

Facilitated transport of $\text{Au}(\text{CN})_2^-$ and other metal-cyanide complexes using amines^(*)

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- Abstract** The use of different amines, Hostarex A327 (tertiary), Amberlite LA2 (secondary) and Primene JMT (primary), as carriers in the facilitated supported liquid membrane transport of metal-cyanide complexes, with special attention to gold, along with the addition of neutral organophosphorous derivatives (Lewis bases) to the amine organic phase as synergistic agents for the transport of $\text{Au}(\text{CN})_2^-$, at alkaline pH values and selectively against other metal-cyano complexes, is investigated.
- Keywords** Supported liquid membranes. Facilitated transport. Amines. Organophosphorous derivatives. Metal-cyano complexes.

Transporte facilitado mediante aminas de $\text{Au}(\text{CN})_2^-$ y otros complejos metálicos cianurados

- Resumen** Se estudia el empleo de las aminas Hostarex A327, Amberlite LA2 y Primene JMT (terciaria, secundaria y primaria, respectivamente) como reactivos del transporte facilitado, con membranas líquidas soportadas, de complejos metálicos cianurados, con especial atención al caso del oro. También se estudia la adición de derivados organofosforados neutros (bases de Lewis) a la fase orgánica de la amina, como agentes sinérgicos del transporte de $\text{Au}(\text{CN})_2^-$, a pH alcalinos, y de forma selectiva frente a otros complejos metálicos cianurados.
- Palabras clave** Membranas líquidas soportadas. Transporte facilitado. Aminas. Derivados organofosforados. Complejos metálicos cianurados.

1. INTRODUCTION

Liquid membranes technologies, containing small volumes of carrier, have been suggested as a potential alternative to conventional liquid-liquid extraction. They have different applications in the field of separation science, i.e. in metallurgical extraction and in the removal of toxic metals from liquid effluents.

Among liquid membranes processing, supported liquid membranes, in various configurations, are gaining considerable importance in the above mentioned field. In supported liquid membrane technologies, the carrier solution (extractant and diluent) filled the pores of the (normally) hydrophobic microporous membrane support, which separates both the aqueous feed phase (containing the metal to be transported) and the receiving phase (from which the metal is finally

recovered). Hence, extraction, stripping and regeneration steps of liquid-liquid extraction are reduced to a single stage. Applications of supported liquid membranes technologies in the processing of metal-bearing solutions have been reviewed^[1 and 2].

Amines had been used to extract metals. Quaternary ammonium salts (strong bases) can be used to extract metals at practically every pH value but with not an easy stripping phase. On the other hand, primary, secondary and tertiary amines (normally referred as weak bases) can be protonated, and thus, they can be used in the extraction of metals only from acidic or near neutral solutions, with the subsequent loss in their effectiveness to extract metals if compared with quaternary ammonium salts. The addition of a Lewis base to an amine-organic phase had been proposed in order to extend the pH range of utilization of these weak-base compounds^[3 and 4].

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Various amines had been used in supported liquid membrane systems for metal separation (Table I), with few data available concerning the liquid membrane transport of aurocyanide-bearing solutions^[5-8].

In the present work, the facilitated transport of $Au(CN)_2^-$ using amines or amine-Lewis base systems as carriers had been investigated.

2. EXPERIMENTAL

All the extractants were used as received. Amine Primene JMT (Rhom and Haas Co.) is a primary aliphatic amine with highly branched alkyl chains in which the amino-nitrogen atom is linked to a tertiary carbon atom. The reagent consists of a mixture of isomeric amines in the C_{16-22} range.

Amberlite LA2 (Rohm and Haas Co.) is a secondary aliphatic amine (R_2NH) with an average molecular weight 375.

Hostarex A327 (Hoechst) is a mixture at 50 % of tertiary n-octyl and n-decylamines. The average molecular weight is 395.

Organophosphorous derivatives Cyanex 923, DBBP and TBP were obtained from Cytec Ind., Albright & Wilson and Fluka, respectively.

