Modeling $Au(CN)_2^-$ Extraction by Mixtures of Primene JMT and Cyanex 925 Reagents

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A chemically based thermodynamic model to predict the distribution coefficient has been developed for the $Au(CN)_2^-$-Primene JMT-Cyanex 925 system. The predictive model makes use of the extraction mechanism, speciation in the organic phase, and the equilibrium constant for the extraction reaction. The distribution coefficient of gold can be predicted by the equation $D_{Au} = K'[H^+]$, where K' is an effective extraction constant and $[H^+]$ is the proton concentration of the aqueous phase at equilibrium. Excellent agreement between the experimental data and the predicted value was obtained. Furthermore, for the present extraction system, the equilibrium isotherm was determined at 20°C.

Introduction

Gold is usually recovered from various raw and secondary materials by cyanidation. The corresponding metal-rich solutions need to be concentrated to produce a higher grade solution, from which gold can be obtained most efficiently by the corresponding recovery methods.

The concentration of the gold-bearing solutions is normally carried out by carbon adsorption or ion exchange (Yannopoulos, 1991; Marsden and House, 1992). Solvent extraction had no known practical application in this field; although during last few years there has been a renewed interest in the application of this technique to the recovery of precious metals from such alkaline solutions using various extractants (Mooiman and Miller, 1984, 1986, 1991; Alguacil et al., 1994; Alguacil and Caravaca, 1996; Alguacil et al., 1997).

On the other hand, solvent extraction has been applied industrially for the separation in chloride media of gold, platinum group metals, and base metals during precious metal refining (Cox, 1992).

Solvent extraction modeling can be used advantageously to predict, from a limited number of chosen conditions and with acceptable accuracy, the finished or equilibrium values, and thus reduce the experimentation required.

Modeling in solvent extraction has been used on different extractant-metal systems (Hoh and Bautista, 1978; Lee and Tavlarides, 1983; Bart et al., 1992; Cote et al., 1994; Veglio and Slater, 1996; Bandyopadhyay et al., 1996; Giles et al., 1996; Cote and Jakubiak, 1996; Doungdeethaveeratana and Sohn, 1998), but no data are available in the literature on predicting gold distribution from cyanide solutions using solvent extraction.

This work was undertaken to develop a chemical-based model for predicting the solvent extraction of gold from cyanide media by a recently developed solvent extraction system (formed by the amine Primene JMT and the phosphine oxide Cyanex 925) that has been proposed for gold extraction, and using the available data in the literature. Additional experimental data were obtained for the system $Au(CN)_2^-$-Primene JMT−Cyanex 925−toluene to test the accuracy of the predictive model further. This system was also used to develop a mathematical equation for the corresponding gold-loading isotherm.

Experimental

The characteristics and properties of the primary amine Primene JMT and the phosphine oxide Cyanex 925 have been published elsewhere (Rohm and Haas, 1992; CYTEC, 1994). Concentrations were measured by titration in an ethanolic medium, with standard sodium hydroxide solutions using Bromothymol Blue as an indicator. The desired extractant mixture concentrations were prepared by diluting the as-received extractants with toluene (AR grade). Stock solutions of gold were prepared by dissolving potassium aurocyanide (AR grade) in distilled water. All other chemicals were also of AR grade.

Extraction experiments were carried out in thermostatically controlled separatory funnels by shaking (700 rpm) together equal volumes of the corresponding aqueous and organic phases at 20°C for 15 min. Previous experiments have shown that this is enough time to achieve equilibrium.

The equilibrium isotherm for extraction was obtained by bringing the aqueous and organic solutions to equilibrium at various A/O ratios. The contacting was achieved by mechanically shaking (700 rpm) the corresponding aqueous and organic solutions in thermostatted separatory funnels.

The concentration of gold in the aqueous solutions was measured by AAS using a Perkin-Elmer 1100B spectrophotometer. The concentration of the metal in the organic solution was calculated from the mass balance. The pH of the aqueous phases was measured by a pH-meter (Crison 506).

