

Properties of polyacryloylacetone for adsorption of divalent metal ions

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Polyacryloylacetone (PAA) was prepared by polymerizing acryloylacetone in a sealed tube, and examined as an adsorbent of divalent metal ions. The dissociation constant of PAA and overall binding constants of PAA-metal complexes were determined from experimental data on pH titration. The adsorptions of metal ions on PAA were in the order $\text{Hg(II)} \gg \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Cd(II)}$, showing high selectivity for Hg(II) . The adsorption depended significantly on the pH of the solution. The uses of a PAA column for separation and concentration of metal ions were also examined.

(Keywords: polyacryloylacetone; chelating resin; metal ions; adsorption; separation)

INTRODUCTION

Reagents containing a β -diketone group are used as chelating agents to extract metal ions owing to their high ability to form complexes with a number of metal ions.

Adsorption is a useful method for separation and concentration of metal ions, and for this purpose, polymers containing a β -diketone group seem of potential value. There are some reports of polymers containing this group¹⁻³. Hoeschele *et al.*³ prepared polyacryloylacetone by ionic polymerization of vinyl methyl ketone and its simultaneous condensation with acetic anhydride, and examined its chelating properties for metal ions in 4/1 dioxane-water solution.

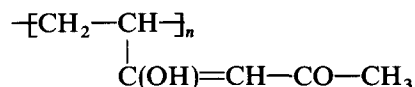
Recently, polyacryloylacetone (PAA) was prepared in our laboratory by polymerization of acryloylacetone in a sealed tube^{4,5}. However, little is known about the characteristics of its adsorption of metal ions. In this study, the adsorption of metal ions, Cu(II) , Co(II) , Ni(II) , Cd(II) and Hg(II) , by PAA and its pH dependence were investigated by batch operations. The dissociation constant of PAA and the binding constants of PAA-metal complexes were determined from the experimental data on pH titration based on the modified Bjerrum method^{3,6}. The uses of a PAA column for separation and concentration of these metal ions were also examined.

EXPERIMENTAL

Polyacryloylacetone (PAA)

Acryloylacetone (AA) was prepared by the method of Ponticello and Furman⁷, and polymerized in sealed tubes at 60°C using a radical initiator (azobisisobutyronitrile) as described before⁵. Three tautomers of AA are theoretically possible (that is, one keto and two enol forms) but n.m.r. spectral data revealed that AA was entirely in the enol form in which the carbonyl group is adjacent to

the methyl group⁵. By analogy with the structure of the monomer, the structure of PAA seems to be as follows:



Anal. calc. for the monomer unit: C, 64.28%; H, 7.14%.
Found: C, 63.83%; H, 7.18%.

Gel permeation chromatography showed that the molecular weight of the PAA used was more than 100 000. The polymer was pulverized to grains of 24-35 mesh for batch operations, and of 40-60 mesh for column processes.

Reagents

All chemicals used were of analytical grade. Metallic acetates and metallic chlorides were used for measuring adsorptivity and pH titration, respectively. Demineralized, distilled water was used. The buffer solution was 0.1 M sodium acetate-acetic acid.

Titration

PAA (50 mg) was swollen in 2-3 ml NaOH solution (0.2 M), and the resulting Na form was converted to the H form by adding HCl solution (0.2 M). After filtration, it was conditioned by washing with NaCl solution (0.1 M). PAA in NaCl solution was titrated in the absence and presence of 0.2 mmol of metal ions (CuCl_2 , NiCl_2 , CoCl_2 , CdCl_2 and HgCl_2) with sodium hydroxide solution (0.05 M) at room temperature. All readings were taken after the pH of the solution attained equilibrium.

Adsorption of metal ions on PAA

The adsorption isotherms of metal ions on PAA were determined by the batch procedure. A series of solutions (40 ml) of different initial concentrations of metal ions adjusted to a given pH were placed in flasks containing

PAA (24–35 mesh, 1 g). The mixtures were shaken continuously in a water bath at 25°C. At fixed time intervals, 1 ml samples were taken for measurement of the metal ion concentration by atomic adsorption spectrometry.

