

Metal Ion Adsorption Behavior of Poly[3-(dimethylamine)propyl acrylate] and Poly[3-(dimethylamine)propylacrylate-*co*-acrylic acid] Resins

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ABSTRACT: Two resins were synthesized by radical polymerization using *N,N'*-methylene-bis-acrylamide and ammonium persulfate as the crosslinking reagent and initiator, respectively. The yields were 98%. The resins were characterized by FTIR and UV-Vis spectroscopy. Sorption behavior of resins toward Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) ions was studied at different pHs depending on the metal ion. Both resins showed selective sorption to Hg(II) ions at pH 2 from a mixture of all ions. The elution of Hg(II) bound to the resins was also investigated using perchloric acid at different concentrations. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1251–1256, 2002; DOI 10.1002/app.10455

Key words: resins; metal-polymer complexes; selectivity

INTRODUCTION

Polymers as metal ion complexing agents have been extensively studied^{1–7} and have also been successfully used in solvent extraction chemistry. The development of metal chelating polymers continues to be a subject of paramount importance.^{8–14} One of the more important problems of environment is related to the decontamination of waste water polluted by heavy metal ions. The process commonly used today in industry are mainly based on hydroxide precipitation, which gives high volumes of sludges difficult to deal with. Several more promising processes are based upon the specific interactions between ions and water swellable or soluble polymeric materials. These resins have been used for the precon-

centration and separation of trace elements from sea water and their analytical use in conjunction with atomic absorption spectroscopy has been well established. For practical applications, strong and selective binding of the target metal ion, rapid complexation of the metal ion, as well as the recovery of the resin are required. Much of the work on these polymers is concerned with the uptake of metal ions from aqueous solution in the wide 1–10 pH range, hence very stable resins are required.

These polymeric substances usually have a polyelectrolyte properties and a very large number of sorption sites per macromolecule, which may be different in their chemical nature or not. Owing to electrostatic and steric effects, these substances display a large range of complexation properties, the respective microscopy stability constants being different for the sorption sites even when they are chemically homogeneous.

The aim of this article is to report the synthesis and the retention properties by batch equilibrium procedure under different experimental conditions of crosslinked 3-(dimethylamine)propylac-

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rylate and their copolymer with acrylic acid for metal ions with impact in the environment as Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III).

EXPERIMENTAL

Reagents

Acrylic acid (Merck) (AA) was purified by distillation.

3-(Dimethylamine)propylacrylate (Aldrich) (DAPA), *N,N'*-methylene-bis-acrylamide (Merck) (MBA), ammonium persulfate (Merck) (APS) were used as received without further purification.

Metal salts (Merck) were analytical grade, perchloric acid (Merck), nitric acid (Merck), and sodium hydroxide (Merck) were used as received.

Synthesis of the Adsorbents

Poly[3-(dimethylamine)propylacrylate] (DAPA) was obtained by aqueous radical polymerization. DAPA was polymerized in water with APS (0.2 mmol) and MBA (4 mol %) as a crosslinking agent at 70°C for 24 h. The resin was washed repeatedly with water and dried in vacuum until constant weight (yield 98%). The dried resin was ground and the particle size of 180–250 μm was used in all the experiments.

Poly[3-(dimethylamine)propylacrylate-*co*-acrylic acid] was obtained by aqueous radical poly-

