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# Open-Chain Thioethers as Extractants of Silver

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NOTE

# Open-Chain Thioethers as Extractants of Silver

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Solvent extraction (SX) is a well-established separation technique which has been widely used in extractive metallurgy when it represents a profitable alternative (1).

The scarcity and particular properties of precious metals justify the interest in the optimization of the related extractive processes in which SX is included (2, 3). In fact, the leaching solutions remaining from the metallurgical treatment of some complex sulfide ores, such as pyrite and chalcopyrite, usually contain traces of silver. Thus, the selective recovery of this precious metal by an organic extractant from sulfuric and especially from hydrochloric media would be quite interesting.

It is widely known that the efficiency in the extraction of precious metals is associated with phosphorus and/or sulfur atoms in the molecules of the organic extractants (4, 5). Therefore, good extraction yields for silver contained in a sulfuric medium have been reported when triisobutylphosphine sulfide is used as the extractant. This organic ligand also exhibits a remarkable selectivity for this metal in the same medium, especially against copper and zinc (4). Different types of open chain and macrocyclic thioethers were also reported to be good extractants for silver ion when contained in a 1-M nitric acid medium (5), but their selectivity of extraction has not been tested.

It is thus evident from the literature that the selective extraction of silver from hydrochloric solutions has not been exhaustively investigated. Therefore, the extraction efficiencies of some open chain thioethers and oxathioethers similar to those tested by Dietze and coworkers (5) were

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evaluated for the extraction of silver from hydrochloric solutions, as well as from 1 M sulfuric acid medium. This work was then carried out in an attempt to analyze the influence of some structural features—the length of the carbon chains between two sulfur atoms, the number of sulfur and/or oxygen atoms and their corresponding environments—in the extraction abilities presented by the ligands toward silver. Some of the ligands were also evaluated regarding their selectivity of extraction from a chloride medium, in which traces of silver coexist with excesses of iron, copper, and lead in solution.

The syntheses of thioethers and oxathioethers tested were performed using classical methods (5), respectively by reaction, under nitrogen atmosphere, of the correspondent alkyl chlorides with the related thiolates and of the alkyl chlorides (or oxaalkyl chlorides) with the related oxathiolates (or thiolates), in refluxing ethanol. Crude products were obtained by extraction and purified by vacuum distillation. The purity of the organic ligands was evaluated by $^1$H NMR and thin-layer chromatography. Octyl sulfide (Aldrich, 96%) was used as received.

Table 1 shows the percentages of extraction and the related extraction coefficients *D* presented by Ligands **1** to **9** in relation to silver contained in sulfuric and in chloride media (experimental conditions as indicated).

From the analysis of the table can immediately be concluded that, for the same experimental conditions regarding the extraction, Ligands **1** to **9** are good extractants of silver from a 1 M sulfuric medium and rather poor extractants of silver from the chloride solution tested.

As the rate of extraction is similar in both media, it seems reasonable to assume that the different behaviors presented by the ligands depend on the distinct nature of the aqueous phases involved. In fact, silver must exist predominantly in the form of the anionic chloro complexes $AgCl_4^{3-}$ and $AgCl_3^{2-}$ in the 5-M chloride medium used. Thus, the interaction of the organic ligands must be established with anionic species and not with silver cation, as is the case in sulfuric medium.

Ligand **1** was revealed to be an optimal extractant of silver from the sulfuric solution, markedly better than Ligand **2**, which can be explained by the lesser steric hindrance of the former. The different percentages of extraction presented by Ligands **3**, **4**, and **5**—in which the effect of increasing the carbon chain between the two sulfur atoms was tested—showed that Ligand **3** presents the most suited geometry to effectively extract silver cation. The ligand with three sulfur atoms proved to be a very good extractant. Nevertheless, Ligand **7**, in which one of the sulfur atoms was replaced by an oxygen atom, showed still more affinity for the silver ion. The inclusion of one more oxygen atom decreased the percentage of extraction, while Ligand **9**, in which the effect of replacing

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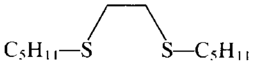
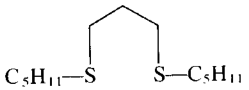
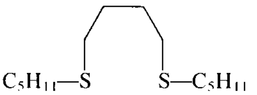
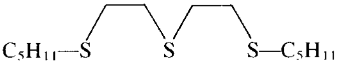
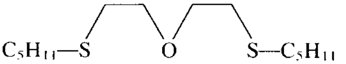
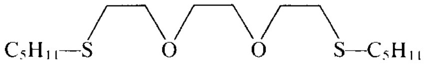
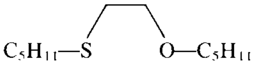
TABLE 1