Results and Discussion

Model development

The equilibrium reaction for the solvent extraction of the gold(I)–cyanide complex by a mixture of the primary amine Primene JMT and the phosphine oxide Cyanex 925 can be represented by the equation (Martín and Alguacil, 1998)

$$\mathrm{Au(CN)_{2_{aq}}}^- + \mathrm{H_{aq}}^+ m\mathrm{L_{org}} + q\mathrm{A_{org}} \rightleftarrows \mathrm{H^+Au(CN)_2}^- \cdot \mathrm{L}_m \cdot \mathrm{A}_{q_{\mathrm{org}}}, \quad (1)$$

where L represents the phosphine oxide, A the amine, and aq and org denote the aqueous and organic phases, respectively. The equilibrium constant K_{ext} for the reaction in Eq. 1 can be represented by

$$K_{ext} = \frac{\left\{\mathrm{H^+Au(CN)_2}^- \cdot \mathrm{L}_m \cdot \mathrm{A}_q\right\}_{\mathrm{org}}}{\left\{\mathrm{Au(CN)_2}^-\right\}_{\mathrm{aq}} \cdot \{\mathrm{H}^+\}_{\mathrm{aq}} \cdot \{\mathrm{L}\}_{\mathrm{org}}^m \cdot \{\mathrm{A}\}_{\mathrm{org}}^q} \quad (2)$$

and

$$K_{ext} = \frac{\left[\mathrm{H^+Au(CN)_2}^- \cdot \mathrm{L}_m \cdot \mathrm{A}_q\right]_{\mathrm{org}}}{\left[\mathrm{Au(CN)_2}^-\right]_{\mathrm{aq}} \cdot [\mathrm{L}]_{\mathrm{org}}^m \cdot [\mathrm{A}]_{\mathrm{org}}^q} \cdot \frac{\gamma_{\mathrm{H^+Au(CN)_2^-L}_m\mathrm{A}_q}}{\gamma_{\mathrm{Au(CN)_2^-}}\gamma_{\mathrm{H^+}}\gamma_{\mathrm{L}}^m\gamma_{\mathrm{A}}^q}, \quad (3)$$

where { } denote activity and [ ] denote concentrations.

The total gold concentration in the organic phase can be expressed as

$$[\mathrm{Au}]_{\mathrm{org}} = \left[\mathrm{H^+Au(CN)_2}^- \cdot \mathrm{L}_m \cdot \mathrm{A}_q\right]_{\mathrm{org}} = K_{ext}\left[\mathrm{Au(CN)_2}^-\right]_{\mathrm{aq}}[\mathrm{H}^+]_{\mathrm{aq}}[\mathrm{L}]_{\mathrm{org}}^m[\mathrm{A}]_{\mathrm{org}}^q \cdot \frac{\gamma_{\mathrm{Au(CN)_2^-}}\gamma_{\mathrm{H^+}}\gamma_{\mathrm{L}}^m\gamma_{\mathrm{A}}^q}{\gamma_{\mathrm{H^+Au(CN)_2^-L}_m\mathrm{A}_q}}. \quad (4)$$

The total metal concentration in the aqueous phase can be written as

$$[\mathrm{Au}]_{\mathrm{aq}} = \left[\mathrm{Au(CN)_2}^-\right]_{\mathrm{aq}}. \quad (5)$$

The distribution coefficient D_{Au} is defined by the ratio of the total concentration of gold in the organic phase to the total gold concentration in the aqueous phase, and is represented by

$$D_{\mathrm{Au}} = \frac{[\mathrm{Au}]_{\mathrm{org}}}{[\mathrm{Au}]_{\mathrm{aq}}}. \quad (6)$$

Substituting Eqs. 4 and 5 into Eq. 6 gives

$$D_{\mathrm{Au}} = K_{ext}[\mathrm{H}^+]_{\mathrm{aq}}[\mathrm{L}]_{\mathrm{org}}^m[\mathrm{A}]_{\mathrm{org}}^q \cdot \frac{\gamma_{\mathrm{Au(CN)_2^-}}\gamma_{\mathrm{H^+}}\gamma_{\mathrm{L}}^m\gamma_{\mathrm{A}}^q}{\gamma_{\mathrm{H^+Au(CN)_2^-L}_m\mathrm{A}_q}}. \quad (7)$$

