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COORDINATING POLYMERS BASED ON PHOSPHINE SULPHIDE FOR THE ADSORPTION OF PRECIOUS METALS

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RESUM

En aquest treball es descriu la preparació de diversos polímers coordinants mitjançant derivatització d'una matriu microporosa de poliestirè a la que s'ha incorporat sulfur de tri-isobutil fosfina com a grup funcional. S'ha estudiat la influència de diferents espaiadors entre la matriu i el grup funcional en l'adsorció d'or (III) o plata (I) a partir de dissolucions d'àcid clorhídric i nítric respectivament. Els resultats obtinguts mostren que la presència d'àtoms d'oxigen a l'espaiador és essencial per a l'efectivitat del procés d'adsorció dels ions metàl·lics esmentats. S'ha observat que aquestes reïnes mostren una major afinitat per la plata que per l'or, obtenint-se tant una major capacitat d'adsorció com una velocitat més ràpida de procés d'adsorció. Aquestes característiques s'han relacionat amb aspectes estequiomètrics i estructurals de les espècies químiques implicades en el procés d'adsorció.

RESUMEN

En este trabajo se describe la preparación de varios polímeros coordinantes mediante derivatización de una matriz microporosa de poliestireno a la que se ha incorporado sulfuro de tri-isobutil fosfina como grupo funcional. Se ha estudiado la influencia de diferentes espaciadores entre la matriz y el grupo funcional en la adsorción de oro (III) o plata (I) a partir de disoluciones de ácido clorhídrico y nítrico respectivamente. Los resultados obtenidos muestran que la presencia de átomos de oxígeno en el espaciador es esencial para la efectividad del proceso de adsorción de los iones metálicos mencionados. Se ha observado que estas resinas muestran una mayor afinidad por la plata que por el oro, obteniéndose tanto una mayor capacidad de adsorción como una velocidad más rápida de dicho proceso. Estas características se han relacionado con aspectos estequiométricos y estructurales de las especies químicas implicadas en el proceso de adsorción.

ABSTRACT

In this work is described the preparation of various coordinating polymers by derivatization of a microporous polystyrene matrix with tri-isobutyl phosphine sulphide as functional group. The influence of different spacers between the matrix and the functional group has been studied in the adsorption of gold (III) and silver (I) from hydrochloric and nitric acid solutions respectively. The results obtained show that the presence of oxygen atoms in the spacer is essential for the effectivity of the adsorption process of the metallic ions mentioned before. These resins show a bigger affinity for silver than for gold, and it is obtained a major adsorption capacity and a faster kinetic for silver in this process. These characteristics have been related with stoichiometrics and structural aspects of the chemical species in the adsorption process.

Keywords: Coordinating polymer, Tri-isobutyl phosphine sulphide, Adsorption, Resin, Au, Ag.

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1. INTRODUCTION

The separation and recovery of precious metals from low grade source is of a high interest due to the high cost and scarcity of these metals. Many efforts in searching and synthesizing new reagents that can selectivity react with these metals have been done in the last decade.

Gold, silver, copper (I) and palladium are classified as "soft acids" by the Pearson theory (1) and can be selectively extracted by reagents containing "soft bases" as donor atoms, such as sulfur.

Some work have been reported on the extraction of various metals by extractants containing both sulfur and phosphorous, e.g. Cyanex 471X® (Cyanamide Inc., USA (2). The active species in Cyanex 471X is tri-isobutylphosphine sulfide (TIBPS) and it has been successfully used in liquid-liquid extraction of silver (3, 4) and gold (5), in liquid membranes (6), and in solvent impregnated resins (7).

Solid-liquid separation is the most appropriate method for mineral and hydrometallurgical applications since big volumes can be treated. On the other hand, the use of organic solvents, which may cause environmental problems, is avoid. For these reasons, the applicability of ionic (8, 9, 10) and coordinating resins (11, 12) has increased in the last years.

