doi:10.20944/preprints202103.0117.v1

Article

Insight the liquid-liquid extraction system $AuCl_4^-/HCl/A327H^+Cl^-$ ionic liquid/toluene

Francisco J. Alguacil[1], Félix A. Lopez[1*]

[1] National Center for Metallurgical Research (CENIM), Spanish National Research Council (CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, Spain; fjalgua@cenim.csic.es (F.J.A.)
* Correspondence: f.lopez@csic.es (F.A.L.); Tel.: (+34-915 538 900)

Abstract: The ionic liquid $A327H^+Cl^-$ is generated by reaction of the tertiary amine A327 (industrial mixture of tri-octil and tri-decyl amines) and hydrochloric acid solutions. Further, the extraction of Au(III) by $A327H^+Cl^-$ ionic liquid under various variables, including metal and ionic liquid concentrations, has been investigated. Results indicate that $A327H^+AuCl_4^-$ is formed, by an exothermic (ΔH^o= -3 kJ/mol) reaction, in the organic solution. Aqueous ionic strength influences the formation constants values and the specific interaction theory (SIT) is used to estimate the interaction coefficient between $AuCl_4^-$ and H^+. Gold (III) is stripped using thiocyanate media, and from the strip solutions, gold is precipitated as gold nanoparticles.

Keywords: gold(III); $A327H^+Cl^-$; liquid-liquid extraction; ionic liquids; nanoparticles

1. Introduction

The concept of urban mining becomes of widespread use, because nowadays, recycling is of the foremost importance, and modern life resulted in the generation of wastes containing a variety of valuable or non-valuable materials.

Including under the term of valuable items, electronic wastes, jewelry scraps, and similar products are of interest because they contained metals, and among them, gold pointed out not only by its bright but also, due to its price, in terms of money or profits. Thus, the separation and recovery of this precious metal, from any of the above materials, focuses a wide interest, whereas different separation technologies are proposed for this task: adsorption [1,2], ion exchange [3], liquid membranes [4,5] and liquid-liquid extraction using ethers [6–8], amides [9], amines [10], ionic liquids [11] or phosphinic acid derivatives [12].

Basically, the procedure of recovery gold begins by as leaching step, normally done with *aqua regia*, followed by a number of separation steps, to yield, at the process end, pure gold. Liquid-liquid extraction or solvent extraction is one of these separation steps, being currently used in the production of a series of metals, specially copper. The technology uses an organic extractant, normally diluted in a suitable diluent, which is characteristic to each case, to make the operation selective in relation with the targeted metal. The advantages of liquid-liquid extraction on other separation technologies (i.e. liquid membranes, adsorption, ion exchange) rely in its operational characteristics, i.e. short operational times (often in the few minutes range), possibility of the treatment of great feed solution volumes at these short times, and selectivity towards gold compounds in solution.

Including in the organic extractants used in liquid-liquid extraction, ionic liquids present a further interest due to their inherent properties [13,14], which make of them to be considered as *green solvents*. Ionic liquids had been amply used, in the recovery of metals, being some recent applications given in the literature, i.e. base metals [15–17], rare earths [18–20], indium [21,22], gold [23,24] and others [25,26].

This work joins the points mentioned above: i) ionic liquids, ii) gold price and the opportunity of its recovery from urban wastes, ii) the usefulness of liquid-liquid extraction in this profitable and environmental field of interest and iii) ionic liquid. $A327H^+Cl^-$ ionic liquid, prepared from the reaction of a tertiary amine, A327, and HCl, is used as extractant, since no data were apparent available about its use in the recovery of gold(III)-bearing aqueous solutions. In the liquid-liquid extraction operation, different variables influencing the extraction of Au(III) are investigated: contact time, temperature, gold(III), HCl and ionic liquid concentrations in the aqueous and organic phases, respectively, the performance of the organic reagent in presence of other metals in the aqueous phase, and also the comparison of the performance of $A327H^+Cl^-$ ionic liquid against that of other ionic liquids. The stripping step is investigated using different strippants, and from the gold-bearing strip solution gold nanoparticles are finally yielded.

2. Materials and Methods

The ionic liquid used in this investigation was generated from the tertiary amine Hostarex A327 (Sanofi), with molecular weight: 395 and density 20º C: 0.82 g/cm^3), being an *ad hoc* industrial mixture of tri-isooctyl $(C_8H_{17})_3N$ and tri-decyl $(C_{10}H_{21})_3N)$ amines. The reagent used without further purification. Toluene (AR grade) was used to dilute the amine. It was claimed in the literature, that organic diluents were of no necessity when ionic liquids were used in the extraction of metal, but the experience of the author of this work showed that the use of an organic diluent was needed in this particular use (liquid-liquid extraction) of the ionic liquids because: i) the high viscosity of the ionic liquids makes doubtful an easy and quick phases separation, moreover, this viscosity will causes flowing problem in the eve of scaling-up to mixer-settlers the process, and ii) the use of a diluent allowed to use the correct concentration of the ionic liquid in each case (and this work is an example of the extreme low ionic concentrations that can be used to extract gold from the feed solution). Being the extractant one of the most, if not the most, expensive input in the circuit, it had no sense to work with a concentration of non-used extractant in the liquid-liquid extraction circuit.

