processes

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Insight into the Liquid–Liquid Extraction System $AuCl_4^-/HCl/A327H^+Cl^-$ Ionic Liquid/Toluene

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

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

Citation: Alguacil, F.J.; Lopez, F.A. Insight into the Liquid–Liquid Extraction System $AuCl_4^-/HCl/A327H^+Cl^-$ Ionic Liquid/Toluene. *Processes* **2021**, *9*, 608. https://doi.org/10.3390/pr9040608

Academic Editors: Paolo Trucillo, Amedeo Lancia and Francesco Di Natale

Received: 2 March 2021
Accepted: 29 March 2021
Published: 30 March 2021

1. Introduction

The concept of urban mining has widespread application because recycling is now of primary importance, and modern life results in the generation of waste that contains a variety of valuable and non-valuable materials.

Valuable items include electronic wastes, jewelry scraps, and similar products, which are of interest because they contain metals. Among these, gold is significant due to both its color, and its sales price and profit potential. Thus, the separation and recovery of this precious metal, from any of the above materials, has attracted wide interest, and different separation technologies have been 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 phosphonic acid derivatives [12].

The basic procedure of gold recovery begins with a leaching step, which is normally undertaken with aqua regia, followed by a number of separation steps, to finally yield pure gold. Liquid–liquid extraction or solvent extraction is one of these separation steps, and is currently used in the production of a series of metals, particularly 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 to the targeted metal. The advantages of liquid–liquid extraction compared to other separation technologies (i.e., liquid membranes, adsorption, ion exchange) rely on its operational characteristics, i.e., short operational periods (often in the range of a few minutes), possibility to treat high feed solution volumes in these short periods, and selectivity towards gold compounds in solution.

The organic extractants used in liquid–liquid extraction include ionic liquids, which have attracted further interest due to their inherent properties [13–16], including high selectivity and conductivity [17], negligible vapor pressure and low volatility [18], inflammability or low flammability [19], strong thermal stability [20], high refractive index [21], and solvation power of organic and inorganic compounds [22,23]. Due to these properties, these liquids are considered to be green solvents. Ionic liquids are used in several fields, e.g., biochemistry [24], electrochemistry [25], pharmaceutics [26,27], and analytical chemistry [28], and in the recovery of metals, with recent applications discussed in the literature including base metals [29–31], rare earths [32–34], indium [35,36], gold [37,38], and others [39,40].

This work builds on the factors mentioned above, namely, (i) ionic liquids, (ii) high gold price and the opportunity of gold recovery from urban wastes, and (iii) the usefulness of liquid–liquid extraction in this profitable and environmental field of interest. $A327H^+Cl^-$ ionic liquid, prepared from the reaction of a tertiary amine, A327, and HCl, was used as an extractant because no data were apparently 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) were investigated: contact time; temperature; gold(III) and HCl and ionic liquid concentrations in the aqueous and organic phases, respectively; the performance of the organic reagent in the presence of other metals in the aqueous phase; and the comparison of the performance of $A327H^+Cl^-$ ionic liquid against that of other ionic liquids. The stripping step was investigated using different strippants, and gold nanoparticles were finally extracted from the gold-bearing strip solution.

2. Materials and Methods

The ionic liquid used in this investigation was generated from the tertiary amine Hostarex A327 (Sanofi), with average molecular weight of 395 g/mol and density of 20 °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 was used without further purification. Toluene (AR grade) was used to dilute the amine. It is claimed in the literature that organic diluents are not required when ionic liquids are used in the extraction of metal; however, the experience of the authors 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 impairs easy and quick phase separation; moreover, this viscosity results in a flowing problem in the process of scaling-up to mixer-settlers. (ii) The use of a diluent allowed the correct concentration of the ionic liquid to be used in each case (this work is an example of the extremely low ionic concentrations that can be used to extract gold from the feed solution). Because the extractant is arguably the most expensive input in the circuit, it was not desirable to work with a concentration of unused extractant in the liquid–liquid extraction circuit.

Other chemicals were of AR grade, with the exception of Cyphos IL101 (Solvay), Aliquat 336 (Fluka) Hostarex A324 (Sanofi), and Primene 81R (Dow Chemicals), which were used without further purification.

