesis reaction leading to the formation of an hydrophilic ionic liquid phase or a precipitate constituted by ion-pair [AlkylGBOEt][AuX4]. The reaction can be written as follows:

\[
\text{AlkylGBOEt}^+ + \text{AuX}_4^- \rightleftharpoons [\text{AlkylGBOEt}^+][\text{AuX}_4^-]_{\text{ill}} \quad (1)
\]

The compound [AlkylGBOEt][AuX4]ill corresponds to the precipitate formed or the liquid phase at the bottom of the tube. The solubility products of [AlkylGBOEt][AuCl4]ill ionic liquids are written as follows:

\[
K_{\text{Au}} = [\text{AlkylGBOEt}^+]_{\text{ill}}[\text{AuX}_4^-]_{\text{ill}} \quad (2)
\]

where [AlkylGBOEt]ill and [AuX4]ill are the concentrations of organic cation and tetrahalogenoaaurate anion in aqueous solution after precipitation. The concentration of organic cation ([AlkylGBOEt]ill) was deduced from its initial concentration before precipitation ([AlkylGBOEt]initial), determined from sulphur analysis by ICP-OES, and the amount of AuCl4^- consumed by the precipitation.

\[
[\text{AlkylGBOEt}^+]_{\text{ill}} = [\text{AlkylGBOEt}^+]_{\text{initial}} - ([\text{AuX}_4^-]_{\text{initial}} - [\text{AuX}_4^-]_{\text{ill}}) \quad (3)
\]

The concentrations of AuCl4^- and AuBr4^- were determined by UV-vis spectroscopy.

The average values for pK_Au for [EtGBOEt][AuX4], [PrGBOEt][AuX4] and [BuGBOEt][AuX4], (X = Cl or Br) are reported in Table 1. In order to allow the interpretation of the obtained results, the values of solubility product of IL with Tf2N and Dca anions (see below) were also reported. These results reveal that the ILs containing AuCl4^- are practically immiscible in water (solubility ranging from 5×10^-4 to 5×10^-3 mol L^-1). For the same anion, the solubility of [AlkylGBOEt][AuX4] ionic liquid decreases as the length of alkyl chain of the cation (hydrophobicity) increases. With the same cation, the AuBr4^- ILs are less soluble than those containing AuCl4^-.

The ILs containing AuCl4^- are composed of Au(III) complexes with the ILs containing chloride ions. Indeed, the ILs containing chloride are 3.92 Å and 3.62 Å, respectively. So, AuBr4^- is expected to be larger and softer than AuCl4^-; the larger the ion, the lower the charge density and the solvation energy (weaker ion-solvent) interaction. This explains the lower solubility of the AuBr4^- ILs compared to the AuCl4^- ILs.

**Table 1**: Solubility products (pK_Au) of [AlkylGBOEt][AuX4] and (pK_Au) of [AlkylGBOEt][Tf2N] and [AlkylGBOEt][Dca] compounds (Alkyl = ethyl or n-butyl)

<table>
<thead>
<tr>
<th>IL</th>
<th>AuCl4^-</th>
<th>AuBr4^-</th>
<th>Tf2N</th>
<th>Dca^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtGBOEt][Br]</td>
<td>4.6 (0.1)</td>
<td>6.6 (0.1)</td>
<td>3.4 (0.1)</td>
<td>-</td>
</tr>
<tr>
<td>[BuGBOEt][Br]</td>
<td>5.2 (0.1)</td>
<td>10.3 (0.1)</td>
<td>5.7 (0.1)</td>
<td>3.5 (0.1)</td>
</tr>
</tbody>
</table>

Values in parentheses refer to estimated uncertainty.

These results show that the direct use of [AlkylGBOEt][Br] hydrophilic IL can be a good alternative for removing gold from water by the formation of [AlkylGBOEt][AuX4] giving an immiscible phase. The results for precipitation experiments using bromide salt of [AlkylGBOEt] cations are given in Table 2 and pictures of an intense yellow or orange precipitate obtained are depicted in figure 2. The precipitates, isolated for a ratio ([AlkylGBOEt][Br])/Au = 10, have been analysed. For the three studied systems, elemental analysis (ESI) reveals a partial or total substitution of chloride anions by bromide anions. Indeed, the stoichiometries of precipitates correspond to [PrGBOEt][AuClBr4^-], [BuGBOEt][AuClBr4] and [EtGBOEt][AuBr4^-]. In aqueous solution AuCl4^- anion exhibits a square planar geometry and its UV-vis spectra show a specific absorption with a maxima at 313 nm due to a ligand (π)-metal (σ^*) charge transfer (LMCT) transitions.