If it is assumed that there is ideal behavior in the organic phase and that the activity coefficients of the aqueous species are constant (and near unity), then

$$D_{\mathrm{Au}} = K_{ext}[\mathrm{H}^+]_{\mathrm{aq}}[\mathrm{L}]_{\mathrm{org}}^m[\mathrm{A}]_{\mathrm{org}}^q. \quad (8)$$

If, for the model application, it is also assumed that at a very low gold concentration range the organic concentration varies sligthly before and after the equilibration, then Eq. 8 can be rewritten as

$$D_{\mathrm{Au}} = K'[\mathrm{H}^+]_{\mathrm{aq}}, \quad (9)$$

where

$$K' = K_{ext}[\mathrm{L}]_{\mathrm{org}}^m[\mathrm{A}]_{\mathrm{org}}^q. \quad (10)$$

Equation 9 is the model equation for predicting the distribution coefficient that is directly first-power dependent on the hydrogen ion concentration in the aqueous phase, m-power dependent on the phosphine oxide concentration, and q-power dependent on the amine concentration in the organic solution.

Application of the model on the Primene JMT–Cyanex 925 system

The model was applied to the Primene JMT–Cyanex 925 system, for which experimental data are available from the literature (Martín and Alguacil, 1998). Xylene was used as the diluent for the organic phase. The gold extraction can be explained by the formation of two species in the organic phase (Table 1). Since a species ratio of 1:3 is predominant over the

Table 1. Species for $\mathrm{Au(CN)_2}^-$ Extraction by the Mixture Primene JMT–Cyanex 925 in Xylene

Coefficient*		
m	q	log K_{ext}
3	1	12.80 ± 0.13
1	1	10.27 max 10.55

*In agreement with the stoichiometry of Eq. 1.

Table 2. Calculated log D_{Au} Compared with the Equilibrium Data for the $Au(CN)_2^-$ −Primene JMT−Cyanex 925−Xylene System

[Primene JMT] mol/L	[Cyanex 925] mol/L	pH_{eq}	log D_{exp}	log D_{cal}
0.125	0.114	8.85	0.35	0.229
		9.15	0	−0.070
		8.59	0.54	0.489
		9.62	−0.44	−0.541
		9.09	−0.017	−0.011
0.250	0.288	10.25	0	0.005
		9.80	0.60	0.455

pH range studied, this ratio is used to make numerical calculations.

Table 2 shows some of these equilibrium data for the $Au(CN)_2^-$−Primene JMT−Cyanex 925−xylene system at two extractant mixture concentrations. The equilibrium data were obtained by interpreting the corresponding plot. Figure 1 shows the good agreement between the experimental and calculated distribution coefficients. The correlation coefficient r^2 between the predicted and reported data is equal to 0.975.

The equilibrium data obtained in the present work at different pH equilibrium values for the $Au(CN)_2^-$−Primene JMT−Cyanex 925−toluene system are given in Table 3. The gold concentration analysis for the aqueous-phase gave excellent reproducible results.

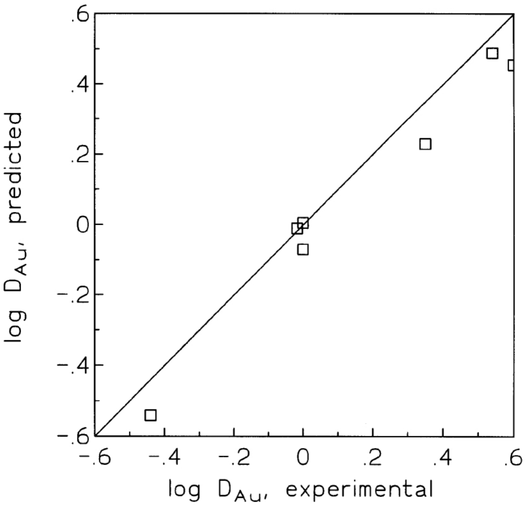

Figure 1. Predicted gold distribution coefficient vs. the experimental data using results from the literature (Martin and Alguacil, 1998) for the Primene JMT−Cyanex 925−Xylene system (temperature 20°C).

Furthermore, to obtain the composition and formation constant of the extracted species, numerical calculations were made using the LETAGROP-DISTR program (Liem, 1971).

