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Solvent Extraction of Au(III) by 2-ethylhexanol and Kinetic Modelling of the Facilitated Transport Across a Liquid Membrane

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Abstract: The solvent extraction of gold(III) by undiluted 2-ethylhexanol or dissolved in toluene from HCl solution has been investigated. The numerical analysis of gold distribution data suggests the formation of $HAuCl_4{\cdot}L$ and $HAuCl_4{\cdot}2L$ (L= 2-ethylhexanol) species in the organic phase with formation constants K_{11}= 38 and K_{12}= 309, respectively. The results derived from gold(III) distribution have been implemented in a solid-supported liquid membrane system. The influence of several variables on gold transport was considered: feed and receiving phases stirring speeds, HCl and gold concentrations in the feed phase and carrier concentration in the membrane phase as well as the presence of base metals (Fe,Cu,Ni) and PGMs in the feed phase. Also, diffusional resistances to mass transfer are estimated. Gold is recovered as zero valent nanoparticles.

Keywords: gold(III); 2-ethylhexanol; extraction; membrane transport; gold nanoparticles

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1. Introduction

Over the last years, there were an increasing interest in the recovery and utilization of the so-named strategic metals (rare earth elements, lithium, neodymium and tantalum, etc.), less mentioned was the recovery, from secondary materials or wastes, of gold and platinum group metals which always were of interest.

The recovery of gold has two main tendencies: i) recovery from raw materials, which is dominated by cyanidation and gold adsorption, and ii) recovery from secondary materials or wastes (printed circuit boards, jewelry scraps, e-wastes, etc.), in which the precious metal is usually dissolved in non-cyanide medium i.e. *aqua regia*, thiourea, tiosulphate, etc, From the leachates, gold is purified and recovered by the use of different options.

Though yet with not any apparent or definitive practical application, the scientific community considered of importance the recovery of gold from these various non-cyanide media, importance which is reflected by the series of publications that every year appeared in journals. In the case of gold adsorption onto different materials recent several approaches are considered by the use of metal organic frameworks [1], metal sulphides microspheres [2] or Aliquat 336 (quaternary ammonium salt) impregnating Nitrolite adsorbent [3].

It is well known the recovery of metals by solvent extraction processing, this is also demonstrated by the number of publications produced over the years. Gold (III) solvent extraction has attracted interest, with recent publications involving the use of ionic liquids [4] or pseudo-protic ionic liquids [5] as extractants for this precious metal.

Due to some environmental concerns, liquid membranes emerged as an alternative to solvent extraction, however, it must say here that at the present time still there is not any plant using any of the different liquid membranes operational variations. Indeed, the interest of scientists for the utilization of these membranes technologies on the recovery of metals or other pollutants still is alive as some recent publications also demonstrated. Several reviews about the general use of liquid membranes included: the transport of actinide elements using diglycolamides as carriers [6] and the application of membranes on the recovery of various elements [7-10], with mention to the use of polymer-inclusion membranes (PIMs) [11]. Experimental papers were devoted to investigate the transport of both, inorganic and organic solutes or harmful species of potential appearance in liquid wastes. As organic compounds, it was investigated the transport of diclofenac and iboprufene by supported liquid membrane technology and using Cyanex 923 (mixture of tri-alkylphosphine oxides) dissolved in kerosene as carrier phase [12,13]. By the use of flat-sheet supported liquid membrane operational mode, the transport of chromium(VI), indium(III) and the separation of Nd(III) and Er(III) were investigated [14-16]; a variation of the above operation was the investigation of the transport process (copper, zinc or cobalt) using electromembranes [17-19].

The utilization of a more dynamic supported liquid membrane procedure as is the operation in hollow fiber modules, found applications in the simultaneous removal of arsenic and mercury [20] or only mercury [21]. A yet more advanced hollow fiber operation, as it is the so-called (though other names are using) pseudo-emulsion based hollow fiber membrane with strip dispersion technology (PEHFMSD), in which, differently to conventional hollow fiber operation using two modules (one for extraction and other for stripping), just one module was used for extraction and stripping. Moreover, in this PEHFMSD operation the organic and the receiving or stripping phase were mixed in one tank, and continuously pumped to the module, to improve the transport and the removal of the solute from the feed to the organic and from the organic to the receiving phases. This PEHFMSD operation was recently used in the removal of iron(III) [22] and in the treatment of stainless steel rinse waters [23]. It is worth to note that against all the literature favoring the use of liquid membranes in the treatment of wastewaters, these technologies seemed to be unpopular in the case of acid mine wastewater treatment [24].