The spectrum of AuBr4^- shows two transitions with maxima at 380 nm and 254 nm. The band at 380 nm has a shoulder at 450 nm. The substitution reaction of chloride by bromide ion is justified by the softer character of the latter, leading to the formation of Au^III-Br bonds with higher stability.

**Figure 2**: Snapshots of precipitate taken after mixing [AlkylGBOEt][Br] with HAuCl4.

This substitution reaction was studied by Usher et al. in aqueous solution. According to their study, the progressive substitution of chloride ions by bromide one induces a gradual shift of the LMCT transitions.

[Image 412x124 to 444x232]
transition from 313 nm (AuCl₄⁻) to 380nm (AuBr₄⁻). The molar absorbance of all the intermediate AuClₓBr₄₋ₓ⁺ (x = integer and 1 ≤ x ≤ 4) complexes have been resolved. In our case, the UV-Vis spectra of the precipitates [BuGBOEt⁺][AuClBr₄⁻], [PrGBOEt⁺][AuClBr₄⁻] and [EtGBOEt⁺][AuBr₄⁻] dissolved in ethyl acetate, show only one transition in the region 300-500 nm, with a maxima at 355, 363 and 378 nm, respectively (figure 3). This means that these precipitates correspond more likely to complexes of AuClₓBr₄₋ₓ⁺ stoichiometry rather than a mixture between [AlkylGBOEt⁺][AuCl₄⁻] and [AlkylGBOEt⁺][AuBr₄⁻] in variable proportion. For all [AlkylGBOEt⁺][AuX₄⁻] precipitates, the location of the maximum of the absorbance corroborates the stoichiometry of the complexes deduced from elemental analysis.

Table 2: Extraction efficiency of gold complexes (%E) in water with hydrophilic ionic liquid.

<table>
<thead>
<tr>
<th>[AlkylGBOEt⁺][Br⁻] (mol L⁻¹)</th>
<th>% Au removed (Eₐₚ)</th>
<th>[EtGBOEt⁺][Br⁻]</th>
<th>[PrGBOEt⁺][Br⁻]</th>
<th>[BuGBOEt⁺][Br⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4x10⁻³</td>
<td>99.8</td>
<td>94.7</td>
<td>96.2</td>
<td></td>
</tr>
<tr>
<td>8x10⁻³</td>
<td>99.9</td>
<td>99.8</td>
<td>97.2</td>
<td></td>
</tr>
<tr>
<td>2x10⁻²</td>
<td>99.9</td>
<td>99.9</td>
<td>95.3</td>
<td></td>
</tr>
<tr>
<td>4x10⁻²</td>
<td>99.9</td>
<td>99.9</td>
<td>97.1</td>
<td></td>
</tr>
</tbody>
</table>

The concentration values of [AlkylGBOEt⁺][Br⁻] are those after the mixing of gold(III) and bromide salt solutions; [Au(III)] = 4x10⁻³ mol L⁻¹; a Alkyl = ethyl, n-propyl or n-butyl.

To obtain direct information about the interaction between [AlkylGBOEt⁺] and [AuX₄⁻], the IR spectra of precipitates were carried out. The presence of [AlkylGBOEt⁺] cation in the precipitate was confirmed by the presence of aliphatic C-H stretch (2989, 2938 (Alkyl = C₂H₅) 2980, 2920 (Alkyl = n-C₃H₇) and 2961, 2873 (Alkyl = n-C₄H₉) and C=O stretch (1741, 1620 (Alkyl = C₂H₅) 1736, 1629 (Alkyl = n-C₃H₇) and 1740, 1622 (Alkyl = n-C₄H₉). The carbonyl vibrations in [AlkylGBOEt⁺][AuX₄⁻] are only slightly shifted, compared to those of the corresponding bromide salts which crystallize with one water molecule. This means that the interaction of the organic cations and AuX₄⁻ is mainly of electrostatic nature and the association is less soluble than the corresponding bromide salt of organic cations. In [AlkylGBOEt⁺][AuX₄⁻], the O-H stretch present in the IR spectrum of the bromide salt, is attenuated because of the lesser hydrophilicity of these complexes.

