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EXTRACTION OF GOLD AND SILVER BY THIOUREA-BASED REAGENTS

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ABSTRACT

The synthesis and properties of some novel solvent extractants that are highly selective for gold and silver in very acidic chloride solutions are described. In this paper we also report on the study of one of these reagents; Dodecyl-thiourea (DTH), which has shown to be a very selective extractant for Au(III) and Ag(I) in the presence of Cu(II) and Fe(III). The extraction of Au and Ag was found to be fast. The Gold-DTH extraction data were explained by the formation of $AuCl_3.(DTH)_3$ species while silver forms $AgCl.(DTH)_2$ complex. The extractant has been also tested for practical application by determining the loading and stripping isotherms.

INTRODUCTION

In the past two decades the use of chloride hydrometallurgy for the processing of complex ores has received increasing attention (See e.g. Ref.[1]). Because of improvements made in materials of construction, future processes to leach gold and silver could use an

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acid chloride solution. Acid chloride leaching solutions are effective on sulphidic materials that are refractory to conventional methods of processing. Sulphidic materials contain appreciable amounts of gold and silver that are associated with base metals. While most of the gold produced at present, via hydrometallurgical route, is by leaching with alkaline cyanide solutions, there is a significant interest to use acidic leach solutions instead (1,2). There is, therefore, a great interest to develop extractants for the selective extraction of gold and silver from acidic chloride solutions.

A variety of extractants were studied for the extraction of precious metals from dilute aqueous solutions, where gold exists mainly as Au(I). Alkyl phosphorus esters (3) and long-chain amines (4,5) have been investigated quite widely for the extraction of gold from alkaline cyanide solutions.

In acidic chloride leaching solutions, Au(III) is the stable oxidation state. Tertiary amines have been studied for the extraction of gold and platinum metals from acidic chloride solutions (6) and it was found to be not sufficiently selective. Tri-iso-butylphosphine Sulfide (Cyanex 471X) (7,8) has been reported to have high loading capacity and fast extraction kinetics for the extraction gold and silver from acidic chloride solutions. Recently, two extractants; 1,3,4-thiadiazole-2-nonylmercapto-5-thiol (TNSTH) (9) and 2-nonylpyridine-N-oxide (NPO) (10), have been reported. Also these reagents have good extraction characteristics but TNSTH has a slow rate of extraction and can be easily oxidized especially by Cu(II). NPO can be used in hydrochloric acid solutions, but at high acidity, the selectivity of NPO for Au(III) against Fe(III) decreases significantly.

The present study is a part of a program aiming at developing selective extractants for the recovery precious metals in the presence of base metals from acidic chloride solutions. The hard-soft acid-base concept, can be used to select the donor atoms of a selective extractant. The precious metal (Au and Ag) ions, being soft acids, form strong complexes with reagents containing S or N atom. Thiourea is one of those reagents containing both donor atoms and is suggested to be used in leaching gold and silver in acidic chloride solutions (11-13). It can be used as extractant by incorporating a suitable alkyl-chain thus render it water-insoluble.

This paper describes the synthesis of some thiourea-based reagents. The extraction characteristics of one of these reagents, dodecylthiourea, are studied in more detail.

PREPARATION OF THE REAGENTS

The synthesis of alkyl-thiourea is carried out by a two-temperature step reaction. The alkyl group is introduced by using the corresponding alkyl primary amine which is reacted with ammonium thiocyanate as given by the following reaction equation: (14)

$$R\text{-}NH_2 + NH_4SCN = R\text{-}NH\text{-}CS\text{-}NH_2 + NH_3(g) \quad (1)$$

Where R denotes the alkyl chain. Three reagents were prepared, nonylthiourea(NTH), dodecyltiourea(DTH), and benzylthiourea(BTH).

Procedure

0.25--0.5 mole of nonylamine, dodecylamine, or benzylmaine and equivalent mole number of ammonium thiocyanate were charged into a reactor equipped with heating, stirring, and condensing facilities. The diluent, butyl alcohol, was added in an amount equivalent to the gross weight of the amine and ammonium thiocyanate. The mixture was gradually heated while stirring to about 110°C. The time required is 30-50 minutes. The temperature was then maintained until the evolution of ammonia ceased. The mixture was then heated up to 125-127°C, and the temperature maintained thereat for 2.5 hours for NTH or DTH and 4 hours for BTH. The resultant solution was then cooled to -20 °C in the case of NTH. For DTH and BTH, it was sufficient to cool the resultant solution to room temperature to obtain a good yield. For BTH, the same amount of diluent was added to the resultant solution before cooling. The crystallized products were separated by filtration and washed with butyl alcohol. The remainder of solvent was then removed by evaporation in a vacuum desiccator for about 24 hours.