Ion exchangers are not soluble in aqueous solutions but they can effectively exchange their ions for other ions present in the aqueous phase. Most of the commercial resins are cation or anion exchangers. They are very effective to adsorb some ionic species from aqueous solutions, but their selectivity is very poor. In order to solve this problem, coordinating resins containing selective functional groups are a good alternative. In this sense, ligands usually utilized as extractants in liquid-liquid separations can also be covalently bound to a cross-linked polymeric matrix.

In a previous work (13) new microporous coordinating resins selective to gold and silver with a functional group based on TIBPS were synthesized. In this work, spacers between the polymeric matrix and the functional group of different nature have been introduced during the synthesis process. The use of a spacer can affect the kinetics of the adsorption process and the capacity of the resin. These effects depend mainly on two factors :

- *Spacer length* (number of atoms in the spacer). Generally, increasing the distance between the matrix and the functional group helps to form more stable complexes due to an increase of the flexibility of the chain (4).
- The presence of *heteroatoms* in the spacer molecule can increase the capacity of the polymer by either coordinating the metal or increasing the hydrophilicity of the polymer that leads to a higher intimate contact with the aqueous solution.

In order to understand the effect of the spacer three functional polymers have been prepared by inserting the specific spacer between the polymer matrix and the coordinating group.

The solid extractants have been studied for the adsorption of some precious metals (Au(III) and Ag(I)) from acidic solutions.

2. EXPERIMENTAL

2.1. Reagents

The matrix polymer used in the synthesis was Merrifield's Peptide Resin (chloromethylated divinylbenzene cross-linked polystyrene, with approx. 1 meq. Cl per gram and 2% cross-linked) (Aldrich). The spacers that have been introduced in it were 2-(2-(2-Chloroethoxy)-Ethoxy)-Ethanol (Aldrich), 6-Chloro-1-Hexanol (Aldrich) and 8-Chloro-1-Octanol (Aldrich). Other reagents used were Tetrahidrofurane (THF) (Aldrich), Sodium (Probus), Benzophenone (Scharlau), Acetone (Carlo Erba), 1-4 Dioxane (Aldrich), Diethyl Ether (BDH), Natrium Hydride (Aldrich), Diethylphosphite (Aldrich), Isobutylmagnesium chloride 2 M in Diethyl Ether (Aldrich), N,N-Dimethylaniline (Aldrich) and Phosphorus pentasulfide (Aldrich).

Stock standard solutions of 1000 ppm of Ag(I) or Au(III) were prepared by dissolving $AgNO_3$ (Johnson and Mattey Chemicals Ltd.) in HNO_3 1.0 M and $HAuCl_4$ (Merck) in 1.0 M HCl. All the reagents were of analytical grade.

2.2. Preparation of the polymeric matrix

The solid matrices are copolymers of styrene and divinylbenzene chloromethylated (Merrifield Polymer).

In all cases, the starting polymers were carefully washed sequentially as follows :

- Purification washes: 1:1 (v/v) Tetrahydrofurane (THF):Water, 1:4 (v/v) THF:Water, 1:5 (v/v) THF:Water, 1:1 (v/v) THF:Acetone, 1:2 (v/v) THF:Acetone and 1:1 (v/v) THF:Acetone.
- Dry washes: 4:1 (v/v) THF:Diethyl Ether, 2:1 (v/v) THF:Diethyl Ether, 1:1 (v/v) THF:Diethyl Ether, 1:2 (v/v) THF:Diethyl Ether, 1:2 (v/v) THF:Diethyl Ether, 1:4 (v/v) THF:Diethyl Ether and pure Diethyl Ether.

The samples were then dried under vacuum until the OH band was observed to disappear in the infrared spectra (IR) of the resins.

2.3. Apparatus

Gold and silver were determined with a SpectrAA-300 (Varian Instruments) Atomic Absorption Spectrometer. IR were measured in a Nicolet 205 FT-IR Spectrometer. Spectrophotometric UV measurements were done on a HP8452A Diode-Array Spectrophotometer (Hewlett-Packard), using 10 mm UV quartz cuvettes (Hellma).