Other chemicals are of AR grade, with the exception of Cyphos IL101 (Solvay), Aliquat 336 (Fluka) Hostarex A324 (Sanofi) and Primene 81R (Rohm and Haas), which were used without further purification. The active groups of these reagents were given in Table 6.

Extraction-stripping tests were carried out in jacketed separation funnels using mechanical shaking, *via* a flour blades impeller. The process normally works with dispersed aqueous phases and continuous organic ones. In extraction tests, 20 mL of the corresponding phases were used, and after phase separation (in the order of 5 min time), hydrochloric acid concentrations in the organic phases were analyzed by titration, in ethanol medium and using bromothymol blue as indicator, with standard NaOH solutions and the HCl concentrations in the aqueous phases were estimated by the mass balance; metals were analyzed in the raffinate (associated error ±3%) by AAS (Perkin Elmer 1100B spectrophotometer); and the corresponding concentration in the extracted phase was calculated also by the mass balance. Stripping experiments were carried out following the same procedure than above, except in the case of using different V_{org}/V_{aq} relationships.

Gold precipitation was done in a glass reactor containing, under gentle stirring, the gold-bearing strip solution to which a weighed amount (0.1 g) of sodium borohydride were sequentally added. After filtration, gold nanoparticles were visualized using a magnifier, whereas microstructural characterization had been carried out using a Hitachi S-4800 Scanning Electron Microscope equipped with an Oxford Instrument energy dispersive X-ray (EDX) microanalyzer.

3. Results

3.1. Preparation of A327H$^+$Cl$^-$ ionic liquid

This ionic liquid was prepared by reaction of the tertiary amine A327 diluted in toluene and 1M HCl solutions, and the results were estimated by the distribution coefficient D, defined as:

$$D = \frac{[HCl]_{org}}{[HCl]_{aq}} \quad (1)$$

where $[HCl]_{org}$ and $[HCl]_{aq}$ were the HCl concentrations in the extracted phase and in the raffinate, at the equilibrium, respectively. A plot of log D versus log $[A327]_{org}$ was shown in Fig.1.

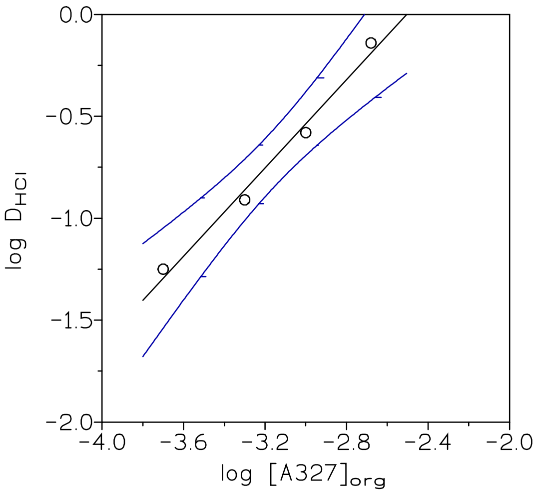

Figure 1. Variation of log D_{HCl} with log $[A327]_{org}$. Aqueous phases: 1 M HCl. Organic phase: 0.05-0.4 M amine A327 in toluene. Temperature: 20º C. Time: 10 min. V_{org}/V_{aq}: 1. Dotted line showed 95% confidence interval of the regression line.

3.2. Gold extraction

3.2.1. Influence of the equilibration time

The influence of this variable on gold extraction was investigated with an aqueous solution of 1.0×10^{-4} M Au(III) in 2 M HCl, and an organic solution containing 2.1×10^{-4} M ionic liquid in toluene, temperature was of 20º C, and a V_{org}/V_{aq} ratio of 1 was used.

3.2.2. Influence of the temperature

The variation of this variable in the 20-50º C range on gold extraction was investigated. In this case the aqueous solution was of 5.1×10^{-4} M gold(III) in 4 M HCl, whereas the organic solution was a 5.3×10^{-5} M ionic liquid in toluene solution. Equilibration time was 10 min and again using a V_{org}/V_{aq} ratio of 1. The experimental results were given in Table 1.

Table 1. Influence of the temperature on gold extraction

Temperature, (ºC)	Gold extraction (%)	log D_{Au}
20	66	0.28
30	59	0.15
40	52	0.04
50	40	-0.17

3.2.3. Influence of the HCl concentration in the aqueous solution

The extraction of gold at various HCl concentrations in the aqueous solution was investigated, and the experimental results were shown in Fig. 2, which represented the percentage of gold extraction versus the HCl concentration in the raffinate phase.

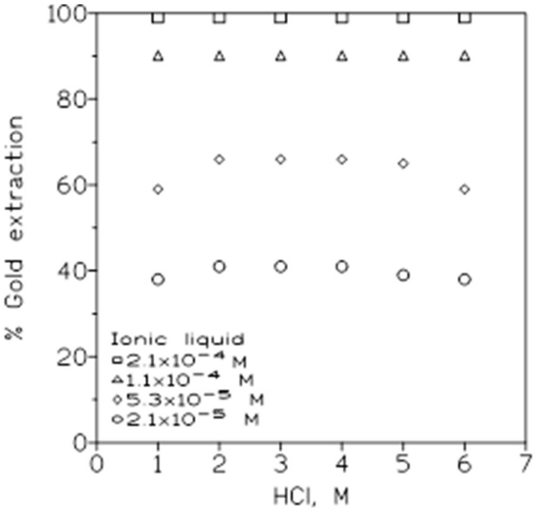

Figure 2. Gold extraction at different HCl and ionic liquid concentrations. Aqueous phase: $5.1\text{x}10^{-5}$ M gold in HCl. Organic phase: different ionic liquid concentrations in toluene. Temperature: 20º C. Time: 10 min. V_{org}/V_{aq}: 1.