All chemicals used were of analytical grades. Table 1 summarizes the reactants, diluent used as well as the yield of the

Table 1. Reactants, yields and melting point of reagents.

REAGENT	REACTANTS		YIELD(%)	MELTING POINT
NTH	nonylamine,	NH_4SCN	13.91	91.0 - 91.5 °C
DTH	dodecylamine,	NH_4SCN	31.47	100.5 - 101.0 °C
BTH	benzylamine,	NH_4SCN	75.72	159.5 - 160.5 °C

different products. Melting points of the reagents were measured with BÜCHI SMP-20 mp equipment.

Composition

The elemental analysis of the reagents have been performed by Micro Kemi AB, Uppsala, Sweden. The atomic molar ratio is given in Table 2 together with theoretical atomic molar ratio, which confirms the composition of these reagents.

Table 2. Experimentally determined and theoretically calculated atomic ratio of the reagents

	EXPERIMENTAL				THEORETICAL			
	C	H	N	S	C	H	N	S
NTH	9.87	22.08	1.95	1.00	10	22	2	1
DTH	12.89	28.64	1.98	1.00	13	28	2	1
BTH	7.98	9.82	2.01	1.00	8	10	2	1

Solubility of Reagents

Tests were conducted in order to determine the solubility of NTH, DTH, and BTH in g/l. The results are summarized in Table 3.

Table 3. Solubility of NTH, DTH, and BTH (g/l)

DILUENT\REAGENT	NTH	DTH	BTH
hexane	0.54	<0.05	<0.01
toluene	2.02	0.27	0.18
chloroform	12.05	2.49	1.03
butyl alcohol	-	12.10	6.80
isoamyl alcohol	-	-	5.95
acetone	-	10.45	47.90
methylisobutylketone	-	-	7.49
dimethyl formamide	-	170.0	191.5
pyridine	-	130.2	218.6
shellsol D-100*	-	-	2.50

The reagents were found to have very low solubility in the following solvents:
Shellsol* (D-40, D-70, A, AB, H, J and K) (trademark of Shell). Isopar G, Escaid(100, 120) and Solvesso 150 (trademark of ESSO).

- The solubility was not determined.

In the following parts, we report in more detail on the extraction of Au(III) and Ag(I) from acidic chloride solutions by DTH in chloroform.

EXTRACTION STUDIES

A gold stock solution was prepared by dissolving 1.000 g pure gold metal in aqua regia, boiling to dryness and then dissolving the residue in 20 ml 37% HCl and diluted to 1000 ml with deionized water. The stock solution of silver was prepared by dissolving 0.787 g silver nitrate in 1000 ml 1% HNO_3.

Aliquots of the aqueous and organic phases of known concentrations were taken in stoppered glass tubes at 25°C. The tubes were shaken for a certain time, within which equilibrium was established as ascertained in preliminary experiments. The analyses of metal ions in aqueous phase, before and after extraction, were carried out using PERKIN-ELMER 603 atomic absorption spectrophotometer. The metal concentrations in the organic phase was calculated by mass balance. In later stage, inductively coupled plasma ICP-OES (ARL-3520) was used for the analyses of metals. The organic phase was stripped by 5% thiourea solution containing 1% HCl. The concentration of gold and silver in these solutions were determined in the same manner.

RESULTS

Extraction Speed for Au(III) and Ag(I)

The kinetics of the extraction of metals were investigated and the results, shown in Figure 1, suggest that gold and silver extraction are quite fast. The equilibrium can be achieved in less than one minute.

Analysis of Equilibrium Data

The distribution data for the extraction of Au(III) and Ag(I) in 2.0 N HCl medium with various concentration of DTH in chloroform are collected in Figures 2 and 3, respectively, in the form of logD versus log[DTH], where the distribution coefficient D is given by

$$D = [M]_{org.}/[M]_{aq.} \qquad (2)$$

The extraction of gold and silver can be expressed by the following general reaction:

$$p.M^{z+} + p.zCl^- + \overline{q.DTH} = \overline{(MCl_z)_p.(DTH)_q} \quad (3)$$

The formation constant, ß, for this reaction is defined as

$$ß = \frac{\overline{[(MCl_z)_p.(DTH)_q]}}{[M^{z+}]^p\ [Cl]^{pz}\ \overline{[DTH]^q}} \quad (4)$$

Where M denotes the metal with charge z+, p and q express the coefficients of reaction species. The bars denote that the species exists in the organic phase.

