

# Chelation Ion-Exchange Properties of Copolymer Resin Derived from 4-Hydroxyacetophenone, Oxamide, and Formaldehyde

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**ABSTRACT:** A copolymer (4-HAOF) prepared by condensation of 4-hydroxyacetophenone and oxamide with formaldehyde in the presence of an acid catalyst proved to be a selective chelating ion-exchange copolymer for certain metals. Chelating ion-exchange properties of this copolymer were studied for Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Hg<sup>2+</sup> ions. A batch equilibrium method was employed in the study of the selectivity of metal-ion uptake involving the measurements of the distribution of a given metal ion

between the copolymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths. The copolymer showed a higher selectivity for Fe<sup>3+</sup> ions than for Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Hg<sup>2+</sup> ions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 787–790, 2003

**Key words:** copolymerization; ion exchange; resins; polyamides

## INTRODUCTION

The chelation properties of 4-hydroxyacetophenone and its substituted derivatives have been extensively studied. Hence, it is obvious that copolymers prepared from 4-hydroxyacetophenone are also the subject of extensive investigations. Synthetic resins derived from hydroxy and amino compounds have attracted the attention of many research workers because of their versatile use as ion-exchangers, photographic binders, thermal stabilizers, etc. Chelating ion-exchange resins prepared by copolycondensation of 8-hydroxyquinoline or phenol derivatives like *o*-aminophenol,  $\beta$ -resorcylic acid, or resorcinol with formaldehyde were reported by Pennington and Williams<sup>1</sup> and by Aristov and Kostantinov.<sup>2</sup> Sykora and Dubsy<sup>3</sup> prepared a selective ion-exchange resin by reacting a condensation product of resacetophenone and anthranilic acid with formaldehyde. Parmar et al.<sup>4</sup> synthesized a resacetophenone formaldehyde resin in an acidic medium and studied its chelation ion-exchange properties. Recently, Pal and Kharat<sup>5,6</sup> reported the synthesis and characterization of some resin polymers derived from salicylic acid, biuret, di-thiooxamide, and trioxane and studied their ion-exchange properties. Nayak et al.<sup>7</sup> and Mohanty and

Lenka<sup>8</sup> reported the synthesis and characterization of some resins obtained from a large number of hydroxyl and amino acetophenones. The present communication deals with the systematic study of the selectivity and capacity of copolymers from 4-hydroxyacetophenone, oxamide, and formaldehyde (4-HAOF copolymers) in an ion-exchange reaction.

## EXPERIMENTAL

### Materials

The chemicals used were all of an A.R. or chemically pure grade.

### Synthesis of 4-HAOF copolymer resins

The copolymer resin 4-HAOF was synthesized by condensing 4-hydroxyacetophenone, oxamide, and formaldehyde in a mol ratio of 1:1:2 in the presence of 2M HCl as a catalyst at 115°C for 5 h.<sup>5,6,9</sup> During the course of the reaction, a periodical shaking was needed to ensure thorough mixing. The separated copolymer was washed with hot water and finally with ether to remove an excess of acid monomers and the 4-hydroxyacetophenone–formaldehyde polymer. The copolymer was purified by dissolving it in 8% NaOH and reprecipitating it by dropwise addition of 1:1 (v/v) HCl/water. The process was repeated twice. The copolymer sample thus obtained was washed with boiling water, dried, and kept *in vacuo* over silica gel. The purified copolymer was finally ground to

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**TABLE I**  
**Evaluation of the Effect of Different Electrolytes on the Uptake of Several Metal Ions**