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

Gold precipitation was performed in a glass reactor containing, under gentle stirring, the gold-bearing strip solution to which a weighed amount (0.1 g) of sodium borohydride was sequentially added. After filtration, gold nanoparticles were visualized using a magnifier, whereas microstructural characterization was 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 1 M HCl solutions, and the results, of these HCl extractions, were calculated by the distribution coefficient D, defined by means Equation (1):

$$D = \frac{[HCl]_{org}}{[HCl]_{aq}} \tag{1}$$

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

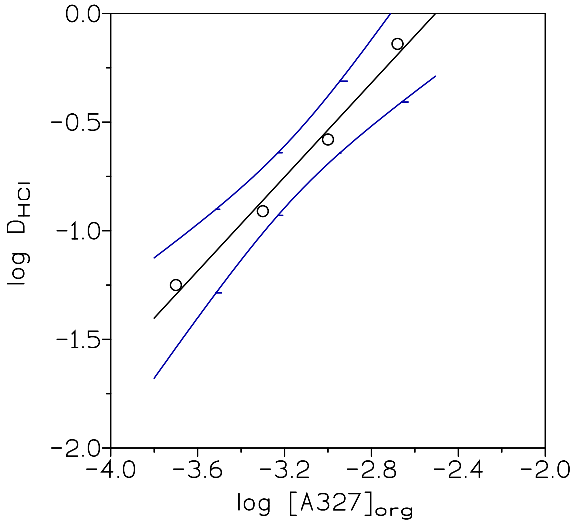

Figure 1. Variation of log D_{HCl} with log $[A327]_{org}$. Aqueous phases: 1 M HCl. Organic phase: 0.05–0.4 M amine A327 in toluene. Temperature: 20 °C. Time: 10 min. V_{org}/V_{aq}: 1. Dotted line shows 95% confidence interval of the regression line.

3.2. Gold Extraction

3.2.1. Influence of the Equilibration Time

The influence of the equilibration time 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 of 20 °C, and a V_{org}/V_{aq} ratio of 1.

3.2.2. Influence of the Temperature

The variation of the temperature, in the 20–50 °C range, on gold extraction was investigated. In this case the aqueous solution was 5.1×10^{-5} 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, again using a V_{org}/V_{aq} ratio of 1. The experimental results are given in Table 1.

Table 1. Influence of the temperature on gold extraction.

Temperature, (°C)	**Gold Extraction (%)**	**log D_{aub}**
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 are shown in Figure 2, which represents the percentage of gold extraction versus the HCl concentration in the raffinate phase.

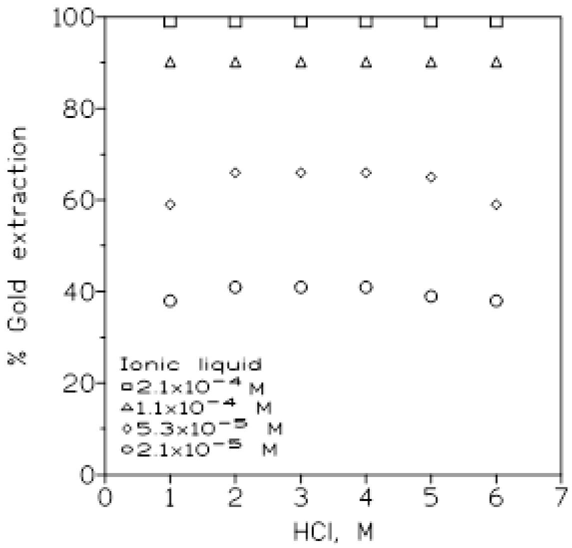

Figure 2. Gold extraction at different HCl and ionic liquid concentrations. Aqueous phase: 5.1×10^{-5} M gold in HCl. Organic phase: different ionic liquid concentrations in toluene. Temperature: 20 °C. Time: 10 min. V_{org}/V_{aq}: 1.