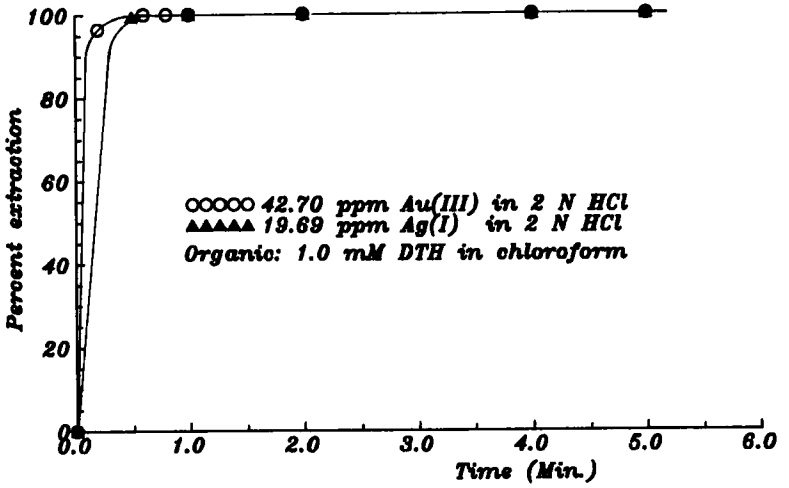

Figure 1. The kinetics of extraction of Au and Ag by DTH.

For the analysis of data, the binary interactions between Au^{3+} or Ag^+ and Cl^- are needed, i.e. the reactions (5) and (6).

$$Au^{3+} + rCl^- = [AuCl_r]^{(r-3)-} \quad (5)$$

$$Ag^+ + rCl^- = [AgCl_r]^{(r-1)-} \quad (6)$$

where r expresses the coefficients of Cl^-. The formation constants for Au-Cl complexation were taken from reference (15). In the case of silver, the corresponding constants at the ionic strength used in this study are not available. They were calculated using the specific interaction approach, developed by Guggenheim and Scatchard (16,17), as described below.

In this approach, the activity coefficient γ_i of an ion of

charge Z_i in a solution of ionic strength I is expressed by

$$\log\gamma_i = -Z_i^2 D(I) + \Sigma\epsilon(i, k)m_k \quad (7)$$

The summation is made over all ions k in the solution with molality m_k. D(I) is the Debye-Hückel term, $A\sqrt{I} / (1+1.5\sqrt{I})$ with A = 0.5107. $\epsilon(i,k)$ is the ionic interaction coefficient between the species i and k, and has a value of zero when both ions are of the same charge sign.

The dependence of the formation constant β^I on the ionic strength I is given by equation (8).

$$\log \beta^I = \log \beta^0 - \Delta Z^2 D(I) + \Sigma\epsilon(i, k)m_k \quad (8)$$

$$\text{with } \Delta Z^2 = \Sigma n_j Z_j^2 - \Sigma p_i Z_i^2 \quad (8a)$$

where n_j denotes the stoichiometric coefficients of the reacting ionic species of charge Z_j, p_i is the coefficient of ionic species of charge Z_i formed in reaction (5) or (6). β° represents the formation constant at zero ionic strength in the molal scale.

The first step is to determine β° using the two known values $\log\beta_1$=3.36 and $\log \beta_2$=5.20 (25°C, I=1) and equation (8) where the interaction coefficient between H^+ and Cl^-, $\epsilon(H^+,Cl^-)$=0.12, is taken from reference (18). The interaction coefficient between $Cl^-$and Ag^+ is not available. Therefore the interaction coefficients between Cl^- and monovalent cation Li^+, Na^+ and K^+ are used instead in the calculations. It is found that by using $\epsilon(K^+,Cl^-)$(18), $\log \beta_1$=3.62 and $\log \beta_2$=5.46 are obtained (at I=4) which are close to the reported values: $\log \beta_1$ = 3.45 and $\log \beta_2$ = 5.67 (15).

Further we got, at I=2, $\log \beta_1 = 3.43$
$\log \beta_2 = 5.27$
$\log \beta_3 = 5.20$
$\log \beta_4 = 5.70$

The analysis of distribution data was carried out by using the general minimizing computer program LETAGROP-DISTR (19). In these calculations a set of species are assumed to exist and their formation constants are determined by minimizing the error square-sum, U, defined by:

$$U = \sum_{i=1}^{N_p} (\log D_{calc} - \log D_{exp})^2 \quad (9)$$

and the standard deviation σY, i.e. (σlogD) defined by

$$\sigma Y = (U/N_p)^{1/2} \quad (10)$$

Where D_{exp} is the experimental distribution coefficient and D_{calc} is the corresponding values calculated by solving the mass balance equation for the different components. N_p is the number of experimental points.