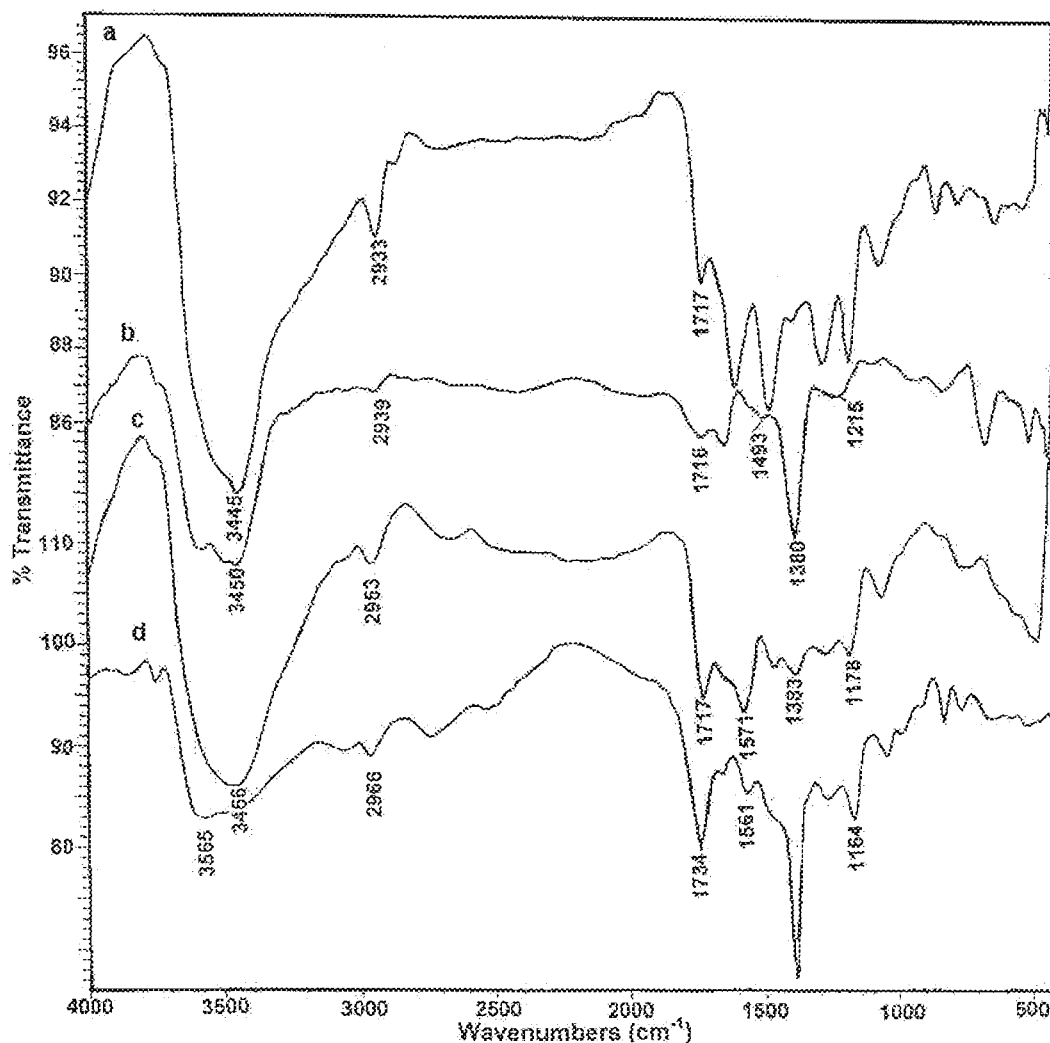


Figure 1 FTIR spectra of the resin DAPA (a), DAPA-Hg (II) (b), DAPA-AA (c), and (d) DAPA-AA-Hg (II).

Table I Thermal Stability of the Unloaded and Loaded Resins.

Resin	Weight Loss (%) at Different Temperatures (°C)				
	100	200	300	400	500
DAPA	0.0	7.6	39.2	57.7	89.0
DAPA-AA	0.7	5.8	32.7	54.7	89.0
DAPA-Hg(II)	0.6	7.2	34.0	55.4	82.1
DAPA-AA-Hg(II)	0.0	0.3	26.0	51.2	75.6

merization. DAPA (0.1 mol) and AA (0.1 mol) were copolymerized in presence of APS (0.2 mmol) and MBA (4 mol %) at 70°C for 24 h. The resin was washed repeatedly with water and dried in vacuum until constant weight (yield 98%). The dried resin was ground, and the particle size of 180–250 μm was used in all the experiments.

Sorption Equilibrium Procedure

A batch-type equilibrium procedure was employed in all the sorption runs. The sorption equilibrium experiments included the effect of the pH values on sorption, determination of the maximum binding capacity, and selectivity sorption from mixtures of metal ions.

