

NOTES

Preconcentration of Cadmium Ion in Aqueous Phase on Poly(methyl methacrylate), Polymethacrylonitrile, and Their Copolymers

INTRODUCTION

With increasing attention to the effect of toxic materials on public health, development of analysis methods capable of determining trace amounts of such materials has become necessary. On the other hand modern technology requires extremely pure materials and it is important to determine trace amounts of impurities in any of these processes. For these reasons determination of trace element concentration is an important subject of chemistry.

Cadmium is an important cation in connection with public health. The poisonous nature of cadmium is analogous to that of mercury and arsenic. In industry, cadmium poisoning frequently occurs when metal alloys are heated. Among the toxic manifestations of cadmium poisoning are dermatitis and, in severe cases, chest and abdominal pains. The physiological action of cadmium ions is similar to that of zinc and mercury in that the central nervous system is affected.

The most common technique for determining trace amounts of metal ions is preconcentrating the element to be determined. This is done on a matrix of polymeric resins that selectively adsorb the desired material. After this procedure the concentrated material can be analyzed by spectrophotometric methods. There are numerous reports on this subject in the literature.¹⁻¹⁰

In this work preliminary results on the preconcentration of a highly toxic ion, cadmium, on a polymeric matrix is reported. The polymeric resins used are poly(methyl methacrylate) (PMMA), polymethacrylonitrile (PMAN), and their copolymers, all synthesized by group transfer polymerization (GTP).¹¹⁻¹⁴ GTP is a new polymerization method introduced by the DuPont group in 1983. In GTP, polymeric chains grow from one active end only and linear unbranched chains are obtained by this method.

In such chains the N and O groups, which should be mostly responsible for the interaction between metal ions and resins, are not masked. This property is believed to enhance the ability to hold metal ions. Another important property of GTP is to give monodisperse polymers at room temperature. The molecular weights and heterogeneity indices of the resins studied in this work are given in Table I.

Because the pH value of the solution affects the holding ability of the resin, the pH dependence was also studied for a wide pH range.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and methacrylonitrile (MAN) (Aldrich Co.) were freed from inhibitor by treating with 5% aqueous sodium hydroxide solution, washing with distilled water several times, then drying over calcium hydride. The monomers were obtained by fractional distillation. The purification of the inert gas (N₂) followed standard methods.¹² Tetrahydrofuran (THF; Aldrich Co.) was refluxed over Na/benzophenone (Aldrich Co.) until dry, then distilled into a reaction flask prior to use. Methyl trimethyl silyl dimethylketene acetal(1-methoxy 2-methyl-1-trimethylsilyl-1-propene) (MTS; Aldrich Co.), tris(dimethylamino)sulfonium difluoride (TASHF₂) (Aldrich Co.), and other chemically pure materials were used without further purification.¹¹⁻¹⁴

Cd(ClO₄)₂ stock solution was prepared from Cd(CO₃)₂ and HClO₄ solutions and its concentration was determined by EDTA titration. Standard cadmium solutions were prepared from the above solution. The pH value of the solutions were adjusted by NaOH and HCl.

Polymerization

The monomer or the monomer mixtures (5.0 mL), the initiator MTS (0.10 mL), and THF as solvent (50 mL), were mixed in a dry nitrogen atmosphere. The catalyst, TASHF₂, was then added as a solution (0.10M) in acetonitrile. The mixture immediately warmed and after cooling the polymer was precipitated in petroleum ether (bp 30–40°C). It was redissolved and reprecipitated, and then dried *in vacuo* at room temperature overnight.¹²

Preconcentrations were performed by batch and column techniques.

Batch Technique

In the batch technique 50 mL of 5 ppm cadmium solution and 0.2 g resin were vigorously stirred at a rate of 350 min^{-1} for 1 h. After filtering the resins, 5 mL of this solution was diluted up to 25 mL and cadmium concentration was determined by atomic absorption spectrometry (AAS).

To recover the amount of Cd in the resins, the resins were washed with 30 mL 2N HCl and the eluent was diluted to 50 mL. The amount of cadmium in this solution was determined by AAS. The above procedure was repeated for pH values 3, 4, 5, 6, 7, 8, and 9, respectively.

After each experiment homopolymers and copolymers were washed first with HCl and then with distilled water. Eluent water was then tested by AgNO_3 to check the removal of the acid.

The experiment was repeated for homopolymer PMMA and PMAN resins and 2 and 5 ppm cadmium solutions containing 2% NaCl at pH 8.5 to determine the influence of the sodium ion on the retention capacity of the resins.

Column Technique

Resins were left in distilled water for 24 h and the columns were filled by a compression pump. In an 8-mm diameter column, 1-g resin height was 4.5 cm and in a 9-mm diameter column, 1-g resin height was 3.2 cm. Two hundred-fifty milliliters of 0.5-ppm cadmium solution at pH 8.5 was passed through the columns at a flow rate of 2 mL/min. The columns were then washed with 25 mL distilled water and cadmium ion was eluted with 100 mL 2N HCl solution. Cadmium in the reference solution of 0.5 ppm and the cadmium in the eluent were determined by AAS.

Cadmium Analysis

The amount of cadmium in the solvent remaining after the removal of the resin and the recovered cadmium in the eluent were analyzed by AAS (Perkin-Elmer 1100 B). The working conditions were wavelength, 228.8 nm; filament current, 4 mA; cavity cathode lamp, Cd; and slit width, 0.7 nm.

Table I Molecular Weights and Heterogeneity Indexes of Homopolymers and Copolymers Used in Preconcentration Studies

System	$M_n \times 10^{-4}$	M_w/M_n
PMMA	2.45	1.15
PMAN	2.30	1.05
Cop I	2.40	1.10
Cop II	2.45	1.05

Cop I is 1MMA + 4MAN and Cop II is 4MMA + 1MAN.