The Eₐₚ values first reveal that gold is successfully removed from water using hydrophilic bromide salt of [AlkylGBOEt⁺] cations. Starting with an aqueous gold solution of 8x10⁻⁵ mol L⁻¹, the values of Eₐₚ exceed 95%. The extraction efficiency is comparable, whatever the salt used, and seems not to be related to the length of alkyl groups.

Liquid-liquid extraction of AuX₄⁻

The values of the extraction percentage (E) and of the distribution coefficient (D) for AuCl₄⁻ and AuBr₄⁻ with [BuGBOEt⁺][Tf₂N⁻] and [EtGBOEt⁺][Tf₂N⁻] ILs are given in Table 3. Snapshots of the extraction of AuX₄⁻ are depicted in figure 4.

Figure 4: Snapshot of ionic liquid phases after extraction of AuCl₄⁻ (left) and AuBr₄⁻ anions (right).
Mechanism of extraction

It is generally assumed, that the transfer of anionic complexes such as AuX₄⁻ from aqueous to IL phase proceeds either by ion-pairing or by anionic exchange. [12-15,22-24]. Ion pairing and anionic exchange are described by the equilibria (4) and (5):

**Ion-pairing (IP):**

\[ \text{AuX}_4^- (\text{w}) + \text{C}^+ (\text{IL}) \rightleftharpoons \text{C}^+ (\text{IL}) + \text{AuX}_4^- (\text{IL}) \]  (4)

**Anionic exchange (AE):**

\[ \text{AuX}_4^- (\text{w}) + \text{A}^- (\text{IL}) \rightleftharpoons \text{AuX}_4^- (\text{IL}) + \text{A}^- (\text{w}) \]  (5)

In general case, the related equilibria constants for the ion pair extraction and the ion exchange reaction are expressed by eqs (6) and (7), respectively.

\[ K_{\text{IP-ex}} = \frac{[\text{AuX}_4^- \text{IL}] [\text{AuX}_4^- \text{w}][\text{C}^+]_{\text{w}}} \]  (6)

\[ K_{\text{AE-ex}} = \frac{[\text{AuX}_4^- \text{IL}] [\text{A}^-]_{\text{IL}} [\text{AuX}_4^- \text{w}]} \]  (7)

These equations are based on the assumption of dilute solutions. Therefore, it is assumed that the activities of C⁺ and A⁻ in the ionic liquid phase are equal to unity, and that no aggregates or micelles are formed.

The anionic exchange and the ion-pairing extraction are connected (or concerted) processes that may occur simultaneously. These processes are interrelated by the solubility product of ionic liquid that describes the relationship between the cation and the anion of the aqueous phase. The eqs. 8 and 9 are the equilibrium and the mass action law for ionic liquid in contact with an aqueous phase. [25]

\[ \text{C}^+ (\text{IL}) + \text{A}^- (\text{IL}) \rightleftharpoons \text{C}^+ (\text{w}) + \text{A}^- (\text{w}) \]  (8)

\[ K_{\text{sp}} = [\text{C}^+] [\text{A}^-] = s^2 \]  (9)

where s is the ionic liquid solubility in water and \( K_{\text{sp}} \) the solubility product of ILs. In both cases the subscripts "IL" and "w" indicate a species present in the IL and aqueous phases, respectively. In water, the solubility of \([\text{EtGBOEt}^+] [\text{Tf}_2\text{N}^-] \) [BuGBOEt⁺][Tf₂N⁻] and [BuGBOEt⁺][Dca⁺] are 1.46×10⁻⁵, 1.88×10⁻⁵ and 1.80×10⁻⁷ mol L⁻¹, respectively and their corresponding solubility products are 2.13×10⁻⁶, 3.53×10⁻⁴ and 3.24×10⁻⁵, respectively. Before extraction the concentration of C⁺ and A⁻ are equivalent. The ionic liquid phases can be considered as infinite reservoirs of their individual components, whatever the process involved for the extraction of AuX₄⁻. After extraction, the concentrations of the organic cation and the anion in aqueous phase, should verify the solubility product of ionic liquid. For example, if the overall extraction process involves only ion-pairing mechanism, the consumption of organic cations due to the formation and solubilisation of \([\text{C}^+][\text{AuX}_4^-]\) in ionic liquid phase should be compensated by an increase of the concentration of \([\text{A}^-]\) in aqueous solution. Conversely, a pure anionic exchange mechanism induces an increase of the \([\text{A}^-]\) concentration in aqueous solution that should be compensated by a decrease of the concentration of organic cation in water. These considerations render difficult the discrimination between ion-pairing mechanism and anionic exchange. Nevertheless, with \([\text{EtGBOEt}^+] [\text{Tf}_2\text{N}^-] \) and [BuGBOEt⁺][Tf₂N⁻], it is possible to determine which mechanism operates or prevails from the analysis of sulphur release in aqueous solution which accompanies, the transfer of AuX₄⁻ from the aqueous to the ionic liquid phase. If we assume a pure ion-pairing process, the concentration of \([\text{AlkylGBOEt}^+]\) in water can be estimated from the extraction yield of AuX₄⁻ (\( E_{\text{Au}} \)):