All other chemicals were of reagent grade, except $K_2Ni(CN)_4$ which was synthesized according to the literature^[9], and Exxsol D100 diluent which was obtained from ExxonMobil Chem. Iberia (Spain) and its characteristics were given elsewhere^[10].

The flat-sheet membrane used was Millipore Durapore GVHP4700 of 12.5×10^{-3} cm thick

microporous PVDF film with nominal porosity of 75 %, effective pore size of 0.22 μm and tortuosity 1.67. The membrane was impregnated with carrier solution containing the extractant dissolved in the corresponding diluent by immersion for 24 h, then leaving it to drip for 10 s before being placed in the transport cell.

The batch transport experiments were carried out in a permeation cell consisting of two compartments made of methacrylate and separated by the microporous membrane. The effective geometrical membrane area was 11.3 cm^2 and the volume of the feed and receiving solutions were 200 cm^3 .

The experiments were performed at the temperature of 20 °C and using a mechanical stirring speed of 1400 min^{-1} in the feed phase, and 1000 min^{-1} in the receiving phase. Previous experiments had shown that, within these stirring speeds range, the transport of the metal becomes independent of the stirring speed; consequently, the thickness of the aqueous diffusion layer and the aqueous resistance to mass transfer were minimized and the diffusion contribution of the aqueous species to the mass transfer process was assumed to be constant.

The transport of metals were monitored by sampling the feed phase, and metals were analyzed by AAS using a Perkin Elmer 1100B spectrophotometer. The percentage of metal transport (%T) was then calculated according to:

$$\%T = \frac{100([M]_0 - [M]_t)}{[M]_0} \quad (1)$$

where $[M]_t$ is the metal concentration in the feed phase at an elapsed time t and $[M]_0$ is the initial metal concentration in the aqueous feed phase.

3. RESULTS AND DISCUSSION

3.1. Influence of the amine type

The transport of gold(I)-cyanide through the membrane was studied using organic solutions of the amines Hostarex A327, Amberlite LA2 and Primene JMT (20 % v/v in xylene) and aqueous solutions of 0.005 g/L Au(I). Receiving phases were of 10^{-2} M NaOH. Results obtained from these experiments are shown in figure 1; it can be seen that the percentage of gold transported was not

Table I. Amines used in SLM technologies

Tabla I. Aminas empleadas en tecnologías de membranas líquidas soportadas

Amine	Type	Metal	Aqueous Solution
Aliquat 336	Qaternary ammonium salt	Cr(VI)	chloride
Aliquat 336		Cd(II)	phosphoric acid/chloride
Trioctylamine	Tertiary	Cr(VI)	sulphuric acid
		Hg(II)	chloride
LIX 79*	Guanidine derivative	Au(I)	cyanide

*LIX 79, not being an amine, is considered as such due to its similar behaviour in the extraction of metals

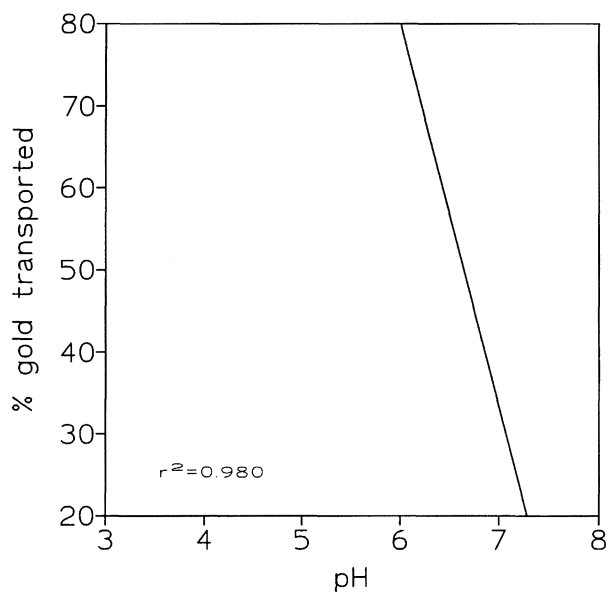


Figure 1. Regression line for the averaged percentage of gold transported by the three amines. Time: 3 h.