Dried samples (0.1 g each) of the chelating resin were equilibrated by 1 h in 10 mL of metal ion solutions at 20°C. The various metal ion aqueous solutions were adjusted to the desired pH values with nitric acid or sodium hydroxide prior to equilibrium. The loaded sample resins were filtered and washed with distilled water. The concentrations of metal ions in the filtrate were determined by atomic absorption spectroscopy. Batch metal uptake experiments under competitive conditions were also carried out. The following metal ion mixture was made: batches of 0.1 g resin were added together with a mixture of 10 mL (4.4×10^{-4} M) of each metal ion Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III). After shaking for 1 h, the samples were further handled as described above for noncompetitive conditions. To obtain the maximum sorption capacity for Hg(II) ions, 50 mL of an aqueous solution (5.2×10^{-3} M) was shaken with 1 g of dry resin for 1 h at 20°C. The mixture in the flask was filtered and washed with distilled water and transferred into a calibrated flask. The process was repeated three times, the volume was made up to 250 mL, and the metals were determined by atomic absorption spectroscopy.

Removal of Mercury(II) Ions

The loaded resin with mercury(II) (0.1 g) was stirred with HClO_4 (10 mL, 1–4 M). The desorbed metal ions were collected and estimated as above.

Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital H. Jurgens & Co. pH meter. A Unicam Solaar M series atomic absorption spectrometer was used for the determination of single and mixed metal ions. The FTIR spectra of the sample were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded, unloaded resins were recorded on a STA-625 thermoanalyzer (Polymer Laboratories). Approximately 5 mg of the dry sample was heated at 10°C/min heating rate under dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

The water-insoluble poly[3-(dimethylamino)propylacrylate] and poly[3-(dimethylamino)propylacrylate-co-acrylic acid] were synthesized by radical

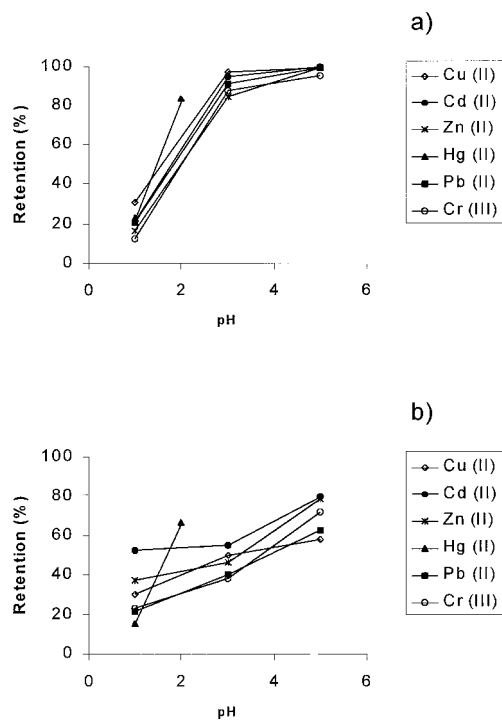
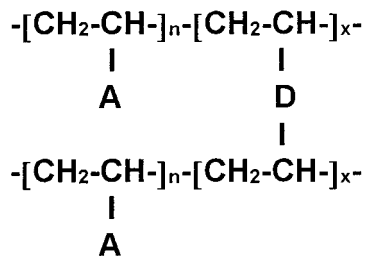
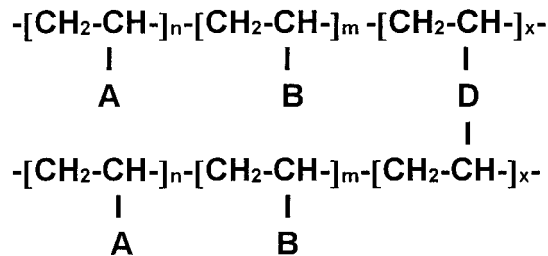


Figure 2 Effect of the pH under noncompetitive conditions of DAPA (a) and DAPA-AA resins (b).

copolymerization by using ammonium persulfate, and *N,N'*-methylene-bis-acrylamide as initiator and crosslinking reagent, respectively. An equimole feed monomer ratio of DAPA and AA was



DAPA



DAPA-AA

Both adsorbents were characterized by FTIR spectroscopy. Figure 1 shows, among others, the more characteristic absorption signals (in cm^{-1}) for DAPA (a): 3445 (N—H, secondary amine), 1717 (C=O, ester), 1598 (N—C=O, secondary amide), and DAPA-AA (c): 3456 (N—H, secondary amide and O—H, carboxylic acid), 1717 (C=O, carboxylic acid), and 1571 (N—C=O, secondary amide).

The thermal behavior demonstrated that the resins were very stable up to 200°C with a weight loss lower than 8%. As the temperature increases, the thermal stability decreases. At 500°C only about 15% remained. The polymeric materials lost basically carbon dioxide and ammonium. No important effect of the mercury ions on the thermal stability was observed (see Table I).

