SHORT PAPER

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Use of liquid–liquid extraction with neutral organophosphorous derivatives in the estimation of ($AuCl_4^-$,H^+) interaction coefficients[†]

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The liquid–liquid extraction of Au(III) from HCl solutions by a series of solvation extractants had been studied. The reagents are neutral organophosphorous derivatives such as phosphine oxides (Cyanex 921 and Cyanex 923) and phospholene derivatives (DMPL, EHMPL and NMPL). The distribution of gold between the aqueous and organic phases has been investigated under different variables. Experimental data were treated numerically in order to define the corresponding extracted species. Both experimental and numerical data were used to estimate the interaction coefficient between $AuCl_4^-$ and H^+ by using the specific interaction theory (SIT). Moreover, experimental data on the liquid–liquid extraction of HCl by these phosphorous derivatives were given.

Keywords: liquid–liquid extraction, Au(III), organophosphorous derivatives

During the last 20 years the price of gold has grown, thus there has been renewed interest in studying new approaches for the recovery of this precious metal from primary or secondary resources and also from corresponding gold-bearing solutions. Of all the separation processes used for the recovery of gold, liquid–liquid extraction seems to be the least used, in spite of being a popular method. There are some industrial processes for recovery of gold and other precious metals by liquid–liquid extraction.[1-6] In the present study the application possibilities of liquid-liquid extraction have been evaluated and compared for various neutral extractants such as phosphine oxides and phospholene derivatives in the extraction of gold(III) from acidic (HCl) tetrachloroaurate solutions; the extraction mechanisms are also defined and the ($AuCl_4^-$, H^+) interaction coefficients were estimated using both experimental and numerical data and the SIT. Results on HCl extraction are also presented.

Experimental

The extractant used were obtained from CYTEC Ind. (phosphine oxides) and Bayer Leverkusen (phospholene derivatives) and were used as received from the manufacturers. Their compositions are given in Table 1. The desired extractant concentration was prepared by diluting the as-received extractant with the as-received corresponding diluent: xylene (Fluka) and cumene (Fluka). Stock solutions of gold were prepared by dissolving tetrachloroauric acid (Fluka) in distilled water. All other chemicals were also of AR grade. Extraction experiments were carried out in thermostatically controlled separatory funnels by shaking (600/min) together equal volumes of the corresponding aqueous and organic phases at 20°C and for the time required. The concentration of gold in the aqueous solutions were measured by AAS. The concentration of the metal in the organic solution was calculated from the mass balance. From these data, the distribution coefficient D_{Au} was calculated as the ratio

$$D_{AU} = \frac{[Au]_{org}}{[Au]_{aq}} \qquad (1)$$

where $[Au]_{org}$ and $[Au]_{aq}$ are the total gold concentration in the organic and aqueous phases, respectively. Experiments on HCl extraction were performed as described above and hydrochloric acid concentration was determined by titration with standard sodium hydroxide solutions using Bromothymol Blue as indicator. The HCl distribution coefficient was calculated using a similar relationship as in Eqn (1).

Table 1 Reagents investigated

Commercial name	Type	Composition
Cyanex 921	Phosphine oxide	Tri-*n*-octylphosphine oxide
Cyanex 923	Phosphine oxide	Mixture of phosphine oxides
DMPL	Phospholene derivative	1-(dodecyloxy)-3-methyl-1-oxo-Δ^3-phospholen
EHMPL	Phospholene derivative	1-(2-ethylhexyloxy)-3-methyl-1-oxo-Δ^3-phospholen
NMPL	Phospholene derivative	1-(2,6-dimethylhept-4-yloxy)-3-methyl-1-oxo-Δ^3phospholen

Table 2 Log ß values for the extraction of HCl

Extractant	Diluent	log ß
Cyanex 921	Xylene	0.10
DMPL	Cumene	–0.59
EHMPL	Cumene	–0.37
NMPL	Cumene	–0.54