Metal ion	Electrolyte (mol L <sup>-1</sup> )	pH	Weight of the metal ion (in mg) taken up in the presence of			
			NaClO <sub>4</sub>	NaCl	NaNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>
Fe <sup>3+</sup>	0.01	2.5	0.87	0.14	0.93	2.21
	0.05		1.84	0.80	1.38	1.24
	0.10		2.12	1.43	1.73	1.13
	0.50		2.46	1.88	1.80	0.68
	1.00		2.83	2.60	2.31	0.11
Cu <sup>2+</sup>	0.01	4.5	1.58	0.96	1.01	3.22
	0.05		2.03	1.93	1.58	2.54
	0.10		2.43	2.40	2.13	1.67
	0.50		2.93	3.06	2.50	0.83
	1.00		4.28	3.32	2.63	0.01
Ni <sup>2+</sup>	0.01	4.5	1.75	1.00	0.80	2.67
	0.05		1.96	1.51	1.46	2.00
	0.10		2.30	2.30	2.31	1.42
	0.50		2.45	2.80	2.87	0.66
	1.00		3.28	3.40	3.07	0.06
Co <sup>2+</sup>	0.01	5.0	1.58	1.73	1.37	1.56
	0.05		1.22	1.03	0.97	1.14
	0.10		0.90	0.87	0.84	0.72
	0.50		0.62	0.71	0.45	0.26
	1.00		0.28	0.28	0.16	0.10
Zn <sup>2+</sup>	0.01	5.0	2.24	2.58	1.31	1.08
	0.05		1.92	2.26	1.24	0.74
	0.10		1.40	0.52	0.90	0.58
	0.50		0.62	0.22	0.80	0.40
	1.00		0.41	0.03	0.20	0.10
Cd <sup>2+</sup>	0.01	5.0	1.20	1.58	1.48	1.50
	0.05		0.90	1.12	1.02	1.08
	0.10		0.67	0.85	0.90	0.67
	0.50		0.28	0.27	0.51	0.20
	1.00		0.18	0.18	0.22	0.05
Pb <sup>2+</sup>	0.01	6.0	0.01	1.33	1.48	—
	0.05		0.05	1.23	0.40	—
	0.10		0.10	0.97	0.28	—
	0.50		0.50	0.80	0.84	—
	1.00		1.00	0.40	0.50	—
Hg <sup>2+</sup>	0.01	6.0	1.08	0.60	0.80	—
	0.05		0.90	0.18	0.38	—
	0.10		0.75	0.08	0.20	—
	0.50		0.08	0.03	0.18	—
	1.00		0.01	—	0.02	—

[M<sup>n+</sup> (NO<sub>3</sub>)<sub>n</sub>] = 0.1 mol L<sup>-1</sup>; volume = 2 mL; volume of electrolyte solution 25 mL; weight of resin = 25 mg; time 24 h; room temperature.

pass through a 300-mesh-size sieve and used in all the experiments carried out in the ion-exchange study.

#### Determination of metal uptake in the presence of electrolytes of different concentrations

The copolymer sample (25 mg) was suspended in an electrolyte solution (25 mL) of a known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M HNO<sub>3</sub> or 0.1M NaOH. The suspension was stirred for 24 h at 25°C. To this sus-

pension, 2 mL of a 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 h and filtered.<sup>10,11</sup> The solid was washed and the filtrate and washings were combined and the metal-ion content was determined by titration against standard EDTA. The amount of the metal-ion uptake of the polymer was calculated from the difference between a blank experiment without the polymer and the reading in the actual experiments. The experiments were performed in the presence of several electrolytes with

TABLE II  
Comparison of the Rates of Metal Ion Uptake

Metal ion	Percentage of metal ion uptake <sup>a</sup> at different times (h)						
	1	2	3	4	5	6	7
Fe <sup>3+</sup>	60	80	96	—	—	—	—
Cu <sup>2+</sup>	41	50	60	80	94	—	—
Ni <sup>2+</sup>	30	50	60	80	94	—	—
Co <sup>2+</sup>	30	46	60	76	90	—	—
Zn <sup>2+</sup>	30	45	59	76	88	—	—
Cd <sup>2+</sup>	18	28	40	60	70	80	—
Pb <sup>2+</sup>	17	27	39	58	69	79	—
Hg <sup>2+</sup>	—	—	30	43	66	74	90

[M<sup>n+</sup> (NO<sub>3</sub>)<sub>n</sub>] = 0.1 mol L<sup>-1</sup>; volume = 2 mL, NaNO<sub>3</sub> = 1 mol L<sup>-1</sup>; volume 25 mL; room temperature.

$$^a\text{Percentage of metal ion uptake} = \frac{\text{amount of metal ion absorbed} \times 100}{\text{amount of metal ion absorbed at equilibrium}}$$

eight different metal ions: Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Hg<sup>2+</sup>.

