

Extraction of AuCl_4^- from HCl solutions by the chloride salt of the secondary amine Amberlite LA2 and estimation of the interaction coefficient between AuCl_4^- and H^+

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The equilibrium distribution of AuCl_4^- between hydrochloric acid and the chloride salt of the secondary amine Amberlite LA2 in xylene was investigated. The extraction reaction is exothermic ($\Delta H^\circ = -20.8$ kJ/mol). The stoichiometry of the complex formed in the organic phase can be represented by $\text{R}'\text{R}''\text{NHH}^+\text{AuCl}_4^-$ and the extraction equilibrium constant depends on the ionic strength. From this dependency it was found that $\log K^\circ = 3.9$ and the interaction coefficient between AuCl_4^- and H^+ is 0.24.

Keywords: AuCl_4^- , Amberlite LA2

Introduction

Among solution purification and concentration treatments, solvent extraction has found the most extensive application.¹ In the case of gold–cyanide hydrometallurgy the operation is far from reaching its full potential but this is not the case for gold–chloride hydrometallurgy in which the effectiveness of the technique is demonstrated by its implementation in various industrial processes.^{2–5} This had led researchers to study various reagents for gold extraction from HCl media. Extractants included amines and solvation reagents.^{6–13} The extraction order often found in the case of amines is quaternary ammonium salts > tertiary > secondary > primary, thus, the conversion of the amine, *viz.* primary, secondary or tertiary to its amine salt derivative increases the extractability properties of the corresponding reagent. The present work is a study of the distribution dependence of AuCl_4^- between hydrochloric acid solutions and the chloride salt of the secondary amine Amberlite LA2 in xylene. Experimental data were treated numerically to obtain the equilibrium constant, furthermore, the interaction coefficient ($\text{AuCl}_4^-/\text{H}^+$) was estimated using specific interaction theory (SIT).

Experimental

The secondary amine Amberlite LA2 (Fluka) was used as received, the purity was greater than 95% (experimentally determined by titration of the reagent with standard HCl solutions). The organic phase was prepared by diluting a measured volume of the amine with xylene (AR grade). The amine chloride salt was prepared by shaking the amine solutions with aqueous phases containing 1.0 M HCl for 10 min at 20 °C. Previous investigations had shown that complete conversion to the amine chloride salt occurs under these experimental conditions. Aggregation of the amine/amine salt depends strongly on the organic diluent and the reagent concentration. In the present study, very dilute solutions of the amine salt were used, so it can be assumed that the monomer form of the reagent predominates in the organic phase. All other chemicals were of AR grade. Gold extractions were carried out by mechanical agitation (600/min) in separatory funnels, thermostatted at the required temperature and for 10 min (time necessary to achieve metal extraction equilibrium) of the appropriate volumes of the corresponding aqueous and organic solutions. Gold content in the equilibrated aqueous solutions was analysed by AAS, whereas metal concentration in the organic phase was obtained after stripping of the loaded organic solutions with

0.5 mol/l sodium tiosulphate solution and analysis of the aqueous phases by AAS. Thus in each experiment, the gold mass balance was calculated by analysing the gold concentration in both aqueous and organic phases before and after the reaction. Experimental data with a 97% mass balance accuracy were accepted, and other data were rejected.

Results and discussion

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

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

The influence of temperature (20–70 °C) on gold extraction was studied using an organic solution of 0.12 mmol/l chloride salt of Amberlite LA2 in xylene and aqueous solution of 0.05 mmol/l gold in 5 mol/l HCl using a volume phase ratio of 1:1 (organic:aqueous). The results indicated a decrease in gold extraction as the temperature is increased; the value of ΔH° (change of enthalpy) is -20.8 kJ/mol, the extraction reaction being exothermic.