In these membranes operations is of the utmost importance gain knowledge on interfacial phenomena associated to metal-carrier (extractant) chemical reactions occurring in the feed phase and the membrane interfaces when the metal (solute) is transported against its concentration gradient. Before scaling up the flat-sheet supported liquid membrane operation (the most simple form of supported liquid membranes), in spiral wound or hollow fiber modules operational modes, a theoretical model of the membrane system is welcomed in order to design an efficient and stable process.

The present work implemented solvent extraction investigations in a solid-supported liquid membrane configuration. Firstly, a quantitative characterization of the solvent extraction of gold(III) by 2-ethylhexanol was undertaken. Further, a liquid membrane system was designed by using the extraction process mentioned above, and the parameters affecting the liquid membrane: stirring speeds applied on both feed and receiving phases, compositions of the feed and organic phases, etc. were investigated. A model was developed to estimate the mass transfer coefficients relative to the transport of gold across the 2-ethylhexanol-immobilized supported liquid membrane.

2. Materials and Methods

2.1. Materials

A stock solution of gold(III) was prepared by dissolving $HAuCl_4$ (Fluka) in HCl. The aqueous solutions for solvent extraction or membrane transport experiments were prepared by dilution of this stock solution. The extractant 2-ethylhexanol (Merck) was used without further purification. The PGMs stock solution was a commercially available standard solution for ICP analysis. All other reagents used in the investigation were of AR grade.

The support for the liquid membrane was a polydifluoroethylene film (Millipore GVHP4700) with thickness of $125 \cdot 10^{-4}$ cm, porosity 75%, tortuosity 1.67, and 0.22 μm average pore size.

2.2. Methods

2.2.1. Liquid-liquid extraction experiments

Before experimentation, undiluted 2-ethylhexanol was pre-saturated with 6 M HCl in order to avoid change in the organic and aqueous phases volume after gold extraction, and from this pre-saturated alcoholic solution all the organic phases used in the investigation were prepared. Distribution ratio experiments were performed at 20º C by shaking (800 min^{-1}) equal volumes (25 cm^3) of the aqueous and organic phases in glass separatory funnels for the required time. After phase separation, the metal remaining in the raffinate was analysed by AAS using a Perkin Elmer 1100B spectrophotometer. The amount of metals extracted in the organic phase was calculated by difference with the initial concentration in the aqueous phase. The percentage of extraction was calculated as:

$$\%\mathbf{E} = \frac{[\mathbf{M}]_{\mathbf{aq,0}} - [\mathbf{M}]_{\mathbf{aq,t}}}{[\mathbf{M}]_{\mathbf{aq,0}}} \cdot \mathbf{100} \tag{1}$$

where $[M]_{aq,0}$ and $[M]_{aq,t}$ were the metal concentrations in the initial aqueous phase and in the raffinate, respectively.

2.2.2. Liquid membrane experiments

The batch transport experiments were carried out in a methacrylate permeation cell having two (200 cm^3 each) compartments separated by the solid support. One compartment was for the feed phase and the other for the receiving or stripping phase. The liquid membrane was prepared by impregnation of the laminar microporous support by the carrier phase during 24 hours, and then leaving it to drip during twenty seconds, before placing in the cell. Metal contents in the feed and receiving phases were periodically analyzed by AAS or ICP (Platinum Group Metals), whereas the overall mass transfer coefficient (K_0) was calculated from:

$$\mathbf{ln}\frac{[\mathbf{M}]_{\mathbf{f,t}}}{[\mathbf{M}]_{\mathbf{f,0}}} = -\frac{\mathbf{A}}{\mathbf{V}}\mathbf{K_0 t} \tag{2}$$

where $[M]_{f,0}$ and $[M]_{f,t}$ were the metal concentrations in the feed at time zero at an elapsed time, respectively, A was the effective membrane area 11.3 cm^2, V the volume of the feed phase (200 cm^3), and t the elapsed time.