3.2.4. Influence of the Ionic Liquid Concentration in the Organic Phase

The investigation into the influence of the extractant concentration on gold(III) extraction was performed using the same conditions as described in Figure 2, which also shows the results derived from this investigation.

3.2.5. Influence of the Initial Gold Concentration

The effect of the variation of the initial metal concentration in the aqueous phase 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 1.1×10^{-4} M ionic liquid in the diluent, was investigated. The results are summarized in Table 2.

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

$[Au]_0$ (M)	log D_{Au}
2.5×10^{-5}	0.96
5.1×10^{-5}	0.95
1.0×10^{-4}	0.95

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

3.2.6. Gold Extraction from Multi-Elemental Solutions

In the recycling of, e.g., electronic waste, gold can be accompanied in the solution by a series of base metals, with the most common found to be 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 are summarized in Table 3. Taking into consideration the definition of the separation factor, $\beta_{Au/M}$ (Equation (2)):

$$\beta_{Au/M} = \frac{D_{Au}}{D_M} \tag{2}$$

where D_{Au} and D_M represent the experimental values of the distribution coefficients (see Equation (1)), of gold and the corresponding metals, respectively, Table 4 shows the values of these separation factors.

Table 3. Variation of log K (log K_m) at different I values.

HCl (M)	**I (m)**	**log K or log K_m**	**U**
1	1.022	5.54	0.310
2	2.080	5.90	0.280
3	3.196	5.99	0.265
4	4.357	6.22	0.259
5	5.573	6.30	0.302
6	6.851	6.35	0.354

I values were given in the molal scale. K_m represented the value of the extraction constant in the molal scale.

Table 4. Values of β for the present system.

Pair	**HCl**	**$\beta_{Au/M}$**
	(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 for gold extraction was also compared against the extraction of gold by other ionic liquids. In these experiments, the aqueous solutions were 5.1×10^{-5} M gold in 1 or 6 M HCl, and the organic solutions were 1.1×10^{-4} M of the extractant in toluene. The results are shown in Table 5.

Table 5. 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: 20 °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 using thiocyanate solutions, as the matrix component of the solution, due to the great affinity that Au(III) has with thiocyanate ions, forming the $Au(SCN)_4^-$ complex in the solution with log β_4 of 43.66 [41].

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 20 °C and using a V_{org}/V_{aq} ratio of 1. A 0.5 M NaSCN solution was used as the 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 6 summarizes the results from these experiments. Moreover, the addition of LiCl or HCl to the NaSCN solution was investigated. A second stripping step was performed on the organic solution, resulting from the first strip, using fresh strippant solutions. The results are given in Table 7.

Table 6. 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: 20 °C. Time: 15 min. V_{org}/V_{aq}: 1.

Table 7. 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 6. The percentage of gold stripped, in the second step, was calculated on the basis of the residual gold concentration in the organic phase after the first 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 are shown in Tables 8 and 9, respectively.

Table 8. 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 6.

Table 9. 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 6.

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 are summarized in Table 10.

Table 10. Influence of temperature on gold stripping.

Temperature (°C)	**% 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 as those in Section 3.3.3. The results from these tests are shown in Table 11, and a stripping isotherm was also generated (Figure 3).

Table 11. 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: 20 °C. Time: 15 min.

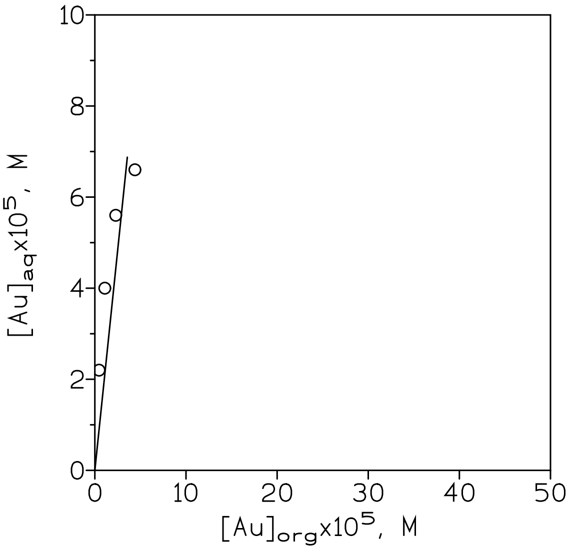

Figure 3. Gold stripping isotherm. Data from results shown in Table 11.

