This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Liquid-Liquid Extraction of Silver From Chloride Media by *N,N'*-Tetrasubstituted Dithiomalonamide Derivatives

Osvaldo Ortet[a]; Ana Paula Paiva[a]
[a] Centro de Química e Bioquímica, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa (DQB-FCUL), Lisbon, Portugal

Online publication date: 06 May 2010

To cite this Article Ortet, Osvaldo and Paiva, Ana Paula(2010) 'Liquid-Liquid Extraction of Silver From Chloride Media by *N,N'*-Tetrasubstituted Dithiomalonamide Derivatives', Separation Science and Technology, 45: 8, 1130 — 1138
To link to this Article: DOI: 10.1080/01496391003697408
URL: http://dx.doi.org/10.1080/01496391003697408

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Separation Science and Technology, 45: 1130–1138, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003697408

Liquid–Liquid Extraction of Silver From Chloride Media by *N,N′*-Tetrasubstituted Dithiomalonamide Derivatives

Osvaldo Ortet and Ana Paula Paiva

Centro de Química e Bioquímica, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa (DQB-FCUL), Lisbon, Portugal

---

***N,N′*-dimethyl-*N,N′*-diphenyldithiomalonamide (DMDPHDTMA) and *N,N′*-dimethyl-*N,N′*-dicyclohexyldithiomalonamide (DMDCHDTMA) were synthesized and tested as extractants for silver in chloride solutions. Even when relatively low concentrations are used, both compounds effectively extract Ag(I) from 2–5 M chloride concentrated aqueous phases. Ag(I) is successfully stripped by a stabilized sodium thiosulfate solution. Results obtained from sequential cycles of extraction-stripping suggest that both extractants exhibit a high Ag(I) loading capacity. The effects of the equilibration time, concentrations of extractant, chloride and hydrogen ions on Ag(I) extraction have been investigated. The chemical reactions involved on Ag(I) extraction are proposed. There is no selectivity of DMDPHDTMA or DMDCHDTMA for Ag(I) when Cu(II) and Fe(III) co-exist in the chloride aqueous solution.**

Keywords chloride media; dithiomalonamide derivatives; silver

INTRODUCTION

Chloride hydrometallurgy is nowadays generally considered to process and refine base, refractory and particularly precious metals (1). The involvement of chloride leaches in the separation of precious metals is a reality (2) and several claims for availability of specific precious metals without any silver contamination have been addressed by the electronics industry (3).

One of the most followed routes to recover Ag(I) from chloride media is through its precipitation as the silver chloride form, but it is well known that the solubility of this precious metal rises when the chloride content in the aqueous solutions increases (3) and this fact, if ignored, can obviously result in significant economic losses, as well as in some contamination of other precious metals with silver. Accordingly, a few research efforts to efficiently and selectively recover Ag(I) from chloride media can be found in literature and liquid-liquid extraction (or solvent extraction, SX) has been the main route proposed to achieve that aim (2–17). The widely known affinity between ligands with sulfur donor atoms (considered as "soft bases") and Ag(I) (a "soft acid") justifies the extensive use of sulfur-containing extractants to recover Ag(I) from any aqueous medium (4,5).

The Ag(I)-chloride-Cyanex 471X (triisobutylphosphine sulfide, TIBPS) extractive system is the one which deserved a more extensive investigation (4–7), all studies pointing out to the remarkable potential of TIBPS to recover Ag(I), either in terms of extraction efficiency or selectivity over several base metals. The involved Ag(I) extraction reactions have also been extensively addressed (6–8). The commercial acidic extractants Cyanex 302 (bis-(2,4,4-trimethylpentyl)-monothiophosphinic acid) (3,9) and Cyanex 301 (bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid) (3,9,10) also showed a good extraction performance towards Ag(I); however, both extractants have been reported as not selective when Ag(I) coexists with Cu(II) in concentrated chloride solutions (9,10), in addition to other precious metals such as Pd(II), Au(III), or Pt(IV), at least.

Other neutral sulfur-phosphorus organic compounds with a comparable structure to TIBPS were specifically synthesized, namely tri-*n*-butylphosphine sulfide (TBPS) and tri-*n*-octylphosphine sulfide (TOPS), and their performance towards Ag(I) extraction from chloride media evaluated (11). Generally it can be said that these ligands behaved similarly to TIBPS but presented lower selectivity factors against Fe(III) and Cu(II).

Some sulfur-nitrogen ligands have also been tested as Ag(I) extractants from chloride media: dodecylthiourea has been referred to as an efficient and selective extractant for Ag(I), over Fe(III) and Cu(II), from highly acidic chloride leaches (12), but other derivatives such as dibutyl- and diphenylthiourea (DPHT and DBT, respectively), although presenting a good Ag(I) extraction performance (13,14), did exhibit low selectivity profiles for the precious metal over the same base metals (14).

Received 18 January 2009; accepted 26 January 2010.

Address correspondence to Ana Paula Paiva, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa (DQB-FCUL), Rua Ernesto de Vasconcelos, Ed. C8, Lisboa 1749-016, Portugal. Fax: +351 217500088. E-mail: appaiva@fc.ul.pt

Additional fundamental studies were also carried out involving extractants with more elaborate structures, such as a monomeric amide derivative of a calix[4]arene (15) or an trialkylthiophosphonate compound (16); both systems were well characterized in terms of the extraction process but no data were achieved regarding their selectivity behavior. Selectivity has not been checked again when some tri- and tetraalkylammonium salts were reported as adequate to recover Ag(I) (17), although exhibiting a lower performance as the chloride content in the aqueous solutions was increased.

In spite of their general use throughout the hydrometallurgical industry, it is well known that phosphorus-containing extractants are less environmentally friendly than other organic compounds bearing oxygen, nitrogen, or sulfur as heteroatoms. It would be worthwhile, if one takes the environmental point of view into account, that alternative extractants with similar efficiency and selectivity patterns as the phosphorus ones could be found. Having that idea in mind, and after an extensive use of *N,N′*-tetrasubstituted malonamide derivatives to recover some metal ions (Fe(III) (18), Rh (19), and Pt (20)), it was decided to carry out the synthesis of two model *N,N′*-tetrasubstituted dithiomalonamides and check their efficiency and selectivity towards Ag(I) in chloride media.