The extraction of gold at different concentrations using an organic phase of 0.23 mmol/l of the amine salt in xylene was studied. Experiments were carried out at 20 °C, varying the metal concentration in the aqueous phase and using various concentrations of HCl. Figure 1 shows that higher D_{Au} values were reached at lower HCl concentrations and they tend to decrease as the acid concentration increases in the aqueous solution. For each HCl concentration, the values of D_{Au} increase as the initial metal concentration decreases; this behaviour can be explained considering that the total concentration of the amine salt in the organic solution is:

$$[\text{R}'\text{R}''\text{NHH}^+\text{Cl}^-]_{\text{TOTAL}} = [\text{R}'\text{R}''\text{NH}^+\text{Cl}^-]_{\text{org}} + \frac{[\text{R}'\text{R}''\text{NHH}^+\text{AuCl}_4^-]_{\text{org}}}{[\text{R}'\text{R}''\text{NHH}^+\text{AuCl}_4^-]_{\text{org}}} \quad (2)$$

where $\text{R}'\text{R}''\text{NH}$ represents to the amine Amberlite LA2, and the extraction reaction of gold(III) by the amine salt:



then:

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

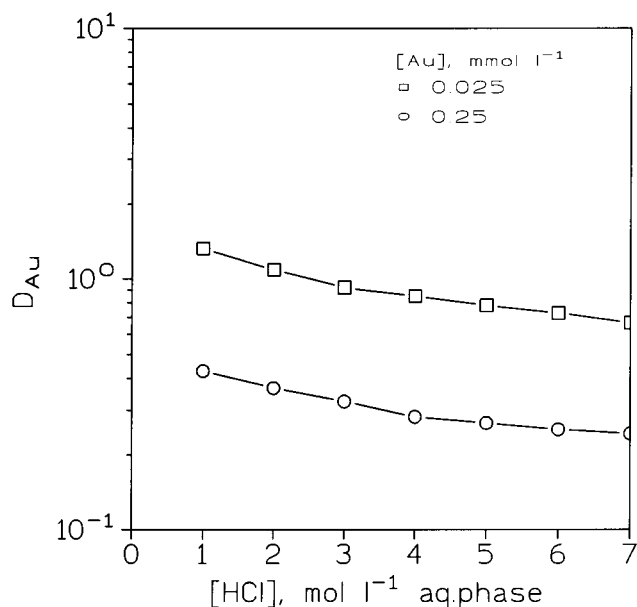


Fig. 1 Influence of metal concentration on the gold distribution ratio in the extraction from HCl solutions. Organic:aqueous phase ratio 1:1.

$$K_{\text{ext}} = \frac{[\text{R}'\text{R}''\text{NHH}^+\text{AuCl}_4^-]_{\text{org}} [\text{Cl}^-]_{\text{aq}}}{[\text{AuCl}_4^-]_{\text{aq}} [\text{R}'\text{R}''\text{NHH}^+\text{Cl}^-]_{\text{org}}} \quad (4)$$

and:

$$[\text{R}'\text{R}''\text{NHH}^+\text{AuCl}_4^-]_{\text{org}} = \frac{K_{\text{ext}} [\text{AuCl}_4^-]_{\text{aq}} [\text{R}'\text{R}''\text{NHH}^+\text{Cl}^-]_{\text{org}}}{[\text{Cl}^-]_{\text{aq}}} \quad (5)$$

Substitution of eqn (5) in eqn (2) leads, after rearranging, to:

$$[\text{R}'\text{R}''\text{NHH}^+\text{Cl}^-]_{\text{org}} = \frac{[\text{R}'\text{R}''\text{NHH}^+\text{Cl}^-]_{\text{TOTAL}}}{1 + \frac{K_{\text{ext}} [\text{AuCl}_4^-]_{\text{aq}}}{[\text{Cl}^-]_{\text{aq}}}} \quad (6)$$

From eqn (4), considering the definition of the distribution coefficient eqn (1) and rearranging, the following expression is obtained:

$$D_{\text{Au}} = \frac{K_{\text{ext}} [\text{R}'\text{R}''\text{NHH}^+\text{Cl}^-]_{\text{org}}}{[\text{Cl}^-]_{\text{aq}}} \quad (7)$$

From eqn (6), as the equilibrium gold concentration is increased, the concentration of the amine chloride salt in the equilibrated organic phase decreases and thus in eqn (7) the value of D_{Au} also decreases (Fig.1). The influence of the variation in the concentration of the extractant on the distribution of gold was studied using aqueous phases of 0.05 mmol/l gold and organic phases of the amine salt in xylene. Figure 2 shows an increase in gold extraction as the extractant concentration is increased. However, the extraction of gold tends to decrease as the HCl concentration of the aqueous solution is increased, indicating a competition between gold and hydrochloric acid for the extractant.