3. RESULTS AND DISCUSSION

3.1. Preparation of the coordinating polymers

The procedure for the preparation of coordinating polymers is quite similar to the synthesis of analogous reagents ((by reaction of Merrifield Polymer and different spacers (fig. 1a). To introduce the spacer, a first reaction was carried out in THF at 80 ºC for 24 hours. In a second step, the polymeric matrix bearing the spacer reacts with $ClMgP(O)(iBu)_2$ in order to introduce the functional group (fig. 1b). This reaction takes place in THF at 80 °C for 15 hours. Finally, the phosphine oxide group was modified to a phosphine sulphide group by reaction with P_4S_{10}, obtaining then the functionalysed polymer (fig. 1c). This reaction was carried out in N,N-DMA at 120 °C for 15 hours.

In table 1, the spacers used and the obtained resin in each case are presented.

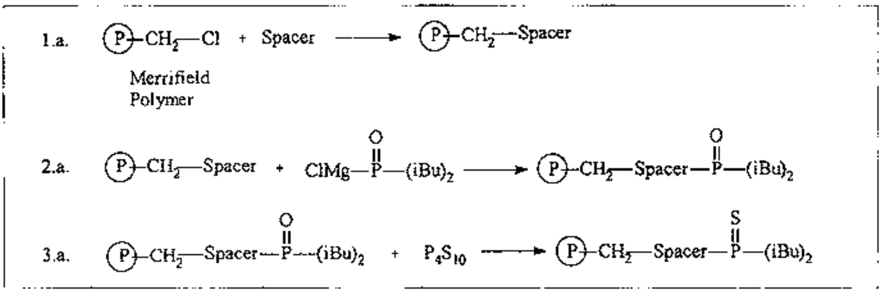

Fig. 1. Schematic preparation of resins. Ⓟ *represents the polymer matrix.*

	SPACER	POLYMER
TIBPS 1	$Cl—CH_2—(CH_2—O—CH_2)_2—CH_2—OH$	$Ⓟ—CH_2—(O—CH_2—CH_2)_3—\overset{S}{\overset{\|}{P}}—(iBu)_2$
TIBPS 2	$Cl—(CH_2)_6—OH$	$Ⓟ—(CH_2)_6—\overset{S}{\overset{\|}{P}}—(iBu)_2$
TIBPS 3	$Cl—(CH_2)_8—OH$	$Ⓟ—(CH_2)_8—\overset{S}{\overset{\|}{P}}—(iBu)_2$

Table 1. Spacers used in synthesis and result polymers.

3.2. Characterization of the functionalysed polymers

Due to the insolubility of the polymer, only elemental analysis and IR spectra are available for the characterization of the resins.

The content of S and Cl in the synthesized resins was determined by elemental analysis. The results collected in table 2 show that the functionalization of Merrifield Polymer is more than 99 % for TIBPS-1 and TIBPS-3. This percentage is calculated from the mmols of sulfur in the final polymer related to the mmols of chloride in the initial polymer. From the S content, the theoretical capacity of the resins has been calculated to have a value of 1 mmol/g for TIBPS-1 and TIBPS-3, and 0.5 mmols/g for TIBPS-2.

	Elements %				Ligand concentration (mmol/g)
	C	H	Cl	S	by S content
MP*	89.3	7.4	3.7	—	—
TIBPS-1	75.8	6.9	< 0.5	3.2	1.00
TIBPS-2	82.9	7.4	< 1.0	1.5	0.47
TIBPS-3	82.3	7.6	< 0.5	3.1	0.97

