

## Polyethyleneimine supports for resins with retention properties for heavy metals. Part 3

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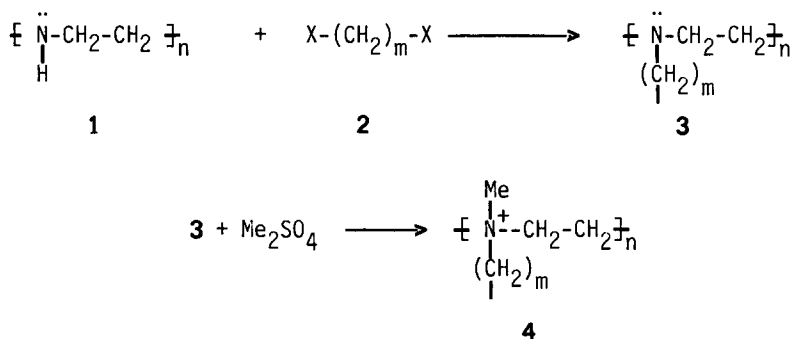
### SUMMARY

Resins with retention properties for copper(II) and uranium(VI) were synthesized by crosslinking of polyethyleneimine with 1,9-dibromononane and 1,10-dibromodecane, and subsequent alkylation with dimethylsulphate. The effect of the pH on the retention, elution assays in acid and basic medium, and maximum capacity of load were determined. Moreover, the thermal behaviour was studied.

### INTRODUCTION

Polymer-metal complexes are now of great interest (1-3). The formation of chelates by polymers has been used for concentration, separation, and extraction of metal-ion (4-5). The potential applications of the polymer-metal complexes probably outweigh the limitations for their study. The ability of polyethyleneimine (PEI) to complex heavy metal salts is well known (6-13).

In this paper are reported water-insoluble resins which were obtained by crosslinking reaction of PEI with organic halides, such as 1,9-dibromononane and 1,10-dibromodecane.



### EXPERIMENTAL PART

*Materials:* Polyethyleneimine (Aldrich Chem.Co.). All the chemicals were used such as except dimethylsulphate which was distilled (b.p. 188°C).

*Crosslinking of Polyethyleneimine:* The branched polyethyleneimine was crosslinked with 1,9-dibromononane (IM-2) and 1,10-dibromodecane (IM-3). The

reaction was carried out in heterogeneous phase using Span 65 as emulsifier (12).

*N-Alkylation of Crosslinked Polyethyleneimine:* This reaction was carried out at 95°C for 6 h using dimethylsulphate as alkylating agent and acetonitrile solvent (12).

*Measurements:* Uranium was analyzed on a PMQ II Carl Zeiss spectrophotometer. Copper and iron were analyzed on a Perkin Elmer 306 atomic absorption spectrophotometer. The thermal behaviour was studied by a Perkin Elmer TGS-1 Thermobalance.

## RESULTS AND DISCUSSION

To obtain resins with retention properties, particularly for copper (II), the branched polyethyleneimine was crosslinked with 1,9-dibromononane and 1,10-dibromodecane. To increase the selectivity for uranium(VI) these resins were N-alkylated with dimethylsulphate. All the resins are insoluble in water. The name used for the resins are shown on Table 1.

Table 1.- Crosslinkers and names of the resins.

Crosslinker	Name	
	Crosslinked Resin	N-Alkylated Resin
1,9-dibromononane	IM-2	IM-2M
1,10-dibromodecane	IM-3	IM-3M

The retention properties of the resins were determined by studying the effect of the pH; maximum capacity of load and elution.

### *Effect of pH on copper retention.*

To determine this parameter, a copper solution (1.0 g/l) was prepared at different pH's (0-4). Ten ml of these solution were contacted with 0.1 g of dry resin over 2 h with constant stirring; copper was analyzed in the aqueous solution. The results are shown in Table 2.

Table 2.- Percent adsorption of copper(II).

Resin	pH				
	0	1	2	3	4
IM-2	0.0	1.6	0.4	6.3	7.6
IM-2M	0.8	0.8	0.4	8.0	8.2
IM-3	3.3	72.4	76.9	76.0	76.9
IM-3M	0.0	0.0	0.0	0.3	0.3

Resins IM-2, IM-2M and IM-3M practically did not retain copper at any pH range assayed. Only resin IM-3 retains copper above 70% from pH=1 to 4.0. At pH=0 it retains only 3.3%. This behaviour is important as it retains significant amounts of copper at pH=2.0 and the resin can be recuperated by changing the pH.