3.4. Precipitation of Gold Nanoparticles

The importance of recovering gold as a type of nanomaterial was recognized elsewhere [42]. In the present investigation, to the strip solution of 0.75 M NaSCN + 0.25 M LiCl containing 5.1×10^{-5} M gold, 0.1 g of sodium borohydride was slowly added under gentle (50 min^{-1}) stirring. Almost immediately a dark precipitate appeared, which was filtered and washed with distilled water. The dry as-obtained solid resulted in gold nanoparticles (Figure 4).

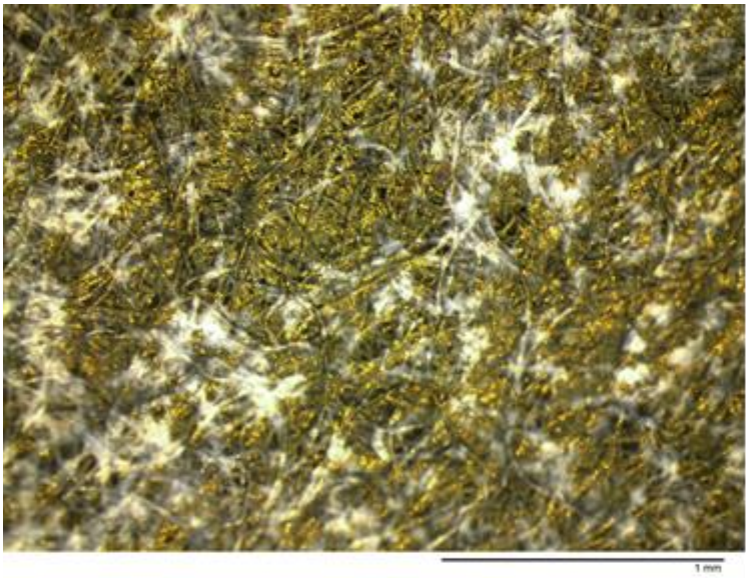

Figure 4. View of the precipitated gold nanoparticles under a magnifier.

4. Discussion

4.1. Preparation of A327H⁺Cl⁻ Ionic Liquid

The plot shown in Figure 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 (Equation (3)):

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

where org and aq subscripts are the extracted phase and the raffinate, respectively.

To verify the above, the experimental data were treated by a tailored computer program to minimize the U function, defined by means Equation (4):

$$U = \sum (\log D_{cal} - \log D_{exp})^2 \quad (4)$$

where D_{exp} and D_{cal} are the experimental distribution coefficients and the corresponding values calculated by the program. The results indicated that the ionic liquid was formed as indicated in Equation (2), with log K = 2.65 (where K is the equilibrium constant related to Equation (3)) and U = 2.3×10^{-5}.

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 demonstrates the affinity of this ionic liquid towards the gold(III)-chloride complex.

4.2.2. Influence of the Temperature

As shown in Table 1, the experimental results indicated that an increase in 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 Equation (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). This allowed the estimation of ΔH° (−3 kJ/mol) and ΔS° (−0.1 kJ/mol K) for the present extraction process, indicating an exothermic reaction. From the above, ΔG° resulted as −0.07 kJ/mol.

4.2.3. Influence of the HCl Concentration in the Aqueous Solution

As observed in Figure 2, the variation in the HCl concentration had little if any influence on the percentage of gold extraction for each ionic liquid concentration used in the experiments.