***Table 2.** Elemental analysis of the resins and Merrifield Polymer**

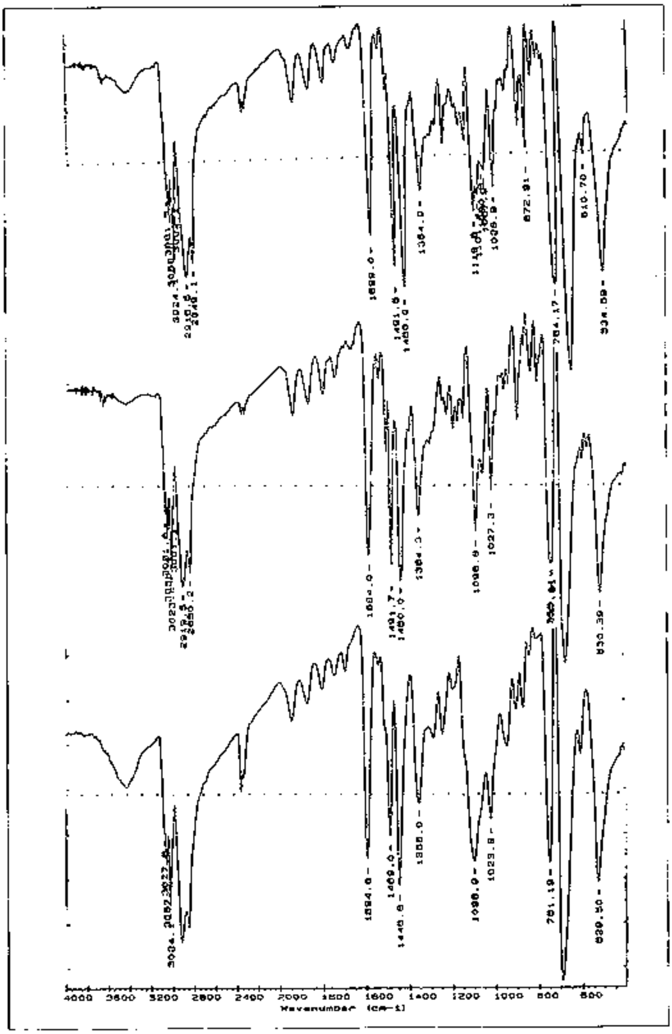

***Fig. 2.** IR spectra of the synthesized polymer.*

The IR spectra of all the resins are collected in fig. 2. From these spectra is possible to verify if the spacer molecules are present in the solid matrix. TIBPS-1 which carries a tri-ethoxylated spacer shows in its IR spectrum a strong absorption at ≈1100 cm^{-1} belonging to the $-CH_2-O-CH_2-$ stretching band. The C-Cl band (≈ 1200 cm^{-1}) has disappeared in all cases. The phosphine sulfide group (P=S) shows an absorption band at 600-610 cm^{-1} in all polymers.

The morphology of the beads was analyzed by scanning electron microscopy (SEM). Fig. 3 shows the photographs obtained by this technique. A particle size of about 50 μm of diameter can be determined.