*Effect of pH on uranium retention:*

In this case a solution containing 1.0 g/l in uranium was prepared. The pH range is 0-4. The procedure is similar to that with copper(II). The results for all resins are shown in Table 3.

Table 3.- Percent adsorption of uranium(VI).

Resin	pH				
	0	1	2	3	4
IM-2	36.9	80.1	86.1	80.5	66.3
IM-2M	41.3	75.0	97.2	98.1	97.2
IM-3	15.0	68.7	60.0	28.9	22.5
IM-3M	41.7	92.3	94.0	92.3	93.0

The N-alkylated resins retain more uranium than crosslinked resins. The N-alkylated resins contain mostly ammonium group ligands. Both resins, IM-2M and IM-3M, retain above 90% at pH=2.0 and have a good selectivity for uranium as they do not retain copper at this pH.

*Determination of the maximum capacity of load for copper(II) and uranium(VI)*

This parameter was determined at pH=2.0. Solutions containing 1.0 g/l uranium or 2.0 g/l copper were prepared. Three contacts were carried out(12).

Maximum capacity of load for copper(II) was determined only for IM-3 as the other resins did not retain this ion (see Table 4). For uranium it is between 2.0 and 4.4 meq/g dry resin. The best resin is IM-2M whose value is 4.4 which is similar to IRA-400, a commercial resin (10).

Table 4.- Maximum capacity of load for copper(II) and uranium(VI).

Resin	IM-2	IM-2M	IM-3	IM-3M
meq uranium per g dry resin	4.0	4.4	3.4	3.0
meq copper per g dry resin	-	-	1.5	-

*Elution assays for copper(II) and uranium(VI).*

Elution assays were carried out in basic ( $\text{Na}_2\text{CO}_3$ ) and acid medium ( $\text{H}_2\text{SO}_4$ ).

Loaded resins with copper(II) or uranium(VI) were contacted with  $\text{Na}_2\text{CO}_3$  or  $\text{H}_2\text{SO}_4$ . Results after one contact are shown in Table 5.

Table 5.- Percent elution of copper(II).

	Na <sub>2</sub> CO <sub>3</sub>				H <sub>2</sub> SO <sub>4</sub>			
	0.25M	0.5M	0.75M	1.0M	1.0M	2.0M	3.0M	4.5M
IM-2	-	-	-	-	-	-	-	-
IM-2M	1.1	1.2	1.3	1.4	18.5	19.0	19.1	19.5
IM-3	0.4	0.5	0.6	0.4	86.0	84.8	84.2	84.6
IM-3M	-	-	-	-	-	-	-	-

IM-2 and IM-3M were not examined as they did not retain practically any copper(II).

Table 6.- Percent elution of uranium(VI).

Resin	Na <sub>2</sub> CO <sub>3</sub>		H <sub>2</sub> SO <sub>4</sub>	
	0.25M	0.75M	1.0M	3.0M
IM-2	64.0	62.7	47.3	55.0
IM-2M	47.3	55.6	49.9	67.9
IM-3	61.0	65.6	44.1	49.1
IM-3M	47.0	56.3	72.9	91.2

For IM-3, sulphuric acid is a good eluent at any concentration range for copper. Elution is selective as copper is practically not eluted with sodium carbonate.

#### *Thermal stability.*

All resins are stable till 140°C. Above 140°C the resins loose of different amount of weight (See Table 7).

Table 7.- Thermogravimetric analyses of the resins.

	weight loss at various temperatures (%)					
	100°C	200°C	300°C	400°C	500°C	600°C
IM-2	0.0	2.0	30.0	68.0	82.0	98.0
IM-2M	0.0	3.0	46.0	64.0	80.0	98.0
IM-3	0.0	6.0	14.0	25.0	54.0	75.0
IM-3M	0.0	3.0	40.0	55.0	77.0	97.0

IM-2 remains constant till 160°C and between 160°-400° it loses 68% weight. IM-2M and IM-3M are stable till 150°C; in the temperature range 150-400° they loose 48% and 64% weight, respectively. Finally IM-3 does not loose weight up to 140°C but it loses 25% between 140-400°C.

There is an important difference between IM-3 and other resins in respect to weight loss.

In addition, resins with retention for copper and uranium were synthesized. These resins did not retain iron in the range pH 0-2, and they show good thermal stability.

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