4.2.4. Influence of the Ionic Liquid Concentration in the Organic Phase

The experimental results represented in Figure 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 each HCl concentration used in the experiments. It is worth noting that almost quantitative gold extraction (99%) resulted for an ionic liquid concentration as low as 2.1×10^{-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 shown in Table 2, it was deducted that the variation in the initial gold concentration had no effect on gold extraction (in terms of the distribution coefficient D_{Au}). This signifies the non-existence of polynuclear complexes in the corresponding gold-loaded organic phases, thus indicating 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 on the results, the next equilibrium is representative of the gold extraction by the present extractant equilibrium (Equation (5)):

$$\mathrm{A327H^+\ Cl^+_{org} + AuCl^-_{4\ aq} \leftrightarrow A327H^+AuCl^-_{4\ org} + Cl^-_{aq}} \tag{5}$$

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

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

The extraction constant, K^0, corresponding to the equilibrium represented in Equation (5), is correlated with the value of I_m (aqueous ionic strength in the molal scale.), according to the Equation (6):

$$\mathrm{K^0 = K_m \frac{\gamma_{A327H^+AuCl_4^-}\gamma_{Cl^-}}{\gamma_{A327H^+Cl^-}\gamma_{AuCl_4^-}}} \tag{6}$$

Ideal behaviour in the organic phase results in the following Equation (7):

$$\log \mathrm{K^0} = \log \mathrm{K_m} + \log \gamma_{\mathrm{Cl^-}} - \log \gamma_{\mathrm{AuCl_4^-}} \tag{7}$$

In solutions with a given ionic strength, I_m, the activity coefficient, γ, of a given ion of charge Z, is represented by the Equation (8):

$$\log\ \gamma = -z^2\ D_1 + \Sigma\varepsilon I_m \tag{8}$$

where D_I is the Debye–Hückel term (in the molality scale) and ε is the interaction coefficient between the charged species of the given system. Considering Equation (8) for any of the charged species of the present system, that is $AuCl_4^-$, Cl^-, and including it in Equation (7), a final equation is derived according to the Equation (9):

$$\mathrm{logK_m = logK^0} + \left(\varepsilon_{\mathrm{AuCl_4^- H^+}} - \varepsilon_{\mathrm{Cl^-\ H^+}}\right)\mathrm{I_m} \tag{9}$$

Thus, plotting log K_m versus I_m (Figure 5), a line of intercept log K^0 and slope $\varepsilon_{AuCl_4^- H^+} - \varepsilon_{Cl^- H^+}$ can be obtained. In the present case, this plot yields log $K^0 = 5.5$ and slope 0.13 ($r^2 = 0.900$); because $\varepsilon_{Cl^- H^+}$ is 0.12 [43,44], $\varepsilon_{AuCl_4^- H^+}$ was estimated to be 0.25.

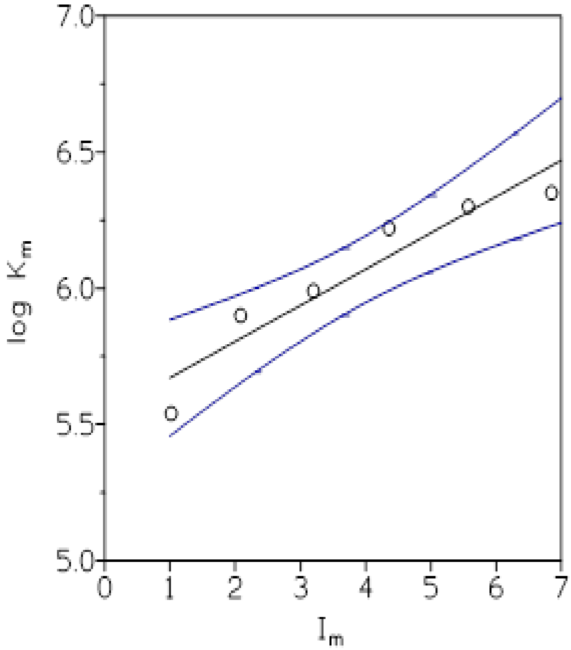

Figure 5. Plot of log K_m versus I_m. Dotted lines show 95% confidence interval of the regression line.

4.2.7. Gold Extraction from Multi-Elemental Solutions

The results from Table 12 demonstrate that gold was extracted in greater percentages than those of the accompanying metals, whereas the value of Table 4 showed the gold can be separated from these metals, because β > 1, using the present experimental conditions.