\[ [\text{AlkylGBOEt}^+]_{\text{IP}} = s - C_{\text{AuX}_4^- \text{w}} \times E_{\text{Au}} \]  (10)

Since the concentrations of \([\text{AlkylGBOEt}^+]\) and \([\text{Tf}_2\text{N}^-]\), in the presence of \( E_{\text{Au}} \), should check the solubility product of \([\text{AlkylGBOEt}^+] [\text{Tf}_2\text{N}^-]\), the concentrations of \( E_{\text{Au}} \) in the aqueous phase can be calculated from the following equation:

\[ [\text{Tf}_2\text{N}^-]_{\text{IP}} = \frac{K_{\text{sp}}}{[\text{AlkylGBOEt}^+] \times K_{\text{sp}}} - \frac{C_{\text{AuX}_4^- \text{w}} \times E_{\text{Au}}}{s} \]  (11)

Inversely in a case of a pure anionic exchange process the concentration of \([\text{Tf}_2\text{N}^-]\) in water is estimated from the extraction yield of AuX₄⁻:

\[ [\text{Tf}_2\text{N}^-]_{\text{AE}} = s + C_{\text{AuX}_4^- \text{w}} \times E_{\text{Au}} \]  (12)

\[ [\text{AlkylGBOEt}^+]_{\text{AE}} = \frac{K_{\text{sp}}}{[\text{Tf}_2\text{N}^-] \times s} - \frac{C_{\text{AuX}_4^- \text{w}} \times E_{\text{Au}}}{s} \]  (13)

It is clearly seen, that the concentration of \([\text{Tf}_2\text{N}^-]\) in aqueous solution will be different according to the type of mechanism involved in the transfer of AuX₄⁻. The determination of sulphur content in aqueous solution makes it possible to estimate that of \( E_{\text{Au}} \) after extraction. Then it is possible to identify the mechanism involved in the transfer of AuX₄⁻ from aqueous solution to IL phase. Figure 5 shows experimental and calculated concentrations of \([\text{Tf}_2\text{N}^-]\) in aqueous solution for anionic exchange or ion-pairing mechanisms, with \([\text{BuGBOEt}^+] [\text{Tf}_2\text{N}^-]\) and [EtGBOEt⁺][Tf₂N⁻], and for several concentrations of \( HAuCl_4 \). Similar trends are observed with the AuBr₄⁻ ions for both ionic liquids.

![Figure 5](image-url)

**Figure 5**: Release of \( \text{Tf}_2\text{N}^- \) in aqueous solution after extraction of AuCl₄⁻ in (a) \([\text{EtGBOEt}^+] [\text{Tf}_2\text{N}^-]\) IL and (b) \([\text{BuGBOEt}^+] [\text{Tf}_2\text{N}^-]\) IL as a function of \( HAuCl_4 \) initial concentration. ○ experimental data \((\text{E})\) calculated from eq.11 considering anionic-exchange mechanism (○) calculated from eq. 10 considering ion-pairing extraction mode for \([\text{EtGBOEt}^+] [\text{Tf}_2\text{N}^-] - \text{HAuCl}_4 \text{ system};

○ experimental data \((\Delta)\) calculated from eq. 12 considering anionic-exchange mechanism for \([\text{BuGBOEt}^+] [\text{Tf}_2\text{N}^-] - \text{HAuCl}_4 \text{ system.}