Figura 1. Regresión lineal del tanto por ciento (medio) de transporte de oro mediante las tres aminas. Tiempo: 3 h.

dependent of the amine type, obtaining an averaging pH_{50} value of 6.6 (pH_{50} value is defined as the pH value of the feed phase in which 50 % gold transport is achieved). These carriers systems are not suitable for the facilitated transport of the aurocyanide complex at alkaline pH values.

Further experiments were carried out to investigate the performance of these amines on the transport of other metal-cyano complexes. Results of this study are summarized in table II; it can be seen that the transport of these metallic complexes is limited to pH values lower than 7, also being the selectivity, on the transport of these metal-cyano complexes by these amine systems, rather poor.

Table II. pH_{50} values for the transport of metal-cyano complexes

Tabla II. Valores del pH_{50} para el transporte de complejos metálicos cianurados

Amine	$\text{Au}(\text{CN})_2^-$	$\text{Ni}(\text{CN})_4^{2-}$	$\text{Fe}(\text{CN})_6^{3-}$
Primene JMT	6.6	6.3	6.1
Amberlite LA2	6.6	6.3	6.0
Hostarex A327	6.6	5.8	5.5

Aqueous phase: 2.5×10^{-5} M metal.
Organic phase: 20 % v/v amine in xylene.
Receiving phase: 10^{-2} M NaOH.
Time: 3 h.

3.2. Influence of the organic diluent

The influence of the organic diluent on the transport of the aurocyanide complex was also studied. The organic diluent chosen as a water-resistant barrier in any liquid membrane process exerts a major influence on the membrane performance. The polarity of the diluent is of a major importance in determining effectiveness of the membrane, though membrane stability versus rapid transport is the primary choice to be made in choosing a membrane diluent^[11].

The influence of various diluents on the transport of gold by the amine Amberlite LA2 was studied using aqueous phases with 0.005 g/L Au(I) at $\text{pH} 6.0 \pm 0.02$ and organic solutions of 20 % v/v amine in each diluent. Receiving solutions were of 10^{-2} M NaOH.

Results obtained are shown in table III; in the present study, the gold transport was dependent upon the organic diluent. Xylene was the diluent giving the best percentage of transport value. It is also evident, from these results, that the supported liquid membrane performance was not only dependent of the diluent type (i.e. aromatic versus aliphatic) but also on intrinsic membrane diluent properties such as viscosity, surface tension, etc.

3.3. Influence of the amine and metal concentrations

The pH_{50} value for the transport of gold increased as the amine concentration in the organic phase increased; that is, better transport results were obtained at more alkaline pH values as the amine concentration is increased. These results are shown in figure 2 for transport investigations carried out

Table III. Influence of the organic diluent on the transport of gold(I)

Tabla III. Influencia del diluyente orgánico sobre el transporte de oro(I)

Diluent	Type	% Transport
Toluene	Aromatic	23.8
Cumene	Aromatic	35.0
Decane	Aliphatic	38.7
Exxsol D100	Aliphatic	21.9
Xylene	Aromatic	76.2

Time: 3 h.