3.2.4 Influence of the ionic liquid concentration in the organic phase

The investigation about the influence of this variable on gold(III) extraction was performed using the same conditions as described in Fig. 2, showing this same Figure the results derived from this investigation.

3.2.5. Influence of the initial gold concentration

The effect of this variable on the extraction of gold, by $A327H^+Cl^-$ ionic liquid in toluene, using aqueous phases containing different metal concentrations in 4 M HCl and organic phases of $1.1\text{x}10^{-4}$ M ionic liquid in the diluent, was investigated, being the results summarized in Table 2.

Table 2. Influence of the initial metal concentration on gold extraction

$[Au]_0$ (M)	log D_{Au}
$2.5x10^{-5}$	0.96
$5.1x10^{-5}$	0.95
$1.0x10^{-4}$	0.95

Temperature: 20ºC. Equilibration time: 10 min. V_{org}/V_{aq}: 1

3.2.6. Gold extraction from multielemental solutions

In the recycling of, i.e electronic wastes, gold can be accompanied in the solution by a series of base metals, being the most commonly found Fe(III), Cu(II) and Ni(II), thus, their possible influence on gold extraction was also investigated, and in this case, metal equimolar concentrations were used. The results from these investigations were summarized in Table 4. Taking into consideration the definition of the separation factor, $\beta_{Au/M}$:

$$\beta_{Au/M} = \frac{D_{Au}}{D_M} \quad (2)$$

where D_{Au} and D_M represented to the experimental values of the distribution coefficients (see eq. (1)), of gold and the corresponding metals, respectively, Table 5 showed the values of these separation factors.

Table 4. Percentages of metals extraction from multielemental solution

System	HCl (M)	Au (%)	Fe (%)	Cu (%)	Ni (%)
Au-Fe-Cu-Ni	2	89	19	-	-
Au-Fe-Cu-Ni	4	91	15	3	-

Aqueous phase: $5.1x10^{-5}$ M (each) Au(III), Fe(III), Cu(II), Ni(II) in HCl solutions. Organic phase: $1.1x10^{-4}$ M ionic liquid in toluene. Temperature: 20º C. Time: 10 min. V_{org}/V_{aq}: 1

Table 5. Values of β for the present system

Pair	HCl (M)	$\beta_{Au/M}$
Au-Fe	2	37
	4	59
Au-Cu	2	quantitative
	4	>300
Au-Ni	2	quantitative
	4	quantitative

3.2.7. Gold extraction using various ionic liquids

The performance of $A327H^+Cl^-$ ionic liquid towards gold extraction was also compared against the extraction of this precious metal by other ionic liquids. In these experiments, the aqueous solutions were of $5.1x10^{-5}$ M gold in 1 or 6 M HCl, and the organic solutions were of $1.1x10^{-4}$ M of the extractant in toluene. The results were shown in Table 6.

doi:10.20944/preprints202103.0117.v1

Table 6. Gold extraction using various ionic liquids

Ionic liquid	**Active group**	**HCl (M)**	**gold extraction (%)**
Cyphos IL101	QPS-chloride form	1	98
		6	96
Aliquat 336	QAS-chloride form	1	10
		6	10
$A324H^+Cl^-$	QAS-chloride form	1	78
		6	60
$P81RH^+Cl^-$	QAS-chloride form	1	15
		6	8
$A327H^+Cl^-$	QAS-chloride form	1	90
		6	90

Temperature; 20º C. Time; 10 min. V_{org}/V_{aq}: 1. QPS: quaternary phosphonium salt. QAS: quaternary ammonium salt. A324: tertiary amine, precursor of the ionic liquid. P81R: primary amine, precursor of the ionic liquid.

3.3. Gold stripping

The stripping of gold from loaded organic phases was accomplished by the use of thiocyanate solutions, as the matrix component of the solution, due to the great affinity that Au(III) had on thyocianate ion, forming the $Au(SCN)_4^-$ in the solution with log β_4 of 43.66 [27].

3.3.1. Influence of the equilibration time

Experiments were carried out with organic phases of 2.1×10^{-4} M of the ionic liquid in toluene loaded with 5.1×10^{-5} M gold at 20º C and using a V_{org}/V_{aq} ratio of 1. A 0.5 M NaSCN solution was used as strippant.

3.3.2. Influence of the composition of the stripping solution

Gold stripping was accomplished using various strippants and organic phases of 2.1×10^{-4} M of the ionic liquid in toluene loaded with 5.1×10^{-5} M gold. Table 7 resumed the results from these experiments. Moreover, the addition of LiCl or HCl to the NaSCN solution was investigated. A second stripping step was done on the organic solution resulting from the first strip, using fresh strippant solutions. The results were given in Table 8.

