

SYNTHESES OF POLYSTYRENE RESINS CONTAINING POLYETHER OLIGOMERS AND THEIR EXTRACTION FOR GOLD (III)*

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ABSTRACT

Three polystyrene resins containing polyether oligomers as extractants were synthesized and their extraction properties were studied. Gold (III) ion could be extracted rapidly by the resins ($T_{1/2} < 1\text{min.}$) with high efficiency and capacity (for LS-B resin that were 99.8% and 95.8mg/gR respectively) from aqueous solution but most of the co-existing metal ions such as Pd (II), Cu(II), Zn (II), Pb (II) and Cd (II) were remained. The extraction capacity and stripping percentage for gold (III) remained unchanged in four extraction-stripping cycles. The resins also showed good column extraction-elution properties.

INTRODUCTION

Despite the wide uses of Levextrel-type resins in the analytical and hydrometallurgical separation and in the enrichment of uranium and rare earth metals^[1], only a few of them were applied for the recovery of noble metals.

Xue^[2] has shown that Levextrel-type resin containing tributylphosphate (TBP) could extract gold (III) ion with high efficiency ($>95\%$) and selectivity in hydrochloric acid. The separation and enrichment of gold (III) with Levextrel-type resins containing Alamine 336 or 7402 ($\text{R}_3\text{NCH}_3^+\text{Cl}^-$) have been reported by Belfer^[3] and Zhuang^[4].

The above approaches did not meet the satisfaction of the hydrometallurgical industry. This seems to be due to the deficiency of the low-molecular-weight extractants which the resins contained.

Oligomer extractants, which have high extraction capacities and selectivity for noble metal ions, would hardly leak from the substrate due to their comparative high molecular weight and low solubility in aqueous solution as well as the expectable tangle of the reagent and matrix chains when the extractants were encapsulated in the resins. Thus the flexibility of the resins will be reduced and the lifetime prolonged.

The work described in this paper consists of the syntheses of three novel Levextrel-type resins containing poly (epoxypropyl alkyl ether) oligomer as extractant (LS resins) and the study on the extraction of these resins for gold (III).

EXPERIMENTAL

Chemicals and materials

Styrene (ST) and divinyl benzene (DVB C. P.) were washed with a 5% aqueous solution of sodium hydroxide prior to polymerization. All epoxypropyl alkyl ethers and boron-trifluoride etherate (C. P.) were distilled before use. Gold perchloride ($\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$, AR), palladium chloride (PdCl_2 , AR) and platinum sheet (purity 99%) were used without further purification.

Syntheses of polyethers

Poly (epoxypropyl alkyl ether) oligomers were synthesized according to the method described before.^[5] All polymerization of epoxypropyl alkyl ethers were carried out under dry nitrogen atmosphere with stirring at the temperature of -15°C — 10°C using $\text{BF}_3\text{-Et}_2\text{O}$ as catalyst. A typical procedure was as follows: 20g of epoxypropyl ethyl ether was polymerized in presence of 0.68ml of anhydrous n-butanol and 20ml of a solution of 10% $\text{BF}_3\text{-Et}_2\text{O}$ in 1,2-dichloroethane as catalyst under dry nitrogen atmosphere with stirring for about 5 hrs and at 20°C for 24 hrs. The resulting mixture was subsequently dissolved in 50ml of 1,2-dichloroethane and washed with water until neutral. After removal of the solvent and unreacted monomer the resultant oligomers were dried to constant weight in vacuum ($80^\circ\text{C}/134\text{Pa}$). The molecular weight of polyethers was determined by VPO.

Syntheses of LS resins

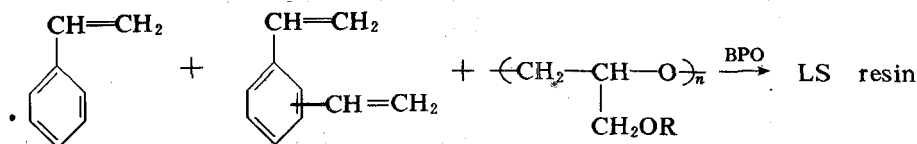
A typical procedure was described in detail as follows: A solution of divinyl benzene (5.6g, content of divinyl benzene is 45%), styrene (4.4g), benzoyl peroxide (0.1g), toluene (5ml) and polyether oligomer (10g) as extractant was introduced into a mixture of 75 parts of water and 25 parts of a 2% polyvinyl-alcohol solution at 50°C . The suspension copolymerization was carried out for about 4 hrs at 80°C and subsequently heated at 95°C for 1 hr, and finally refluxed for 1 hr. After cooling, the resulting polymer beads were washed with boiling water and then dried to a constant weight in vacuum ($60 \pm 5^\circ\text{C}/670\text{Pa}$).