Table 3. Equilibrium Data for $Au(CN)_2^-$ − Primene JMT−Cyanex 925−Toluene System

[Primene JMT] mol/L_{org}	[Cyanex 925] mol/L_{org}	pH_{eq}	[Au(I)] $mmol/L_{aq}$	Au(I)] $mmol/L_{org}$	log D_{exp}	log D_{cal}
0.063	0.057	7.30	0.102	0.406	0.60	0.563
		7.89	0.254	0.254	0	−0.027
		8.05	0.330	0.178	−0.27	−0.187
		7.20	0.025	0.101	0.61	0.663
		7.43	0.030	0.095	0.50	0.443
		7.64	0.051	0.079	0.19	0.223
		7.92	0.061	0.066	0.03	−0.057
		8.05	0.086	0.039	−0.34	−0.187
		7.40	0.015	0.036	0.38	0.463
		7.53	0.020	0.030	0.18	0.333
		8.00	0.030	0.021	−0.15	−0.137
		8.35	0.036	0.103	−0.44	−0.487
0.125	0.114	8.80	0.157	0.350	0.35	0.279
		9.17	0.254	0.254	0	−0.091
		9.24	0.269	0.239	−0.05	−0.161
		9.28	0.325	0.183	−0.25	−0.201
		9.63	0.366	0.142	−0.41	−0.551
		8.54	0.030	0.096	0.51	0.539
		8.88	0.051	0.078	0.18	0.199
		9.10	0.061	0.065	0.03	−0.021
		9.62	0.091	0.034	−0.43	−0.541
		8.47	0.010	0.040	0.60	0.609
		8.83	0.020	0.028	0.25	0.249
		9.09	0.025	0.025	0	−0.011
		9.35	0.036	0.017	−0.33	−0.271
0.250	0.228	9.90	0.127	0.381	0.48	0.304
		10.25	0.254	0.254	0	0.029
		10.44	0.355	0.152	−0.37	−0.161
		9.70	0.025	0.102	0.61	0.579
		10.30	0.071	0.061	−0.07	−0.021
		9.87	0.015	0.036	0.38	0.409
		10.10	0.020	0.030	0.18	0.179
		10.46	0.030	0.020	−0.18	−0.181
		10.51	0.036	0.015	−0.38	−0.231

Table 4. Species for Gold Extraction by the Mixture Primene JMT–Cyanex 925 in Toluene

Species	log K_{ext}	σ(log K_{ext})
$HAu(CN)_2 \cdot L_3 \cdot A$	12.78 ± 0.12	0.04
$HAu(CN)_2 \cdot L_2 \cdot A$	9.76 max 11.16	0.14

$U = 0.285$ ($\sigma = 0.09$); L = phosphine oxide; A = amine.

For a given model, this program searches the best set of equilibrium constants that would minimize the sum of squares defined by

$$U = \Sigma\left(\log D_{cal} - \log D_{exp}\right)^2, \tag{11}$$

where D_{exp} is the distribution coefficient determined experimentally, and D_{cal} is the value calculated by the program solving the mass-balance equation for gold, amine, and phosphine oxide, assuming a particular set of species and constants. Different models with species of different stoichiometries were tried in order to investigate the possibility of finding different species that could improve the fit to the experimental results. For the present system, the program defines the existence of two species in the gold-loaded organic phases. The corresponding stoichiometries are summarized in Table 4, with their respective log K_{ext} values.

Figure 2 shows the distribution diagram of gold vs. pH equilibrium with the $[\text{amine}]_{total}/[\text{phosphine oxide}]_{total}$ constant. For these conditions the 1:3 species (amine:phosphine oxide) is predominant in the entire range, and thus is used to make the chemical model calculations.

The predicted values of the gold distribution coefficients are given in Table 3, while Figure 3 shows the plots of the experimental and predicted values of the gold distribution coefficients. Good agreement between the experimental and calculated data is indicated by the reasonable r^2 value 0.934 between these two results and the standard deviation 0.09 of residuals from the line.