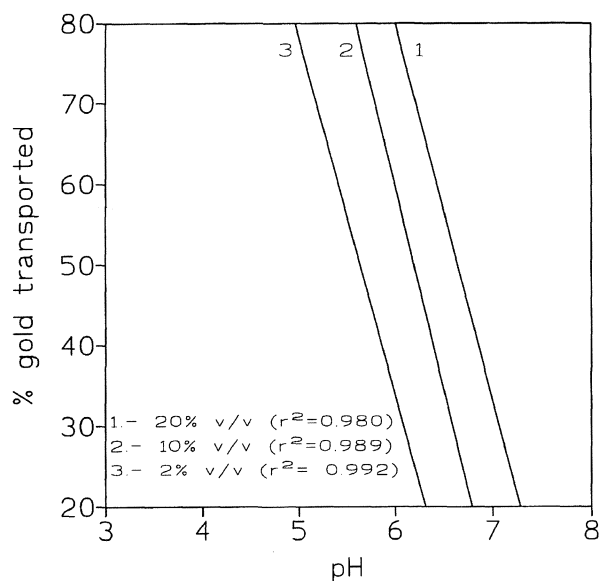
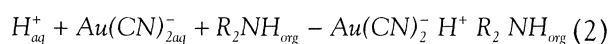


Figure 2. Regression line for the percentage of gold transported by Amberlite LA2. Receiving phase: 10^{-2} M NaOH. Time: 3 h.

Figura 2. Regresión lineal del porcentaje de transporte de oro mediante Amberlite LA2. Fase de recepción: 10^{-2} M NaOH. Tiempo: 3 h.

with various Amberlite LA2 concentrations and aqueous phases of 0.005 g/L Au(I).

This behaviour is due to the mass action law which shifted to the right the corresponding extraction equilibrium:



It had been shown in the literature^[12 and 13], that the extraction of the $Au(CN)_2^-$ complex by different extractants can be enhanced by the use of an electrolyte, specially if the latter is a source of lithium ions in the extraction process. Thus, the presence, in the aqueous feed phase, of an electrolyte such as $LiNO_3$ on the transport of the aurocyanide complex was also investigated. The experiments were carried out with aqueous phases of 0.02 g/L Au(I) at $pH\ 5.0 \pm 0.02$ which also contained 1 M $LiNO_3$. The organic phase was of 20 % v/v Amberlite LA2 in xylene and the receiving phase of 10^{-2} M NaOH. The results obtained, after 3 h, showed that the ionic strength of the feed phase influenced the transport of gold (i.e. 9.7 % transport at $I = 1$ against 36.7 % at $I = 0$). Similar results were obtained using various amine or metal concentrations. It can be concluded that the ionic strength may be a significant parameter to consider in the facilitated transport of the gold(I)-cyanide complex by alkylamines.

Also, the influence of varying the initial gold concentration on the transport of the metal by the amines was investigated. Experiments were performed using aqueous solutions with different gold concentrations and organic phases of the amines Hostarex A327, Amberlite LA2 and Primene JMT (20 % v/v in xylene). A 10^{-2} M NaOH solution was used as receiving phase throughout all the tests. Results obtained are shown in table IV, in which it is observed that the increase of the initial gold concentration decreases the percentage of gold transport, being this effect similar for the three amines investigated.

The results obtained showed that the alkylamines investigated transported the aurocyanide complex from acidic or near neutral aqueous phases, they can not be used in the transport of gold from aqueous solutions with a pH value higher than 6-7. On the other hand, the use of synergic mixtures may increase the pH range of extraction by amines. Phosphorous organic derivatives seemed to be the reagents with greater possibilities in this field.

3.4. Facilitated transport of the aurocyanide complex with synergic mixtures

It is known the use of synergic mixtures in various facilitated transport systems, being these mixtures effective in the transport of gold by amines.

As it is mentioned above, addition of an organophosphorous derivative, acting as a Lewis base, to weak-base amines increases the pH range in which these reagents can facilitate the transport of specific anions. This effect is particularly important in the case of the transport of the aurocyanide complex and, thus, increasing the

Table IV. Influence of the metal concentration on the percentage of gold(I) transported

Tabla IV. Influencia de la concentración inicial del metal sobre el tanto por ciento de transporte de oro(I)

Amine	A	B	C
Primene JMT	35.3	76.0	>99
Amberlite LA2	36.7	75.1	>99
Hostarex A327	36.9	79.7	>99

A: aqueous phase: 0.02 g/L Au(I) at $pH\ 5.0 \pm 0.02$.
B: aqueous phase: 0.01 g/L Au(I) at $pH\ 5.0 \pm 0.02$.
C: aqueous phase: 0.005 g/L Au(I) at $pH\ 5.0 \pm 0.02$.
Time: 3 h.

possibilities in the use of these supported liquid membrane systems.

