# Study of Polymer-Metal Ions Triple Complex as Materials for Adsorption and Separation

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**ABSTRACT:** Diethylenetriamine and a copolymer of sodium acrylate and maleic anhydride were used for the adsorption and separation of  $Au^{3+}$ ,  $Ru^{3+}$ ,  $Bi^{3+}$ , and  $Hg^{2+}$  ions by forming polymer-metal ions triple complex. The acidity, temperature, capacity, and interference on the adsorption of these ions on the complex, as well as the conditions of desorption of these ions from the complex, were investigated by means of inductively coupled plasma optical emission spectrometry. The results were satisfactory. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 819–821, 1999

Key words: polymer-metal ions triple complex; adsorption; separation

## **INTRODUCTION**

It is well known that polyelectrolytes form complexes with metal ions. This is widely used in the case of ion-exchange resin.<sup>1-7</sup> Also, polyacid can form insoluble polymer-polymer complex with polybase,<sup>8-12</sup> so metal ions are adsorbed by forming polymer-metal ions triple complex. These ions can be separated from the complex with small amounts of mineral acid.<sup>8,9</sup> In this article, the diethvlenetriamine (polybase)-copolymer of the sodium acrylate and maleic anhydride (polyacid) system was the first time used for concentration and separation of traces of Au<sup>3+</sup>, Ru<sup>3+</sup>, Bi<sup>3+</sup>, and  $Hg^{2+}$  ions from a sample solution to form the triple complex (most of the maleic anhydride in the polyacid existed as carboxylic acid, because it was hydrolyzed in aqueous solution):

+c	H <sub>2</sub> —CH	I—СН-	-сн—	$-M^{n+}-H_2NCH_2CH_2NHCH_2CH_2NH_2$
L		O = C		
	NaO	но	OH	

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The conditions and properties of enrichment and separation of these ions in the complex system were investigated by inductively coupled plasmaoptical emission spectrometry (ICP-OES) with satisfactory results.

#### **EXPERIMENTAL**

#### Instrument

An ICP/6500 ICP spectrometer (Perkin-Elmer) was used. The determined conditions by ICP-OES were: forward power, 1100 W; viewing height, 15 mm; argon outer gas flow rate, 14 L min<sup>-1</sup>; nebulizer gas flow rate, 1.0 L min<sup>-1</sup>; and wavelengths—Au 242.795 nm, Ru 240.272 nm, Bi 223.601 nm, and Hg 253.652 nm.

#### **Reagents and Standards**

Reagents of analytical or spectroscopic purity were used for preparing stock solution of 1 mg mL<sup>-1</sup> of Au<sup>3+</sup>, Ru<sup>3+</sup>, Bi<sup>3+</sup>, and Hg<sup>2+</sup>, respectively. The mixed standard solution of 50  $\mu$ g mL<sup>-1</sup> of Au<sup>3+</sup>, Ru<sup>3+</sup>, Bi<sup>3+</sup>, and Hg<sup>2+</sup> ions was prepared with the stock solution in 0.5*M* HCl. Other reagents in the

		Recovery (%)						
Element	pH 1	pH 2	pH 3	pH 4	pH 5			
Au Ru Bi Hg	97 80 95 100	$100 \\ 84 \\ 99 \\ 100$	100 90 100 100	100 89 100 100	100 89 100 100			

Table IEffect of pH Value on EnrichmentRecovery

Table II	Influence of Desorption Acidity (HCl					
Concentration in M) on Recovery						

	Recovery (%)					
Element	1M	2M	3M	4M		
Au	33	69	93	95		
Ru	17	55	90	92		
Bi	41	78	93	96		
Hg	12	55	90	90		

experiments were analytically pure, and the molecular weight  $(M_v)$  of the polyacid was  $1.1 \times 10^5$  ([maleic anhydride]/[sodium acrylate] = 3/7).

#### **Analytical Procedure**

0.2 g of copolymer of sodium acrylate and maleic anhydride was dissolved in 50 mL of distilled water and added to the mixed standard solution of  $Au^{3+}$ ,  $Ru^{3+}$ ,  $Bi^{3+}$ , and  $Hg^{2+}$  (1 mL) in it. The solution was adjusted to pH 1-5, with 0.1MNaOH and 0.1M HCl, then 0.2 mL of diethylenetriamine was added to form an insoluble compound. The precipitate was filtered to obtain filtrate 1. The ions in the precipitate were desorbed with 15 mL of 3M HCl and filtered again to obtain filtrate 2. The two filtrates were evaporated to small volumes at a lower temperature, transferred into 10 mL of flasks, and made up to volume with distilled water, respectively, so that the ions of the solution could be determined by ICP-OES.