To our knowledge only one work has appeared in literature that envisaged the study of a specific *N,N′*-disubstituted dithiomalonamide derivative as a complexing and SX reagent for Ag(I) in nitrate medium (21); however, the difficulties that arose in the synthesis of that compound did not allow its testing (it was produced in a quite small quantity). Additionally, only a few complexation data involving dithiomalonamide and *N,N′*-disubstituted dithiomalonamides and diverse metal ions have been reported so far (22–27). Actually, it must be pointed out that any sort of work with *N,N′*-tetrasubstituted dithiomalonamide derivatives, either involving SX or complexing studies with metals, has not been found.

EXPERIMENTAL

Synthesis and Characterization

N,N′-dimethyl-*N,N′*-diphenyldithiomalonamide (DMDPHDTMA) and *N,N′*-dimethyl-*N,N′*-dicyclohexyldithiomalonamide (DMDCHDTMA) were obtained from their correspondent malonamides, *N,N′*-dimethyl-*N,N′*-diphenylmalonamide (DMDPHMA) and *N,N′*-dimethyl-*N,N′*-dicyclohexylmalonamide (DMDCHMA), whose synthetic and characterization details have already been published (18).

DMDPHMA (5 g, 0.018 mol) or DMDCHMA (5 g, 0.017 mol) were dissolved in dry toluene (60 mL) and about 200 mL of a dry toluene solution of the Lawesson reagent (Fluka, 98%) (7.43 g, 0.018 mol; 7.02 g, 0.017 mol, respectively), were added dropwise. The reaction mixtures were refluxed and left under nitrogen atmosphere, being periodically controlled by thin-layer chromatography (TLC). After 4–5 h, DMDPHMA or DMDCHMA disappeared in TLC, hence both reactions were stopped. The resulting yellow solutions were evaporated in a rotary evaporator and prepared solutions of the crude solid products were passed through silica chromatographic columns. The fractions containing the desired products were evaporated from the solvent and further dried under vacuum. The yields were 67% for DMDPHDTMA and 80% for DMDCHDTMA. Both syntheses were repeated to obtain reasonable quantities to pursue to the SX experiments.

Several characterization methods were used: determination of melting points (Stuart Scientific, model SMP3), Fourier transform-infrared spectroscopy (Satellite FT-IR Mattson, with a resolution of 2 cm^{-1}) proton nuclear magnetic resonance (^1H, 400 MHz NMR, Bruker 400 Avance spectrometer), and ion trap mass spectrometry fitted with an electrospray ionization source (ESI-MS, Thermoquest LCQ Duo). The characterization results obtained for both DMDPHDTMA and DMDCHDTMA are presented in Table 1.

Solvent Extraction Experiments

Aqueous solutions for the extraction experiments were prepared using hydrochloric acid alone or mixed with sodium chloride. The most utilized aqueous phases contained 5 M HCl or 2 M HCl + 3 M NaCl; however, for the study of the chemical reactions involved or the influence of acidity, different proportions of both reagents, or HCl alone, were also used. Ag(I) feed solutions, with concentrations varying between 3.7×10^{-4} M and 1.4×10^{-3} M, were made by dissolution of the required amount of $AgNO_3$ (Merck, 99.5% purity) in the correspondent chloride solutions. In addition to Ag(I), solutions containing 3×10^{-2} M Cu(II), 9×10^{-2} M Fe(III), and 1×10^{-2} M Pb(II) were prepared from the respective chloride salts either in 2 M HCl + 3 M NaCl or 5 M HCl and were used for the selectivity experiments. All chemicals were of analytical quality. For the stripping experiments, a stabilized sodium thiosulfate solution whose composition is referred to by Rickelton and Robertson (28) was employed. Organic phases containing DMDPHDTMA or DMDCHDTMA, with concentrations varying between 5×10^{-3} M and 7×10^{-2} M, were prepared in 1,2-dichloroethane (1,2-DCE, Riedel-de-Haen, 99.8%).

Extraction and stripping experiments were generally carried out by mixing equal volumes of aqueous and organic phases (A/O = 1) for 30 minutes, at room temperature and at a constant stirring speed of 1000 rpm, which was enough to guarantee a good emulsion. A similar procedure was also adopted for the evaluation of the selectivity of both extractants towards Ag(I).

TABLE 1
Physical and spectroscopic data obtained for DMDCHDTMA and DMDPHDTMA

Collected data	DMDCHDTMA	DMDPHDTMA
Physical appearance and melting point (°C)	Light yellow crystals 147.5–149.2	Yellow crystals 156.4–158.3
FT-IR (ν_{max}, NaCl pellets / cm^{-1})	1395, 1261, 1070 (-N-C=S)	1471, 1263, 1070 (-N-C=S)
^{1}H NMR (400 MHz; $CDCl_3$, Me_4Si, δ in ppm)	1.1–1.9 (20 H, multiplet, 2 × -CH_2 cyclohexyl), 3.2–3.3 (6 H, double doublet, 2 × CH_3-N), 4.3–4.4 (2 H, triplet, CS-CH_2-CS), 4.5–4.6 (2 H, multiplet, 2 x -CH cyclohexyl)	3.7 (6 H, singlet, 2 × CH_3-N), 3.8 (2 H, singlet, CS-CH_2-CS), 7.1–7.2 (4H, duplet, aromatic in *ortho* position), 7.4–7.5 (6H, multiplet, aromatic in *meta*- and *para*- positions)
ESI-MS (CH_3OH, m/z)	327 ([Molecular + H]$^+$), 245 (base peak), 216, 214, 112	315 ([Molecular + H]$^+$), 300, 210 (base peak), 208, 150

The determination of the metal contents in the aqueous phases, before and after extraction, was carried out by Flame Atomic Absorption Spectrophotometry (AAS) using a Pye Unicam SP9 model. For each sample, two aliquots were analyzed and the values obtained were critically treated and only accepted if a reasonable relative standard deviation was obtained. Metal ion concentrations in organic phases were calculated by mass balance. For the majority of the cases, at least two sets of experiments were accomplished in order to confirm all data obtained.