Separation and concentration of metal ions with a PAA column

A column of 5.5 mm inside diameter, packed with powdered PAA (40–60 mesh) to a height of 14 cm, was used for the concentration and separation of metal ions. For experiments on concentration of metal ions, a buffer solution containing the metal ions at 0.1 mM was passed through the column, and then the metal ion adsorbed on PAA column was eluted with 0.2 M HCl solution.

Fractions of effluent were collected with an automatic fraction collector, and the concentration of metal ion in each fraction (2 ml) was determined by atomic absorption spectrometry. For examination of separation of metal ions, solution in the concentration range of 0.5 to 1 mM was pulsed into the column. The mobile phase was a buffer solution of the required pH. Fractions were collected automatically, and analysed as mentioned above.

RESULTS AND DISCUSSION

Complexing properties of PAA

Figure 1 shows the titration curves of PAA and PAA–metal ions (about 2/1 molar ratio) in 0.1 M NaCl solution. The degree of neutralization, α , is defined as the equivalent of base (NaOH) added per equivalent of PAA present initially. In each titration curve of PAA–metal ions, a buffer region can be observed, suggesting that PAA–metal complexes are formed. However, in the case of the PAA–Hg(II) system with sodium hydroxide solution, no buffer region was observed (plots are omitted). This may be due to the formation of salts such as $\text{HgCl}_2 \cdot \text{HgO}$ and/or HgO other than PAA–Hg(II) complex by addition of NaOH. Therefore, the results of pH titration for the Hg(II) system seem to be inaccurate. As seen from the figure, the complex of PAA–Cu(II) seems to be more stable than the other complexes. The titration curves of PAA with Cd(II) and Co(II) were very similar.

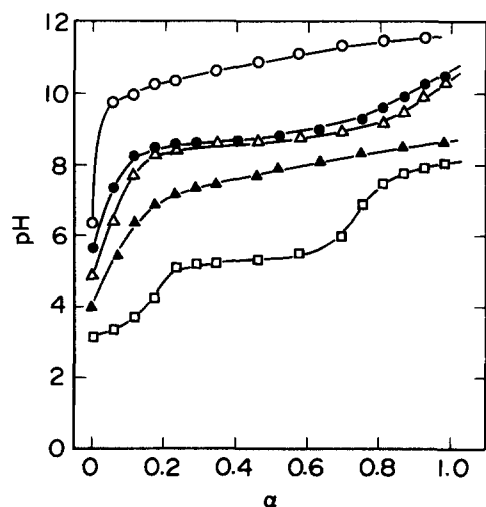


Figure 1 Titration of PAA and PAA–metal ions (0.2 mmol) in 0.1 M NaCl solution with NaOH solution: no metal ion (○), Cd(II) (●), Co(II) (△), Ni(II) (▲), Cu(II) (□)

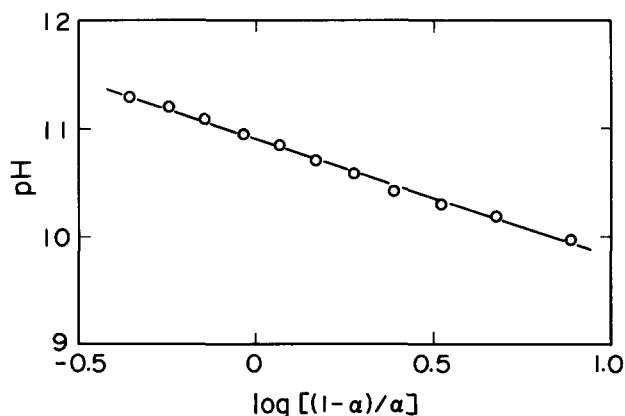


Figure 2 Henderson–Hasselbalch plot for PAA in 0.1 M NaCl solution

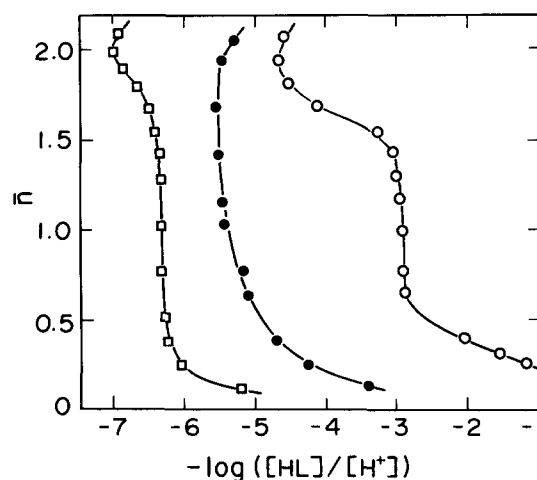
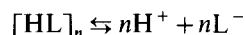