Table 7. Gold stripping using various strippants

Strip solution	% gold stripping
0.5 M NaSCN	47
0.5 M NaSCN+0.5 M LiCl	61
0.5 M NaSCN+0.5 M HCl	55
aqueous solution of pH 2.5 (HCl)	3
aqueous solution of pH 5	-

Temperature: 20º C. Time: 15 min. V_{org}/V_{aq}: 1

Table 8. Gold stripping after two steps

Strip solution	% gold stripping (1st step)	% gold stripping (2nd step)
0.5 M NaSCN+0.5 M LiCl	61	>99
0.5 M NaSCN-0.5 M HCl	55	>99

Operational conditions as in Table 7. The percentage of gold stripped in the second step was calculated on the basis of the residual gold concentration in the organic phase after 1st step

The influence of the NaSCN or LiCl concentrations, in the strip solution, on gold stripping was also investigated with the same organic phase as described above. The results from this investigation were shown in Tables 9 and 10, respectively.

Table 9. Influence of the NaSCN concentration on gold stripping

Strip solution	% gold stripping
0.1 M NaSCN+0.5 M LiCl	26
0.25 M NaSCN+0.5 M LiCl	47
0.5 M NaSCN+0.5 M LiCl	61
0.75 M NaSCN+0.5 M LiCl	70
1 M NaSCN+0.5 M LiCl	68

Operational conditions as in Table 7

Table 10. Effect of LiCl concentration on gold stripping

Strip solution	% gold stripping
0.75 M NaSCN	75
0.75 M NaSCN+0.25 M LiCl	79
0.75 M NaSCN+0.5 M LiCl	70
0.75 M NaSCN+0.75 M LiCl	70
0.75 M NaSCN+1 M LiCl	67

Operational conditions as in Table 7.

3.3.3. *Influence of the temperature*

The influence of the temperature on gold stripping was also investigated using the same gold-loaded solutions as in previous investigations, and aqueous strip solutions of 0.75 M NaSCN+0.25 M LiCl. The results were summarized in Table 11.

Table 11. Influence of temperature on gold stripping

Temperature (ºC)	% gold stripping
20	79
50	93

Time: 10 min. V_{org}/V_{aq}: 1

3.3.4. Influence of varying the V_{org}/V_{aq} relationship

The effect of varying the V_{org}/V_{aq} relationship, on gold stripping, was investigated using the same strip and organic phases that in subsection 3.3.3.; the results from these tests were shown in Table 12, whereas a stripping isotherm was also generated (Fig. 3).

Table 12. Gold stripping under various V_{org}/V_{aq} ratios

V_{org}/V_{aq}	% gold stripping
0.5	88
1	79
2	59
4	33

Temperature: 20º C. Time: 15 min

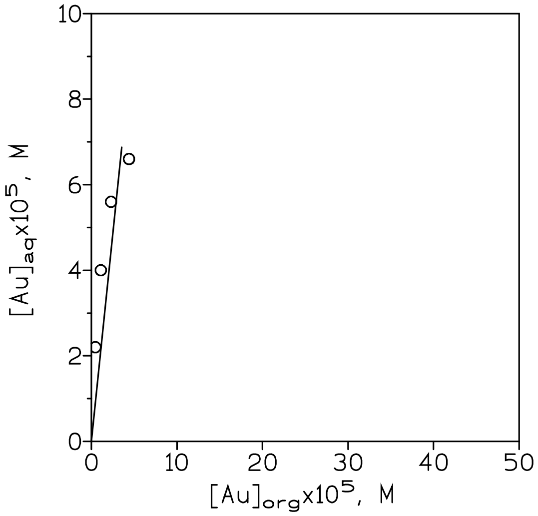

Figure 3. Gold stripping isotherm. Data from results showed in Table 12.

3.4. Precipitation of gold nanoparticles

It was recognized elsewhere [28], the importance of gold recovering as some type of nanomaterial. In the present investigation, to the strip solution of 0.75 M NaSCN+0.25 M LiCl containing $5.1\text{x}10^{-4}$ M gold, 0.1 g of sodium borohydride was slowly added under gentle (50 min^{-1}) stirring. Almost immediately a dark precipitate appeared, this was filtered and washed with distilled water. The dry as-obtained solid, resulted in gold nanoparticles (Fig. 4).

4. Discussion

4.1. Preparation of $A327H^+Cl^-$ ionic liquid

The plot showed in Fig. 1 resulted in a straight line of slope 1.08 (r^2= 0.986), thus, the ionic liquid was formed (99.8% amine conversion) accordingly to the equilibrium:

$$\mathrm{H}\,+_{aq} + \mathrm{Cl}\,-_{aq} + \mathrm{A327}_{org} \Leftrightarrow \mathrm{A327H^+Cl^-_{org}} \quad (3)$$

org and aq subscripts were the extracted phase and the raffinate, respectively.

To verify the above, the experimental data were treated by a tailored computer program with minimizes the U function, defined as:

$$\mathrm{U} = \Sigma\left(\log \mathrm{D_{cal}} - \log \mathrm{D_{exp}})^2\right) \quad (4)$$

being D_{exp} and D_{cal} the experimental distribution coefficients and the corresponding values calculated by the program. The results indicated that the ionic liquid was formed as indicated in eq.(2), with log K= 2.65 (K being the equilibrium constant related to eq.(3)) and U $2.3x10^{-5}$.