## RESULTS

## Effect of Acidity on Enrichment

Equal concentrations of mixed standards were diluted to equal volumes and enriched in the pH range of 1–5 as previously described. Results (Table I) show that  $Au^{3+}$ ,  $Ru^{3+}$ ,  $Bi^{3+}$ , and  $Hg^{2+}$  can be enriched with recoveries of 80–100% at pH 1–5. To determine these elements simultaneously, pH 3.0 was selected as the enrichment pH.

## Influence of Desorption Acidity on Recovery

After traces of Au<sup>3+</sup>, Ru<sup>3+</sup>, Bi<sup>3+</sup>, and Hg<sup>2+</sup> ions had been enriched, following the procedure herein, the precipitate was eluted with 15 mL of 1M, 2M, 3M, and 4M HCl, respectively. Table II shows that these ions can be desorbed with 15 mL of 3M or 4M HCl.

## Effect of Temperature on Recovery

At pH 3, equal concentrations of mixed standards were diluted to equal volumes and enriched at different temperatures as the analytical procedure herein. The results, summarized in Table III, show that the recoveries of  $Au^{3+}$ ,  $Ru^{3+}$ ,  $Bi^{3+}$ , and  $Hg^{2+}$  are all >80% at different temperatures. In the experiments, 20°C was selected as the experimental temperature.

## **Adsorption Capacity**

Four portions of the polyacid (0.2 g) and polybase (0.2 g) were placed in four conical flasks. One mg

 Table III
 Effect of Temperature (°C) on Recovery

	Recovery (%)								
Element	5°C	10°C	15°C	20°C	30°C	40°C	50°C	60°C	
Au	99	99	100	100	100	100	100	100	
Ru	82	82	85	90	91	91	90	92	
Bi	100	99	100	100	100	100	100	99	
Hg	100	100	100	100	99	100	99	99	

Element	Recovery (%) <sup>a</sup>							
	Ca <sup>2+</sup> (100)	${ m Mg^{2+}}\ (50)$	Sn <sup>4+</sup> (100)	${\mathop{\rm Cu}}^{2+}$ (50)	${ m Al}^{3+}$ (50)	${ m Fe}^{3+ b}$ (50)	Zn <sup>2+</sup> (100)	Ti <sup>4+</sup> (100)
Au	92	95	98	95	100	95	90	100
Ru	63	42	80	58	60	80	70	70
Bi	97	100	95	91	95	99	100	100
Hg	100	100	92	95	90	96	100	98

Table IV Interference of Other Ions (Conc., in  $\mu g m L^{-1}$ ) Present in 50 mL of Solution

 $^a$  Concentration of each Au  $^{3+},$  Ru  $^{3+},$  Bi  $^{3+},$  and Hg  $^{2+}$  was 1  $\mu g$  mL  $^{-1}.$ 

 $^{\rm b}\,{\rm Fe^{3+}}$  was masked with 5 mL of 10% NaSCN solution.

mL<sup>-1</sup> stock solution of Au<sup>3+</sup>, Ru<sup>3+</sup>, Bi<sup>3+</sup>, and Hg<sup>2+</sup> was added into the each flask and diluted to 50 mL. The acidity of each solution was adjusted to pH 3.0, and the flasks were shaken on a mechanical shaker. The concentration of these ions in each solution was measured by ICP-OES until equilibrium was reached. Thus, the adsorption capacity of the complex could be calculated to be 220 mg g<sup>-1</sup> for Au<sup>3+</sup>, 105 mg g<sup>-1</sup> for Ru<sup>3+</sup>, 155 mg g<sup>-1</sup> for Bi<sup>3+</sup>, and 176 mg g<sup>-1</sup> for Hg<sup>2+</sup>.

#### Interference

Different interfering ions were added to diluted analytes. The analytes were adsorbed and determined as described. The results, summarized in Table IV, show that 50- to 100-fold excesses of other ions caused a little interference in the recoveries of  $Au^{3+}$ ,  $Bi^{3+}$ , and  $Hg^{2+}$ ; however, they cause a little interference for  $Ru^{3+}$ , which is due to the complex ability of  $Ru^{3+}$  that is lower than that of  $Au^{3+}$ ,  $Bi^{3+}$ , and  $Hg^{2+}$ .

#### CONCLUSIONS

The proposed method for adsorption of some metal ions is quick, convenient, and precise. Its application is reliable and satisfactory. The diethylenetriamine copolymer of the sodium acrylate and maleic anhydride complex system can effectively concentrate and separate traces of  $Au^{3+}$ ,  $Ru^{3+}$ ,  $Bi^{3+}$ , and  $Hg^{2+}$  from the aqueous solution.

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