Table 12. Percentages of metal extraction from multi-elemental 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: 5.1×10^{-5} M (each) Au(III), Fe(III), Cu(II), Ni(II) in HCl solutions. Organic phase: 1.1×10^{-4} M ionic liquid in toluene. Temperature: 20 °C. Time: 10 min. V_{org}/V_{aq}: 1.

It was observed that gold was separated quantitatively from Ni(II) at both HCl concentrations of the aqueous phase. This was because nickel(II) did not form any type of anionic complex in chloride medium. Thus, as shown in Equation (4), it was not possible for an anion exchange reaction to occur.

4.2.8. Gold Extraction Using Various Ionic Liquids

The results from Table 5 indicate that Cyphos IL101 responded slightly better than $A327H^+Cl^-$ for gold extraction, and that the latter performed significantly better than the other ionic liquids tested in this investigation and under these experimental conditions. Although in all cases gold(III) was extracted via an anion exchange mechanism (see Equation (5)), it appears the type of the ionic liquid has a key influence on gold(III) extraction from HCl media. In the case of the structure of Cyphos IL101, a quaternary phosphonium salt or $R_4P^+Cl^-$ is more able to exchange chloride ions with $AuCl_4^-$ ions from the aqueous phase, than the quaternary ammonium salt ($R_3HN^+Cl^-$) of the amine derivative. Thus, the ionic character in the N^+Cl^- pair appeared to be stronger than in the P^+Cl^- ionic pair. The comparison of the performance of amine derivatives showed that the exchange properties of the ionic liquids derived from tertiary amines are better than those of, e.g., the primary amine derivative; in a chloride medium, tertiary amines extracted better metal-chloride complexes than primary amines. In the case of the ionic liquids derived from the tertiary amines, the results showed that the amine composition has a definitive role in the extraction of the metal: tri-octyl in the case of amine A324 versus an ad hoc tri-octyl and tri-decyl mixture in the case of amine A327, with the latter performing better than the former.

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 high affinity of gold(III) to form a stable complex with thiocyanate ions.

4.3.2. Influence of the Composition of the Stripping Solution

Results from Table 6 show 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 favored gold stripping, which is attributable to an increment of the ionic strength in the strip phase when these chemicals were added to the phase. Results from Table 7 indicate that near complete gold recovery was achieved after the second step, at the same time the ionic liquid was regenerated according to the Equation (10):

$$A237H^{+}AuCl^{-}_{4\ org} + 4SCN^{-}_{aq} \leftrightarrow A237H^{+}Cl^{-}_{org} + Au(SCN)^{-}_{4\ aq} + 3Cl^{-}_{aq} \tag{10}$$

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

The results presented in Table 8 show that there was an increment in the percentage of gold stripped with the increase in the NaSCN concentration, in the strip solution, up to 0.75 M, before then stabilizing. The effect of adding LiCl to the strip solution (0.75 M NaSCN), as shown in Table 9, indicates 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, as in the case of using 0.5 M NaSCN solution (Table 6).

4.3.3. Influence of the Temperature

Table 10 shows an increment in the percentage of gold stripping as the temperature increased to 50 °C. The strip reaction had an endothermic character.

4.3.4. Influence of Varying the V_{org}/V_{aq} Relationship

Results presented in Table 11 indicate that the increase in the V_{org}/V_{aq} relationship led to a decrease in the percentage of gold stripping. From these results, a stripping isotherm was generated, as shown 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 Equation (11):

$$2Au(SCN)^{-}_{4} + 3H_2 2Au^{0} + 6H^{+} + 8SCN^{-} \tag{11}$$

5. Conclusions

The results indicate 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 is 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 ($\Delta H^{\circ} = -3$ kJ/mol) and log K^{0} for the extraction equilibrium of 5.5. Using the specific interaction theory approach, the interaction coefficient was estimated for the pair ($AuCl_4^-$, H^+), with a value of 0.25. Gold was effectively recovered from gold-loaded organic phases using thiocyanate solutions, yielding zero valent gold nanoparticles from these strip solutions.

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.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank CSIC Agency (Spain) for support, P Adeva for her help in SEM and EDX analysis, and D. Martinez for assistance in taking the picture of Figure 4; the above are 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.

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