#### Evaluation of the rate of metal uptake

To determine the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out, in which the metal ion taken up by the chelating resins was estimated from time to time at 25°C in the presence of 25 mL of 1M NaNO<sub>3</sub> solutions. It is assumed that, under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as the percentage of the amount of metal ions taken up after a certain time related to that in the state of equilibrium.

#### Evaluation of the distribution of metal ions at different pH

The distribution of each one of the eight metal ions, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, and Fe<sup>3+</sup>, between the polymer phase and the aqueous phase

was estimated at 25°C and in the presence of a 1M NaNO<sub>3</sub> solution. The experiments were carried out as described earlier at pH 3, 4, 5, 6, and 7. The distribution ratio *D* is defined by the following relationship:

$$D = \frac{\text{weight (in mg) of metal ion taken up by 1 g of polymer}}{\text{weight (in mg) of metal ion present in 1 mL of solution}}$$

#### RESULTS AND DISCUSSION

The results of the batch equilibrium study carried out with the copolymer sample 4-HAOF is presented in Tables I–III. From this study, carried out with eight metal ions under a limited variation of experimental conditions, certain generalizations may be made about the behavior of the copolymer sample selected for study.

#### Influence of electrolytes on metal uptake

Table I reveals that the amount of metal ions taken up from a given amount of a copolymer depends on the

TABLE III  
Distribution Ratio *D* of Different Metal Ions as a Function of the pH

Metal ion	Distribution ratio of the metal ion at different pH									
	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Fe <sup>3+</sup>	11.9	150.8	266.8	409.1	—	—	—	—	—	—
Cu <sup>2+</sup>	—	—	—	40.9	89.7	176.4	351.4	1179.8	1588.0	1689.3
Ni <sup>2+</sup>	—	—	—	30.9	87.5	129.9	300.9	448.8	1009.1	1085.9
Co <sup>2+</sup>	—	—	—	27.1	38.8	89.4	109.7	182.2	251.1	266.6
Zn <sup>2+</sup>	—	—	—	26.9	33.6	49.2	88.3	124.7	236.0	247.7
Cd <sup>2+</sup>	—	—	—	—	10.0	25.5	30.0	37.2	77.2	127.2
Pb <sup>2+</sup>	—	—	—	23.0	32.6	46.8	87.2	109.7	196.5	206.4
Hg <sup>2+</sup>	—	—	—	—	—	10.1	10.9	41.2	102.0	—

$$D = \frac{\text{Weight (in mg) of metal ions taken up by 1 g of terpolymer}}{\text{Weight (in mg) of metal ions present in 1 mL of solution}}$$

[M<sup>n+</sup> (NO<sub>3</sub>)<sub>n</sub>] = 0.1 mol L<sup>-1</sup>; volume = 2 mL; NaNO<sub>3</sub> = 1 mol L<sup>-1</sup>; volume 25 mL, time 24 h; (equilibrium state); room-temperature.

nature and concentration of the electrolyte present in the solution. In the presence of perchlorate, chloride, and nitrate ions, the uptake of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  ions increases with an increasing concentration of the electrolytes, whereas in the presence of sulfate ions the amount of the above-mentioned ions taken up by the copolymer resin sample decreases with an increasing concentration of the electrolyte. In the case of the remaining metal ions, namely,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$ , the amount of the metal ions taken up by the copolymer samples increases with a decreasing concentration of the chloride, nitrate, perchlorate, and sulfate ions.<sup>5,6,10,11</sup> This observation can be explained on the basis of the stability constant with these metal ions.<sup>12</sup> This type of trend was also observed by earlier research workers.<sup>12,13</sup> It was also observed that the amount of the metal ions taken up by the copolymer increases in the order 4-HAOF-1 < 4-HAOF-2 < 4-HAOF-3 < 4-HAOF-4. This above-observed increasing order of metal-ion adsorption by the resin samples may be due to the introduction of more and more ligand groups in the repeat unit of the copolymer resins.