3. Results and discussion

3.1. Solvent extraction experiments

Firstly, it was studied the influence of equilibration time on attachement gold(III) extraction equilibrium. In these series of experiments the aqueous phase contained 35 g/L Au(III) in 6 M HCl, whereas the organic phase was of 75% v/v 2-ethylhexanol in toluene. From results showed in Table 1 it can be concluded that equilibrium was almost reached within 2 minutes of contact between both phases, and the same conclusion was reached when the aqueous phase contained other (15-100 g/L) gold concentrations.

In this Table 1, the fractional attachment to equilibrium (F) was calculated as:

$$\mathrm{F} = \frac{[\mathrm{Au}]_{\mathrm{org,t}}}{[\mathrm{Au}]_{\mathrm{org,e}}} \tag{3}$$

where $[Au]_{org,t}$ and $[Au]_{org,e}$ were the gold concentrations in the organic phase at an elapsed time and at the equilibrium, respectively. According with these experimental data, all subsequent experiments were carried out using 5 minutes of contact between the respective organic and aqueous phases.

Table 1. Influence of equilibration time on the fractional attachment to equilibrium.

Time, min	F
1	0.71
2	0.98
5	1
10	1

15	1

Temperature: 20º C. Org/Aq volume ratio: 1.

The variation of the initial gold concentration on the extraction of this precious metal from 6 M HCl medium was also investigated. In these cases, the initial aqueous solutions contained varying gold concentrations in the 5-200 g/L range, and the organic phases were of undiluted 2-ethylhexanol. The results from this set of experiments were shown in Table 2.

Table 2. Percentages of gold extraction at various initial metal concentrations in the aqueous phase.

$[Au]_0$, g/L	% Extraction
5	98
15	98
25	98
35	98
50	98
75	97
100	96
150	93
200	87

Temperature: 20º C. Org/Aq volume ratio: 1.

These results concluded that in the 5-100 g/L gold concentrations range the variation in the percentage of gold extraction in the organic phase was almost negligible (96-98%), whereas at higher initial gold concentrations in the aqueous solutions these percentages decreased from 93% at 100 g/L gold to 87% at 200 g/L gold. This decrease in the percentage of gold extraction with the increase of the initial metal concentration was not rare [25-28], and it can be due to polymerization of the metal in the aqueous phase and also to the common ion effect, in which the organic phase was dominated by the metal anion ($AuCl_4^-$ in this work) and the aqueous phase by the halide ions (Cl^- in this case) [29].

The influence of the variation of the initial extractant concentration on gold extraction was also investigated using organic phases containing 25-90% v/v 2-ethylhexanol in toluene or undiluted extractant. The aqueous phase were of 35 g/L Au(III) in a 6 M HCl medium, showing Table 3 the results from the experiments.

Table 3. Percentages of gold extraction at various extractant concentrations in the organic phase.

[2-ethylhexanol], % v/v	% Extraction
25	57
35	75
50	88
60	92
70	94
75	95
80	96

90	98
undiluted	98

Temperature: 20º C. Org/Aq volume ratio: 1.

These results indicated that there was an increase of the percentage of gold extraction with the increase of the extractant concentration in the organic phase from 25 to 60% v/v, though for extractant concentrations higher than 70% v/v the variation in gold extraction did not exceed 5%.

The stoichiometry of the extracted species and their equilibrium constants were determined by the treatment of the experimental data by a numerical program, which minimized the U function defined as:

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

being D_{cal} and D_{exp} the respective distribution ratios calculated from the mass balance equations for the various models and experimentally calculated as:

$$D_{exp} = \frac{[Au]_{org}}{[Au]_{aq}} \qquad (5)$$

The results of the numerical treatment indicated that the extraction of gold(III) can be explained (U= 0.009) by formation of $HAuCl_4{\cdot}L$ (log K_{ext}= 1.58±0.09) and $HAuCl_4{\cdot}2L$ (log K_{ext}= 2.49±0.26) species in the gold-loaded organic phases. In the above formulations, L represented 2-ethylhexanol molecules.