The solubility of \([\text{BuGBOEt}^+] [\text{Tf}_2\text{N}^-]\) is lesser than the concentrations of AuCl₄⁻ used in our experiments, so that a pure ion-pairing process can not be considered. In this case, it is not possible to calculate the release of sulphur in water associated to this process.
Moreover, as seen in figure 5, with [BuGBOEt⁺][Tf₂N⁻], whatever the initial concentration of AuCl₄⁻, the experimental concentrations of [Tf₂N⁻]ex are really close to those calculated with a pure anion exchange mechanism meaning that this process prevails in this system. It is interesting to note that the calculations of the Tf₂N⁻ release in aqueous solution, carried out by considering a mixed process, anion exchange and ion pairing, would lead to higher values of Tf₂N⁻ release than those calculated with a pure ion exchange process.

The extraction mode with [EtGBOEt⁺][Tf₂N⁻] involves simultaneously a mixed process by ion pairing and anionic exchange (figure 5), for concentrations of AuX₄⁻ lower than 6x10⁻⁵ mol L⁻¹. However, we observe a gradual increase of AuX₄⁻ extraction by anionic exchange with the increase of the AuCl₄⁻ concentration in solution. The extraction of AuX₄⁻ for a concentration of 8x10⁻⁵ mol L⁻¹ proceeds at 95% via anionic exchange. The higher rate of AuX₄⁻ extraction via ion-pairing for [EtGBOEt⁺][Tf₂N⁻] compared to [BuGBOEt⁺][Tf₂N⁻] is related to its higher solubility which leads to a greater concentration of organic cation in solution, enhancing the formation of ion-pairs in aqueous solution.

To further confirm the validity of anionic exchange and ion-pairing mechanism, for the partitioning of AuX₄⁻ between water and the IL phases, extraction experiments were carried out with Li[Tf₂N] solutions at concentrations ranging between 0.05 and 0.5 mol L⁻¹. These experiments allow us to examine the influence of Tf₂N⁻ concentration in aqueous solution on the distribution coefficient of gold between aqueous and the IL phases. Similar extraction experiments of tetrahalogenoaurate anions in NaDca aqueous solutions, with concentrations ranging between 0.2 and 1 mol L⁻¹, are carried out using [BuGBOEt⁺][Dca] as extractant phase. Considering the mass action law relative to anionic exchange (eqs. 5 and 7), the distribution coefficient of AuX₄⁻ should decrease with the increase of the [A⁺] concentration in aqueous solution. This is confirmed by experimental results (figure 6), which show a drastic effect of the increase of the anion concentration, in aqueous phase, on the coefficient distribution values. This indicates that the anions constitutive of ILs compete with tetrahalogenoaurate anions in metathesis reactions with organic cations. This result confirms the predominance of the anionic exchange as a main extraction mode for all the studied systems.

The equilibrium constants associated to anionic exchange and ion-pairing transfer of tetrahalogenoaurate anions from aqueous to IL phase (eqs. 6 and 7) were determined by the approach developed by Katsuta et al. 25, 26

According to the mass action laws (eqs. 6 and 7), the distribution coefficient are related to the concentrations of [A⁺]w and [C⁻]w, by the following equations:

\[
\log D = \log K_{IP,ex} + \log [C^-]_w \tag{14}
\]

\[
\log D = \log K_{AE,ex} - \log [A^-]_w \tag{15}
\]

Therefore \(K_{IP,ex}\) and \(K_{AE,ex}\) are related by the relation:

\[
K_{AE,ex}/K_{IP,ex} = K_{IP} \tag{16}
\]

The equilibrium constants of eqs. 6 and 7 can be determined from eq. 15, by plotting \(\log D_{Au}\) as a function of the logarithm of the anion concentration of \(\log [A^-]\) (figure 7). The slope of the graph should be equal to unity and the intercept gives the \(K_{AE,ex}\) Value. Then the \(K_{IP,ex}\) value can be deduced from the value of \(K_{AE,ex}\) and the solubility product of ionic liquid \(K_{IP}\). In our fitting procedure, a slope equal to unity was imposed. For the Tf₂N⁻ based ILs, the Katsuta model fits quite well the experimental data (figure 7) obtained with AuBr₄⁻, with good correlation coefficients (\(r^2 > 0.98\)). The applicability of Katsuta’s model remain acceptable, in the case of AuCl₄⁻, but with less good correlation coefficients (\(r^2 \geq 0.93\)).