The adsorption properties by the resins towards the following di- and trivalent cations: Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) were assayed by a batch equilibrium procedure at different pH values (see Fig. 2).

In these experiments, buffer solutions deliberately were not used to avoid any possible interferences coming from the components of the buffer.

Due to the protonation and deprotonation properties of the acidic and basic groups of the adsorbents, its sorption behavior for metal ions is influenced by the pH value, which influences the

employed. The yield was 98%. The polymeric materials were ground, and the particle size particle 180–250 μm was used for further metal ion retention properties.

surface structure of the sorbents, the speciation of the metal ions, and the interaction between sorbents and metal ions. Moreover, it is well known that the constant K_a of polyacids dissociation is not constant like that a monomeric weak acids, but depends strongly on various parameters¹⁵ such as the charge density and the concentration of the polymer as well as the ionic strength of the solution. Therefore, the pH dependence of the adsorption for the metal ions was examined in detail. In general, both resins show a high retention ability to bind metal ions depending on the pH and metal ion.

The retention properties of DAPA are higher than those DAPA-AA, especially at pH 3. This is

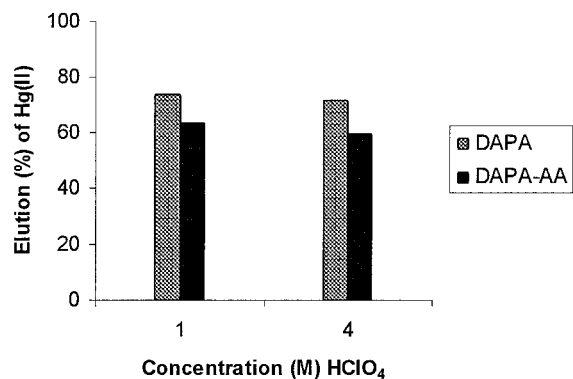


Figure 3 Elution behavior of Hg(II) from DAPA (a) and DAPA-AA (b) with 1 M and 4 M HClO₄.

attributed to the fact that the amine groups would form more stable complexes with the various metal ions than with the carboxylate groups. This difference is larger at pH 3 than at 5.

At pH 1, both resins did not significantly retain all the metal ions. According to the properties of Hg(II) in aqueous solution, only the retention behavior for these ions were studied up to pH 2. DAPA and DAPA-AA did retain 83.1% (0.528 mEq/g dry resin) and 66.3% (0.288 mEq/g dry resin), respectively. These values demonstrate a higher retention respect to the other metal ions. The resin-metal ion interaction is evidenced in the FTIR spectra (see Fig. 1) by shifting the one placed at 1380 cm^{-1} (DAPA) and 1384 cm^{-1} (DAPA-AA) indicating an important involvement of the tertiary amine groups in coordination with mercury ions. At pH 3, DAPA retain above 75% all the metal ions. The highest value was obtained for Cu(II) ions 99% (0.630 mEq/g dry resin). DAPA-AA show a lower retention behavior than DAPA. Thus, the metal ions adsorption ranged between 35–50%.

At pH 5 the retention behavior for DAPA is similar to pH 3, but DAPA-AA shows an increase of the retention values varying between 50 and 75%.

According to these data, the following experiments were carried out.

The maximum retention capacity (MRC) values of Hg(II) at pH 2 for DAPA and DAPA-AA were determined. The MRC values are 0.845 mEq/g dry resin and 0.608 mEq/g dry resin for DAPA and DAPA-AA, respectively. To recover the resin, elution was run with 1 and 4 M perchloric acid (see Fig. 3). The elution varied between 60–75%. No important effect of the concentration and the sorbent was observed.

The retention behavior at pH 5 from a mixture containing all the metal ions, except Hg(II) ions, was carried out. The concentration of each one was 0.0001 M. The results are shown in Figure 4. It is very relevant that there is no important difference with those metal ion retention values obtained under noncompetitive conditions. Only the adsorption of Zn(II) ions decreased from 80 to 40% for DAPA but it was not observed for DAPA-AA.