In the present work, various synergic mixtures of Amberlite LA2 (20 % v/v in xylene) with each one of the reagents shown in table V were investigated.

The transport experiments were carried out with aqueous solutions of 0.005 g/L Au(I) and organic phases of Amberlite LA2 20 % v/v and each of the reagents, shown in table V, in xylene. The results obtained are shown in figure 3, in which the percentage of gold transported is plotted against the pH of the aqueous phase.

Table V. Phosphorous derivatives used in the transport of gold(I)

Tabla V. Derivados del fósforo empleados en el transporte del oro(I)

Name	Type	Structure
Tributylphosphate (TBP)	phosphoric ester	$(RO)_3P = O$
Dibutyl butylphosphonate (DBBP)	phosphonic ester	$(RO)_2RP = O$
Cyanex 923	phosphine oxide	$R_3P = O$

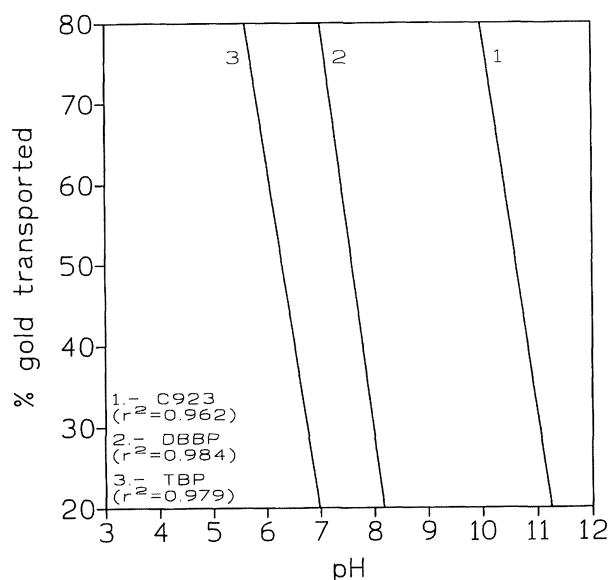


Figure 3. Regression line for the percentage of gold transported by mixtures of Amberlite LA2 and neutral organophosphorous derivatives (20 % v/v each). Other experimental conditions as in figure 2.

Figura 3. Regresión lineal del porcentaje de transporte de oro mediante mezclas de Amberlite LA2 y derivados organofosforados neutros (20 % v/v de cada uno). Resto de condiciones experimentales como en la figura 2.

These results shown that the addition of an organophosphorous derivative, as the investigated, to the amine shifted to the right, that is to more alkaline pH values, the transport results. This effect is more evident in the case of Cyanex 923, which gives a variation in the pH_{50} for metal transport of near 4 pH units (i.e. pH_{50} values of 6.6 and 10.6 for systems using Amberlite LA2 alone of a mixture of the amine with Cyanex 923, respectively). From figure 3, it is deduced that the influence in the transport follows the apparent order: Cyanex 923>DBBP>TBP. This sequence follows the order in the increase of the Lewis base character of the reagents, that is, the electron donor properties of the synergic agent, and shows that the transport of the aurocyanide complex with these synergic mixtures is probably due to a solvation of the anion together with the transport mechanism shown in eq.(2).

Due to that best transport results were obtained using Cyanex 923, further facilitated transport investigations were carried out using this organophosphorous derivative.

Figure 4 shows the percentage of gold transported against aqueous pH for transport tests performed with organic solutions using various Amberlite LA2-Cyanex 923 concentrations in xylene. It can be seen that as the concentration of the synergic mixture is increased, the percentage of gold transported is shifted to more alkaline pH values; within the present experimental conditions a pH_{50} value of near 10.6 is achieved.