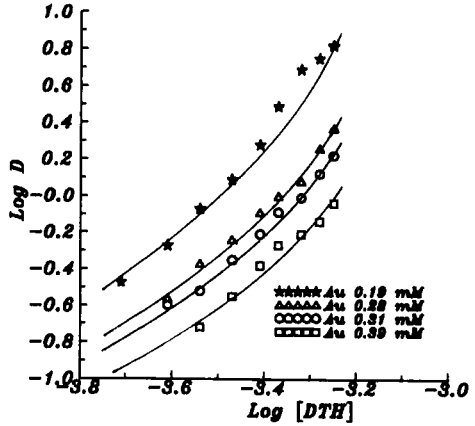

Fig. 2. Extraction of Au by DTH. The aqueous phase contained 2N HCl. The curves are calculated using the models given in Table 4.

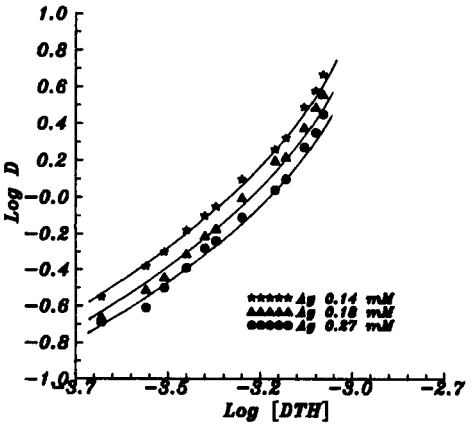

Fig. 3. Extraction of Ag by DTH. The aqueous phase contained 2N HCl. The curves are calculated using the models given in Table 5.

Several models were tested to search for the best fit of the experimental data. The best model is the one which gives the lowest values for both U and σ.

Summary of the results of the numerical analysis for the distribution equilibrium data of Au(III) and Ag(I) are listed in Tables 4 and 5.

Table 4. Summary of the results of the numerical treatment of extraction data for the system Au(III)-DTH in chloroform at 25°C.

Model	logß	U	σ	Remarks
$AuCl_3.(DTH)$	33.50±0.19	2.40	0.28	
$AuCl_3.(DTH)_2$	37.72±0.23	0.67	0.15	
$AuCl_3.(DTH)_3$	43.64 max 44.04	0.26	0.09	
$AuCl_3.(DTH)$	0	0.67	0.15	Rejected*
$AuCl_3.(DTH)_2$	37.72±0.25			
$AuCl_3.(DTH)$	0	0.26	0.09	Rejected*
$AuCl_3.(DTH)_3$	43.67 max 44.10			
$AuCl_3.(DTH)_2$	0	0.26	0.09	Rejected*
$AuCl_3.(DTH)_3$	43.66 max 44.14			
$AuCl_3.(DTH)$	0	0.26	0.09	Rejected*
$AuCl_3.(DTH)_2$	0			Rejected*
$AuCl_3.(DTH)_3$	43.67 max 44.15			
	Data at [DTH] = 0.05-0.34 mM:			
$AuCl_3.(DTH)$	33.23 max 33.45	4.87	0.40	
$AuCl_3.(DTH)_2$	33.76 max 37.86	2.50	0.28	
$AuCl_3.(DTH)_3$	42.69 max 43.26	1.56	0.22	
	Data at [DTH] = 0.34-0.57 mM:			
$AuCl_3.(DTH)$	33.54±0.21	1.85	0.28	
$AuCl_3.(DTH)_2$	37.77±0.25	0.51	0.16	
$AuCl_3.(DTH)_3$	43.84 max 44.22	0.14	0.08	

* For the rejected species, logß = 0.

Table 5. Summary of the results of the numerical treatment of extraction data for the system Ag(I)-DTH in chloroform at 25°C.