Figure 3 Modified Bjerrum plots for 8.9 mM PAA with metal chlorides at 4 mM; Cu(II) (○), Ni(II) (●), Cd(II) (□)

The dissociation reaction of PAA may be represented by the following equation:



where HL denotes the monomeric unit of PAA. In this case, the dissociation constant, K_a , and the value of n may be determined by a Henderson–Hasselbalch plot, which is shown in Figure 2. The plot is almost linear over a wide range of α values. The intercept of the line at $\alpha=0.5$ and its slope gave values of $\text{p}K_a=10.9$ and $n=1$, respectively. The value of n implies that the monomeric unit of PAA corresponds to an equivalent weight.

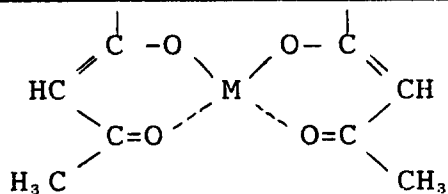
We determined the overall binding constants of PAA–metal complexes from the modified Bjerrum plots^{3,6} shown in Figure 3, where \bar{n} is the degree of formation, and $[\text{HL}]$ and $[\text{H}^+]$ mean the total concentration of PAA and the hydrogen ion concentration, respectively. In each case, the value of \bar{n} increased with decrease in the value of the abscissa, and then the curves converged to $\bar{n}=2$ or broke in the vicinity of $\bar{n}=2$. This shows that the maximum coordination number is close to 2. The values of the overall binding constant, K' , were determined from the values on the abscissa corresponding to $\bar{n}=1$, and the value of K_a obtained above. These values are summarized in Table 1. The binding constant of PAA for Cu(II) was larger than those for the other metal ions examined. The values of the dissociation constant of PAA and its binding constant for Cu(II) are similar to those

Table 1 Overall binding constants of metal ions

| Ions | Cu(II) | Ni(II) | Co(II) | Cd(II) |
|----------|--------|--------|--------|--------|
| log K' | 16 | 11 | 9.3 | 9.2 |

of acetylacetonate rather than those of PAA in the dioxane-water system presented by Hoeschele *et al.*³.

Acetylacetonate, which is a model compound of PAA, is well known to react with bivalent metal ions to form bis(acetylacetonato) compounds^{8,9}. On consideration of both this fact and the observation that the Bjerrum plots for PAA-metal(II) systems converged to $\bar{n}=2$, the structure of the complexes is presumed to be as follows:

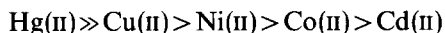


where M denotes bivalent metal ion.

Adsorption

The adsorption equilibria of PAA with Cu(II), Ni(II), Co(II), Cd(II) and Hg(II) were determined. The adsorption was initially fast, but gradually became slower with time and reached a constant value after 24 h. Therefore, the metal concentration in solution after 24 h was taken as the equilibrium concentration. Figure 4 shows the adsorption isotherms for Co(II) as typical examples. Data treatment showed that the adsorption behaviour conformed to the Langmuir isotherm rather than the Freundlich isotherm. This seems reasonable, because the number of β -diketone groups, that is adsorption sites, in PAA is limited.

The effects of the pH of the solution on the maximum adsorptions of metal ions on PAA are shown in Figure 5. The maximum adsorption was strongly influenced by the pH, increasing with increase in the pH value. But, in most cases, the maximum adsorption was low, suggesting that only a limited number of ligands were available for chelation due to the small interfacial area owing to the low porosity of PAA. The adsorption of Hg(II), however, was selective. The maximum adsorptions at the same pH value were in the following order:



This order was the same as that of the stability constant.

From these results, it is expected that PAA may be useful for concentration of metal ions, and separation of the respective metal ions from mixtures.