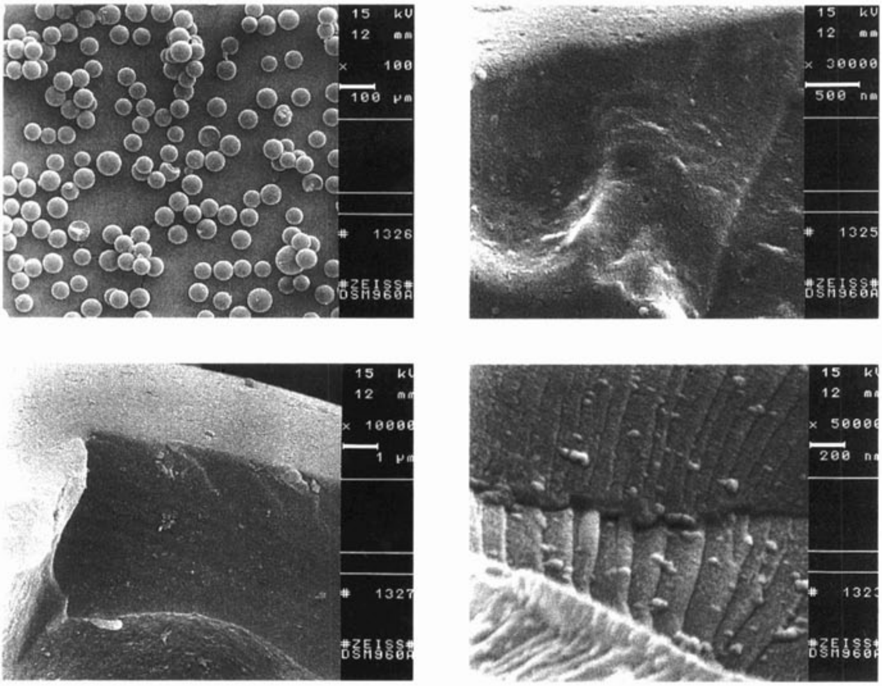

Fig. 3. Morphology of the beads of TIBPS-1 polymer. (Scaning Electronic Microscopy)

After their preparation, the resins were washed for their purification and dried before use.

3.3. Kinetics of metal adsorption.

In order to determine the capacity of the resins for gold (III), about 0.02 g of the polymer were stirred with 10 ml of acidic solution containing different concentrations of metal for 24 hours. Afterwards, the concentration of metal ion remaining in the aqueous solution was determined by AAS and the amount of loaded metal ion (in mmol/g resin) was calculated by applying mass balance. As seen in fig. 4, the amount of metal adsorbed increases with the initial concentration of gold solution until 0.020 mmols of Au(III), where a constant value is achieved. This result corresponds to TIBPS-1 resin, the other resins, TIBPS-2 and TIBPS-3, have shown a very low adsorption of the metal during the same period of time.

On the other hand, the absence of the functional group in the polymer produces no adsorption of the metal ions, i.e. either Merrifield Polymer or the polymer bearing the spacer show that gold (III) and silver (I) are not adsorbed after a long period of contact with the respective solutions.

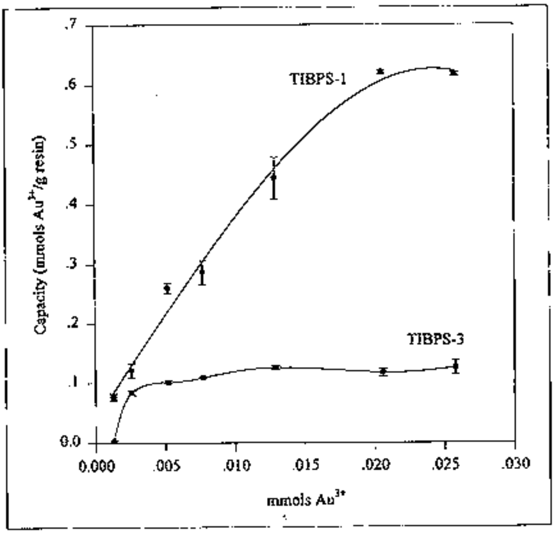

Fig. 4. Study of Au-binding in front of the amount of gold in the feed solution. Experimental conditions: 0.02g of resin, 10 ml feed solution in 1.0 M HCl, room temperature.