Model	logß	U	σ	Remarks
$AgCl.(DTH)$	10.05±0.11	1.25	0.189	
$AgCl.(DTH)_2$	13.58±0.03	0.07	0.045	
$AgCl.(DTH)_3$	17.27±0.11	0.45	0.114	
$AgCl.(DTH)_4$	21.19±0.25	0.11	0.172	
$AgCl.(DTH)$ $AgCl.(DTH)_2$	0 13.58±0.03	0.07	0.045	Rejected*
$AgCl.(DTH)$ $AgCl.(DTH)_3$	9.61±0.10 16.94±0.11	0.07	0.046	
$AgCl.(DTH)$ $AgCl.(DTH)_4$	9.77±0.10 20.51±0.22	0.15	0.067	
$AgCl.(DTH)_2$ $AgCl.(DTH)_3$	13.55±0.08 16.07 max 16.56	0.06	0.043	
$AgCl.(DTH)_2$ $AgCl.(DTH)_4$	13.57±0.04 19.26 max 19.85	0.07	0.044	
$AgCl.(DTH)_3$ $AgCl.(DTH)_4$	17.27±0.12 0	0.45	0.115	Rejected*
$AgCl.(DTH)$ $AgCl.(DTH)_2$ $AgCl.(DTH)_3$	9.13 max 9.64 13.39 max 13.69 16.50 max 16.93	0.06	0.043	
$AgCl.(DTH)$ $AgCl.(DTH)_2$ $AgCl.(DTH)_4$	7.91 max 9.35 13.57±0.13 19.30 max 19.93	0.07	0.045	

* For the rejected species, logß = 0.

As the concentrations of both metals are relatively low, it is reasonable to assume that only monomeric species, with respect to the metal, are formed. The extraction data of Ag(I) - DTH system were first treated using a one complex model, i.e. a model assuming the formation of only one complex with the general formula $(AgCl)_p(DTH)_q$. Several models were tested with different p:q values i.e. 1:1, 1:2, 1:3, 1:4, etc. As shown in table 4, the model containing the species 1:2 $[AgCl.(DTH)_2]$ gives the best fit. The 1:1 species (and also the 1:3 species) gives higher U and σY values than

those obtained with the 1:2 species.

Further to this models assuming the formation of two and three species were tested. When the model "1:1 and 1:2" (i.e.[AgCl.(DTH)] and [$AgCl.(DTH)_2$]) was tested, the program sets the formation constant of the species 1:1 equal to zero indicating that its existence, under these experimental conditions, is improbable. No significant improvement of the fit was obtained when testing other models. The data can thus be explained by assuming the presence of only the $AgCl.(DTH)_2$ species.

For the Au(III)-DTH system, the model which contains only one complex, $AuCl_3.(DTH)_3$, gives the best fit to all the experimental data. The 1:1 complex i.e. $AuCl_3.DTH$ was rejected by the program meaning that its existence is improbable. Also the 1:2 complex was rejected.

In order to further check the possibility of the existence either of 1:1 and 1:2 species, we divided the data into two parts in the respect to low and high DTH concentrations. The different models were then tested using each set of data independently. In both cases, the data were best explained by the presence of the 1:3 species only.

Reagent Selectivity

The extraction of some metals, at similar concentrations, from various acidic solutions was carried out using 1.0 mM DTH. The results are given in Fig. 4. As seen, Au and Ag were extracted to almost 100% while other metals were extracted to a much lower degree.

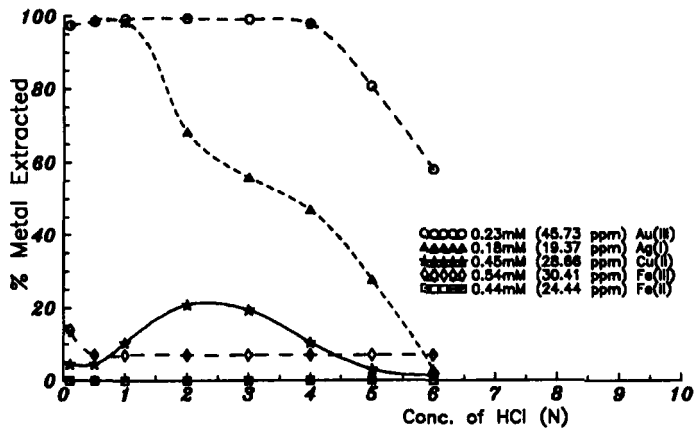

Figure 4. Extraction of different metals by 1.0 mM DTH.

The selectivity of DTH was also tested by using different concentrations of DTH to extract metals from a solution of Au(III), Ag(I) in the presence of much higher concentrations of Cu(II) and Fe(III) in 2.0 N HCl medium. The results are collected in Fig. 5.