The reutilization experiments consisted of three successive cycles of extraction/stripping. A solution containing 1.4×10^{-3} M Ag(I) in 5 M HCl was contacted with 5×10^{-2} M DMDPHDTMA or DMDCHDTMA in 1,2-DCE under the usual set of experimental conditions and, after each stripping stage with the stabilized sodium thiosulfate solution, the same organic extract was again equilibrated with a fresh portion of aqueous feed phase.

For the application of spectroscopic techniques (FT-IR and ^{1}H NMR), equal volumes of a 5 M HCl solution alone (or with 1.4×10^{-3} M Ag(I)) and an organic phase containing 2×10^{-2} M DMDPHDTMA or DMDCHDTMA in dichloromethane were equilibrated, adopting the same experimental scheme reported previously. After phase separation, the organic solutions were dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness. Some portions of the residues were used to prepare potassium bromide pellets for FT-IR and others were dissolved in $CDCl_3$ with tetramethylsilane for ^{1}H NMR. Apart from that, the given volumes of the previously equilibrated organic phases were contacted with equal volumes of distilled water, to check if some HCl would transfer from the loaded organic phases to the new ones (by control of the pH values of water before and after equilibration).

RESULTS AND DISCUSSION

Preliminary Ag(I) Extraction Studies

Time Necessary to Reach Equilibrium

Preliminary experiments were carried out to evaluate how much time would be necessary for the extraction systems to attain equilibrium. Hence, a general set of experimental conditions was adopted for both dithiomalonamide derivatives, for which an aqueous solution 1.4×10^{-3} M Ag(I) in 5 M HCl was used. The contact time considered for the experiments varied between 1 and 60 min.

As can be seen in Fig. 1, the equilibrium for both systems is reached at about 15 min; the percentage (%E)

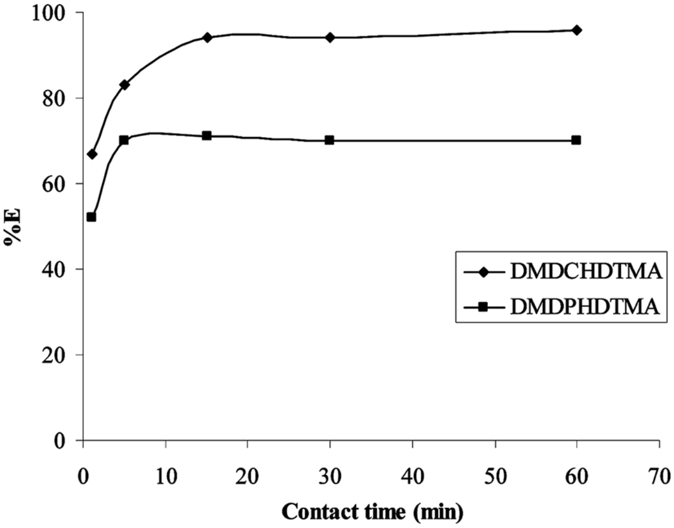

FIG. 1. Dependence of %E Ag(I) on different contact times for both DMDCHDTMA and DMDPHDTMA (1.4×10^{-3} M Ag(I) in 5 M HCl, 3×10^{-2} M DMDCHDTMA or DMDPHDTMA in 1,2-DCE, A/O = 1, room temperature, 1000 rpm). Standard deviation: ±1%.

TABLE 2
Extraction percentages of 1.4×10^{-3} M Ag(I) by 5×10^{-2} M DMDPHDTMA or DMDCHDTMA in 1,2-DCE (A/O = 1, room temperature, 1000 rpm, 30 minutes equilibration)*

	%E Ag(I)	
Extractant	2 M HCl + 3 M NaCl	5 M HCl
DMDPHDTMA	69	80
DMDCHDTMA	94	97

*Associated standard deviation: ±2%.

Ag(I) extraction values achieved after that period of time are practically similar to the ones obtained for longer periods of contact. Earlier studies involving trialkylphosphine sulfides were carried out adopting 15 min (7) or 30 min (11) for equilibration, hence it was decided to proceed with a 30 min contact for the subsequent experiments with DMDPHDTMA or DMDCHDTMA. It is also observed that DMDCHDTMA is more efficient to extract Ag(I) than DMDPHDTMA (%E ~95% against 71%).

Use of Two Different Chloride Media

The most used aqueous medium to perform the research with the trialkylphosphine sulfides was composed of 2 M HCl + 3 M NaCl (7,11); hence, in order to directly compare the present results with the earlier ones, some preliminary experiments were carried out with the above-mentioned aqueous phase. Under the same set of experimental conditions, a 5 M HCl medium was also tested. The Ag(I) extraction results obtained are displayed in Table 2.

It can be observed that both compounds extract Ag(I) more effectively from 5 M HCl than from 2 M HCl + 3 M NaCl, the difference in performance for both chloride media being more accentuated for DMDPHDTMA. Higher Ag(I) extraction efficiencies from more acidic aqueous phases, for a similar chloride concentration, were detected with TIBPS (7), revealed to be appreciable with TBPS and TOPS (11), but were nonexistent with DBT, whose performance was independent on the nature of the chloride source (14). Additionally, it should be emphasized that DMDPHDTMA and DMDCHDTMA are more efficient than all the other organic compounds already tested by this group (7,11,14), as the %E Ag(I) now obtained are similar to the best ones already reported, but were achieved with half of the extractants concentration in the organic phase.