Test of extraction properties

The procedure to determine the extraction properties of LS resins for metal ions was described as the previous paper^[5].

RESULTS AND DISCUSSION*Syntheses of LS resin*

LS resins were synthesized through the copolymerization of styrene and divinyl benzene in the presence of the polyether oligomers, as shown below:



The experimental results of preparation of LS resins were listed in Table 1. The densities of LS-E and LS-B resins were given in Table 2.

Extraction properties of LS resins

Extraction efficiency dependence on medium acidity:

Table 1 Preparation of Levextrel-type resins

Resin *	Styrene (g)	Divinyl benzene (g)	Polyether **			Degree of crosslinking (%)
			R	M_n	(g)	
LS-M	4.4	5.6	CH ₃	970	10	25
LS-E	4.4	5.6	C ₂ H ₅	1370	10	25
LS-B ₁₅	6.6	3.4	n-C ₄ H ₉	1210	10	15
LS-B	4.4	5.6	n-C ₄ H ₉	1210	10	25
LS-B ₃₅	2.2	7.8	n-C ₄ H ₉	1210	10	35
LS-B ₄₅	0	10.0	n-C ₄ H ₉	1210	10	45

* The yield of LS-resins by this method was 90–95%.

** The structure of polyether is $\left(\text{CH}_2 - \underset{\text{CH}_2\text{OR}}{\text{CH}} - \text{O} \right)_n$

The influence of acidity on the extraction efficiency of LS-B resin was investigated in the different concentration of hydrochloric acid containing 100ppm Au(III), 100ppm Pd(II) or 100ppm Pt(IV) respectively. As shown in Fig. 1, the extraction efficiency of LS-B for Au(III), Pd(II), or Pt(IV) increased with the increasing of medium acidity. In a wide range of acidity,

the extraction efficiency of LS-B for Au(III) was more than 96%, and in more concentrated acid (4–6mol/L HCl) that was over 99%, whereas the extraction efficiency of LS-B for Pd(II) or Pt(IV) was rather low.

The extraction efficiency for Pd(II) increased 6% to 16% and that for Pt(IV) increased from 21% to 23% when the acidity increased from 1–6mol/L HCl. It was obvious that LS-B possessed high extraction efficiency and selectivity for gold (III) over a wide range of acidity.

Table 2 Density of LS resins (g/ml)

Resin(20–100 mesh)	LS-E	LS-B
Bulk density	0.32	0.53
Specific density	0.99	1.00

Extraction efficiency and capacity:

The extraction efficiency of LS resins for noble metal ions from hydrochloric acid solution containing 100 ppm Au(III), Pd(II) or Pt(IV) was given in Table 3. Table 4 summarized the capacities of these resins for metal ions. The results indicated that:

1. LS resins could extract strongly for Au(III) and Hg(II). Among these resins LS-B possessed the greatest extraction efficiency and capacity for Au(III) which was 99.8% and 95.8mg/gR respectively. Only a small percentage of Pd(II) ($\leq 6.1\%$) and Pt(IV) ($\leq 3.8\%$) was extracted whereas Cu(II), Pb(II) and Cd(II) ions were remained in the solution.

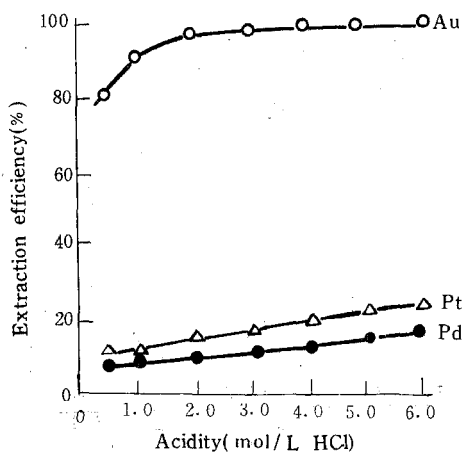


Fig. 1 The dependence of extraction efficiency of LS-B resin on acidity
○—Au; ●—Pd; △—Pt