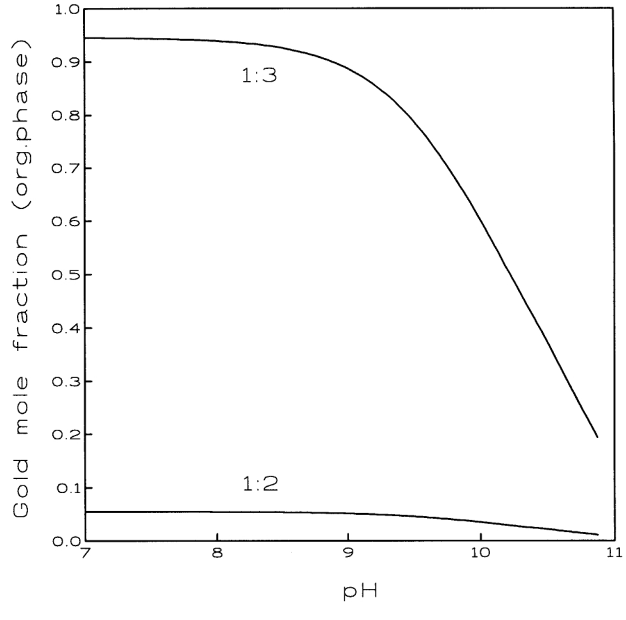

Figure 2. Molar fraction of gold plotted as a function of pH for Primene JMT (0.250 mol/L) and Cyanex 925 (0.228 mol/L) and gold concentration of 0.025 g/L; organic phase diluent: toluene.

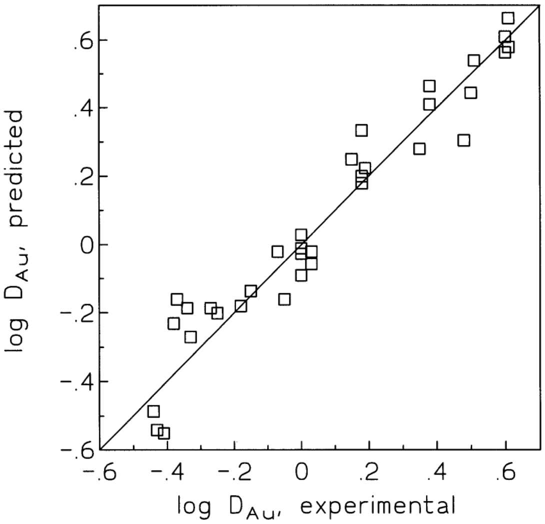

Figure 3. Predicted gold distribution coefficient vs. the experimental data for the Primene JMT–Cyanex 925–Toluene system.

Figure 4 shows the relationship between the aqueous proton concentration at equilibrium $[H^+]_{eq}$ vs. the experimental and predicted log D_{Au} values. The distribution coefficient decreases as the hydrogen-ion concentration decreases. The dashed line denotes the regressed line for the experimental data, and the solid line denotes the regressed line for the predicted data. Good agreement between both these data was obtained.

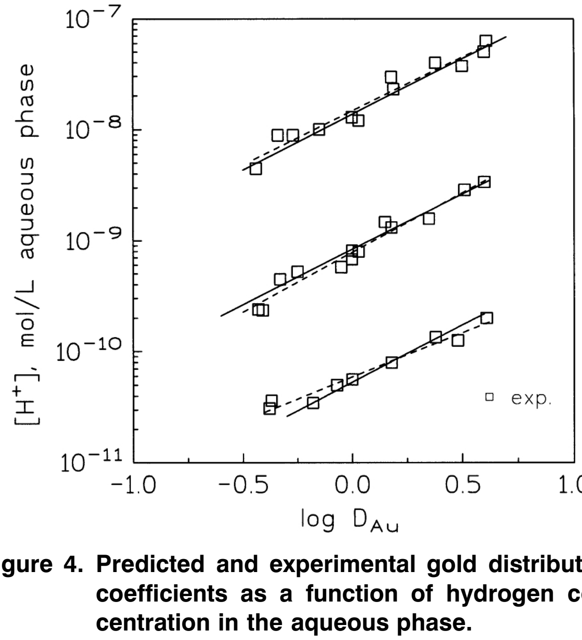

Figure 4. Predicted and experimental gold distribution coefficients as a function of hydrogen concentration in the aqueous phase.