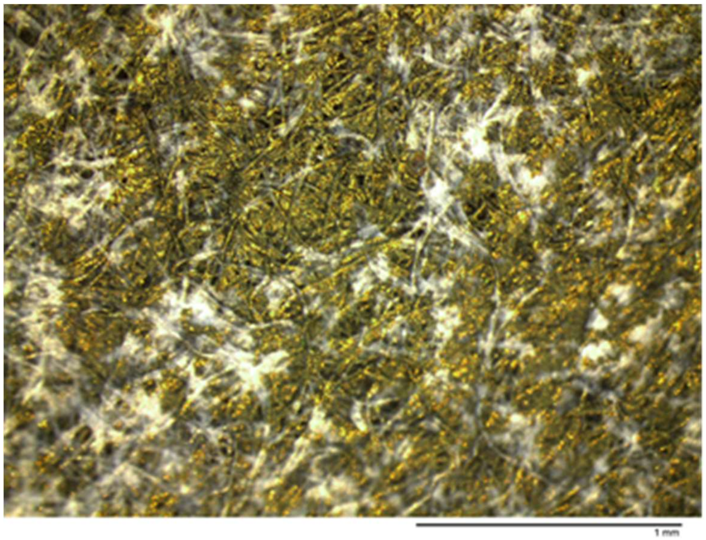

Figure 4. View of the precipitated gold nanoparticles under a magnifier.

4.2. Gold extraction

4.2.1. Influence of the equilibration time

The results showed that equilibrium was reached (93% gold extraction) after 5 min contact time between both phases. Thus, gold extraction equilibrium was achieved in a relatively short time, which it can be a demonstration about the affinity that this ionic liquid had towards gold(III)-chloride complex.

4.2.2. Influence of the temperature

As it was shown in Table 1, the experimental results indicated that an increase of the temperature resulted in a decrease in the percentage of gold extracted into the organic phase.

A plot of log D_{Au} (D defined as in eq. (1), but considering metal concentrations in the equilibrated organic solution and in the raffinate versus 1000/T (T in Kelvin degrees) resulted in a straight line (r^2= 0.979), allowing to estimate ΔH^{o} (-3 kJ/mol) and ΔS^{o} (-0.1 kJ/mol K) for the present extraction process, indicating an exothermic reaction. From the above, ΔG^{o} resulted as -0.07 kJ/mol.

4.2.3. Influence of the HCl concentration in the aqueous solution

As it was observed in Fig. 2, the variation in the HCl concentration had little if any influence in the percentage of gold extraction for every ionic liquid concentration used in the experiments.

4.2.4 Influence of the ionic liquid concentration in the organic phase

doi:10.20944/preprints202103.0117.v1

The experimental results represented in Fig. 2 showed that, the increment in the ionic liquid concentration was associated with an increment in the percentage of gold extracted into the organic phase, and for every HCl concentration used in the experiments. It was worth to note here, that almost quantitative gold extraction (99%) resulted for an ionic liquid concentration as low as 2.1x10^{-4} M (equivalent to a 0.01 % v/v ionic liquid concentration) in toluene.

4.2.5. Influence of the initial gold concentration

From the results showed in Table 2, it was deducted that the variation in the initial gold concentration had not effect on gold extraction (in therms of the distribution coefficient D_{Au}), this should be an indication about the non-existence of polynuclear complexes in the corresponding gold-loaded organic phases, that should be indicative about the formation of $A327H^+AuCl_4^-$ species in this phase.

4.2.6. Determination of the extraction constant and estimation of the $AuCl_4^-$,H^+ interaction coefficient

Based in the results, the next equilibrium should be representative of the gold extraction by the present extractant:

$$\mathrm{A327H^+Cl^-_{org}} + \mathrm{AuCl^-_{4_{aq}}} \Leftrightarrow \mathrm{A327H^+AuCl^-_{4_{org}}} + \mathrm{Cl^-_{aq}} \qquad (5)$$

equilibrium where the subscripts org and aq represented the species in the organic solution and in the raffinate, respectively. Thus, the extraction of gold was associated to an anion exchange reaction.

By the use of the same computer calculation that showed in eq.(4), it was shown that, gold extraction under various HCl concentrations was represented by eq.(5); however, the value of the extraction constant vary with the acid concentration, and thus, with the ionic strength (I) of the raffinate (Table 3).

The extraction constant, K^0, corresponding to the equilibrium represented in eq.(5) can be correlated with the value of I_m (aqueous ionic strength in the molal scale.). Thus:

$$K^0 = K_m \frac{\gamma_{A327H^+AuCl_4^-}\gamma_{Cl^-}}{\gamma_{A327H^+Cl^-}\gamma_{AuCl_4^-}} \qquad (6)$$

If ideal behaviour in the organic phase was considered, the following equation resulted:

$$\log K^0 = \log K_m + \log \gamma_{Cl^-} - \log \gamma_{AuCl_4^-} \qquad (7)$$

In solutions with a given ionic strength, I_m, the activity coefficient, γ, of a given ion of charge Z, is:

$$\log \gamma = -z^2 D_I + \Sigma \varepsilon I_m \qquad (8)$$

where D_I was the Debye-Hückel term (in the molality scale), and ε was the interaction coefficient between the charged species of the given system. Considering eq.(8) for any of the charged species of the present system, that is $AuCl_4^-$, Cl^- , and including it in eq.(7), a final equation was derived as:

$$\log K_m = \log K^0 + \left(\varepsilon_{AuCl_4^-,H^+} - \varepsilon_{Cl^-,H^+}\right) I_m \qquad (9)$$

doi:10.20944/preprints202103.0117.v1

thus, plotting log K_m versus I_m (Fig.5), a line of intercept log K^0 and slope $\varepsilon_{AuCl4-,\ H+}$ -$\varepsilon_{Cl-,H+}$ should be obtained. In the present case, such plot gives log K^0= 5.5 and slope 0.13 (r^2= 0.900), since $\varepsilon_{Cl-,H+}$ was 0.12 [29,30], $\varepsilon_{AuCl4-,H+}$ was estimated as 0.25.