The effect of adding Cyanex 923 to a primary or tertiary amine, Primene JMT or Hostarex A327 respectively, on the transport of gold was investigated with mixtures of each amine and Cyanex 923 (20 % v/v and 20 % v/v of each reagent in xylene) and aqueous phases of 0.005 g/L Au(I). The receiving phase was also a 10^{-2} M NaOH solution. The results obtained are shown in figure 5, in which the percentage of metal transported is plotted versus pH for each of these amine-Cyanex 923 systems.

The comparison of these results with those shown in figure 1, transport using only amines, concluded that in all the present systems the percentage of metal transported shifted to the right (to more alkaline pH values) if compared with results obtained using only alkylamines. It should be pointed out that, using this synergic mixture, the transport order follows the order: primary>secondary=tertiary amines, which somewhat resembles the order found in conventional liquid-liquid extraction.

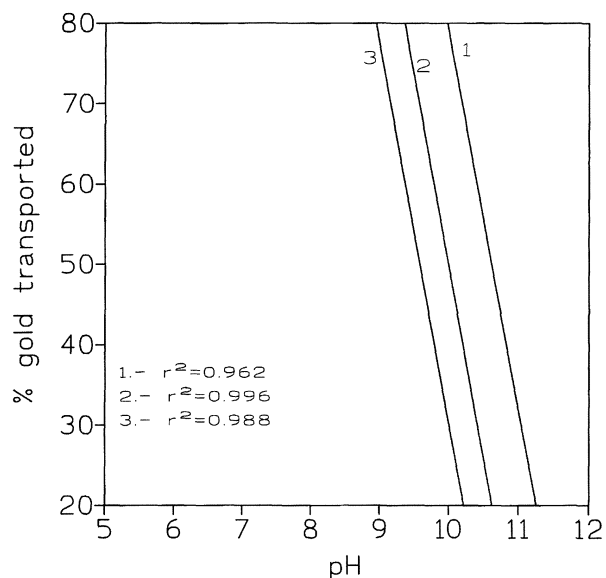


Figure 4. Regression line for the percentage of gold transported by various concentrations of the synergic mixture Amberlite LA2 and Cyanex 923. Feed phase: 0.005 g/L Au(I). Organic phases: 1 (20 % v/v Amberlite LA2 and 20 % v/v Cyanex 923), 2 (5 % v/v Amberlite LA2 and 5 % v/v Cyanex 923), 3 (2 % v/v Amberlite LA2 and 2 % v/v Cyanex 923). Other experimental conditions as in figure 2.

Figura 4. Regresión lineal del porcentaje de transporte de oro mediante distintas concentraciones de la mezcla sinérgica Amberlite LA2 y Cyanex 923. Fase de alimentación: 0,005 g/L Au(I). Fase orgánica: 1 (20 % v/v Amberlite LA2 y 20 % v/v Cyanex 923), 2 (5 % v/v Amberlite LA2 y 5 % v/v Cyanex 923), 3 (2 % v/v Amberlite LA2 y 2 % v/v Cyanex 923). Resto de condiciones experimentales como en la figura 2.

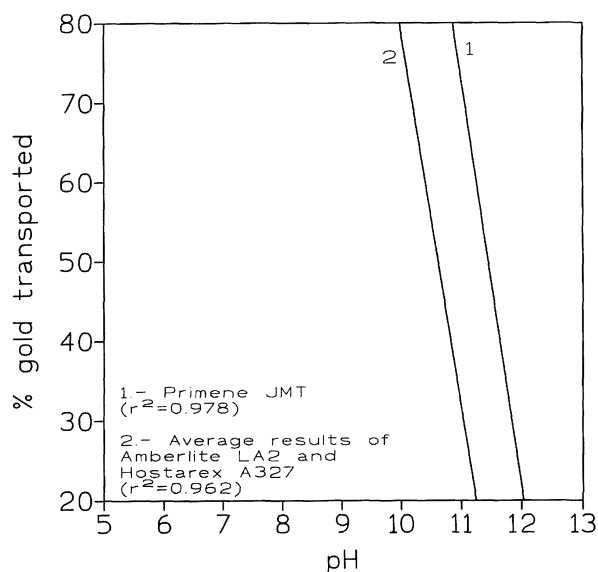


Figure 5. Regression line for the percentage of gold transported by mixtures of amines and Cyanex 923. Time: 3 h.