Table 5. Extraction Isotherm Data

A/O Ratio	[Au], g/L Aqueous	[Au], g/L Organic
0.067	0.002	0.03
0.25	0.012	0.12
0.29	0.017	0.14
0.33	0.021	0.16
0.46	0.046	0.21
0.50	0.065	0.22
0.61	0.089	0.25
0.70	0.13	0.26
0.85	0.18	0.27
1	0.23	0.28
1.21	0.27	0.28
1.61	0.32	0.29
2	0.36	0.30

Processing in a continuous extraction basis requires information about the equilibrium isotherm. Because gold cyanide leaching solutions usually have a pH value above 9 in the present study, an equilibrium isotherm at an equilibrium pH of 9.05 ± 0.05 was determined. The concentration of the initial aqueous phase was 0.5 g/L gold.

The extraction isotherm data for the gold–cyanide–Primene JMT–Cyanex 925–toluene system obtained from the phase-ratio variation procedure are given in Table 5. Figure 5 shows the extraction isotherm for gold, with 0.125 M Primene JMT–0.114 M Cyanex^{TM} 925 in toluene. The loading isotherm curve can be mathematically represented by the following equation:

$$[\mathrm{Au}]_{\mathrm{org}} = \frac{0.304\,[\mathrm{Au}]_{\mathrm{aq}}}{0.0199 + [\mathrm{Au}]_{\mathrm{aq}}}, \qquad (12)$$

where $[\mathrm{Au}]_{\mathrm{org}}$ and $[\mathrm{Au}]_{\mathrm{aq}}$ represent the metal concentrations at equilibrium in the respective organic and aqueous phases.

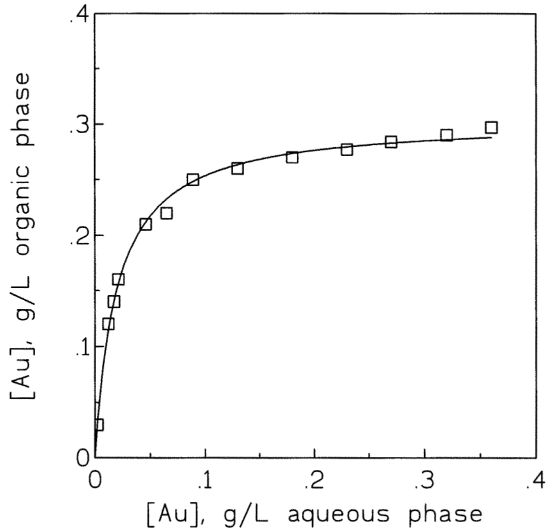

Figure 5. Extraction equilibrium isotherm for the system $Au(CN)_2^-$–Primene JMT (0.125 mol/L)–Cyanex 925 (0.114 mol/L)–Toluene at pH_{eq} 9.05 ± 0.05 (temperature 20°C).

Conclusions

The predictive thermodynamic equilibrium model equation for the $Au(CN)_2^-$–Primene JMT–Cyanex 925 system is found to be first-power dependent on the aqueous proton concentration, first-power dependent on the amine concentration, and third-power dependent on the phosphine oxide concentration in the organic solution.

The model equation can be modified to $D_{Au} = K'[H^+]_{eq}$, so only the equilibrated hydrogen-ion concentration in the aqueous phase needs to be known.

Gold is extracted by the Primene JMT–Cyanex 925 mixture in toluene by a series of complexes with the general stoichiometry $H^+Au(CN)_2^- \cdot L_m \cdot A$, where L represents the phosphine oxide, A the amine, and m is 2–3. The species with stoichiometry 1:3 (amine:phosphine oxide) is predominant in the pH range studied.

The equilibrium loading isotherm for the $Au(CN)_2^-$–Primene JMT–Cyanex 925–toluene system was obtained at 20°C and an aqueous gold concentration of 0.5 g/L.

The predictive thermodynamic equilibrium model was found to give a good estimate of the gold distribution coefficient in the $Au(CN)_2^-$–Primene JMT–Cyanex 925 solvent extraction system.

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