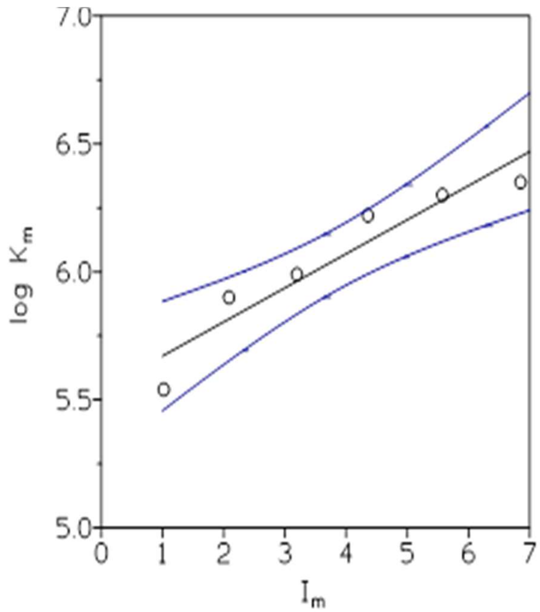

Figure 5. Plot of log K_m versus I_m. Dotted line showed 95% confidence interval of the regression line.

4.2.7. Gold extraction from multielemental solutions

The results from Table 4 demonstrated that gold was extracted in greater percentages than these of the accompanying metals, whereas the value of Table 5 showed the gold can be separated from these metals, since β>1, by the use of the present experimental conditions.

It was observed that gold was separated quantitatively from Ni(II) at both HCl concentrations of the aqueous phase, this was due to that nickel(II) did not form any type of anionic complex in chloride medium, and thus, and anion exchange reaction as shown in eq.(4), it was not possible to occur.

4.2.8. Gold extraction using various ionic liquids

The results from Table 6 indicated that Cyphos IL101 responded slightly better than $A327H^+Cl^-$ towards gold extraction, and that the latter performed much better than the others ionic liquids tested in this investigation and under these experimental conditions.

4.3. Gold stripping

4.3.1. Influence of the equilibration time

Results showed that equilibrium was reached after 10 min of contact time, indicating the great affinity that gold(III) had to form a stable complex with thiocyanate ion.

4.3.2. Influence of the composition of the stripping solution

Results from Table 7 showed that the use of NaSCN solutions was adequate to strip gold from the loaded organic solution, whereas the presence of LiCl or HCl in the strip solution favoured gold stripping, being the above attributable to an increment of the ionic strength in the strip phase when these chemicals were added to the phase. Results from Table 8 indicated that near complete gold recovery was achieved after the second step, at the same time the ionic liquid was regenerated:

$$\mathrm{A327H^+AuCl^-_{4_{org}}} + 4\mathrm{SCN^-_{aq}} \Leftrightarrow \mathrm{A327H^+Cl^-_{org}} + \mathrm{Au(SCN)^-_{4_{aq}}} + 3\mathrm{Cl^-_{aq}} \quad (10)$$

where org and aq subscripts represented the organic and strip phases, respectively.

The results presented in this Table 9 showed that there was an increment in the percentage of gold stripped with the increase of the NaSCN concentration, in the strip solution, up to 0.75 M and then levels off. The effect of adding LiCl to the strip solution (0.75 M NaSCN), showed in Table 10, indicated that from 0.25 M LiCl, an increase in the LiCl concentration of the strip solution decreased the percentage of gold stripping in the first step. However, in the case of 0.75 M NaSCN solutions, the use of LiCl in the strip solution was not as evident, with respect to gold stripping, that in the case of using 0.5 M NaSCN solution (Table 7).

4.3.3. Influence of the temperature

Table 11 showed an increment in the percentage of gold stripping as the temperature increased to 50º C. The strip reaction had an endothermic character.

4.3.4. Influence of varying the V_{org}/V_{aq} relationship

Results presented in Table 12 indicated that the increase of the V_{org}/V_{aq} relationship led to a decrease in the percentage of gold stripping. From these results, a stripping isotherm was generated and showed in Figure 4.

4.4. Precipitation of gold nanoparticles

Gold particles presented various sizes in the nano-range, i.e. 9.3-13.2 nm (SEM derived results). The reduction of gold(III) to zero valent gold responded to the formation of H_2 in the hydrolysis of sodium borohydride and the subsequent next reaction:

$$2\mathrm{Au(SCN)^-_4} + 3\mathrm{H_2} \rightarrow 2\mathrm{Au^0} + 6\mathrm{H^+} + 8\mathrm{SCN^-} \quad (11)$$

5. Conclusions

The results indicated that the ionic liquid $A327H^+Cl^-$ is effectively formed by reaction of the tertiary amine and HCl solutions. This ionic liquid extracts gold(III) in HCl solutions. The extraction mechanism are related to an anion exchange, in which the complex with $A327H^+AuCl_4^-$ stoichiometry in the organic phase is formed, releasing chloride ions in the aqueous solution. The process is exothermic (ΔH^o= -3 kJ/mol) and log K^0 for the extraction equilibrium of 5.5. By the use of the specific interaction theory approach the interaction coefficient was estimated for the pair ($AuCl_4^-$, H^+), the value being 0.25. Gold is effectively recovered from gold-loaded organic phases using thiocyanate solutions, and from these strip solutions, zero valent gold nanoparticles are yielded.