![Figure 6: The distribution ratio (D) of AuX₄⁻ as a function of the concentration of the anion [A^-] (a) AuCl₄⁻, (results obtained with [BuGBOEt⁺][Tf₂N⁻] and [EtGBOEt⁺][Tf₂N⁻] ILs are very close and, for clarity only one curve was depicted in the graph to represent the general trend observed), (b) AuBr₄⁻](image)
[BuGBOEt][Tf₂N] compared to [EtGBOEt][Tf₂N]. Moreover, it appears clearly that partitioning is also dependent on the hydrophilic/hydrophobic character of the anion of the ionic liquid. A hydrophilic anion will be exchanged more easily with tetrahalogenoaurate anion than an hydrophobic anion. The relative values of \( K_{\text{AE-ex}} \) are compatible with the fact that Dca⁻ anion is more hydrophilic than Tf₂N⁻ anion and consequently the \( D_{\text{Au}} \) values are higher with Dca⁻ based ILs than with Tf₂N⁻ based ILs.

**Figure 7**: Plot of log \( D_{\text{Au}} \) versus log [A⁻] concentration, open symbol AuCl₄⁻ filled symbol AuBr₄⁻ (a) [EtGBOEt][Tf₂N] (b) [BuGBOEt][Tf₂N] (c) [BuGBOEt][Dca]

**Table 4**: the \( K_{\text{AE-ex}} \) and \( K_{\text{IP-ex}} \) values determined from figure 7, by application of Katsuta’s model.

<table>
<thead>
<tr>
<th>ILs</th>
<th>Anion</th>
<th>( K_{\text{AE-ex}} )</th>
<th>( K_{\text{IP-ex}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EtGBOEt][Tf₂N]</td>
<td>AuCl₄⁻</td>
<td>2.76</td>
<td>7.82×10⁻³</td>
</tr>
<tr>
<td>[BuGBOEt][Tf₂N]</td>
<td>AuCl₄⁻</td>
<td>2.52</td>
<td>1.18×10⁻⁶</td>
</tr>
<tr>
<td>[BuGBOEt][Dca]</td>
<td>AuCl₄⁻</td>
<td>83.20</td>
<td>3.91×10⁻⁷</td>
</tr>
<tr>
<td>[EtGBOEt][Tf₂N]</td>
<td>AuBr₄⁻</td>
<td>17.93</td>
<td>5.08×10⁻⁴</td>
</tr>
<tr>
<td>[BuGBOEt][Tf₂N]</td>
<td>AuBr₄⁻</td>
<td>48.31</td>
<td>2.27×10⁻⁷</td>
</tr>
<tr>
<td>[BuGBOEt][Dca]</td>
<td>AuBr₄⁻</td>
<td>194.3</td>
<td>9.12×10⁻⁷</td>
</tr>
</tbody>
</table>

We analyzed the coordination of Au(III) in aqueous solution and in ILs phase, dissolved in ethyl-acetate, by UV-vis spectroscopies. The figure 8 shows AuCl₄⁻ and AuBr₄⁻ absorption spectra in water and in ILs phases. The absorption spectra of gold complexes in IL phases, with [EtGBOEt][Tf₂N] and [BuGBOEt][Tf₂N] ILs, show similar features as those in aqueous solutions, regardless of the concentration of AuX₄ extracted. These observations indicate that the coordination of Au(III) does not change and that the ILs phases contain the AuCl₄⁻ orAuBr₄⁻ species. The absorption maximum appears at 323 nm in [BuGBOEt][Tf₂N] phase and at 333 nm in [EtGBOEt][Tf₂N] for AuCl₄⁻ species. The peak shifting may be caused by the interaction between organic cation with AuX₄⁻ or by the change of solvent (ethyl acetate). A similar trend is observed with AuBr₄⁻ with a shift of the absorbance maximum close to 20 nm. The UV-vis spectra of the two tetrahalogenoaurate anion, in [BuGBOEt][Dca], present nearly the same feature with a sharp transition between 250-260 nm and a shoulder between 270-280 nm. As seen earlier, such a shift towards higher energy compared to the spectrum in aqueous media or in Tf₂N⁻ based ionic liquid, can be ascribed to the substitution of bromide or chloride ion by dicyanamide anion. This interpretation was confirmed by a titration of HAuCl₄ and HAUaBr₄ ion by NaDca in aqueous solutions (results not shown here). The substitution is effective for ratio [Dca⁻][AuX₄⁻] higher than 200, this condition is reached in [BuGBOEt][Dca] where the Dca⁻ concentration is estimated close to 3 mol L⁻¹, the concentration of AuX₄ used in all our experiments being less than 1x10⁻⁵ mol L⁻¹.