Stripping and Recycling

The Ag(I) loaded organic phases coming from the extraction experiments involving the 2 M HCl +3 M NaCl or 5 M HCl aqueous solutions were subjected to an equilibration with an equal volume of a 1 M stabilized sodium thiosulfate solution (28), following the usual experimental set. The above-mentioned stripping solution has systematically been adopted to strip Ag(I) from the loaded organic solvents (7,11,14). The Ag(I) stripping results that were obtained are displayed in Table 3.

It can generally be observed that the stabilized sodium thiosulfate solution is a good stripping agent to remove Ag(I) from the loaded organic media, either those coming from the equilibration with a 2 M HCl + 3 M NaCl or with a 5 M HCl feed aqueous phase, with percentages for Ag(I) stripping (%S) always higher than 90%. These %S values are better than the ones found for TIBPS (7), TBPS (11), DPHT and DBT (14), and similar to those of TOPS (11). Hence, it can be concluded that both DMDPHDTMA and DMDCHDTMA are extremely efficient for recovering Ag(I) from concentrated chloride media, being almost completely regenerated by a stabilized sodium thiosulfate solution, as they easily release Ag(I) to the new aqueous medium.

In order to check if both compounds would maintain their high %E Ag(I) if reused, three sequential extraction-stripping experiments were carried out. The initial aqueous phase contained 1.4×10^{-3} M Ag(I) in 5 M HCl and the organic extracts consisted of 5×10^{-2} M concentrations of either DMDPHDTMA or DMDCHDTMA in 1,2-DCE. The %E Ag(I) results obtained for all the cycles are displayed in Fig. 2.

TABLE 3
Stripping percentages of Ag(I) (%S) from the loaded organic solvents (*Extraction*: 1.4×10^{-3} M Ag(I) in 5 M HCl or 2 M HCl + 3 M NaCl, 5×10^{-2} M DMDPHDTMA or DMDCHDTMA in 1,2-DCE; *Stripping*: 1 M stabilized $Na_2S_2O_3$; *Extraction and stripping conditions*: A/O = 1, room temperature, 1000 rpm, 30 minutes equilibration)*

Extractant	%E (from 5 M HCl)	%S (from 5 M HCl)	%E (from 2 M HCl + 3 M NaCl)	%S (from 2 M HCl + 3 M NaCl)
DMDPHDTMA	80	93	69	100
DMDCHDTMA	97	98	94	94

*Associated standard deviation: ±1%.

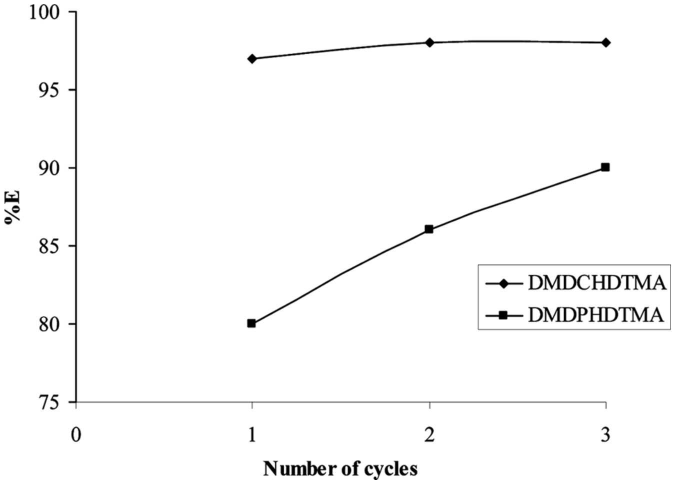

FIG. 2. Variation of the %E Ag(I) values within three sequential extraction-stripping cycles (1.4×10^{-3} M Ag(I) in 5 M HCl, 5×10^{-2} M DMDPHDTMA or DMDCHDTMA in 1,2-DCE, 1 M stabilized $Na_2S_2O_3$, A/O = 1, room temperature, 1000 rpm, 30 minutes equilibration). Standard deviation: ±2%.

It can be seen that both DMDPHDTMA and DMDCHDTMA keep their ability to extract Ag(I) and, for the three experiments, the %E even increases for DMDPHDTMA. This latter result is a bit unexpected, suggesting that the DMDPHDTMA solvent may have suffered some transformation after contacting with the stripping solution. It was additionally noticed that, after the first cycle, the sodium thiosulfate solution somehow decreases its stripping power towards Ag(I): for DMDPHDTMA, the Ag(I) stripping values varied from 93% to 87% for the three cycles, whereas for DMDCHDTMA the range obtained was from 98% to 68%. These experiments also denote that DMDCHDTMA and DMDPHDTMA do show a very good loading capacity to accommodate Ag(I), as they keep the high %E towards the metal ion even when the latter is only partially stripped from the corresponding organic phases.

Selectivity

The selectivity experiments involving both dithiomalonamide derivatives were carried out with solutions containing 1.4×10^{-3} M Ag(I), 3×10^{-2} M Cu(II), 9×10^{-2} M Fe(III), and 1×10^{-2} M Pb(II), either in 2 M HCl + 3 M NaCl or 5 M HCl, adopting the usual set of experimental conditions. The extraction profiles obtained are displayed in Fig. 3.

The results observed show that both compounds do not exhibit selectivity towards the precious metal. In fact, Fe(III) and particularly Cu(II) are extensively extracted along with Ag(I) and probably, as a consequence, the %E Ag(I) are much lower than those obtained when the precious metal was the only metal species in solution. Dark brown precipitates located at the interface were always detected after the equilibration experiments. Only Pb(II) was not significantly extracted, particularly when the 5 M HCl feed aqueous solution was used. For a similar set of extraction conditions, and when 2 M HCl + 3 M NaCl aqueous solutions were involved, the selectivity performances of TBPS and TOPS (11) and particularly that of TIBPS (7) are much more promising. The selectivity results now obtained also denote that the %E Cu(II) are lower, the %E Fe(III) are higher and the %E Pb(II) are similar to the ones reported for DPHT and DBT (14). Hence, within all the extractants already tested for the selective recovery of Ag(I) from concentrated chloride media investigated by this group, the phosphorus-sulfur ones continue to be the most adequate.