Once gold was extracted into the organic phase, the stripping operation was performed using water as strippant. In this case from an organic phase of undiluted 2-ethylhexanol containing 34 g/L gold and using the same volume of water (Org/Aq= 1), near 89% gold was recovered at 20º C in one step. From these solutions, gold can be recovered by precipitation with sodium borohydride, oxalic acid, etc., however, this last step was not investigated here but it was in the case of solutions derived from the supported liquid membrane experimentation (see further).

The selectivity of the present system against the presence of Cu(II), Zn(II) and Ni(II) in the aqueous phase was also investigated. These experiments used organic phases of undiluted 2-ethylhexanol and aqueous phases containing separately 0.18 M of the element in 6 M HCl. The results from these set of experiments were summarized in Table 4.

Table 4. Extraction of Au(III), Cu(II), Fe(III) and Ni(II).

Element	**% Extraction**	**D**	**SF**
Au(III)	98	69	
Cu(II)	21	0.25	276
Zn(II)	11	0.12	575
Ni(II)	12	0.13	530

Temperature: 20º C. Org/Aq volume ratio: 1.

The Separation Factor (SF) values showed the extreme selectivity of the system; these separation factors were calculated within the next relationship:

$$SF = \frac{D_{Au}}{D_M} \qquad (6)$$

Further experiments had been performed to elucidate the separation Au(III)/Cu(II) using this same organic phase, and aqueous phase containing both elements in 6 M HCl and using various Au(III):Cu(II) molar concentration relationships. Table 5 summarized these results.

Table 5. Extraction and separation of Au(III) and Cu(II) at various molar concentration relationships.

$[Au]_0$:$[Cu]_0$	D_{Au}	D_{Cu}	SF
2:1	69	0.045	1533
3:1	69	0.047	1468
6:1	69	0.044	1568
18:1	69	0.049	1408

$[Au]_0$: 0.18 M. temperature: 20º C. Org/Aq volume ratio: 1.

These results that in mixed Au(III)-Cu(II) solutions, the extraction of this last element decreased with respect to the results obtained from the use of single metal-bearing solutions. This is why the SF values resulted in the 1400-1500 order, though the variation in the $[Au(III)]_0$:$[Cu(II)]_0$ relationships seemed not to influence greatly on this separation.

3.2. Supported liquid membrane experiments

In these membrane systems, the extraction (transport) of a given metal-species depends not only of the equilibrium parameters but also the kinetics parameters.

The influence of the variation (600-1600 min^{-1}) of the stirring speed of the feed phase on gold transport was investigated. The results from these experiments were shown in Table 6, and it can be observed that the overall mass transfer coefficient value (K_O) increased with the increase of the stirring speed from 600 to 1000 min^{-1}, and beyond that not increase in gold transport was observed. In fact, there was a decrease of the transport from 1400 min^{-1} due to membrane instability probably attributable to the displacement of the organic phase from the membrane pores caused by the turbulence due to these higher stirring speeds.

Table 6. Influence of the feed phase stirring speed on gold transport.

Stirring speed, min^{-1}	$K_O \cdot 10^3$, cm/s
600	0.95
800	2.6
1000	5.7
1200	5.7
1400	5.5
1600	4.9

Feed phase: 0.01 g/L Au(III) in 6 M HCl. Membrane phase: 50% v/v 2-ethylhexanol in toluene immobilized on GVHP4700 support. Receiving phase: water. Receiving phase stirring speed: 1200 min^{-1}. Temperature: 20º C.

In supported liquid membranes experimentation, two types of diffusional resistances are usually found: i) one due to the feed phase boundary layer, and ii) another in relation with the membrane support. Many times the magnitude of the values of both resistances competed between them [30]. These experimental results show that, in the 1000-1200 min^{-1} range, the feed phase boundary layer reached a minimum and the aqueous resistance to mass transfer are minimized, thus, the diffusion contribution of the aqueous species to the mass transfer phenomena is constant [31].