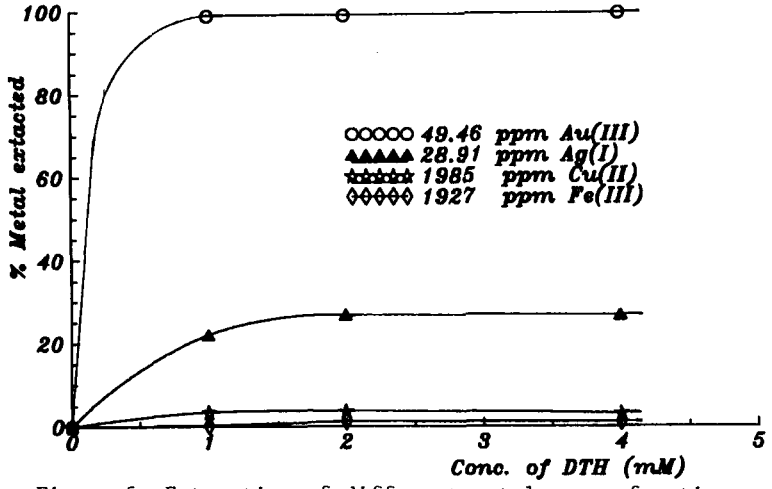

Figure 5. Extraction of different metals as a function of the concentration of DTH in chloroform.

As seen, the reagent shows very high selectivity for Au(III) and Ag(I) over Cu(II), Fe(III) and Fe(II). Very high separation factors could be obtained. For example, when the concentration of DTH was 1.0 mM and the solution contained 49.46 ppm Au(III), 28.91 ppm Ag(I), while [Cu(II)] & [Fe(III)] is about 2 g/l. Separation factors, D_{Ag}/D_{Cu}=7, D_{Ag}/D_{Fe}=140 while D_{Au}/D_{Cu} and D_{Au}/D_{Fe} are more than 1000, were obtained.

The Acidity Influence on Extraction

The extraction behavior of Au(III) and Ag(I) from aqueous solution with various concentration of HCl by 1.0 mM DTH in chloroform was shown in Figure 4. However, the data of Figure 4 are replotted as logD versus [HCl] in Figure 6. It can be seen that, although the percentage of Au(III) extracted at acidity lower than 4 molar did not change significantly, it shows an extraction maximum at about 2.0 N HCl. For Ag(I), the extraction decreases as acidity of aqueous phase increases.

Loading Capacity for Extraction of Au(III) and Ag(I)

The loading and stripping of gold and silver by the reagent were studied in order to assess the practical applicability of the

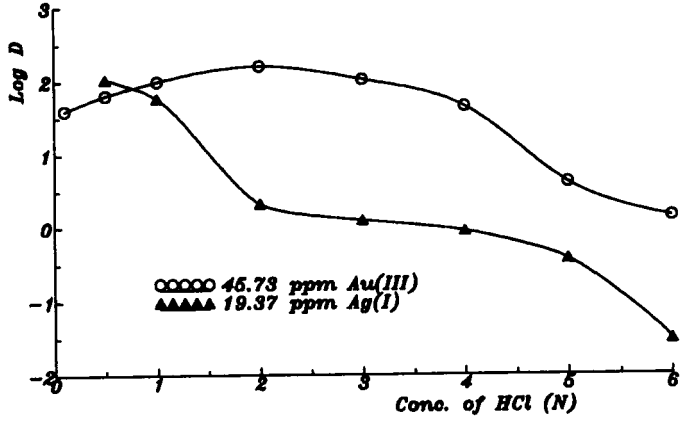

Fig. 6. The influence of concentration of HCl in the aqueous phase on the extraction of Au and Ag by 1.0 mM DTH dissolved in chloroform.

reagent. We used "feed" solutions with higher concentration of Au and Ag there is normally encountered in actual processes in order to determine the maximum loading capacity. The extraction isotherms at 25°C for the gold and silver are shown in Figures 7 and 8 respectively, using 10.0 mM DTH while the acidity in the aqueous phase was kept at 2.0 N HCl.

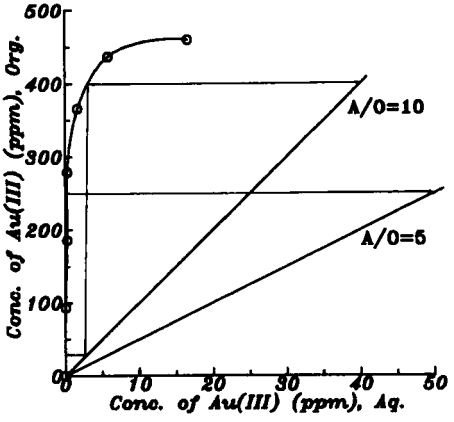

Fig. 7. The extraction isotherm of Au(III) by 10 mM DTH. The aqueous phase contained 2N HCl.