The extraction of gold can be described using the reaction shown in eqn (3). According to this equilibrium, experimental data were treated numerically using the program LETAGROP-DISTR,¹⁴ in order to confirm the proposed equilibrium and to

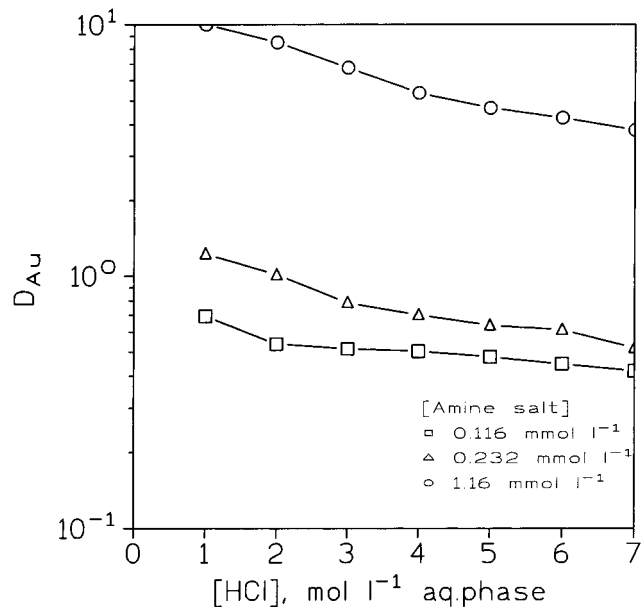


Fig. 2 Influence of extractant concentration on the gold distribution ratio in the extraction from HCl solutions. Temperature 20°C. Organic:aqueous phase ratio 1:1.

obtain the values of the equilibrium constant. In the program, the error square sum U defined as:

$$U = \sum (\log D_{\text{cal}} - \log D_{\text{exp}})^2 \quad (8)$$

was used in the minimisation process. D_{exp} represents the experimental distribution coefficient and D_{cal} is the value calculated by the program for the model tested after solving the mass balance equations of the components of the system. Thus, the best model is the one which gives the lowest value of U . The calculations were carried out taking a set of species and extraction constants as the starting input and considering the influence of the minimised function when partially varying or adding new species to the model. In these calculations, secondary reactions, *i.e.*, the formation of the amine dichloride for HCl concentrations above 4 M were also considered. The results of the numerical calculations are given in Table 1. From these results, it was found that gold extraction at various ionic strengths (I) responded to the equilibrium shown in eqn (3), whereas extraction constants varies with I . The variation can be correlated using SIT and used to determine the interaction coefficient (ϵ) between the species in the aqueous phase.¹⁵⁻²⁰

Taking into account eqn (3), the extraction constant (K°) for this equilibrium can be correlated with the ionic strength by:

$$K^\circ = K_{(m)} \frac{\gamma [\text{R}'\text{R}''\text{NHH}^+\text{AuCl}_4^-]_{\text{org}} \gamma [\text{Cl}^-]_{\text{aq}}}{\gamma [\text{AuCl}_4^-]_{\text{aq}} \gamma [\text{R}'\text{R}''\text{NHH}^+\text{Cl}^-]_{\text{org}}} \quad (9)$$

Table 1 Extraction constants for gold extraction by the chloride salt of the amine Amberlite LA2 from HCl solutions

HCl, mol/l	I^a	$\log K^b$	U
1	1.022	3.84	0.195
2	2.080	4.12	0.211
3	3.196	4.28	0.202
4	4.357	4.42	0.198
5	5.573	4.53	0.179
6	6.851	4.66	0.442
7	8.195	4.68	0.175