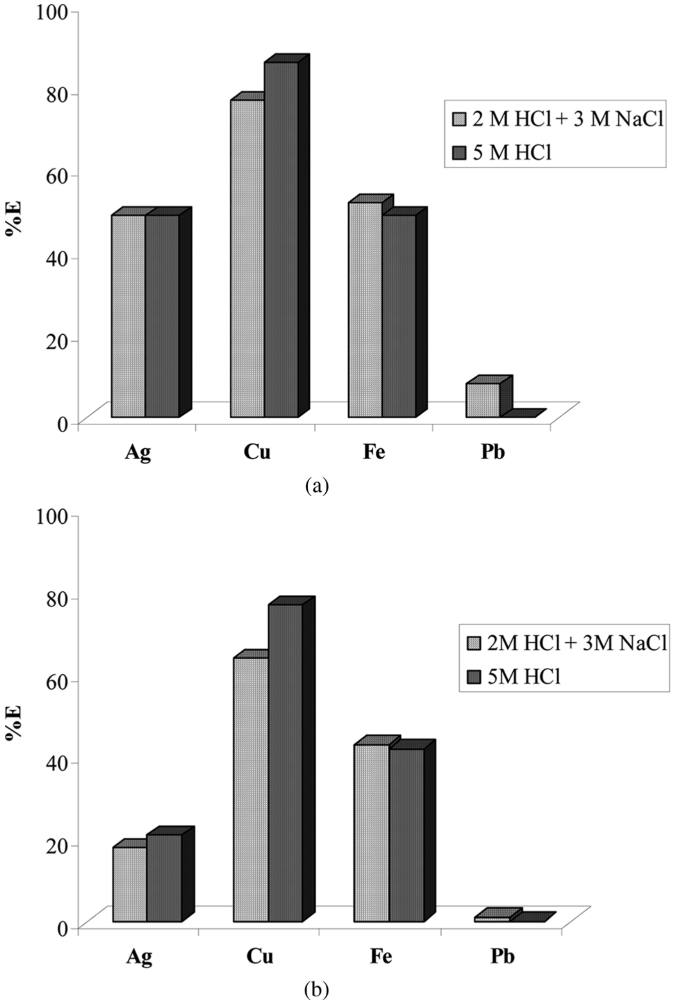

FIG. 3. %E values obtained for Ag(I), Cu(II), Fe(III) and Pb(II) by DMDCHDTMA (a) and DMDPHDTMA (b), respectively (1.4×10^{-3} M Ag(I), 3×10^{-2} M Cu(II), 9×10^{-2} M Fe(III) and 1×10^{-2} M Pb(II) either in 2 M HCl + 3 M NaCl or 5 M HCl, 5×10^{-2} M DMDCHDTMA or DMDPHDTMA in 1,2-DCE, A/O = 1, room temperature, 1000 rpm, 30 minutes equilibration). Standard deviation: ±1%.

Lower chloride concentrated aqueous feed solutions could probably affect the equilibria involving the different metal ion chlorocomplexes and would somehow modify the selectivity profiles presented, but significant changes are not likely to be expected.

Extraction Reactions

In order to identify the reactions responsible for Ag(I) extraction, the dependence of %E Ag(I) or the Ag(I) distribution coefficients on several parameters, namely the initial concentrations of extractant, the acidity, and the chloride content of the aqueous solutions, has been evaluated. In addition to equilibrium results, spectroscopic data have also been obtained, to help with the clarification of the extraction reactions occurring in both systems.

The variation of the Ag(I) distribution coefficients in 5 M HCl with the initial concentrations of both dithiomalonamide derivatives was therefore investigated. The data obtained from the correspondent log-log plots are presented in Fig. 4.

The experimental points achieved for both DMDPHDTMA and DMDCHDTMA adjust well to straight lines within the concentration ranges tested, whose slopes are one for DMDPHDTMA and between one and two for DMDCHDTMA. Based on the slope values obtained, it can generally be estimated that an average of one molecule of DMDPHDTMA and two molecules of DMDCHDTMA for each Ag(I) are involved in the metal ion extraction.

Concerning the effect of acidity (1 to 5 M) for a constant 5 M chloride concentration, for which mixtures of HCl and NaCl have been considered when adequate, a series of experiments have been performed to evaluate the dependence of the %E Ag(I) on increasing acidity (1, 2, 3, and 5 M HCl) of the aqueous phase. The %E of 1.4×10^{-3} M Ag(I) by 1×10^{-2} M DMDPHDTMA in 1,2-DCE were 21, 28, 34, and 44% [standard deviation (sd) ± 1%], respectively, whereas for DMDCHDTMA, using a similar set of experimental conditions, values of 50, 58, 62, and 67% (sd ± 1%), respectively, were obtained instead. These results denote that an increasing acidity in the aqueous phases favors the migration of the metal ion into the organic solutions.

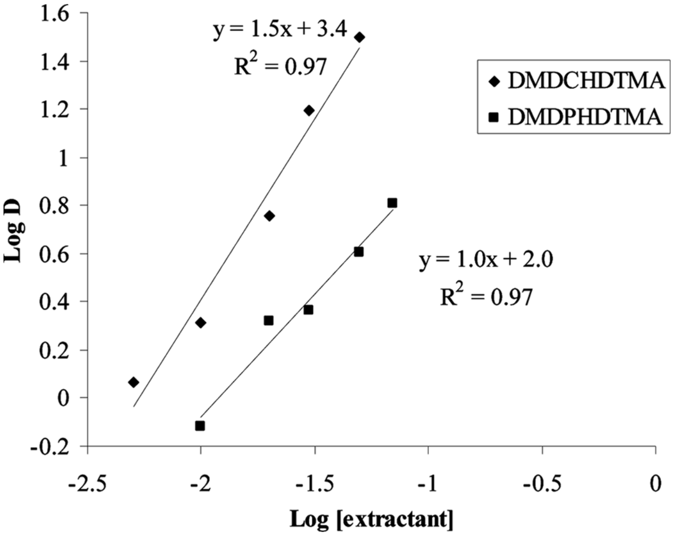

FIG. 4. Dependence of Ag(I) distribution coefficients on the initial extractant concentrations (1.4×10^{-3} M Ag(I) in 5 M HCl, DMDCHDTMA or DMDPHDTMA in 1,2-DCE, A/O = 1, room temperature, 1000 rpm, 30 minutes equilibration). Standard deviation associated to the %E values: ±2%.

