J. Chem. Research (S), 1998, 792–793†

Solvent Extraction of $Au(CN)_2^-$ by Mixtures of the Primary Amine Tridecylamine and the Phosphine Oxide Cyanex 923†

Francisco José Alguacil

Centro Nacional de Investigaciones Metalúrgicas (CSIC), Avda. Gregorio del Amo 8,
Ciudad Universitaria, 28040 Madrid, Spain

Recovery of gold from various resources is accomplished using chloride or cyanide media; from the corresponding gold-containing solutions various alternatives are used to separate it from less valuable metals.

Solvent extraction is less used in cyanide media, although in recent years suitable extractants have been used advantageously in the extraction of gold from these media.[1–5] In the present work, the extraction of the $Au(CN)_2^-$ complex by mixtures of tridecylamine and the phosphine oxide Cyanex 923 have been studied in order to gain knowledge about the performance of such systems and to define the stoichiometry of the reaction species.

Cyanex 923 (Cytec Ind.)[6] and tridecylamine (Fluka) were used as received. Cyanex 923 extractant is a mixture of four trialkylphosphine oxides as follows: R_3PO, $R_2R'PO$, RR'_2PO and R'_3PO, where $R = n$-octyl and $R' = n$-hexyl, average molecular weight 348, density (25 °C) 0.88 g dm^{-3}. Tridecylamine is a primary amine of molecular weight 199.4 and density (25 °C) 0.80 g dm^{-3}. The concentrations of the extractants were checked by titration in ethanolic media of the respective organic solutions with standard hydrochloric acid solution using bromothymol blue as indicator. All other chemicals were of analytical reagent grade. Extractions were carried out by mechanical agitation (700 min^{-1}) in separatory funnels, thermostatted at the required temperature and for 10 min (time necessary to achieve metal extraction equilibrium), of equal volumes of the appropriate organic and aqueous phases. In each test, the metal mass balance was calculated by analyzing the gold concentration in both aqueous and organic phases, before and after the reaction. Gold was analysed by AAS.

The distribution of gold between the organic and aqueous phases was obtained as the ratio of the total metal concentration in the equilibrated phases:

$$D_{Au} = \frac{[Au]_{org}}{[Au]_{aq}}$$

Table 1 shows the values of the pH_{50} (equilibrium pH in which $D_{Au} = 1$) obtained in the extraction of 0.10 mmol dm^{-3} gold by organic solutions which contained different tridecylamine–Cyanex 923 mixtures in xylene on a total 20% vol/vol basis. The best results (gold extraction at more alkaline pH values) were obtained using 1:1 or 1:3 amine to phosphine oxide ratios. However, phase disengagement was improved using the 1:1 ratio, thus all subsequent experiments were done using this ratio.

Table 1 pH_{50} values for the extraction of gold by tridecylamine–Cyanex 923 mixtures in xylene[a]

Extractant concentration ratio B:L	pH_{50}
75:25	11.4
50:50	11.7
25:75	11.7

[a] Temperature 20 °C. B = amine, L = phosphine oxide.

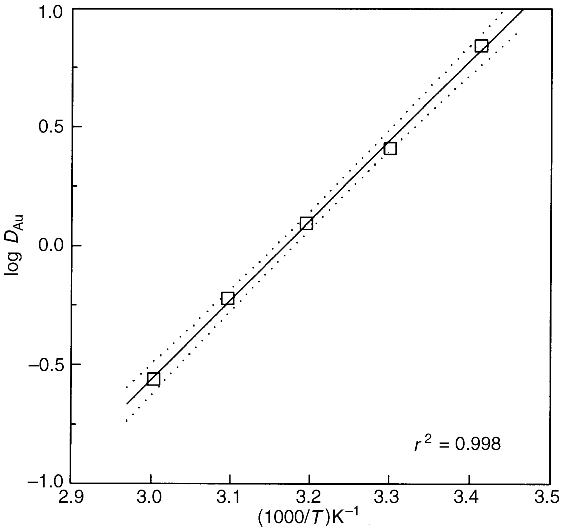

Fig. 1 Arrhenius plot for gold extraction by the mixture tridecylamine–Cyanex 923 in xylene. Dotted line shows 95% confidence interval. Initial gold concentration: 0.1 mmol dm^{-3}. Initial amine and phosphine oxide concentrations: 0.41 and 0.25 mol dm^{-3}. Equilibrium pH: 10.6 ± 0.02

Fig. 1 shows the Arrhenius plot for gold extraction. Increasing temperature decreases gold extraction; the change of enthalpy ($\Delta H°$) for the reaction is –64.2 kJ mol^{-1} and the extraction is exothermic.