^aValues in the molality scale. ^bValues calculated by the numerical program and in the molality scale.

where $K(m)$ is the extraction constant in the molality scale (Table 1). Assuming ideal behaviour in the organic phase and taking logarithms, the next expression is obtained:

$$\log K^{\circ} = \log K(m) + \log \gamma_{[\text{Cl}^-]_{\text{aq}}} - \log \gamma_{[\text{AuCl}_4^-]_{\text{aq}}} \quad (10)$$

The activity coefficient (γ_i) of an ion of charge (z_i) in a solution of ionic strength (I) is defined as:

$$\log \gamma_i = -z_i^2 D(I) + \sum \epsilon_{(i,k)} I \quad (11)$$

where I represents the ionic strength in the molality scale, $D(I)$ is the Debye-Hückel term, also in the molality scale, and ϵ is the interaction coefficient between the charged species. Taking into consideration eqn (11) for each of the charged species of the present extraction system, and ϵ substituting in eqn (10), the next expression is obtained after re-arranging:

$$\log K(m) = \log K^{\circ} + (\epsilon_{(\text{AuCl}_4^-, \text{H}^+)} - \epsilon_{(\text{Cl}^-, \text{H}^+)}) I \quad (12)$$

A plot of $\log K(m)$ vs I should give a line of slope $(\epsilon_{(\text{AuCl}_4^-, \text{H}^+)} - \epsilon_{(\text{Cl}^-, \text{H}^+)})$. Figure 3 shows that $\log K^{\circ} = 3.9$ and since $\epsilon_{(\text{Cl}^-, \text{H}^+)} = 0.12$,¹⁵ it can be estimated that $\epsilon_{(\text{AuCl}_4^-, \text{H}^+)}$ is 0.24, a value which compares well with others obtained from the literature.^{8,10,21-24}

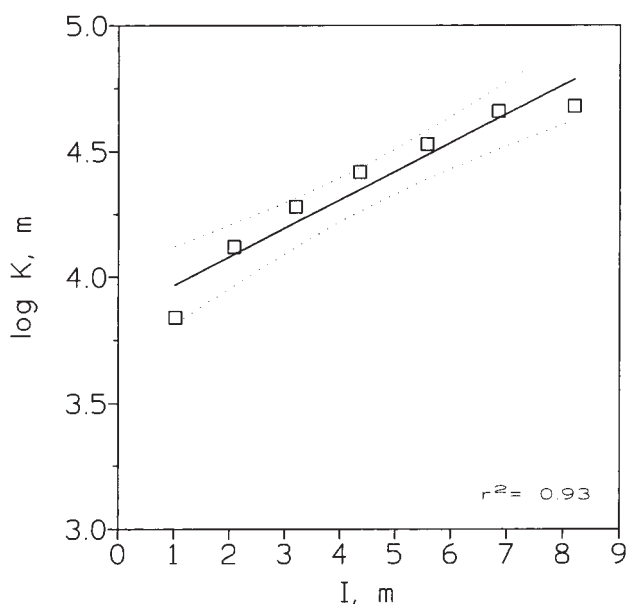


Fig. 3 Plot of $\log K$ vs. I . Dotted line shown 95% confidence interval.

In the precious metal concentrates derived from large scale nickel and copper extraction operations, gold is present together with a number of base metals. The first stage in the treatment of these concentrates is extraction with aqua regia; this aqua regia solution contains gold, other precious metals, and base metals.²⁵ Thus, the possibility of separation gold from those base metals was also studied. For this purpose extraction of iron(III), copper(II) and nickel(II) as representative base metals has been investigated. Extraction experiments carried out at 20 °C and at an organic: aqueous phase ratio of

1:1 using an organic phase containing 1.16 mmol/l of the amine salt in xylene and an aqueous phase with 0.05 mmol/l of each metal (Au, Fe, Cu and Ni) in 1 mol/l HCl show that after 10 min of contact, near quantitative gold(III) extraction is achieved without any of the base metals being extracted, allowing the selective separation of the precious metal.