To study the dependence of the Ag(I) distribution coefficients on the chloride content of the aqueous media, solutions containing about 3.7×10^{-4} M Ag(I) in at least 3 M HCl were considered, the variation of the chloride content achieved by the addition of adequate amounts of NaCl until a maximum of 5 M Cl^-(hence, the acidity was maintained constant). Organic solutions containing 1×10^{-2} M DMDPHDTMA or DMDCHDTMA in 1,2-DCE were used. The log-log plots obtained are displayed in Fig. 5.

The experimental points for both DMDPHDTMA and DMDCHDTMA fit well to straight lines, whose slopes are about minus five for DMDPHDTMA and about minus four for DMDCHDTMA. The slope values obtained suggest that an average of five chloride ions should be displaced from Ag(I) species when DMDPHDTMA is involved and about four for DMDCHDTMA, denoting the negative effect caused by increasing concentrations of chloride in the aqueous phases on Ag(I) extraction by both organic compounds. Similar results for the log D Ag(I) *vs.* log [Cl^-] plots were already found for TIBPS (6,8), TBPS and TOPS (11).

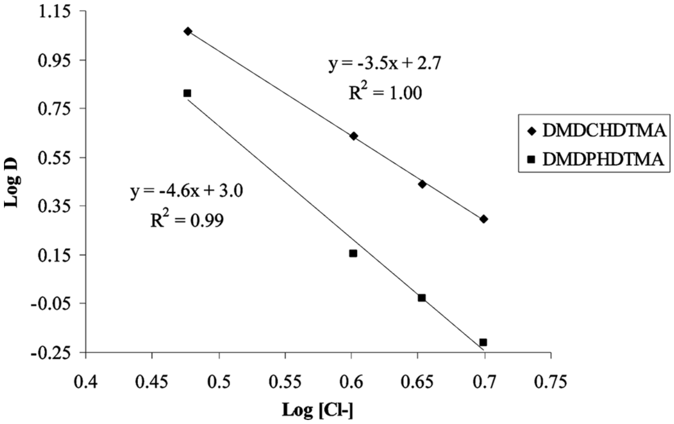

FIG. 5. Dependence of Ag(I) distribution coefficients on the total chloride concentrations in the aqueous phase (3.7×10^{-4} M Ag(I) in at least 3 M HCl, 1×10^{-3} M DMDCHDTMA or DMDPHDTMA in 1,2-DCE, A/O = 1, room temperature, 1000 rpm, 30 minutes equilibration). Standard deviation associated to the %E values: ±1%.

TABLE 4
Variation of the pH of distilled water, measured after contact with pre-equilibrated organic phases containing 2×10^{-2} M DMDPHDTMA or DMDCHDTMA in 1,2-DCE, and the calculated hydrogen ion concentrations transferred to water (Both contacts at similar experimental conditions: A/O = 1, room temperature, 1000 rpm, 30 minutes equilibration)

	ΔpH of distilled water (initial pH – pH after equilibration)	
Extractant	After equilibration with 5 M HCl	After equilibration with 1.4×10^{-3} M Ag(I) in 5 M HCl
DMDPHDTMA	~0	1.3 ($[H^+] = 3.4 \times 10^{-5}$ M)
DMDCHDTMA	1.6 ($[H^+] = 1.2 \times 10^{-4}$ M)	2.2 ($[H^+] = 1.8 \times 10^{-4}$ M)

A few experiments were additionally carried out to check the influence of increasing HCl concentrations on the %E Ag(I) (hence, both the acidity and chloride concentrations were changed). Aqueous phases containing 3.7×10^{-4} M Ag(I) in 3 M, 5 M, and 8 M HCl were equilibrated with 1.0×10^{-2} M DMDPHDTMA or DMDCHDTMA organic solutions. It was found that %E Ag(I), for DMDPHDTMA, were 87, 44, and 25% (sd ± 1%), whereas for DMDCHDTMA they were 92, 68, and 20% (sd ± 1%). It can be concluded that the negative effect on the %E Ag(I) caused by increasing chloride ion concentrations in the aqueous phases is stronger than the beneficial influence of higher acidities; these findings apply for both extracting systems.

FTIR and ^{1}H NMR spectra of both DMDPHDTMA and DMDCHDTMA after equilibration with HCl aqueous solutions (in the absence or presence of Ag(I)) were also plotted, evaluated, and compared with the respective spectra obtained for the initial extractants (see Experimental section for details). The results obtained revealed that the new spectra were similar to the former ones, suggesting that any protonation of the heteroatoms of the extractants or some sort of complexation did not occur.

In an ultimate effort to understand the eventual transfer of HCl from the feed aqueous phases to the organic solutions, 2.0×10^{-2} M Ag(I) DMDPHDTMA or DMDCHDTMA organic phases were contacted with 5 M HCl only or containing 1.4×10^{-3} M Ag(I), under the usual set of experimental conditions, and in sequence again similarly equilibrated with an identical volume of distilled water. The decrease of the pH values of the distilled water fractions achieved from the various experiments, if occurring, would denote the transfer of HCl from the organic solutions to the new aqueous phase. The results obtained are depicted in Table 4, and whenever a relevant pH variation was found, the hydrogen ion concentrations transferred from the pre-equilibrated organic phases to water were calculated.

It can be concluded that there are more significant ΔpH values (initial pH – pH after equilibration) when Ag(I) is present in the 5 M HCl aqueous phases for both dithiomalonamide derivatives, suggesting that Ag(I) favors the transfer of HCl to the organic phases. No Ag(I) was detected by AAS on all the distilled water fractions obtained. Furthermore, there was not any decrease in pH for DMDPHDTMA after equilibration with 5 M HCl only, whereas some HCl has been transferred when DMDCHDTMA is involved.