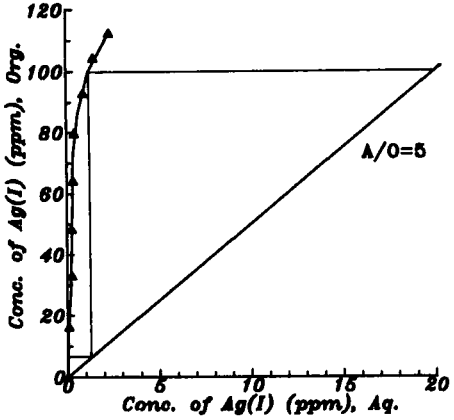

Fig. 8. The extraction isotherm of Ag(I) by 10 mM DTH. The aqueous phase contained 2N HCl.

As seen, DTH has an excellent extraction ability for gold and silver from acidic chloride solutions. For example, a feed solution containing 40 ppm gold can be treated in only two theoretical stages to extract almost all the gold, at phase ratio=10. Silver is extracted to a lesser degree and, as seen from the extraction isotherm, it is possible to extract almost all the silver from a feed solution containing 20 ppm Ag with two theoretical stages at phase ratio=5. For treating solutions with higher concentrations of silver, higher reagent concentration is required.

For stripping the loaded organic solutions, a solution containing 5% thiourea in 1% acidic chloride solution and 5% ammonium thiocyanate solution were used. The first solution can re-extract 99.8% while the second solution can re-extract 96.2% silver form organic phase containing 18.16 ppm silver at phase ratio=1.

Further study showed that, at phase ratio=1, 5% thiourea in 1% acidic chloride solution re-extracted 91.9% Au(III) from organic phase containing 338.65 ppm Au(III) and 98.3% Ag(I) from organic solution containing 150.15 ppm Ag(I).

DISCUSSION

No data are reported for a similar organic reagent. We therefore compare our results with the data available for the complexation of thiourea to metal ions in aqueous solutions.

The extraction of silver, in chloride solutions, by DTH is explained by the formation of the 1:2 species. Literature data for the complexation of silver by thiourea (20, 21) indicate the formation of $(Ag)_p(Tu)_q$ species with p:q value of 1:1, 1:2, 1:3 and 1:4 species in aqueous solutions. Our results confirm the existence of only one species although it does not exclude the possibility of the existence of other species. However, the expected 1:1 complex could not be confirmed from this study. On the other hand, some monovalent metal ions e.g Cu(I) also form a 1:2 species with thiourea (and not 1:1 species) in acidic chloride solutions.

In the case of gold extraction, no report on the complexation of trivalent gold and thiourea was found. In thiourea acidic leach solutions, gold is oxidized to gold(I) which forms only 1:2 species with thiourea, i.e. $(AuTu_2)^+$.(20) The calculations reported here indicate that Au(III) forms only the 1:3 species, $AuCl_3.(DTH)_3$, with this extractant.

The dependence of extraction of both Au and Ag on the HCl concentration in the aqueous phase may be explained by the formation of unextractable species $AuCl_4^-$ and $AgCl_2^-$ respectively. Fig. 9 is constructed using the formation constants of the different species determined for the Ag-H-Cl-DTH system. As seen the calculated percentage of Ag extracted is in a good agreement with the experimental data.

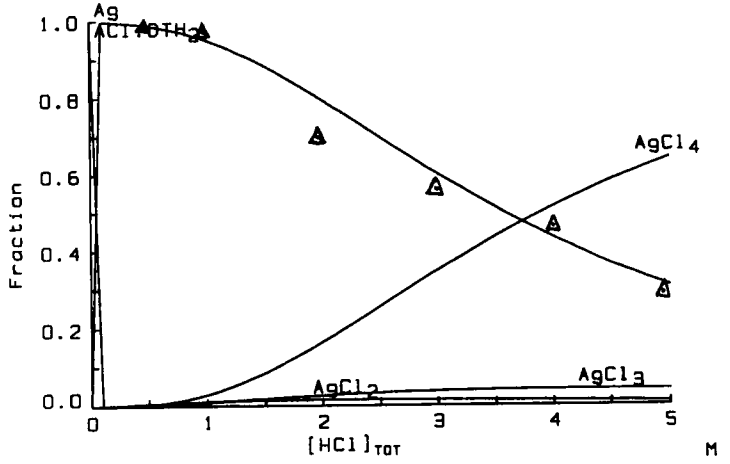

Fig. 9. The extraction of Ag by DTH in chloroform at different concentrations of DTH. The ▲ represent the experimental data, the curve is calculated using the formation constants of different Ag-Cl species and Ag-Cl-DTH species.