The influence of the variation (800-1200 min^{-1}) of the stirring speed of the receiving phase on gold transport was also investigated using the very same experimental conditions as in Table 4, but using a stirring speed of 1000min^{-1} in the feed phase. The results from these experiments showed that the variation of the stirring speed applied to the receiving phase had a negligible influence on gold transport. In the case of the receiving phase, and if the stirrer in the receiving compartment was close to the support, the thickness of the boundary layer was minimized and the resistance in the receiving side was neglected [32]. Thus, subsequent experiments were performed using stirring speeds of 1000 min^{-1} for both feed and receiving phases.

Another variable investigated was the variation (0.5-6 M) of the HCl concentration in the feed phase on gold transport, keeping the carrier concentration in the membrane support constant. The results were shown in Table 7. It can be seen that gold permeation increased when the acid concentration in the feed solution was increased up to 1 M, being metal permeation independent of the HCl concentration in the 3-6 M range due to that the equilibrium:

$$\mathrm{HAuCl_4} \leftrightarrow \mathrm{AuCl_4^-} + \mathrm{H^+} \tag{7}$$

was shifted completely to the left, and $HAuCl_4$ was the predominant species in the feed solution.

Table 7. Gold(III) permeation at various HCl concentrations in the feed phase.

[HCl], M	$K_O \cdot 10^3$, cm/s
0.5	3.8
1	4.7
3	5.7
6	5.7

Feed phase: 0.01 g/L Au(III) and HCl. Membrane phase: 50% v/v 2-ethylhexanol in toluene immobilized on GVHP4700 support. Receiving phase: water. Temperature: 20º C.

The influence of the variation of the carrier concentration on gold transport was next investigated. In these experiments, the feed phase was of 0.01 g/l Au(III) in 6 M HCl, whereas the organic phase contained 10-75% v/v 2-ethylhexanol in toluene or undiluted extractant. Table 8 showed the variation of the overall mass transfer coefficient with the variation of the carrier concentration in the membrane phase.

Table 8. Gold transport at various carrier concentrations.

[carrier], % v/v	**$K_O \cdot 10^3$, cm/s**	**^{a}% Gold recovery**
10	1.2	95
25	2.7	95
35	4.0	94
45	5.6	93
50	5.7	92
65	5.5	93
75	3.0	90
undiluted	1.2	89

Membrane support: GVHP4700. Receiving phase: water. ^{a}In the receiving phase after 3 hours.

These results demonstrated that gold transport increased from 10 to 50% v/v carrier concentration in the membrane phase, then levels off and after decreased at the highest carrier concentrations. These phenomena can be attributable to that at low carrier concentrations, metal transport was dominated by membrane diffusion, whereas in the 50% v/v range the contribution of membrane diffusion was negligible and gold transport was controlled by diffusion in the stagnant film of the feed phase. At this maximum K_O value [33]:

$$K_O = \frac{D_{aq}}{d_{aq}} \tag{8}$$

where D_{aq} represented the average aqueous diffusion coefficient (10^{-5} cm^2/s) of metal species in the feed phase [34], and d_{aq} was the minimum thickness of the feed phase boundary layer, thus, d_{aq} for the present system was estimated as $1.8 \cdot 10^{-3}$ cm. The decrease of gold transport at the highest carrier concentration was due to the increase of the organic phase viscosity, which decreased the Au(III)-2-ethylhexanol complexes diffusion coefficients values [35].

Investigation about the effect of the initial concentration (0.01-0.1 g/l) of gold, in the feed phase, on metal transport (Table 9), it was observed that the increase of the initial gold concentration was accompanied by a continuous decrease of metal transport, whereas the initial metal flux (J) defined as:

$$J = K_O[Au]_0 \tag{9}$$

initially increased from 0.005-0.04 g/L initial gold concentrations, and beyond this concentrations range, J became almost independent of the initial gold concentration in the feed phase.

Table 9. Variation in gold transport and initial flux at various metal concentrations.