Results and discussion

Solvation reagents extract hydrochloric acid from aqueous solutions, the extraction can be represented by the general reaction

$$HCl_{aq} + L_{org} \rightleftharpoons HClL_{org} \qquad (2)$$

and

$$\beta = \frac{[HClL]_{org}}{[HCl]_{aq}\,[L]_{org}} \qquad (3)$$

where L represents the corresponding organic reagent. From the experimental data obtained in this investigation, the extraction constants (ß, Eqn (3)) for the extraction of HCl using these solvation extractants were calculated using the program LETAGROP-DISTR;[7] the program is based on the minimisation of the error square sum defined as

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

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

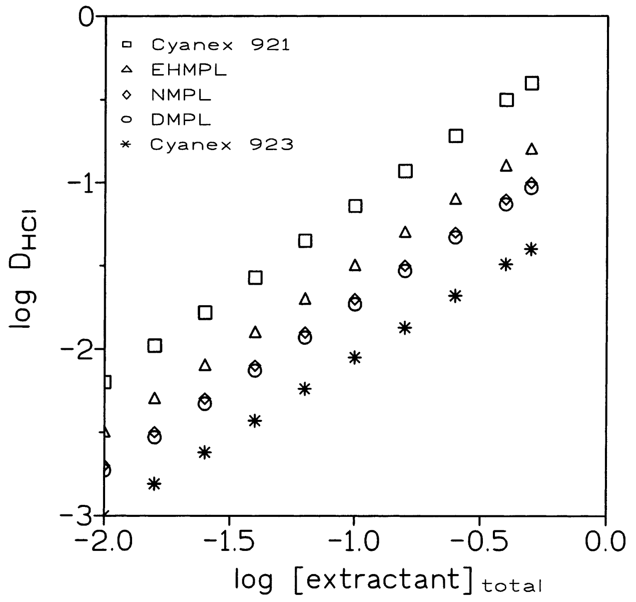

Fig.1 Plot of log D_{HCl} versus log [extractant]$_{total}$ for the various reagents using the extraction constants given in Table 2.

where D_{exp} is the experimental value of the distribution coefficient and D_{cal} is the value calculated by the program solving the mass balance equation for hydrochloric acid and the extractant, assuming a particular set of species and constants. Results at I(HCl) = 1 and 20°C are summarised in Table 2. In the range of extractant concentrations from 0.01 to 0.8 mol/l, the apparent extraction order for HCl is Cyanex 921 > NMPL > > EHMPL = DMPL > Cyanex 923 (Fig. 1).

To study the influence of equilibration time on gold extraction, experiments were carried out using extractant (0.65 mM Cyanex 921 in xylene or 0.1 mol/l NMPL in cumene) and gold concentrations (0.25 mM Au in 6 mol/l HCl media (Cyanex 921) or 0.14 mM Au in 1 mol/l HCl media (NMPL)); the agitation time was varied from 1 to 60 min and temperature of 20°C. The results obtained show that, under the experimental conditions used, the extraction is sligthly dependent upon the agitation time and extraction equilibrium is achieved within 5 min (phospolene derivatives) or 1 min of contact (phosphine oxides).

The influence of temperature was also studied using organic phases of the phosphine oxides and gold solutions in 6 mol/l HCl media. The increase of temperature decreases gold extraction. Table 3 shows the values of the change of enthalpy for these systems. The reactions are exothermic.

The effect of changing the extractant concentration on gold extraction was studied using aqueous solutions which contain 0.25 mM gold at various HCl concentrations and organic solutions of different Cyanex 923 concentrations in xylene. The results of these experiments (Fig. 2) show that there is an increase in gold extraction as the initial phosphine oxide concentration is increased and also as the hydrochloric acid is increased. This reaches a maximum at near 7 mol/l HCl, at higher acid concentration the extraction of gold decreases; this can be explained by the fact that at these high acid concentrations there is competition between gold and HCl extraction by the phosphine oxide.[8,9] The effect of changing the initial metal concentration (0.06 – 0.24 mM) on gold extraction was studied using organic phases of DMPL in cumene. Average results, obtained on three gold concentrations at I(HCl) = 0.5 and 1.5, are shown in Fig. 3. The independence of log D_{Au} with metal concentration suggests that metal polynuclear species were not formed in the extraction reaction.