Author Contributions: Conceptualization, F.J.A.; Methodology, F.J.A. and F.A.L.; Formal analysis, F.J.A. and F.A.L.; Investigation, F.J.A.; Resources, F.A.L.; Writing—original draft preparation, F.J.A.; Writing—review and editing, F.J.A. and F.A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding

Acknowledgments: Author thanks to CSIC Agency (Spain) for support. Also to Prof. Dr. P Adeva for her interest to help in SEM and EDX analysis, also to Mr. D. Martinez for assistance in taking the picture of Fig. 5, all the above from CENIM-CSIC. We acknowledge support of the publication fee by the CSIC Open Access Publication Support Initiative through its Unit of Information Resources for Research (URICI).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Alguacil, F. J.; Garcia-Diaz, I.; Lopez, F.; Rodriguez, O. Removal of Cr(VI) and Au(III) from aqueous streams by the use of carbon nanoadsorption technology. *Desalin. WATER Treat.* **2017**, *63*, 351–356, doi:10.5004/dwt.2017.0264.
2. Alguacil, F. Adsorption of Gold(I) and Gold(III) Using Multiwalled Carbon Nanotubes. *Appl. Sci.* **2018**, *8*, 2264, doi:10.3390/app8112264.
3. Navarro, R.; Lira, M. A.; Saucedo, I.; Alatorre, A.; Avila, M.; Guibal, E. Amberlite XAD Resins Impregnated with Ionic Liquids for Au(III) Recovery. *Macromol. Symp.* **2017**, *374*, 1600134, doi:10.1002/masy.201600134.
4. Alguacil, F. J. Non-dispersive extraction of gold(III) with ionic liquid Cyphos IL101. *Sep. Purif. Technol.* **2017**, *179*, 72–76, doi:10.1016/j.seppur.2017.01.065.
5. Alguacil, F. J.; López, F. A. Permeation of AuCl4− Across a Liquid Membrane Impregnated with A324H+Cl− Ionic Liquid. *Metals (Basel).* **2020**, *10*, 363, doi:10.3390/met10030363.
6. OSHIMA, T.; OHKUBO, N.; FUJIWARA, I.; HORIUCHI, T.; KOYAMA, T.; OHE, K.; BABA, Y. Extraction of Gold(III) Using Cyclopentyl Methyl Ether in Hydrochloric Acid Media. *Solvent Extr. Res. Dev. Japan* **2017**, *24*, 89–96, doi:10.15261/serdj.24.89.
7. Horiuchi, T.; Oshima, T.; Baba, Y. Separation of Au(III) from other precious and base metals using 1-methoxy-2-octoxybenzene in acidic chloride media. *Hydrometallurgy* **2018**, *178*, 176–180, doi:10.1016/j.hydromet.2018.04.014.
8. Oshima, T.; Horiuchi, T.; Matsuzaki, K.; Ohe, K. Effect of structure of aromatic ethers on their extraction of Au(III) from acidic chloride media. *Hydrometallurgy* **2019**, *183*, 207–212, doi:10.1016/j.hydromet.2018.12.017.
9. Doidge, E. D.; Kinsman, L. M. M.; Ji, Y.; Carson, I.; Duffy, A. J.; Kordas, I. A.; Shao, E.; Tasker, P. A.; Ngwenya, B. T.; Morrison, C. A.; Love, J. B. Evaluation of Simple Amides in the Selective Recovery of Gold from Secondary Sources by Solvent Extraction. *ACS Sustain. Chem. Eng.* **2019**, *7*, 15019–15029, doi:10.1021/acssuschemeng.9b03436.
10. OSHIMA, T.; IWAO, S.; MATSUO, N.; OHE, K. Extraction Behavior of Precious Metals in Hydrochloric-acid Media Using a Novel Amine Extractant Bearing a Furan Group. *Solvent Extr. Res. Dev. Japan* **2019**, *26*, 69–80, doi:10.15261/serdj.26.69.
11. Wang, M.; Wang, Q.; Geng, Y.; Wang, N.; Yang, Y. Gold(III) separation from acidic medium by amine-based ionic liquid. *J. Mol. Liq.* **2020**, *304*, 112735, doi:10.1016/j.molliq.2020.112735.
12. Xing, W. D.; Lee, M. S. A Process for the Separation of Noble Metals from HCl Liquor Containing Gold(III), Palladium(II), Platinum(IV), Rhodium(III), and Iridium(IV) by Solvent Extraction. *Processes* **2019**, *7*, 243, doi:10.3390/pr7050243.
13. Billard, I. Green solvents in urban mining. *Curr. Opin. Green Sustain. Chem.* **2019**, *18*, 37–41, doi:10.1016/j.cogsc.2018.11.013.
14. Gu, J.; Zang, H.; Yao, S.; Wang, X.; Zhu, M.; Song, H. Study on Degradation of Benzothiazolium-Based Ionic Liquids by UV-H2O2. *Appl. Sci.* **2020**, *10*, 894, doi:10.3390/app10030894.
15. Belhadj, N.; Benabdallah, T.; Coll, M. T.; Fortuny, A.; Hadj Youcef, M.; Sastre, A. M. Counter-current separation of cobalt(II)–nickel(II) from aqueous sulphate media with a mixture of Primene JMT-Versatic 10 diluted in kerosene. *Sep. Sci. Technol.* **2020**, *55*, 513–522, doi:10.1080/01496395.2019.1577271.
16. Wieszczycka, K.; Filipowiak, K.; Aksamitowski, P.; Wojciechowska, I. Task-specific ionic liquid impregnated resin for zinc(II) recovery from chloride solutions. *J. Mol. Liq.* **2020**, *299*, 112115, doi:10.1016/j.molliq.2019.112115.
17. Zante, G.; Masmoudi, A.; Barillon, R.; Trébouet, D.; Boltoeva, M. Separation of lithium, cobalt and nickel from spent lithium-ion batteries using TBP and imidazolium-based ionic liquids. *J. Ind. Eng. Chem.* **2020**, *82*, 269–277, doi:10.1016/j.jiec.2019.10.023.
18. Khodakarami, M.; Alagha, L. Separation and recovery of rare earth elements using novel ammonium-based task-specific ionic liquids with bidentate and tridentate O-donor functional groups. *Sep. Purif. Technol.* **2020**, *232*, 115952, doi:10.1016/j.seppur.2019.115952.
19. Maria, L.; Cruz, A.; Carretas, J. M.; Monteiro, B.; Galinha, C.; Gomes, S. S.; Araújo, M. F.; Paiva, I.; Marçalo, J.; Leal, J. P.