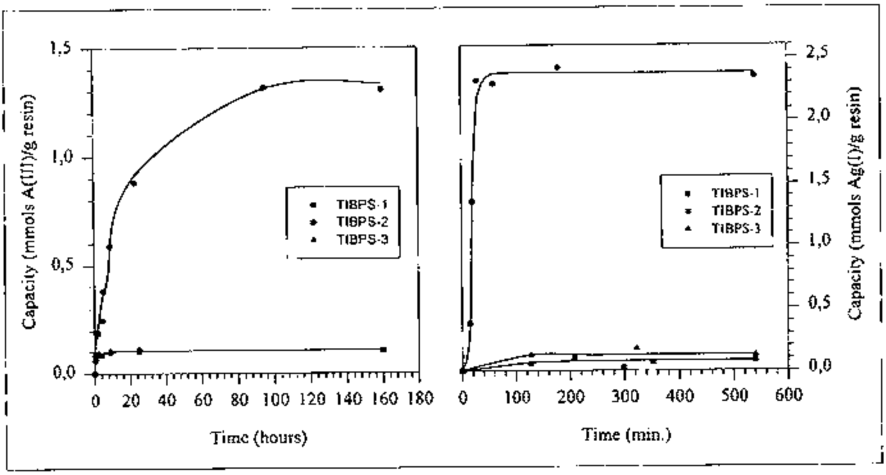

Fig. 5. Capacity for gold adsorption and silver adsorption by different resins. Experimental conditions: batch experiments, 0.02 g resin, 10 ml feed solution containing (1000 ppm of metal and 1.0 M acid, room temperature.

The kinetics of the adsorption process of Au(III) and Ag(I) was studied for the three polymers under similar experimental conditions. The results collected in fig. 5 confirm that only the polymer TIBPS-1 can adsorb these metals giving a capacity of 1.3 and 2.4 mmols/g resin for gold and silver respectively .The other two polymers (TIBPS-2 and TIBPS-3) have a maximum capacity of 0.1 mmols/g resin for each metal. Such a low value compared with the obtained before may be explained by the presence of oxygen atoms in the spacer in the case of TIBPS-1 which seems to favor the adsorption of gold and silver.

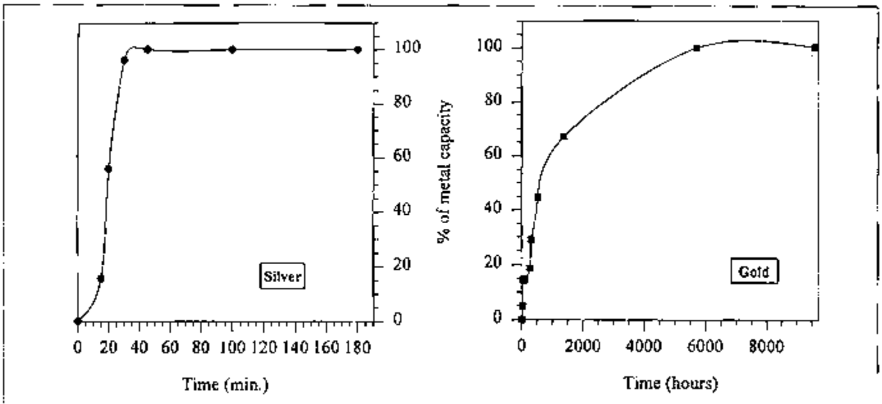

Fig. 6. *The kinetics of Au and Ag for TIBPS-1. Experimental conditions: batch experiments, 0.02 g resin, 10 ml feed solution containing (1000 ppm of metal and 1.0 M acid, room temperature.*

Theoretical capacity of the TIBPS-1 resin was estimated by the S content in the polymer (see table 2). According to literature data (14, 15) were assumed a 1:1 stoichiometry for the corresponding metal complexes. The experimental results obtained with gold are in agreement with this assumption, however the value obtained with silver is two times the theoretical capacity. An explanation for these results can be given on the basis of a possible interaction of one functional group with two silver ions. In the gold case, the stoichiometry is 1:1 probably due to the tetra-chloro complex of this metal in solution and a steric hindrance can be expected from such a complex.

The loading half time, $t_{1/2}$ (time needed to reach 50 % of the resin's final loading capacity), are also different for the two metals, approximately 20 minutes for silver and 75 hours for gold (estimated from fig. 6). Also, in this case, the higher affinity of silver towards the sulfur containing ligand may explain such a differences.

4. CONCLUSIONS

The study has shown the influence of the nature of spacers in the adsorption process of noble metals. The presence of an heteroatom, in our case oxygen, in the structure of the spacer molecule (TIBPS polymer) provide the best results for the adsorption process, due to the increase of hydrophilicity of the resin with a tris-ethoxylated chain (16). In this case, the capacity values obtained are 1.3 mmols Au(III)/g resin and 2.4 mmols Ag(I)/g resin. When the spacer do not contain any heteroatom, the polymers practically do not adsorb these metals.

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