According to all the data collected and assuming that $AgCl_3^{2-}$ and $AgCl_4^{3-}$ are the main Ag(I) species existing in chloride aqueous phases varying between 3 and 5 M (8,29), the general reactions proposed as being responsible for Ag(I) extraction by either DMDPHDTMA or DMDCHDTMA are schematically presented in equations (1) and (2). L stands for DMDPHDTMA or DMDCHDTMA.

$$\begin{aligned} &AgCl_3^{2-}(aq) + m(H^+Cl^-)(aq) + nL(org) \rightarrow \\ &\quad [AgCl \cdot mHCl \cdot nL](org) + 2Cl^-(aq) \end{aligned} \tag{1}$$

$$\begin{aligned} &AgCl_4^{3-}(aq) + m(H^+Cl^-)(aq) + nL(org) \rightarrow \\ &\quad [AgCl \cdot mHCl \cdot nL](org) + 3Cl^-(aq) \end{aligned} \tag{2}$$

The variable *n* is one for DMDPHDTMA and about two for DMDCHDTMA; the variable *m* is expected to be greater for DMDCHDTMA than for DMDPHDTMA, and its magnitude, according to the experimental results collected, may be lesser than one.

It should be taken into account that these "solvation" Ag(I) chlorocomplex extraction reactions proposed are qualitative, as the slopes determined from the log D *vs.* log [Cl$^-$] plots would suggest the release of about four or five chloride anions from the coordination sphere of Ag(I) species and not two or three, as displayed in Eqs. (1) and (2), respectively. As it was written before, similar slope results have already been achieved for other systems studied before (6,8,11) and a totally satisfactory explanation to interpret such data has not still been found.

CONCLUSIONS

Two *N,N′*-tetraalkylated dithiomalonamide derivatives, namely *N,N′*-dimethyl-*N,N′*-diphenyldithiomalonamide (DMDPHDTMA) and *N,N′*-dimethyl-*N,N′*-dicyclohexyldithiomalonamide (DMDCHDTMA) were used as SX reagents towards Ag(I) in concentrated chloride media for the first time. Both dithiomalonamide compounds are very efficient in extracting Ag(I) up to 5 M chloride ion concentrations and a stabilized sodium thiosulfate solution is quite adequate to transfer Ag(I) to a new aqueous phase. DMDCHDTMA and DMDPHDTMA do show a very good loading capacity to accommodate Ag(I), as revealed by successive extraction-stripping stages. Both compounds do not exhibit selectivity towards the precious metal, as Fe(III) and Cu(II) are extensively extracted along with Ag(I). Equilibrium and spectroscopic studies allowed the proposal of qualitative "solvation" Ag(I) extraction reactions involving both DMDPHDTMA or DMDCHDTMA. However, further studies focusing on the clarification of the nature of the extracted species are still needed, eventually through the use of ion trap mass spectrometry fitted with an electrospray ionization source (ESI-MS); furthermore, the consideration of other techniques, able to detect the eventual occurrence of aggregation phenomena of the extractants in the organic phases, would also be worthwhile.

ACKNOWLEDGEMENTS

Thanks are due to Carlos M. Borges (CQB, DQB-FCUL) for the help provided in obtaining the ESI-MS spectra.