$[Au]_0$, g/L	$K_O \cdot 10^3$, cm/s	J, mol/cm^{2}s	^{a}% Gold recovery
0.01	5.7	2.9	95
0.02	4.5	4.6	93
0.04	3.0	6.0	94
0.06	2.2	6.6	93
0.08	1.7	6.8	94
0.1	1.4	7.0	95

Feed phase: gold(III) in 6 M HCl. Membrane phase: 50% v/v 2-ethylhexanol in toluene immobilized on GVHP4700 support. Receiving phase: water. ^{a}In the receiving phase after 3 hours.

According with these results, at low metal concentrations (0.01-0.04 g/L), the transport process was controlled by diffusion of gold species, whereas in the highest metal concentrations range, the near constant metal flux values were due to a change in the rate- determining step for the transport process. At these higher gold concentrations, membrane became saturate by metal-carrier species on the feed-membrane interface, resulting in a lower effective membrane area, which led to a near constant initial flux value.

Following the same considerations described in the literature [36], it can be concluded that the gold transport rate was determined by the rate of diffusion of the $HAuCl_4$ species across the feed phase diffusion layer and the rate of diffusion of the gold species eq. () and () through the liquid membrane. Thus, taking the same assumptions that in [37,38], a final expression for the overall mass transfer coefficient can be derived as:

$$K_O = \frac{K_{11}[ROH]_{org} + K_{12}[ROH]_{org}^2}{\Delta_{org} + \Delta_f(K_{11}[ROH]_{org} + K_{12}[ROH]_{org}^2)} \tag{10}$$

where Δ_{org} and Δ_f were the transport resistances due to diffusion across the membrane and the aqueous feed boundary layer, respectively. The above equation combined in one expression both equilibrium and diffusional parameters involved in the gold(III) transport process from the feed phase, across supported liquid membranes using 2-ethylhexanol as carrier.

To estimate the values of the resistance to the mass transfer, the above equation was linearized, resulting in:

$$\frac{1}{K_O} = \Delta_f + \Delta_{org}\frac{1}{K_{11}[ROH]_{org} + K_{12}[ROH]_{org}^2} \tag{11}$$

and a plot of $1/K_O$ versus $1/(K_{11}[ROH]_{org} + K_{12}[ROH]_{org}^2)$ might result in a straight line with slope Δ_{org} and intercept Δ_f. From the plot, it resulted that Δ_{org} and Δ_f were found to be 2580 s/cm and 147 s/cm, respectively, with r^2= 0.9895. The utility of eq.(11) to describe gold transport across the supported liquid membrane by 2-ethylhexanol was shown in Figure 1, where the experimental and calculated values using this equation have been represented versus the initial carrier concentration.

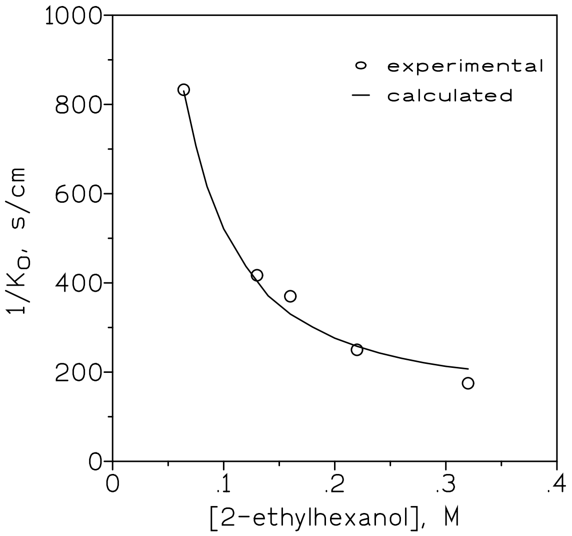

Figure 1. Plot of 1/Ko versus [2-ethylexanol]. Feed phase: 0.01 g/L Au(III) in 6 M HCl. Membrane phase: 10-50% v/v 2-ethylhexanol in toluene immobilized on GVHP4700. Receiving phase: water. .