**Figure 8**: UV-vis spectra of tetrahalogenoaurate anions in ionic liquid phase (a) AuCl₄⁻ (b) AuBr₄⁻: (1) aqueous solution, (2) [EtGBOEt][Tf₂N], (3) [BuGBOEt][Tf₂N] (4) [BuGBOEt][Dca].

**Conclusion**

Tetrahalogenoaurate anions have been successfully removed from water using betaine derivative cations ILs. Such compounds, which are accessible via simple synthetic routes, may constitute good substitutes to the organic solvents and allow the development of proper methodology for the gold recovery from aqueous industrial effluents. Anionic gold complexes may be efficiently extracted from water by using hydrophilic bromide salt of betaine derivative. In all cases gold is removed very efficiently from the aqueous phase with an extraction yield higher than 90%. The liquid-liquid extraction of gold(III) carried out with hydrophilic ionic liquids, constituted by the association of cationic betaine derivatives with bis(trifluoromethanesulfonyl)imide (Tf₂N⁻) or dicyanamide anions (Dca⁻), leads to the extraction yields and the distribution coefficients
higher than 99% and 150, respectively. The affinity of tetrahalogenoaurate anions for the IL phases increases in the order:

\[ [\text{EtGBOEt}^+][\text{TF}_2\text{N}]^- < [\text{BuGBOEt}^+][\text{TF}_2\text{N}]^- < [\text{BuGBOEt}^+][\text{Dca}]^- \]

And the affinity of tetrahalogenoaurate anions for the ionic liquid phases increases in the order:

\[ [\text{AuCl}_4^-]<[\text{AuBr}_4^-] \]

These trends are in accordance with the strength of the interaction between tetrahalogenoaurate anions and organic cation evaluated by the determination of the $K_{AB}$ values. However, the higher affinity of tetrahalogenoaurate anions for dicyanamide based ILs, compared to bis(trifluoromethanesulfonyl)imide one, can be explained by the higher hydrophilicity of dicyanamide anion which favors anionic exchange process.

**Experimental**

**Reagents**

HAuCl$_4$$\cdot$3H$_2$O (99.9%) was purchased from Aldrich. For extraction experiments, a stock solution was prepared with highly purified water and metal salts. The solutions of AuBr$_4^-$ were prepared from HAuCl$_4$ solutions by addition of sodium bromide in a ratio [Br$^-$]/[Au(III)] equal to 10. The complete conversion of AuCl$_4^-$ into AuBr$_4^-$ was checked by UV-vis spectrophotometry.

**Precipitation experiments**

The precipitation experiments are carried out by mixing 1.5 mL of the initial solution of HAuCl$_4$ at a concentration of 8$\times$10$^{-3}$ mol L$^{-1}$, with 1.5 mL of [AlkylGBOEt$^+$][Br]$^-$ at concentrations ranging between 8 $\times$ 10$^{-3}$ and 8 $\times$ 10$^{-2}$ mol L$^{-1}$. For each experiment, the tube was placed on a shaker for 24h and then centrifuged at 2000 rpm for 10 minutes. The residual concentration of AuCl$_4^-$ in aqueous solution was determined by UV-vis spectroscopy. The same experiments were carried out with AuBr$_4^-$ to determine the solubility product of [EtGBOEt$^+$][AuBr$_4^-$], [PrGBOEt$^+$][AuBr$_4^-$] and [BuGBOEt$^+$][AuBr$_4^-$]. Since AuCl$_4^-$ based ionic liquids were more soluble than their analog compounds containing AuBr$_4^-$, the solubility product of [EtGBOEt$^+$][AuCl$_4^-$], [PrGBOEt$^+$][AuCl$_4^-$] and [BuGBOEt$^+$][AuCl$_4^-$] were determined by contacting HAuCl$_4$ solutions with aqueous solutions saturated by [BuGBOEt$^+$][TF$_2$N]$^-$ and [EtGBOEt$^+$][TF$_2$N]$^-$.