The extraction of gold was determined as a function of the initial metal concentration. Fig. 2 shows the plot of

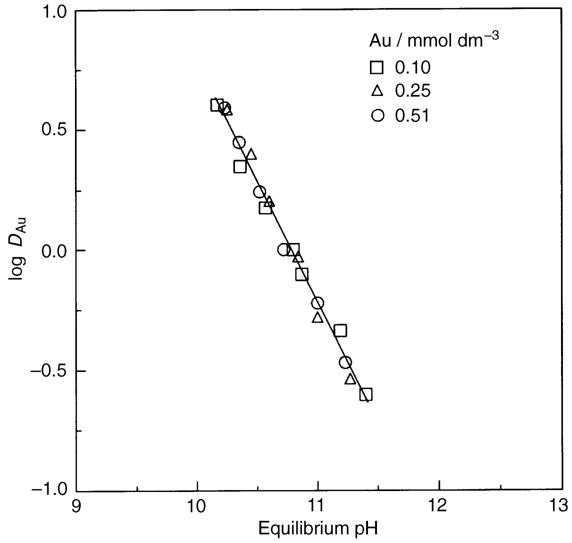

Fig. 2 Gold extraction by the mixture tridecylamine–Cyanex 923 (0.20–0.13 mol dm^{-3}) in xylene at various initial gold concentrations. Temperature: 20 °C

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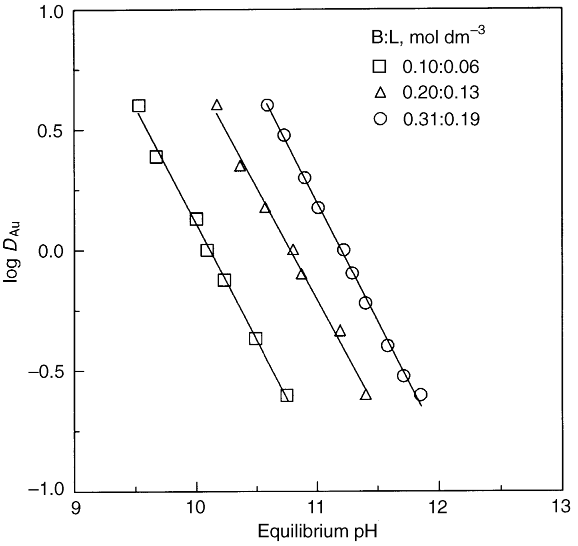

Fig. 3 The influence of the extractant mixture concentration on gold extraction. Initial gold concentration: 0.10 mmol dm^{-3}. Temperature: 20 °C. B = amine, L = phosphine oxide

log D_{Au} *versus* equilibrium pH. The variation of the initial metal concentration does not influence gold extraction. These results are indicative of the apparent lack of formation of polynuclear gold complexes in the organic phase.

Fig. 3 shows the variation of log D_{Au} with equilibrium pH for experiments carried out using different amine and phosphine oxide concentrations. From the results obtained it can be deduced that the increase of the extractant mixture concentration shifted gold extraction to more alkaline pH_{50} values.

The extraction of the gold(I)-cyanide complex with the mixture tridecylamine–Cyanex 923 may be written as:

$$Au(CN)_{2aq}^- + H_{aq}^+ + pB_{org} + qL_{org} \rightleftharpoons HAu(CN)_2 \cdot pB \cdot qL_{org}$$

where B and L represent the amine and the phosphine oxide, respectively.

Experimental data were treated numerically using the program LETAGROP-DISTR[7] in order to obtain the values of the extraction constant as well as to obtain the values of the coefficients p and q and thus the stoichiometry of the extraction reaction. The results are given in Table 2.