Table 3 Extraction efficiency of LS resins (%)

Resin	LS-M	LS-E	LS-B15	LS-B	LS-B35	LS-45
Au(Ⅲ)(6mol/L HCl)	79.8	91.4	99.3	99.8	99.7	99.3
Pd(Ⅱ)(5mol/L HCl)	0.6	2.7	6.1	5.1	4.4	5.4
Pt(Ⅳ)(3mol/L HCl)	1.1	3.8	0.0	1.2	0.0	2.8

Table 4 Extraction capacity of LS resins (mg/gR) (pH=5.4)

Resin	LS-M	LS-E	LS-B15	LS-B	LS-B35	LS-45
Au(Ⅲ)*	25.2	47.2	87.5	95.8	92.6	95.6
Pd(Ⅱ)* *	1.0	0.4	2.0	1.5	1.8	1.2
Cu(Ⅱ)	—	0	0	0	—	0
Zn(Ⅱ)	—	0	0	0	—	0
Pb(Ⅱ)	—	0	0	0	—	0
Cd(Ⅱ)	—	—	0	0	0	—
Hg(Ⅱ)	—	76.2	128.4	128.4	—	126.4

* 6mol/L HCl, * * 5mol/L HCl

2. The extraction properties of LS resins were greatly affected by the structure of the extractants contained. The extraction efficiency and capacity of LS resin increased with the increasing carbon number of R group on the side chain ($-\text{CH}_2\text{OR}$) of the extractants, LS-M, where R was methyl, extracted only 79.8% of Au(III) with the capacity of 25.2mg/gR in 6mol/L HCl. When the R group was changed to n-butyl (LS-B), 99.8% of Au(III) was extracted and the capacity was 95.8mg/gR, about 2.8 times greater than that of LS-M.

3. The influence of the crosslinking degree of the polymer matrix on the extraction properties of LS resins was slight. When the crosslinking degree varied from 15% to 45% (LS-B15-LS-B45), the extraction efficiency for Au(III) almost unchanged (99.3%—99.8%) and the capacity of these resins was close to each other.

Reuse of LS resins:

Gold loaded LS resins could be stripped by the solution of 2.5mg/ml thiourea in 0.1mol/L hydrochloric acid. The extraction capacity and stripping percentage of LS-B in four extraction-elution cycles were given in Table 5.

Table 5 Reuse of LS-B resin

Run No.	1	2	3	4
Extraction capacity (mg/gR)	97.4	112.1	91.2	97.4
Stripping percentage(%)	108.3	86.7	92.4	89.9

The results showed that no significant change in the extraction and stripping properties happened after four extraction-elution cycles. The resin could be reused.

The increase of the capacity after the first cycle may result from the same mechanism of S-PTB resin^[5].

Extraction selectivity:

Au(III) could be extracted with high efficiency (96%) from the mixture of 100ppm Au(III) and 100ppm Pd(II) in 6mol/L HCl by LS-B resin but few of the co-existing Pd(II) ions were taken up (1.2%). Other LS resins also showed in Table 6.

Table 6 Extraction efficiency of LS in the mixture solution of Au(III) and Pd(II) (6mol/L HCl)

Resin	LS-E	LS-B15	LS-B	LS-B45
Au(III)	88.9	95.8	96.0	95.6
Pd(II)	3.4	0.9	1.2	1.5

In another artificial solution containing Au(III) (100ppm), Zn(II), Cu(II), Pb(II) and Cd(II) (0.0025mol/L for each), LS resins demonstrated their selectivity for gold (III) over base metal ions (Table 7). The extraction efficiency of LS-B for Au(III) was as high as 98.7% whereas that for Pb(II) and Cd(II) was very low (1.6% and 0.6% respectively) and none of the Cu(II) and Zn(II) ions was extracted. So it was possible for these resins to be used to recover gold from the solution containing trace Au(III) and other metals.