In this case, to avoid dilution of aqueous saturated ILs solutions by AuCl$_4^-$ solutions, 2 mL of aqueous solution previously contacted during 24 hours with ILs phase, was collected and lyophilized. The lyophilisat of aqueous phase was then contacted with 2 mL AuCl$_4^-$ solution. Thus no dilution occurs upon mixing of the IL and the AuCl$_4^-$ solutions, and the conditions for the precipitation of [AlkylGBOEt$^+$][AuCl$_4^-$] are reached. The solutions were then shaken during 24 hours and centrifugated before analysis. The initial concentration of organic cation was determined from the measurements of sulphur concentration by ICP-OES spectroscopy. It was previously checked, by sulphur and TOC measurements, that the lyophilisation does not affect the composition of aqueous solutions.

**Extraction experiments**

Au(III) aqueous solutions were prepared by dissolution of HAuCl$_4$ 3H$_2$O in deionized water. Extraction yields (E) and distribution ratios (D) were determined by mixing equal volume (1 mL) of IL and aqueous phase. The mixture was shaken for 24h to reach equilibrium and then centrifuged at 2000 rpm during 5 minutes. The phases were then separated for analysis. The Au(III) content metal ion in the aqueous phase was determined by UV-vis spectroscopies applying the Beer–Lambert law at the maximum absorption wavelength ($\lambda_{max} \approx 313$ nm and 380 nm for AuCl$_4^-$ and AuBr$_4^-$, respectively) of gold complexes and using calibration solutions ranging from 10 to 100$\mu$mol L$^{-1}$. Before analysis, the samples were diluted in HCl or HBr 0.05 mol L$^{-1}$ to suppress hydrolysis of solutions before analysis. According to Usher et al.\textsuperscript{21}, AlCl$_3$ is stable below pH 3 and AuBr$_3$ below pH 4. Moreover, in the case of AuCl$_4^-$, a calculation based on the dissociation constant of AuCl$_4^-$ and AuCl$_4$OH determined by Wagman et al.\textsuperscript{22} and Baes and Mesmer\textsuperscript{23}, show that in our conditions, the extent of hydrolysis does not exceed 1%.

Complementary measurements were monitored by ICP-OES from Thermoscientific (cap 6000 series) to confirm the UV-vis measurements. In all cases, the pH of aqueous phase was checked before and after gold extraction. Since solutions are not buffered, the pH was related to the free concentration of H$^+$ ions brought by HAuCl$_4$. 3H$_2$O. The pH variations during the extraction process were negligible. The metal ion concentration in the IL phase was deduced from the difference between the initial concentration of metal ion in the aqueous phase and the concentration of metal ion after extraction.

The efficiency of the extraction process was evaluated by the determination of the extraction percentage (%E) calculated using the following equation:

\[ %E = 100 \times \frac{C_{in} - C_{fin}}{C_{in}} \] (17)

where $C_{in}$ and $C_{fin}$ (mol L$^{-1}$) represent the concentrations in the initial and in the final aqueous solution, respectively. $V_w$ and $V_{IL}$ correspond to the volumes of water and ionic liquid, respectively; in general, $V_w$ and $V_{IL}$ are equal to 1 mL. However, for the analysis of the extraction mode of AuX$_4^-$, some experiments were done with a ratio $V_w/V_{IL}$ equal to 4. The extraction percentages (%E) were determined at 298 K. The concentration of Au(III) solutions lies in the range from 4$\times$10$^{-4}$ to 8$\times$10$^{-3}$ mol L$^{-1}$. The experimental error on the extraction yield values is estimated to be less than 3%.

For the liquid–liquid extraction experiments, the distribution coefficient (D) is calculated using the following formula:

\[ D = \frac{(C_{in} - C_{fin})V_w}{C_{fin}V_{IL}} \] (18)

The maximum D value measurable in this study is assumed to be 5$\times$10$^3$. The relative uncertainty on D is ± 10%. Experimental results, done in duplicate, agree within 5%.

**Physical measurements**

Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 2400 C, H, N element analyzer in our University. UV-visible spectra of Au(III) solutions were recorded using a Cary-5000 Varian spectrophotometer. Total concentration of sulphur and gold were carried out by ICP-OES from Thermoscientific (cap 6000 series).

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Notes and references

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