Percentages of Extraction and Extraction Coefficients *D* of 20–40 ppm of Silver Contained in a 1-M Solution of $H_2SO_4$ (S) and in a 0.3-M HCl + 4.7 M NaCl Chloride Solution (C) (50 g·L$^{-1}$ of ligand in $CHCl_3$, room temperature, A/O = 1, 30 minutes of shaking, metal concentrations evaluated in the aqueous phases, before and after extraction, by Atomic Absorption Spectrophotometry using a SP9 Pye-Unicam model)

| Ligands | | Percent extraction | | Extraction coefficient | |
|---|---|---|---|---|---|
| | | S | C | *D*(S) | *D*(C) |
| **1** | $C_8H_{17}$—S—$CH_3$ | 99.5 | 1.0 | 214 | 0.01 |
| **2** | $C_8H_{17}$—S—$C_8H_{17}$ | 87.5 | 7.7 | 7 | 0.08 |
| **3** |  | 94.6 | 7.5 | 18 | 0.08 |
| **4** |  | 86.7 | 3.0 | 7 | 0.03 |
| **5** |  | 72.5 | 1.5 | 3 | 0.02 |
| **6** |  | 96.7 | 0.3 | 28 | 0.003 |
| **7** |  | 99.0 | 0.0 | 101 | — |
| **8** |  | 87.1 | 15.0 | 7 | 0.2 |
| **9** |  | 53.6 | 15.0 | 1 | 0.2 |

one sulfur atom by an oxygen atom in relation to Ligand **3** was tested, revealed to be the worst of the whole series. This fact can be attributed to the greater hydrophilicity of the formed silver complex involving Ligand **9.**

A quite different approach has to be made in order to explain the results obtained when the chloride medium is involved. In fact, with the exception

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of Ligands **3**, **4**, and **5**, in which the percentages of extraction varied in the same order as in sulfuric solution, the ligands which were the best for the extraction of silver from sulfuric medium were revealed to be the worst for the extraction from chloride solution. The real affinity for silver cation presented by Ligands **1**, **6**, and **7** cannot be spread to silver contained in a chloride solution, in which the existence of $Ag^+$, even considering that the equilibria of the anionic species would be quite forced to produce its formation, can be neglected.

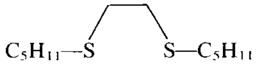
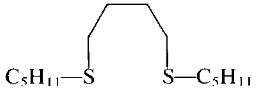
Curiously, Ligands **8** and **9** revealed the best affinities for extracting silver from this medium. As Ligand **7** showed no extraction at all, specific geometrical requirements together with the presence of oxygen atoms may be determinant for increasing of the extraction power presented by them. Moreover, this latter feature, which normally increases the hydrophilicity of the ligand, can possibly contribute to a better efficiency for the extraction from an aqueous medium with these specific characteristics.

Additional experiments with Ligands **1**, **3**, **5**, and **8** were performed in order to evaluate their selectivity in the extraction of silver when copper (500 ppm), lead (2000 ppm), and iron (2000 ppm) coexist in the chloride solution. The results obtained are listed in Table 2.

An increase in silver extraction was observed, caused both by the use of a higher ligand concentration and a possible synergistic effect brought

TABLE 2

Selectivity of Extraction of 20 ppm of Silver Contained in a 0.3-M HCl + 4.7 M NaCl (150 $g \cdot L^{-1}$ of ligand in $CHCl_3$, other experimental conditions as presented in Table 1. All metals were determined by atomic absorption spectrophotometry, except iron, which was determined by a standard volumetric method)

| Ligands | | Percent extraction | | | |
|---|---|---|---|---|---|
| | | Silver | Copper | Lead | Iron |
| **1** | $C_8H_{17}$—S—$CH_3$ | 16 | 3 | 1 | 2 |
| **3** |  | 43 | 13 | 2 | 1 |
| **5** |  | 22 | 0 | 0 | 1 |
| **8** |  | 27 | 3 | 2 | 0 |

about by the other metals. In terms of selectivity, good results were obtained for the ligands tested; only Ligand **3** extracts copper considerably.

This study points out that thioethers, which are easily accessible by synthesis, appear to have promising efficiency for the extraction of silver from sulfuric media. The same is not true for silver extraction from chloride solutions; nevertheless, a remarkable selectivity has been found. From a practical point of view, the selectivity obtained with Extractant **5** in chloride media may justify a specific optimization.

Although there is evidence of the important role played by structural modifications, further study must be carried out of the analysis and interpretation of the interface phenomena in order to clarify the mechanisms of extraction in both media.

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