Table 3 Values of $\Delta H°$ for the extraction of gold by phosphine oxides

Reagent	Diluent	Initial gold	$\Delta H°$
Cyanex 921(0.65 mM)	Xylene	0.25 mM	-44.6 kJ/mol
Cyanex 923(0.63 mM)	Xylene	0.25 mM	-43.7 kJ/mol

Equilibration time: 10 min

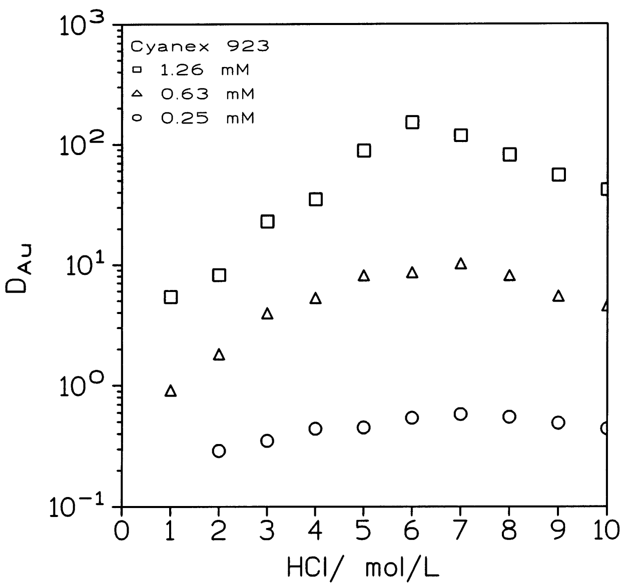

Fig.2 The influence of Cyanex 923 concentration on gold extraction. Temperature: 20°C. Equilibration time: 10 min.

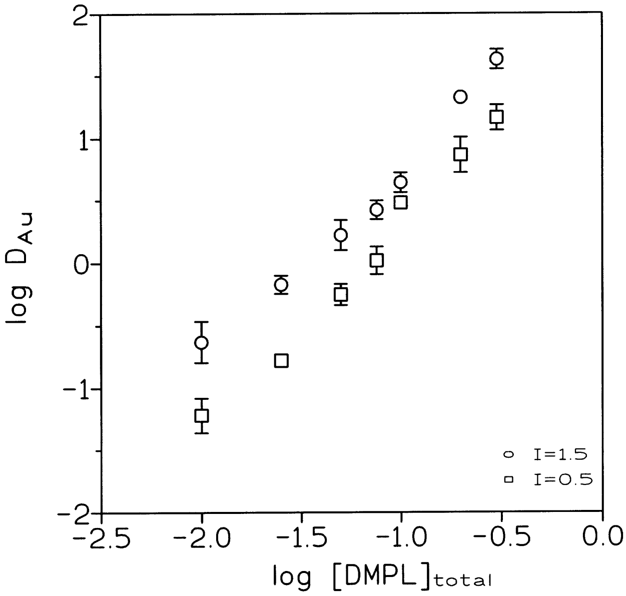

Fig.3 The influence of metal concentration on gold extraction. Temperature: 20°C. Equilibration time: 15 min.

The extraction of gold from acidic tetrachloroaurate solutions by solvation extractants (L) can be represented by the general equation

$$AuCl^-_{4\,aq} + H^+_{aq} + pL_{org} \rightleftharpoons HAuCl_4L_{p\,org} \quad (5)$$

and the extraction constant is defined by

$$K_{ext} = \frac{[HAuCl_4L_p]_{org}}{[AuCl_4^-]_{aq}\,[H^+]_{aq}\,[L]^p_{org}} \quad (6)$$

Table 4 Species for gold extraction and interaction coefficients ($AuCl_4^-$, H^+)

Extractant	Species	log K_{ext}	$\varepsilon_{(AuCl_4^-, H^+)}$
Cyanex 921	$HAuCl_4L_2$	6.78	0.25
DMPL	$HAuCl_4L$	1.11	0.26
	$HAuCl_4L$	3.06	0.28
EHMPL	$HAuCl_4L$	1.28	0.28
	$HAuCl_4L_2$	2.74	0.28
NMPL	$HAuCl_4L$	0.68	0.28
	$HAuCl_4L_2$	2.19	0.28