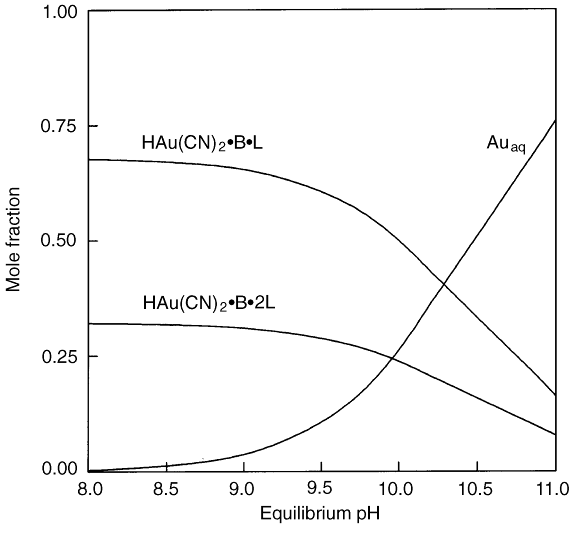

Fig. 4 Gold distribution diagram as a function of equilibrium pH at constant tridecylamine–Cyanex 923 concentrations (0.20–0.13 mol dm^{-3}). Gold concentration: 0.10 mmol dm^{-3}

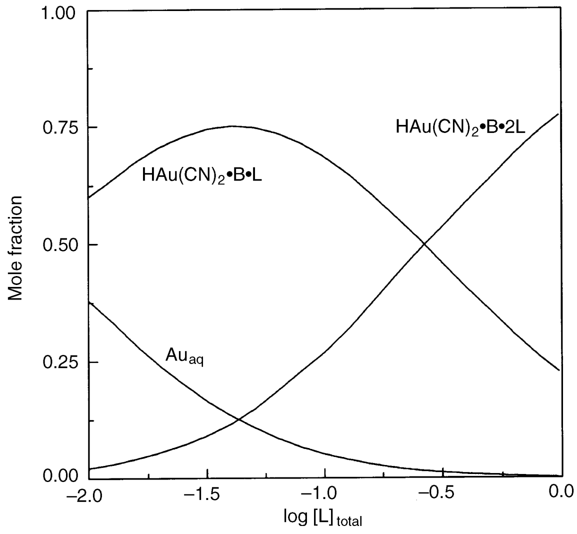

Fig. 5 Gold distribution diagram as a function of the total Cyanex 923 concentration. Amine concentration: 0.20 mol dm^{-3}. Gold concentration: 0.10 mmol dm^{-3}. Aqueous pH: 9.0

The extraction of the $Au(CN)_2^-$ complex by this extraction mixture can be explained by the formation in the organic phase of two species $HAu(CN)_2 \cdot B \cdot L$ and $HAu(CN)_2 \cdot B \cdot 2L$ in the range of concentrations used.

Fig. 4 shows the distribution diagram of gold *versus* equilibrium pH with the $[\text{extractant mixture}]_{tot}/[Au]_{tot}$ ratio kept constant. For such conditions the species $HAu(CN)_2 \cdot B \cdot L$ is predominant in the organic phase at all the equilibrium pH values.

Fig. 5 shows the distribution diagram of gold species as a function of the total Cyanex 923 concentration at constant equilibrium pH. At constant amine concentration and low Cyanex 923 concentrations $HAu(CN)_2 \cdot B \cdot L$ is the dominant species and only at higher Cyanex 923 concentrations does the species $HAu(CN)_2 \cdot B \cdot 2L$ become dominant.

Finally, IR measurements on gold-loaded organic phases show a peak at 2140 cm^{-1}, which is characteristic of the cyanide stretching vibration of the aurocyanide complex;[8] this peak is at the same wavenumber as that obtained for the $Au(CN)_2^-$ complex and indicated that the coordination of this anion is not easily altered.

Table 2 Equilibrium constants for the extraction of $Au(CN)_2^-$ by the mixture tridecylamine–Cyanex 923

Complex[a]	log K_{ext}	σ(log K_{ext})	U[b]
$HAu(CN)_2 \cdot B \cdot L$	12.21 ± 0.07	0.023	0.027
$HAu(CN)_2 \cdot B \cdot 2L$	12.77 ± 0.14	0.047	

[a] B = amine, L = phosphine oxide. [b] U defined by the numerical program.[7]

Received, 11th May 1998; Accepted, 12th August 1998
Paper E/8/03508C

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