The high selectivity of the reagent for Au(III) and Ag(I) may be explained by the formation of complexes that are more stable than those for Cu(II), Fe(III) and Fe(II). The stability of the complexes of DTH with different metals is in the order of Au(III) > Ag(I) > Cu(II) > Fe(III) > Fe(II). The complexation constants of thiourea with different metal ions Au^{+}, Ag^{+}, Cu^{+}, Fe^{3+} and Fe^{2+} in acidic aqueous solutions are given below (20, 21).

Metal ion	$\log\beta_{11}$	$\log\beta_{12}$	$\log\beta_{13}$
Au^{+}	-	21.3	-
Ag^{+}	-	-	12.95
Cu^{+}	-	12.8	14
Fe^{3+}	-	8.44	-
Fe^{2+}	-	6.44	-

The stability of the complexes of thiourea with the different metals is in the same order as that of DTH except for Cu and Ag. The stability constant $\log\beta_3$ for Cu(I) is slightly higher than that for Ag(I). On the other hand, our study shows that DTH has a high selectivity for Ag(I) over Cu(II).

In aqueous solution thiourea is easily oxidized, and in acidic solutions it is hydrolyzed to form urea and hydrogen sulphide. There is also a slow decomposition of thiourea to ammonium thiocyanate (12). The DTH reagent seems to be more stable both in the solid form (no change of the melting point etc) and when dissolved in organic diluents.

CONCLUSION

Alkyl substitution of the thiourea produces a water insoluble reagent that can be used as a selective extractant for gold and silver from acidic chloride solutions. The extractant tested showed to have fast extraction kinetics and high loading capacity.

The complexes formed upon the extraction of gold and silver were obtained from the analysis of distribution data. The selectivity of the extractant towards different metals seems to be consistent with that reported for the thiourea itself.

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REFERENCES

1. Danielssen, T. et al., Zinc Solvent Extraction from Iron Chloride Leach Liquors., "Chloride Hydrometallurgy" - Sympsium. Soc. Chem. Ind. (London), Solv. Extr. & Ion Exch. Group, 1980.

2. Nogueira, E.D., J. M. Regite, M. P. Viegas, Design Features and Operating Experience of the Quimigal Zincex Plant., Chloride Electrometallurgy., Ed. Parker. P.D.,AIME, New York 59-76 (1983).

3. Miller, J. D., R. Y. Wan, M. B. Mooiman and P. L. Sibrell, Separation Science and Technology, 22(2&3), 487-502 (1987).

4. Groenewald, T., Proceedings of the International Solvent Extraction Conference(ISEC'74), Lyon, 2715-2712 (1974).

5. Mooiman M. B., and J. D. Miller, Mineral and Metallurgical Processing, August, 153-157 (1984).

6. Mirza, M. Y., Talanta, 27, 101-106 (1980).

7. American Cyanamid Company, Cyanex 471X Extractant, Technical data sheet.

8. Salvado, V., M. Hidalgo, A. Masana, M. Valiente and M. Muhammed, Extraction of Gold from Hydrochloric Acid Solutions by Triisobutyl Phosphine sulfide in Toluene, Analytical Letters (In press).

9. Hudson, M. J. and M. J. Shepherd, Hydrometallurgy, 14, 23-24 (1985).

10. Hudson, M. J., and L. R. Glaves, Chemistry and Industry, 7, January, 22-24 (1985).

11. Nelson, J. H. James L. H., and Emil M. Metals Speciation, Separation and Recovery, (ed. J. W. Patterson and R. Passino), Lewis Publishers, Inc., 119-146 (1987).

12. Bilston, D. W., S. R. La Brooy and J. T. Woodcock, The Aus. I.M.M. Melbourne Branch, Symposium on "Extractive Metallurgy", November 51-60(1984).

13. Chen, C. K., T. N. Lung and C. C. Wan, Hydrometallurgy, 5, 207-212(1980).

14. Levy, J. (to Universal Oil Products Co.), US Patent 3,282,997, Nov. 1, (1966).

15. Smith R. M. and A. E. Martell, Critical Stability Constants, Plenum Press, New York, 1976.

16. Guggenheim, E. A., Application of Statistical Mechanics, Clarendon Press, Oxford, 1966.

17. Scatchard, G., Equilibrium in Solution, Surface and Colloid chemistry, Harvard University Press, Cambridge, Massachusetts, 1976.

18. Ciavatta, L., Ann. Chim. (Rome), 70, 551 (1980).

19. Liem, D. H., Acta Chem. Scand. 25, 1521-1534 (1971).

20. Hiskey, J. B., Minerals and Metallurgical Processing, November, 174-179 (1984).

21. IUPAC, Stability Constants of Metal-ion Complexes, Part B, Organic Ligands (ed. D. D. Perrin), Pergamon Press, 1979.