Extraction rate:

It has a fast speed for LS-B to extract Au(III) from the solution of 250ppm Au(III) in 6mol/L HCl at 30°C. The extraction efficiency exceeded 98% in five minutes and the equilibrium was reached in 40 minutes with the efficiency of 99.6%. $T_{1/2}$ was less than one minute. (Fig. 2)

Table 7 Extraction efficiency of LS in the mixture solution of metal ions (6mol/L HCl)

Resin	LS-E	LS-B15	LS-B	LS-B45
Au(Ⅲ)	88.1	99.0	98.7	98.6
Cu(Ⅱ)	0	0	0	0
Zn(Ⅱ)	0	0	0	0
Pb(Ⅱ)	3.4	2.3	1.6	1.9
Cd(Ⅱ)	1.6	1.6	0.6	2.0

Column extraction-elution

3.00g dry LS-B was soaked in HCl and then packed into a column ($\phi 9.8 \times 75\text{mm}$). An aqueous solution of 0.98mg/ml Au(III) in 6mol/L HCl was passed until the column was saturated. The eluent was collected every 10ml and the concentration of Au(III) was determined by ICP-AES (Fig. 3a, 3b)

The result indicated that LS-B column had excellent extraction ability for Au(III). When the column was saturated, the capacity was 50.0 mg/ml resin or 94.3mg/g resin, which was very close to that shown in Table 4.

Gold (III) loaded on LS-B could be eluted by 1 mol/L hydrochloric acid. Although the column was saturatedly loaded with gold, the elution curve was still symmetric. The stripping percentage was 88.8% when 200ml acid passed through the column. This may be attributed to the fact that gold (III) was easily subjected to reduction.

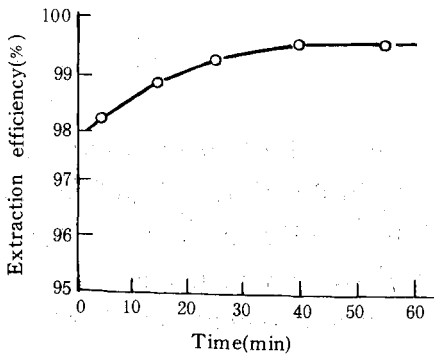


Fig. 2 Extraction rate of LS-B for Au(Ⅲ) (30℃)

Table 8 Column extraction-elution of LS-B resin

Weight of LS-B (g)	Column volume (mm)	Extraction capacity (mg/ml resin)		Stripping percentage %
		Breakthrough	Saturation	
3.00	$\phi 9.8 \times 75$	36.4	50.0	88.8

CONCLUSIONS

Polystyrene resins containing poly(epoxypropyl alkyl ether) oligomer as

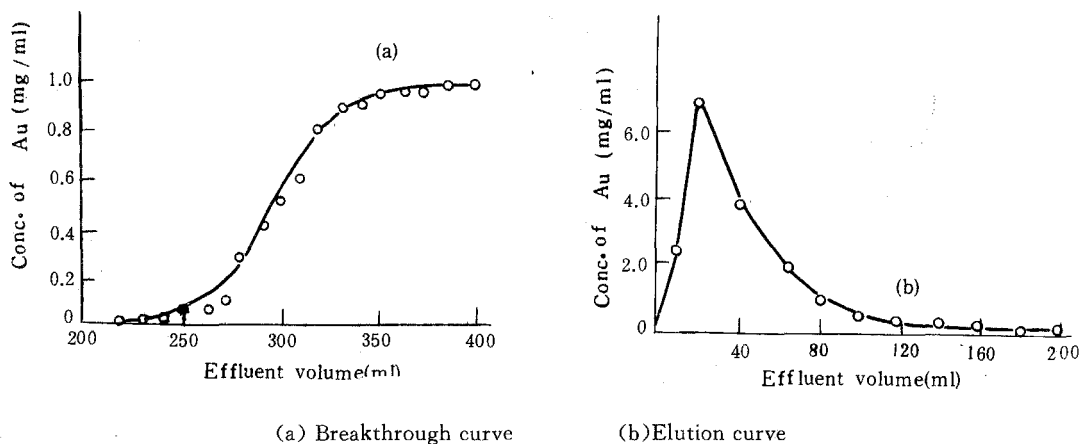


Fig. 3 Extraction-elution of LS-B column for Au(III)

extractants (LS reins) could extract gold (III) with high efficiency and capacity in 6 mol/L HCl and showed high selectivity over Pd(II), Zn (II), Cu(II), Pb (II) and Cd (II) ions. Gold (III) loaded on resins could be stripped and the resins could be reused. The column packed with LS resin also showed good extraction-elution properties for gold (III).

Keywords:

Gold; polyether oligomer; Levextrel-type resin

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