Improving the selective extraction of lanthanides by using functionalised ionic liquids. *Sep. Purif. Technol.* **2020**, *237*, 116354, doi:10.1016/j.seppur.2019.116354.

20. Turanov, A. N.; Karandashev, V. K. Extraction of Lanthanides(III) from Nitric Acid Solutions with Tetraphenylmethylenediphosphine in the Presence of Bis[(trifluoromethyl)sulfonyl]imides of Quaternary Ammonium Bases. *Russ. J. Inorg. Chem.* **2020**, *65*, 113–118, doi:10.1134/S0036023620010180.
21. Dhiman, S.; Gupta, B. Cyphos IL 104 assisted extraction of indium and recycling of indium, tin and zinc from discarded LCD screen. *Sep. Purif. Technol.* **2020**, *237*, 116407, doi:10.1016/j.seppur.2019.116407.
22. Volia, M. F.; Tereshatov, E. E.; Boltoeva, M.; Folden, C. M. Indium and thallium extraction into betainium bis(trifluoromethylsulfonyl)imide ionic liquid from aqueous hydrochloric acid media. *New J. Chem.* **2020**, *44*, 2527–2537, doi:10.1039/C9NJ04879K.
23. Su, H.; Wang, Q.; Wang, N.; Yang, Y. Behavior, mechanism and equilibrium studies of Au(<scp>iii</scp>) extraction with an ionic liquid [C_4-6-C_4BIm]Br_2. *Dalt. Trans.* **2020**, *49*, 504–510, doi:10.1039/C9DT03860D.
24. Wang, N.; Wang, Q.; Geng, Y.; Sun, X.; Wu, D.; Yang, Y. Recovery of Au(III) from Acidic Chloride Media by Homogenous Liquid–Liquid Extraction with UCST-Type Ionic Liquids. *ACS Sustain. Chem. Eng.* **2019**, *7*, 19975–19983, doi:10.1021/acssuschemeng.9b05602.
25. Micheau, C.; Arrachart, G.; Turgis, R.; Lejeune, M.; Draye, M.; Michel, S.; Legeai, S.; Pellet-Rostaing, S. Ionic Liquids as Extraction Media in a Two-Step Eco-Friendly Process for Selective Tantalum Recovery. *ACS Sustain. Chem. Eng.* **2020**, *8*, 1954–1963, doi:10.1021/acssuschemeng.9b06414.
26. Quijada-Maldonado, E.; Allain, A.; Pérez, B.; Merlet, G.; Cabezas, R.; Tapia, R.; Romero, J. Selective liquid-liquid extraction of molybdenum (VI) and rhenium (VII) from a synthetic pregnant leach solution: Comparison between extractants and diluents. *Miner. Eng.* **2020**, *145*, 106060, doi:10.1016/j.mineng.2019.106060.
27. O.Barbosa-Filho, A. J. M. Leaching of gold in thiocyanate solutions - part 1: chemistry and thermodynamics. *Trans. Inst. Min. Met. Sect. C Miner. Process. Extr. Metall.* **1994**, *103*, C105-110.
28. Oestreicher, V.; García, C. S.; Soler-Illia, G. J. A. A.; Angelomé, P. C. Gold Recycling at Laboratory Scale: From Nanowaste to Nanospheres. *ChemSusChem* **2019**, *12*, 4882–4888, doi:10.1002/cssc.201901488.
29. L.Ciavatta The specific interaction theory in equilibrium analysis. Some empirical rules for estimation interaction coefficients of metal-ion complexes. *Ann. Chim.* **1990**, *80*, 255–263.
30. L.Ciavatta The specific interaction theory in evaluating ionic equilibria. *Ann. Chim.* **1980**, *70*, 255–263.