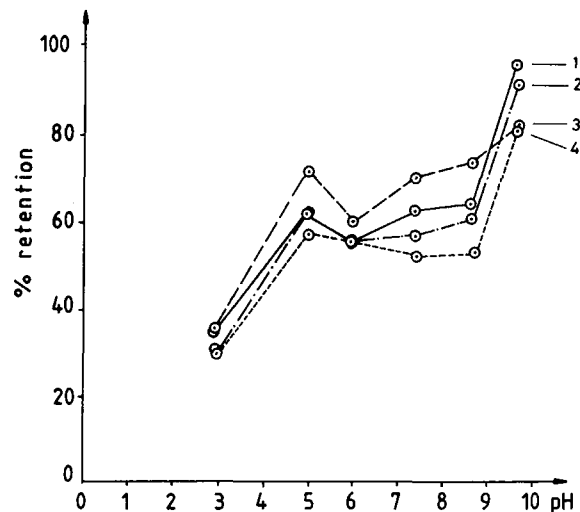


Figure 1 Retention values versus pH values obtained from the batch technique. Lines represent (1) PMMA, (2) PMAN, (3) 4MAN + 1MMA, and (4) 1MAN + 4MMA.

RESULTS AND DISCUSSION

Retention ratios and pH values obtained from the batch technique are plotted in Figure 1. The column method was applied to the homopolymers at pH 8.5. For the 0.5-ppm cadmium solution, retention percentages of polymers were 62% for PMMA and 55% for PMAN.

For all polymers retention was around 60%. The O groups in PMMA and the N groups in PMAN and in copolymers did not make a discernible difference in retention. For all resins, concentration versus retention values are plotted in Figure 2. Evaluating all results together in the Langmuir equation gave

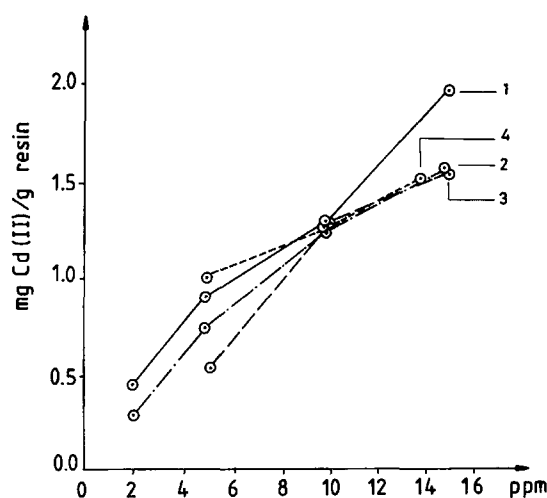


Figure 2 Retention values versus resin concentration at pH 8.5. Lines represent (1) PMMA, (2) PMAN, (3) 4MAN + 1MMA, and (4) 1MAN + 4MMA.

Table II Cadmium Retention of Homopolymers and Copolymers at Different pH Values

pH	% Retention			
	PMMA	PMAN	Cop I	Cop II
3.0	34.6	28.9	27.8	35.8
5.0	60.9	60.8	56.2	70.6
6.0	53.8	54.1	54.4	59.0
7.4	61.7	53.3	55.4	68.9
8.7	63.6	59.1	51.2	72.4
9.7	94.8	89.2	80.1	79.8

Cop I is 1MMA + 4MAN and Cop II is 4MMA + 1MAN.

$$x/m = 0.2405c - 0.7205,$$

where x/m is mg Cd/g resin and c is ppm concentration.

The pH of the solution has a very significant effect on the retention of Cd(II) ion on the homopolymers and copolymers studied (Table II, Fig. 1). At low pH values (pH < 3) retention is about 25–35%, increasing rapidly with pH up to pH 5 in all polymers. At low pH values high H^+ ion concentration located at the interface electrostatically repels positively charged metal ions, preventing their approach to the polymer surface. For this reason low retention is expected at low pH values.

In all polymers a maximum in retention is seen at approximately pH 5 followed by a slight decrease and a slow increase. It is well known that in neutral solutions Cd is in the $Cd(OH)^+$ form. From pH 5 to pH 7 the dissolution of the localized positive ion surface around the resin is compensated by the replacement of the Cd(II) ion by the $Cd(OH)^+$ ion. The decrease of retention is probably caused by this effect.

In basic medium, Cd retention increases slowly with pH. However, around pH 9 the solubility product constant of Cd is exceeded, colloidal hydroxide particles accumulate easily on the polymer body, and retention increases steeply.

From environmental and public health aspects, determination of trace amounts of Cd ion is important. The 60–70% retention by the polymers used is sufficient for the determination of Cd by the methods of analytical chemistry.

The retention capacity of 2 and 5 ppm solutions of these polymers in 2% NaCl solution was also studied. The results show that in this environment both homopolymers have highly reduced retention capacities, the retention capacity of PMAN being reduced to 4.5% and that of PMMA to between 3 and 4%.

We could not find any value in the literature for the retention capacity of PMMA and PMAN. In studies of Co, Mn, Ni, and Fe ions in polyacrylonitrile (PAN) resin, which has a similar structure, a maximum retention was observed at pH 6.^{9,10} The retention ability

quoted in that work is higher than the results obtained here. This reduced retention ability can be due either to the steric hindrance cause by the methyl group or to the larger size of the Cd ion.

Further work is in progress on the retention of Cd on PMAN and PMMA and copolymers synthesized by free radical polymerization. It is hoped that the results will clarify the relationship between retention and the polymerization mechanism.

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