CONCLUSIONS

The radical polymerization of DAPA and DAPA-AA yielded a crosslinked matrix completely insol-

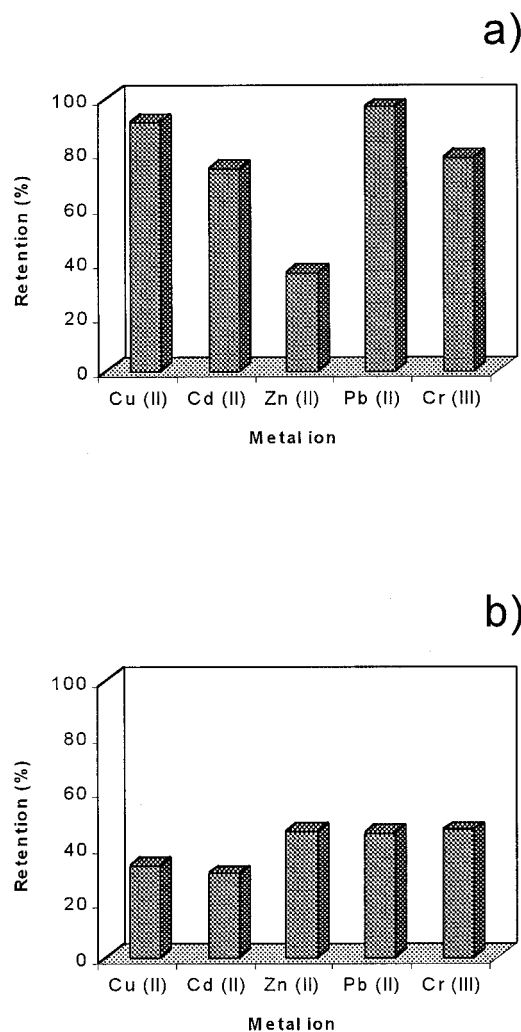


Figure 4 Retention behavior of DAPA (a) and DAPA-AA (b) from a mixture of five metal ions at pH 5.

uble in water. The resins showed a high efficiency to adsorb Hg(II) (DAPA 83% and DAPA-AA 66%) at pH 2. However, at pH 5 both resins also showed a higher retention (>75%) for all the divalent ions except Zn(II) ions (<45%). The maximum load capacity for Hg(II) ($4.4 \times 10^{-4}\text{ M}$) at pH 2 for DAPA was 88% (0.8 mEq/g resin). The amino groups bind the metal ions more strongly than the carboxylate groups. It was partially possible to recover the resins by treatment of the loaded resins with perchloric acid.

Both loaded and unloaded resins showed high thermal stability up to approximately 200°C.

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REFERENCES

1. Reed, B. E.; Matsumoto, M. R. *Sep Sci Technol* 1993, 28, 2179.
2. Konishi, Y.; Asai, S.; Midoch, Y.; Oku, M. *Sep Sci Technol* 1993, 28, 1691.
3. Chiang, W. Y.; Mei, W.-P. *Eur Polym J* 1993, 29, 1047.
4. Kolarz, B. N.; Jezienska, J.; Bartkowiak, D.; Gontarczyk, A. *React Polym* 1994, 23, 53.
5. Allen, S. J.; Brown, P. A. *J Chem Tech Biotechnol* 1995, 62, 17.
6. Lee, Ch. H.; Kim, J. S.; Suh, M. Y.; Lee, W. *Anal Chim Acta* 1996, 339, 303.
7. Chiarizic, R. *Macromolecules* 1996, 29, 1021.
8. Rivas, B. L.; Maturana, H. A.; Villegas, S. *Polym Bull* 1997, 39, 445.
9. Rivas, B. L.; Maturana, H. A.; Villegas, S.; Pereira, E. *Polym Bull* 1998, 40, 721.
10. Rivas, B. L.; Pooley, S. A.; Luna, M. *Macromol Rapid Commun* 2000, 13, 905.
11. Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. *Macromol Chem Phys* 2001, 202, 4432.
12. Rivas, B. L.; Maturana, H. A.; Luna, M. *J Appl Polym Sci* 1999, 74, 1557.
13. Rivas, B. L.; Maturana, H. A.; Villegas, S. *J Appl Polym Sci* 2000, 77, 1994.
14. Rivas, B. L.; Peric, I. M.; Maturana, H. A.; Fuentes, L. *Polym Bull* 1999, 42, 337.
15. Heitz, C.; Binana-Limele, W.; Francois, J.; Biver, C. *J Appl Polym Sci* 1999, 72, 455.