Column operations

Figure 6 shows the elution curves of some metal ions with eluents buffered at pH 5 and pH 6, respectively. Cd(II) was eluted first, followed by Co(II) and Ni(II). The retention volumes of Co(II) and Ni(II) were distributed over wide ranges when the eluent was buffered at pH 6, but, these metal ions were eluted sooner with eluent buffered at pH 5. Thus their elution behaviours were influenced significantly by the pH of the solution in this pH range. In this pH range, Cu(II) and Hg(II) were strongly retained and could not be eluted, but they were

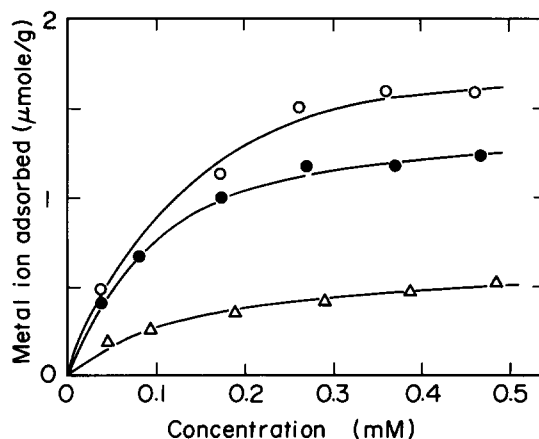


Figure 4 Adsorption isotherms of Co(II) on PAA at 25°C: pH 7 (○), pH 6 (●), pH 5 (△)

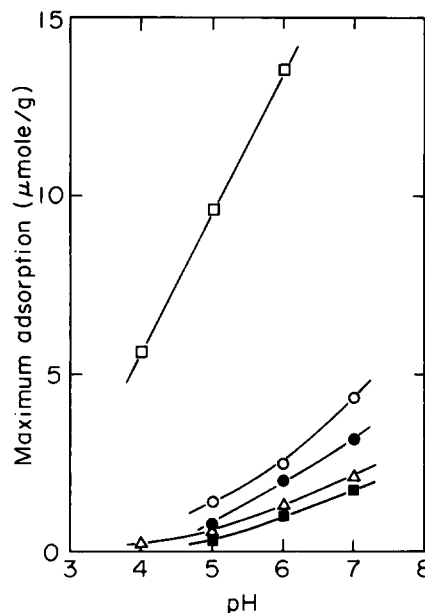


Figure 5 Effect of pH on the maximum adsorption of metal ions by PAA: Hg(II) (□), Cu(II) (○), Ni(II) (●), Co(II) (△), Cd(II) (■)

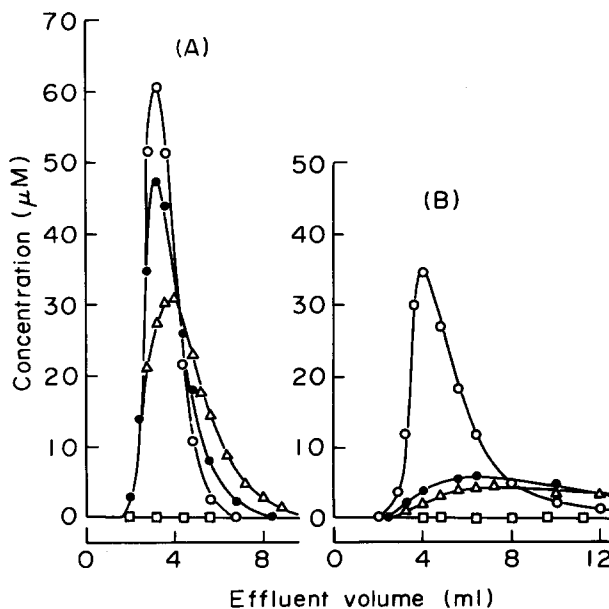


Figure 6 Elution curves for impulses of metal ions (0.5 mM × 0.2 ml): Cd(II) (○), Co(II) (●), Ni(II) (△), Cu(II) and Hg(II) (□). Flow rate of eluent, 0.68 ml min⁻¹. Eluent: sodium acetate-acetic acid buffered at pH 5 (A) and pH 6 (B)