REFERENCES

1. Puvvada, G.V.K.; Sridhar, R.; Lakshmanan, V.I. (2003) Chloride metallurgy: PGM recovery and titanium dioxide production. *JOM*, 55 (8): 38.
2. Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G.R. (Eds.) (2004) *Solvent Extraction Principles and Practice*, 2nd Ed.; Marcel Dekker: New York, U.S.A., pp. 455.
3. Alam Shafiqul, M.; Inoue, K.; Yoshizuka, K.; Dong, Y.; Zhang, P. (1997) Solvent extraction of silver from chloride media with some commercial sulfur-containing extractants. *Hydrometallugy*, 44: 245.
4. Paiva, A. P. (1993) Solvent extraction and related studies on silver recovery from aqueous solutions. *Sep. Sci. Technol.*, 28 (4): 947.
5. Paiva, A. P. (2000) Review of recent solvent extraction studies for recovery of silver from aqueous solutions. *Solvent Extr. Ion Exch.*, 18 (2): 223.
6. Abe, Y.; Flett, D.S. (1992) Solvent extraction of silver from chloride solutions by Cyanex 471X. *Proc. International Solvent Extraction Conference ISEC'1990* (Sekine, T., Ed.), Elsevier Science Publishers, Amsterdam, pp. 1127.
7. Paiva, A.P.; Abrantes, L.M. (1994) Sulfur – phosphorus ligands in the solvent extraction of silver. *Proc. Extraction and Processing Division Congress, TMS Annual Meeting* (Warren, G.W., Ed.), The Minerals, Metals & Materials Society, Warrendale, pp. 243.
8. Paiva, A.P. (2005) Extraction of silver from chloride solutions – how to establish the chemical reactions? *Proc. International Solvent Extraction Conference ISEC'2005* (Conference Proceedings Editorial Department, Chinese Academic Journal), Beijing, pp. 74.
9. Rajesh Kumar, J.; Lee, H.-I.; Lee, J.-Y.; Kim, J.-S.; Sohn, J.-S. (2008) Comparison of liquid-liquid extraction studies on platinum(IV) from acidic solutions using bis (2,4,4-trimethylpentyl) monothiophosphinic acid. *Sep. Purif. Technol.*, 63: 184.
10. Facon, S.; Avila Rodriguez, M.; Cote, G.; Bauer, D. (1993) General properties of bis (2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301®) in acidic liquid-liquid extraction systems. *Proc. International Solvent Extraction Conference ISEC'1993* (Logsdail, D.H., Slater, M.J., Eds.), Society of Chemical Industry, Elsevier Applied Science, London and New York, pp. 557.
11. Capela, R.S.; Paiva, A.P. (2002) Solvent extraction of silver from concentrated chloride solutions: Use of tri-n-butyl- and tri-n-octylphosphine sulphides. *Proc. International Solvent Extraction Conference ISEC'2002* (Sole, K.C., Cole, P.M., Preston, J.S., Robinson, D.J., Eds.), Chris van Rensburg Publications: Melville, pp. 335.
12. Zuo, G.J.; Muhammed, M. (1990) Extraction of gold and silver by thiourea-based reagents. *Sep. Sci. Technol.*, 25 (13–15): 1785.
13. Paiva, A.P. (2001) Silver ion extraction reactions by dibutylthiourea (DBT) or *disulfiram* (DSF) from concentrated chloride solutions. *Proc. Extraction and Processing Division Congress, TMS Annual Meeting* (Taylor, P.R., Ed.), The Minerals, Metals & Materials Society, Warrendale, pp. 665.
14. Paiva, A.P. (2001) Sulphur-nitrogen ligands in the solvent extraction of silver from chloride solutions. *Proc. International Solvent Extraction Conference ISEC'1999* (Cox, M., Hidalgo, M., Valiente, M., Eds.), Society of Chemical Industry, London, pp. 399.
15. Ohto, K.; Yamaga, H.; Murakami, E.; Inoue, K. (1997) Specific extraction behavior of amide derivative of calix[4]arene for silver(I) and gold(III) ions from highly acidic chloride media. *Talanta*, 44 (6): 1123.
16. Sevdić, D.; Meider, H.; Pavković, D. (1990) Solvent extraction of silver and mercury by *O,O*-di-butyl-phenylamino-phenylmethanethio phosphonate from chloride solutions. *Solvent Extr. Ion Exch.*, 8 (4–5): 643.
17. Irving, H.M.N.; Damodara, A.D. (1969) Extraction of silver(I) from hydrochloric acid solutions of tri-normal-hexylammonium and tetra-normal-hexylammonium chloride in organic solvents. *Anal. Chim. Acta*, 48 (2): 267.
18. Costa, M.C.; Peczek, I.; Sadowski, Z.; Natu, S.; Paiva, A.P. (2007) The solvent extraction of iron(III) from chloride solutions by *N,N′*-tetrasubstituted malonamides: Structure-activity relationships. *Solvent Extr. Ion Exch.*, 25 (4): 463.
19. Malik, P.; Paiva, A.P. (2008) Solvent extraction of rhodium from chloride media by *N,N′*-dimethyl-*N,N′*-diphenyltetradecylmalonamide. *Solvent Extr. Ion Exch.*, 26 (1): 25.
20. Malik, P.; Paiva, A.P. (2009) Solvent extraction studies for platinum recovery from chloride media by a *N,N′*-tetrasubstituted malonamide derivative. *Solvent Extr. Ion Exch.*, 27 (1): 36.
21. Daubinet, A. (2001) Design, synthesis and evaluation of silver-specific ligands. *Ph.D. Thesis*, Rhodes University: Grahamstown, South Africa.
22. Pellacani, G.C. (1974) Palladium(II) complexes with dithiomalonamide and *N,N′*-diphenyldithiomalonamide. *Can. J. Chem.*, 52: 3454.
23. Ishii, H.; Minegishi, M.; Odashima, T. (1991) Extractive spectrophotometric determination of micro amounts of palladium with *N,N′*-diphenyldithiomalonamide (DPDTA) and equilibria and kinetics of extraction of palladium with DPDTA. *Anal. Sci.*, 7: 73.
24. Kisenyi, J.M.; Willey, G.R. (1985) *N,N′*-disubstituted complexes of antimony(III). Crystal and molecular structure of $[SbCl_3\{C_2H_5NHC(S)CH_2C(S)NHC_2H_5\}]^*$ with lone-pair occupation of an antimony coordination site. *J. Chem. Soc. Dalton Trans.*, 1073.
25. Pal, T.; Ganguly, A.; Maity, D.S.; Livingstone, S.E. (1986) *N,N′*-diphenyldithiomalonamide as a gravimetric reagent for nickel and cobalt. *Talanta*, 33 (12): 973.

26. Willey, G.R.; Baker, R.J.; Haslop, J.V.; Spry, M.P.; Drew, M.G.B. (1998) Coordination studies of the ligand series $RNH \cdot CØ \cdot (CH_2)_n \cdot CØ \cdot HR$ where R = alkyl, aryl; Ø = O, S and n = 0,1,2. Part 6. Crystal structures and bonding considerations of the ligands MeNH. $CO \cdot CH_2 \cdot CO \cdot NHMe$ (L^1), $MeNH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHMe$ (L^4), $MeNH \cdot CS \cdot CH_2 \cdot CS \cdot NHMe$ (L^5) and the Sn^{IV} complexes $SnBr_4L^1 \cdot L^1$, $SnBr_4L^2 \cdot 2$ THF and $SnBr_4L^3 \cdot MeCN$ where $L^2 = {}^iC_3H_7NH \cdot CO \cdot CH_2 \cdot CO \cdot NH^iC_3H_7$ and $L^3 = {}^iC_3H_7NH \cdot CS \cdot CH_2 \cdot CS \cdot NH^iC_3H_7$. *Polyhedron*, 17 (19): 3291.
27. Mikhailov, O.V.; Kazymova, M.A.; Shumilova, T.A. (2008) Mild template synthesis in the Cu(II)-dithiomalonamide-formaldehyde ternary system. *Russ. J. General. Chem.*, 78 (2): 258.
28. Rickelton, W.A.; Robertson, A.J. (1987) Selective recovery of silver by solvent extraction with triisobutylphosphine sulfide. *Min. Metall. Proc.*, February, 7.
29. Malik, P., Paiva, A.P., Neng, N., Nogueira, J.M.F. (2007) The mutual effect of iron(III) and silver(I) species in concentrated chloride medium. *Sep. Sci. Technol.*, 42 (6): 1267.