Since Cyanex 923 is a mixture of phosphine oxides, species for gold extraction, extraction constants and interaction coefficient values were not provided in the present work, but it could be stated here that the stoichiometry of the extracted species and other values are similar to these obtained for Cyanex 921

In order to determine the composition of the extracted species and their equilibrium constants, the experimental data were numerically treated using the program LETAGROP–DISTR. Each ionic strength was treated separately and the extraction of HCl was also considered. Table 4 summarises the results obtained. These show that the composition of extracted species is independent of the ionic strength, however, the value of the extraction constant depends on the ionic strength. The variation in the equilibrium constant with the ionic strength can be correlated using specific interaction theory.[10–15] In this approach, the activity coefficient of an anion of charge z_i in a solution of strength I can be expressed as

$$\log \gamma_i = -z_i^2 D(I) + \sum \varepsilon_{(i,\,k)}\, m_k \qquad (7)$$

The summation is made over all ions (k) present in the solution at molality m_k, $D(I)$ is the Debye–Hückel term in the molality scale and ε is the interaction coefficient.

From Eqn (6) it has been found that the extraction constant including the activity coefficients can be written as

$$\log k(I) = \log K^\circ + \log \gamma_{AuCl_4^-} + \log \gamma_{H^+} \qquad (8)$$

assuming ideal behaviour in the organic phase. From Eqn (7) the activity coefficients of the aqueous species can be defined in a simplified form as

$$\log \gamma_{AuCl_4^-} = -z^2_{AuCl_4^-} D(I) + \varepsilon_{(AuCl_4^-,\,H^+)}\, m_{HCl} \qquad (9)$$

$$\log \gamma_{H^+} = -z^2_{H^+} D(I) + \varepsilon_{(H^+,\,Cl^-)}\, m_{HCl} \qquad (10)$$

The substitution of Eqns (9) and (10) into Eqn (8) gives, after rearranging

$$\log K(I) + 2D(I) = \log K^\circ + (\varepsilon_{(AuCl_4^-,\,H^+)} + \varepsilon_{(H^+,\,Cl^-)})\, m_{HCl} \qquad (11)$$

A plot of log $K(I) + 2D(I)$ versus m_{HCl} (ionic strength) should give a line with an intercept equal to log K° and slope ($\varepsilon_{(AuCl4-,H+)} + \varepsilon_{(H+,Cl-)}$). To correlate the constant it is necessary to transform the extraction constants to the molality scale,[16] and also the value of $\varepsilon_{(H+,Cl-)} = 0.12$ were obtained from the literature.[10] Results were summarised in Table 4.

From experimental data and using the extraction constants, the extraction order for gold from HCl media can be estimated as: Cyanex 923 > Cyanex 921 >> EHMPL=DMPL > NMPL (Fig. 4).

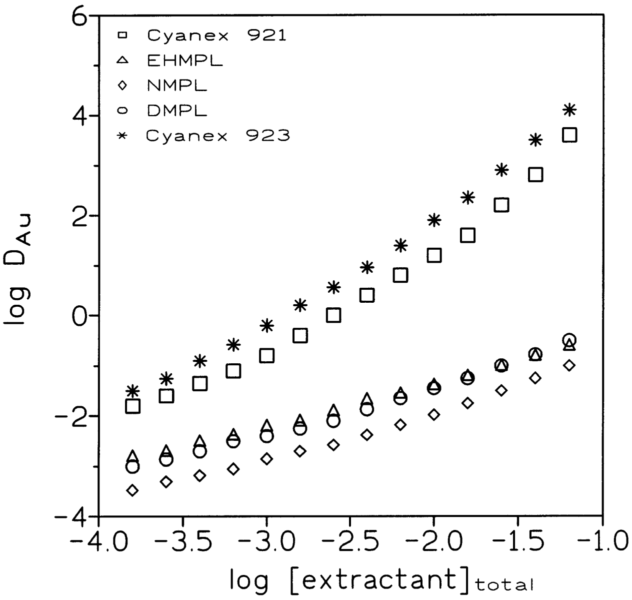

Fig.4 Plot of log D_{Au} versus log [extractant]$_{total}$ for the various solvation reagents using the constants given in Table 4.

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