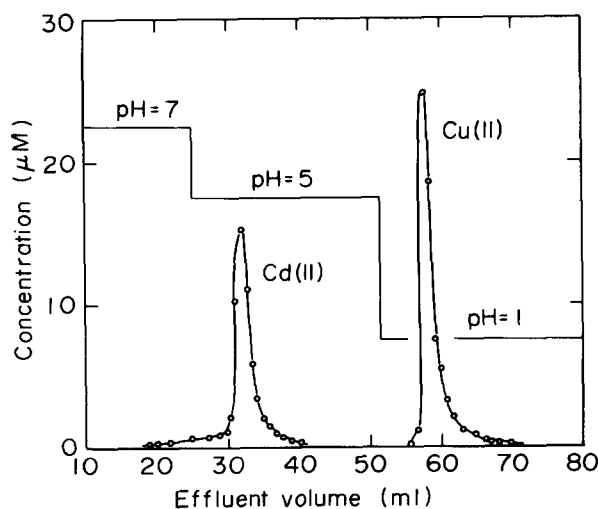


Figure 7 Separation of Cu(II) and Cd(II) by stepwise elution with acetate buffer solution (pH 7–5), and HCl solution (pH 1): 0.06 μmol Cu(II), 0.06 μmol Cd(II). Flow rate, 0.68 ml min^{-1}

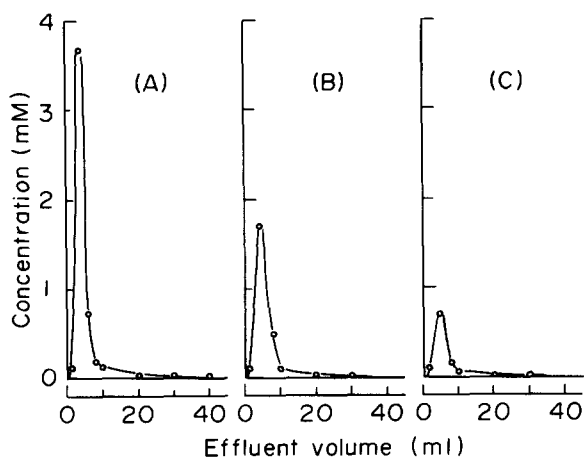


Figure 8 Elution curves of Cu(II) adsorbed at pH 6 (A), pH 5 (B) and pH 4 (C)

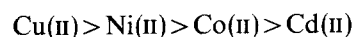
soon eluted completely with a small volume of HCl solution at a concentration above 10 mM. These results imply that stepwise decrease in pH provides a means for resolving a mixture of metal ions.

The separation of metal ions was examined using mixtures of two kinds of metal ions. As seen from Figure 7, Cu(II) and Cd(II) were successfully resolved by stepwise decrease in the pH of the eluent. The separations of Cu(II) from Co(II) and Ni(II) were also achieved successfully by the same technique. However, resolution of a mixture of Co(II) and Ni(II) was not so good because the adsorption characteristics of these metal ions are similar.

Typical examples of the elution curves of Cu(II) at different pH values are shown in Figure 8. With a solution of 0.1 mM Cu(II), the maximum concentration of Cu(II) of 3.8 mM was obtained by passing the solution through the column at pH 6, and then eluting the adsorbed Cu(II) with 0.2 M HCl solution. This means that the feed solution was concentrated about 40 times over its initial concentration by use of 1.56 g of PAA. Thus use of a PAA column is useful for concentrations of metal ions present in dilute solution.

CONCLUSIONS

Polyacryloylacetone (PAA) was synthesized, and examined as an adsorbent of divalent metal ions. Its dissociation constant and overall binding constants for complexing with metal ions were determined from experimental data on pH titration. The results are shown in Table 1. The order of stability of metal complexes was as follows:



The adsorption behaviours of metal ions on PAA conformed to the Langmuir rather than the Freundlich isotherm. The maximum adsorptions of metal ions by PAA were very low, but Hg(II) was adsorbed selectively. The adsorption was strongly dependent on the pH of the solution, and metal ions adsorbed on PAA could be eluted with HCl solution in a concentration above 10 mM.

The separation and concentration of metal ions using a PAA column were examined. Good resolution of Cu(II) and Cd(II) from their mixture was achieved by stepwise decrease in pH of the eluent. But the resolutions of Co(II) and Ni(II) from their mixture was poor because of the similarity in their adsorption characteristics.

The possibility of use of a PAA column for concentration of metal ions from dilute solution was also demonstrated.

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