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References

- 1 C.K. Gupta and T.K. Mukherjee, *Hydrometallurgy in Extraction Processes, Vol. II*, p.74. CRC Press, Boca Raton, 1990.
- 2 G.M. Ritcey and A.W. Ashbrook, *Solvent Extraction, Part II*, p.371. Elsevier, Amsterdam, 1979.
- 3 R.I. Edwards and W.A.M. te Riele, in *Handbook of Solvent Extraction*, p.725. T.C.Lo, M.H.I. Baird and C.Hanson (eds.), J.Wiley & Sons, New York, 1983.
- 4 M. Cox, in *Principles and Practices of Solvent Extraction*, p.357. J. Rydberg, C.Musikas and G.R.Choppin (eds.), Marcel Dekker, New York, 1992.
- 5 J. Marsden and I. House, *The Chemistry of Gold Extraction*, p.368. Ellis Horwood, London, 1993.
- 6 D. Maljkovic and M. Maljkovic, *Proceedings of the International Solvent Extraction Conference (ISEC '88)*, Vol. III, p.206. Moscow, 1988.
- 7 V.A. Drake and R.A. Grant, *Workshop on Innovations in Precious Metals Recovery and Refining*, SCI, London, 1991.
- 8 I. Villaescusa, N. Miralles, J. de Pablo, V.Salvadó and A.M.Sastre, *Solvent Extr. Ion Exch.*, 1993, **11**, 613.
- 9 F.J. Alguacil and C. Caravaca, *Hydrometallurgy*, 1993, **34**, 91.
- 10 S. Martínez, A.M. Sastre, N. Miralles and F.J. Alguacil, *Hydrometallurgy*, 1996, **40**, 77.
- 11 I. Villaescusa, V. Salvadó and J. de Pablo, *Hydrometallurgy*, 1996, **41**, 303.
- 12 F.Z. El Aamrani, A. Kumar, L. Beyer, J.L. Cortina and A.M.Sastre, *Solvent Extr. Ion Exch.*, 1998, **16**, 1389.
- 13 A. Madi, N. Miralles, J.L. Cortina, J. Arnaldos and A. Sastre, *Proceedings of the International Solvent Extraction Conference (ISEC '96)*, p.463. Melbourne, 1996.
- 14 D.H. Liem, *Acta Chem. Scan.*, 1971, **25**, 1521.
- 15 L. Ciavatta, *Ann. Chim.*, 1980, **70**, 551.
- 16 J. de Pablo, M. Aguilar and M. Valiente, *Proceedings of the International Solvent Extraction Conference (ISEC '83)*, p.497. Denver, 1983.
- 17 J.de Pablo, M. Aguilar and M. Valiente, *Chem. Scripta*, 1984, **24**, 147.
- 18 M. Aguilar, J. de Pablo, M.Valiente and E. Högfeltdt, *Chem. Scripta*, 1984, **26**, 635.
- 19 L. Ciavatta, *Ann. Chim.*, 1990, **80**, 255.
- 20 E. Rodríguez de San Miguel, J.C. Aguilar, M.T.J. Rodríguez and J. de Gyves, *Hydrometallurgy*, 2000, **57**, 151.
- 21 S. Martínez, P. Navarro, A.M. Sastre and F.J. Alguacil, *Hydrometallurgy*, 1996, **43**, 1.
- 22 M.A. Barroso, F.A. López, A.M. Sastre and F.J. Alguacil, *Hydrometallurgy*, 1997, **45**, 199.
- 23 S. Martínez, A.M. Sastre and F.J. Alguacil, *Hydrometallurgy*, 1997, **46**, 199.
- 24 S. Martínez, A.M. Sastre and F.J. Alguacil, *Hydrometallurgy*, 1999, **52**, 63.
- 25 M. Iglesias, E. Anticó and V. Salvadó, *Analytica Chimica Acta*, 1999, **381**, 61.