Whereas the first term (1/Ko) of eq. (11) represented the value of the total resistance (R_T), and being this resistance the sum of the mass transfer resistances due to the feed and the membrane phase, eq. (11) can be expressed as:

$$R_T = R_f + R_m \tag{12}$$

The total resistance calculated from experiments in Table 6 presented values in the 175-1052 s/cm range, in comparison the total resistance calculated by the model is 206 s/cm, which indicated that the resistance due to the membrane is dominant at low stirring speeds.

The contribution of the fractional resistances due to each step of the total transport process, R_f^o and R_m^o can be expressed by equations:

$$\%R_f^o = \frac{R_f}{R_T} \cdot 100 \tag{13}$$

$$\%R_m^o = \frac{R_T - R_f}{R_T} \cdot 100 \tag{14}$$

Under various experimental conditions, the values of $\%R_f^o$ and $\%R_m^o$ are summarized in Table 10.

Table 10. Contribution of the mass transfer resistances to gold(III) transport process.

Experimental condition	**R_T, s/cm**	**^aR_T, s/cm**	**$\%R_f^o$**	**$\%R_m^o$**
Carrier 10-50% v/v	370-175	147	40-84	60-16
Gold: 0.01-0.1 g/L	175-714	147	84-21	16-79
HCl 6 M	175	147	84	16

^{a}Value from the theoretical model (eq. (11)).

Taking into account that:

$$D_{org} = \frac{d_m}{\Delta_{org}} \tag{15}$$

where D_{org} represented the diffusion coefficient of the gold-containing species in the organic phase immobilized on the solid support and d_m was the membrane thickness, then, D_{org} was found to be

$4.8 \cdot 10^{-6}$ cm²/s. The diffusion coefficient of the gold transported species in the bulk organic phase can be estimated by the next expression [39]:

$$D_{org,b} = \frac{D_{org}\tau^2}{\epsilon} \qquad (16)$$

where τ and ε were the membrane tortuosity and porosity values, respectively. The above resulted in $D_{org,b}$ calculated as $1.8 \cdot 10^{-5}$ cm²/s. Comparison of D_{org} and $D_{org,b}$ values showed that D_{org} was lower than $D_{org,b}$, which can be attributed to the diffusional resistance caused by the solid support separating the feed and receiving phases.

The selectivity of the present system against the presence of other metals in the feed phase was investigated. In this case, the feed phase contained 0.01 g/L each of Au(III), Ni(II), Cu(II), Fe(III) and PGMs (Ir, Os, Pd, Pt, Re, Rh, Ru) in 6 M HCl medium, being the organic phase of 50% v/v 2-ethylhexanol in toluene immobilized on Durapore GVHP4700 support. Like all the previous experimentation, water was used as receiving phase. The results indicated that PGMs were not transported under the present experimental conditions, whereas the transport of gold and the base metals followed the Au(III)>Fe(III)>Cu(II)=Ni(III) order, with separation factors Au/Fe, Au/Ni and Au/Cu of 1.3, 4.5 and 4,7, respectively. In these transport experiments the separation factors were calculated as:

$$SF = \frac{K_{O,Au}}{K_{O,M}} \qquad (17)$$

However, the presence of all these elements in the feed phase produced a decrease of the gold overall mass transfer coefficient from $5.7 \cdot 10^{-3}$ cm/s to $2.3 \cdot 10^{-3}$ cm/s. This behavior is not rare in supported liquid membrane operations and it is attributable to the multi-ion competition or crowding effect [40].

Once gold was transported from the feed solution to the membrane phase and finally to the receiving phase, it can be recovered from this last solution by precipitation as zero valent gold nanoparticles by the use of sodium borohydride. This procedure was used by one of us from years ago [41], otherwise the importance about the recovery of this precious metal as nanoparticles was also demonstrated [42], and uses of these nanoparticles in different fields (catalysis, medicine, sensors, etc,) regularly appeared in the literature [43-46]. In the present work, the receiving solution containing 0.009 g/L was precipitated by the direct action of solid sodium borohydride, after the reaction stopped, the dark solid was filtered. From this dry solid the next images were obtained.