Figura 5. Regresión lineal del porcentaje de transporte de oro mediante mezclas de aminas y Cyanex 923. Tiempo: 3 h.

3.5. Selectivity of the amine-Cyanex 923-aurocyanide complex against other metal-cyanide complexes

In order to investigate the effect of other metal-cyanide complexes, generally accompanying gold in cyanide solutions, a systematic study was carried out on the selective transport of gold against these metal complexes using the system amine-Cyanex 923.

The transport experiments were running up for 3 h. The aqueous phase contained 2.5×10^{-5} M of each metal and the organic phases contained 20 % v/v Amberlite LA2 and 20 % v/v Cyanex 923 in xylene. The results obtained are shown in figure 6, in which the percentage of metal transported is plotted against aqueous pH.

It is observed that the aurocyanide complex was transported preferably to other metal-cyanide complexes, and a general transport sequence was established as: $\text{M}(\text{CN})_2^- > \text{M}(\text{CN})_4^{2-} > \text{M}(\text{CN})_6^{3-}$, the metal-cyanide complex with lower coordination number and lower charge was transported at higher alkaline pH values with respect to complexes with higher coordination and charge. This sequence is similar to this obtained in conventional liquid-liquid extraction using mixtures of amines and phosphine oxides to extract metal-cyano complexes^[14].

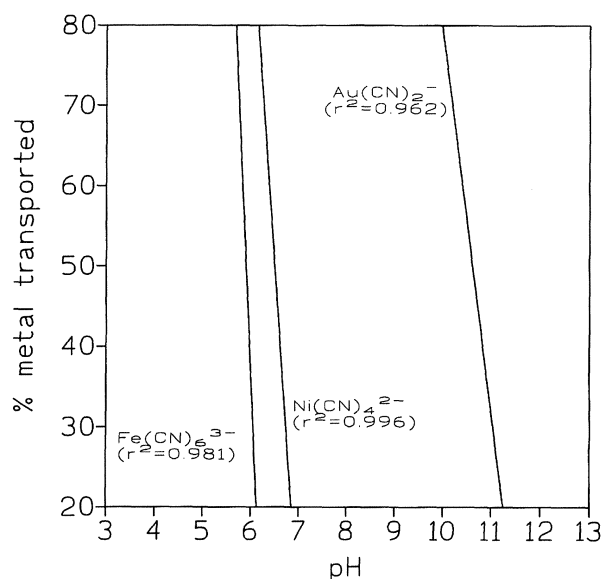


Figure 6. Regression line for the percentage of metal transported by a mixture of Amberlite LA2 and Cyanex 923.

Figura 6. Regresión lineal del porcentaje de transporte de metal mediante una mezcla de Amberlite LA2 y Cyanex 923.

4. CONCLUSIONS

Results obtained from the present research shown that the aliphatic amines Hostarex A327, Amberlite LA2 and Primene JMT dissolved in xylene can be used as carriers in the facilitated transport of $Au(CN)_2$ from acidic or near neutral aqueous phases. The transport of the aurocyanide complex was not dependent of the amine type but the diluent of the organic phase and the aqueous ionic strength influenced the transport of the metal.

The use of synergic mixtures of the amines shifted the transport of the gold(I)-cyanide complex to alkaline pH values; best results were obtained when the synergic reagent was a phosphine oxide, such as Cyanex 923. Moreover, these amine-Cyanex 923 systems facilitated the selective transport of the $Au(CN)_2$ complex against other metal-cyano complexes.

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