#### Evaluation of the rate of metal-ion uptake

Table II shows the dependence of the rate of the metal-ion uptake on the nature of the metal. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The results show that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under the given condition. It was found that  $\text{Fe}^{3+}$  ions require about 3 h for the establishment of the equilibrium, whereas  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Zn}^{2+}$  ions required almost 5 h for equilibrium. Thus, the rate of metal-ion uptake follows the order  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} = \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Hg}^{2+}$  for all the copolymers.<sup>10-12</sup> However, comparison of the uptake capacity of the copolymer resins reveals the order 4-HAOF-4 > 4-HAOF-3 > 4-HAOF-2 > 4-HAOF-1.

#### Distribution ratios of metal ions at different pH

Examination of the data on the distribution ratio as a function of pH, presented in Table III, indicates that the relative amount of the metal ions taken up by the 4-HAOF copolymer resins increases with an increasing pH of the medium. The magnitude of the increase,

however, is different for different metal cations.<sup>14,15</sup> The 4-HAOF copolymer resins adsorb  $\text{Fe}^{3+}$  ions selectively over the other metal cations under investigation. The observed order of the distribution ratios of the metal ions measured in the pH range 3–6.5 is  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Hg}^{2+}$ . Thus, the results of such a type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions.<sup>5,6,10,11</sup> For instance, the results suggest optimum pH 3.5 for the separation of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  with the distribution ratio 221.2 for  $\text{Cu}^{2+}$  and 61.4 for  $\text{Zn}^{2+}$  using the 4-HAOF-4 copolymer resin as the ion-exchanger.

### CONCLUSIONS

1. A copolymer, 4-HAOF, based on the condensation reaction of 4-hydroxyacetophenone and oxamide with formaldehyde in the presence of acid catalyst was prepared.
2. 4-HAOF is a selective chelating ion-exchange copolymer for certain metals.
3. The copolymer showed a higher selectivity for  $\text{Fe}^{3+}$  ions than for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  ions.

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### References

1. Pennington, L. D.; Williams, M. B. *Ind Eng Chem* 1959, 57, 759.
2. Aristov, L. J.; Kostantinov, V. V. *Iz Tomsk Politek Inst* 1961, 111, 104.
3. Sykora, V.; Dubsy, F. *Czech. Patent* 110,864, 1964.
4. Parmar, J. S.; Patel, M. M.; Patel, M. R. *Angew Makromol Chem* 1981, 93, 11.
5. Pal, T. K.; Kharat, R. B. *Angew Makromol Chem* 1989, 173, 55.
6. Pal, T. K.; Kharat, R. B. *Indian J Chem A* 1989, 28, 55.
7. Nayak, P. K.; Lenka, S.; Nayak, P. L. *J Appl Polym Sci* 1990, 41, 1491.
8. Mohanty, P. K.; Lenka S. *J Appl Polym Sci* 1991, 42, 2261.
9. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. *Asian J Chem* 12, 767, 2000.
10. Joshi, R. M.; Patel, M. M. *Proc Indian Acad Sci Chem Sci* 1982, 91, 351.
11. Manavalan, R.; Patel, M. M. *Makromol Chem* 1983, 184, 717.
12. Patel, B. S.; Patel, S. R. *Makromol Chem* 1979, 180, 1159.
13. Patel, H. S.; Patel, S. R. *J Makromol Sci Chem* 1982, 106, 1383.
14. Davadov, S. L.; Plate, N. A. *Coord Chem Rev* 1975, 16, 195.
15. Vernon, F.; Eccles, H. *Anal Chem Acta* 1974, 72, 331.