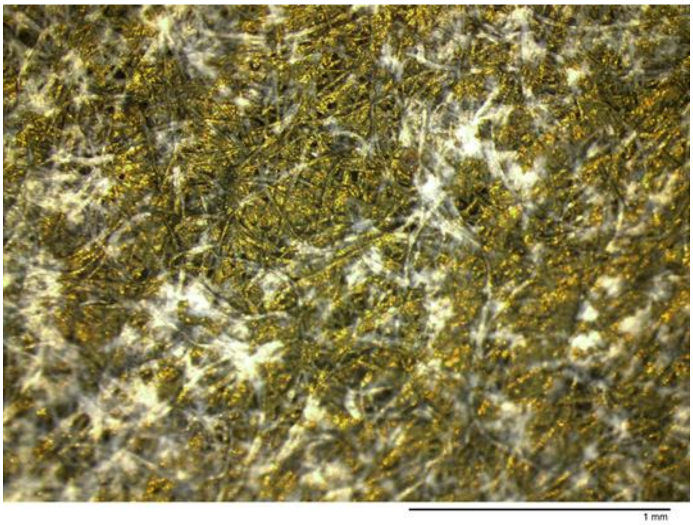

Figure 2. Gold nanoparticles under magnifier.

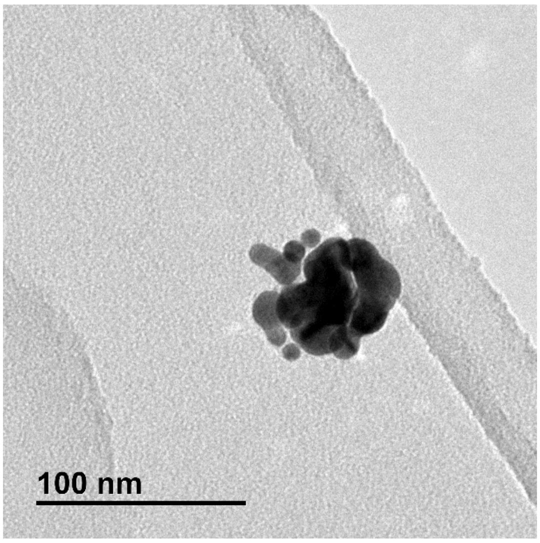

Figure 3. TEM image of gold nanoparticles. Some degree of agglomeration is observed.

Conclusions

2-ethylhexanol was used to extract gold(III) from macro amounts from 6 M HCl medium. The extraction process reached equilibrium within few minutes, being metal extraction dependent on gold and extractant concentrations. On the basis of numerical simulation, gold(III) extraction by 2-ethylhexanol can be explained by formation of $HAuCl_4{\cdot}L$ and $HAuCl_4{\cdot}2L$, with extraction constants of 38 and 309, respectively, and where L represented the extractant molecule. The extraction process is highly selective with respect to gold(III) in the presence of copper(II), nickel(II) and zinc(II). Gold can be stripped from the metal-loaded organic phase with water.

The extraction system was implemented in a solid supported liquid membrane system in which the metal flux was dependent on the initial gold concentration (up to 0.04 g/L) but almost independent of this variable above this concentration. The metal transport was also dependent on extractant concentration but for 2-ethylhexanol concentrations in the 50% v/v range in toluene, a limiting value for the overall mass transfer coefficient was obtained. Mass transfer coefficients in the feed and in the membrane phases were calculated as $6.8{\cdot}10^{-3}$ cm/s and $3.9{\cdot}10^{-4}$ cm/s, respectively. The minimum thickness of the feed boundary layer was calculated to be $1.8{\cdot}10^{-3}$ cm. The transport process was controlled by mixed diffusion of gold across the feed phase and the diffusion of the gold-2-ethylhexanol complexes in the liquid membrane phase. The system was highly selective respect to Au(III) in the presence of Platinum Group Metals and Cu(II), Ni(II) and Fe(III) in the aqueous feed phase. From the water-receiving phase, gold was recovered as zero valent gold nanoparticles by the use of sodium borohydride.

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