

Metal complexes of poly(2-acetamidoacrylic acid)

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Complexation constants of divalent and trivalent metal ions with 2-acetamidoacrylic acid (4A) and its polymer (P4A) were determined by the modified Bjerrum method. P4A has carboxyl and acetamido (acetyl) groups. Although an additive effect of two functional groups was expected in complexing with metal ions, the complexation constants of P4A were essentially the same as those for poly(acrylic acid), while P4A has greater complexing ability than 4A. The interactions of P4A and 4A with Cu(II) and Mn(II) ions were studied using ^{13}C n.m.r. The addition of Cu(II) ion to P4A and 4A solutions selectively broadens the α -carbon and carboxyl carbon signals, and the addition of Mn(II) ion broadens the acetyl and carboxyl carbonyl carbon signals. This finding suggests that Cu(II) and Mn(II) ions form five-membered and seven-membered chelate rings, respectively.

(Keywords: poly(2-acetamidoacrylic acid); di- and trivalent metal ions; complexation constants)

INTRODUCTION

Crosslinked polyacrylic and polymethacrylic acids are compounds well known as metal absorbents. In practice, almost all weakly acidic cation-exchange resins are prepared by hydrolysis of poly(methylacrylate-co-divinylbenzene) and poly(methyl methacrylate-co-divinylbenzene). In this connection, the potentiometric titration of polyacrylic and polymethacrylic acids has been studied by many investigators¹⁻⁴.

The introduction of a functional group to polycarboxylic acid, such as the iminoacetic acids⁵, can be expected to increase the complexing ability because of an additive effect of two functional groups. Poly(2-acetamidoacrylic acid) (P4A) has an acetamido (acetyl) group other than the carboxyl group, and therefore may form more stable complexes than poly(acrylic acid) (P2A).

This paper describes titrations of P4A in the absence or presence of various divalent transition and trivalent rare earth metal ions. The complexation constants are calculated using a modified Bjerrum method⁶, and the complexation constants of P4A are compared with those of P2A and 2-acetamidoacrylic acid (4A). Experiments on determination of formation constants for the complexes of rare earth metal ions with P4A offer preliminary data on chromatographic separation of the rare earth metal ions, which is paid much attention by many investigators.

EXPERIMENTAL

Materials

2-Acetamidoacrylic acid (4A) was prepared by refluxing a benzene solution of pyruvic acid and acetamide⁷. On recrystallization of the resulting crude product from ethanol, 4A precipitates as white needles with a melting point of 198–199°C. 4A was polymerized with 2,2'-azobisisobutyronitrile (AIBN) as the initiator. The number-average molecular weight of the polymer obtained was estimated to be 44 000 by means of gel permeation chromatography (g.p.c.). P4A is readily soluble in water, whereas 4A is only slightly soluble. Poly(acrylic acid) (P2A) ($M_w = 90\,000$) was commercially available, and purified by dialysis and lyophilization. Other reagents and solvents were of a special grade available commercially, and purified prior to use.

Measurements

The molecular weight of P4A was determined by g.p.c. (pump, Jasco Trirotor-V; detector, Showa Denko SE-31 refractometer; column, TSK Gel G6000PW + G3000PW; carrier, 0.1 M phosphate buffer; standard sample, poly(ethylene oxide) from Toyo Soda; flow rate, 0.5 ml min⁻¹; temperature, 40°C).

^{13}C n.m.r. spectra were taken in D₂O or D₂O/CD₃OD solvent on a Jeol GX-400 spectrometer, relative to the dioxane signal as 67.40 ppm or the deuterated methanol signal as 47.05 ppm.

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Titration

Titrations of pH were performed with a TOA HM-60S pH meter equipped with automatic titrator at 25°C for constant ion strength ($\mu = 1.0$, KNO_3 or KCl); aqueous solutions of P4A, 4A and P2A were titrated with potassium hydroxide in the absence or presence of the nitrate salt of divalent metal ions or the chloride salt of rare earth metal ions.

RESULTS AND DISCUSSION

Complexation of P4A with metal ions

Figure 1 shows titration data for P4A, 4A and P2A in the absence of metal salts. Henderson-Hasselbalch plots (plot of pH versus $\log(1-\alpha)/\alpha$) gave a straight line in a certain range of the degree of dissociation (α). Table 1 summarizes values for apparent ionization constant ($\text{p}K_a$) and the constant n which are estimated from the pH value at $\alpha=0.5$ and the slope of the straight line.

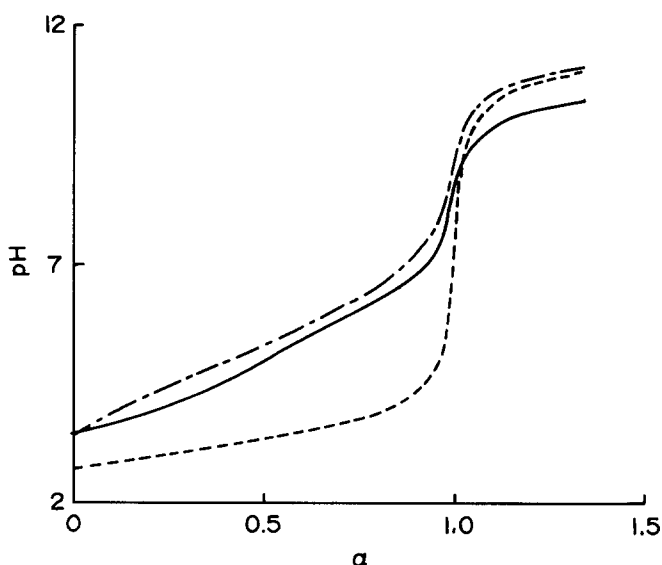


Figure 1 Titration of 4A (0.01 M, ---), P4A (0.01 M, —), and P2A (0.01 M, -·-·-) with aqueous NaOH (0.01 M) at 25°C ($\mu = 1.0$, KNO_3)

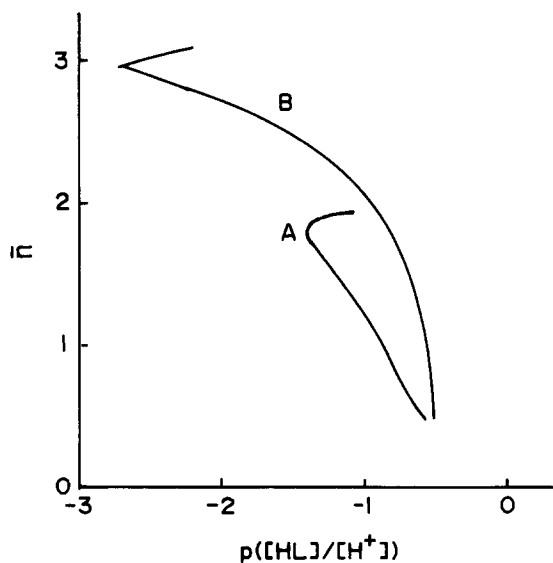


Figure 2 Modified Bjerrum plots for (A) P4A-Cu(II) and (B) P4A-Ce(III) systems

Table 1 $\text{p}K_a$ and n values for the Henderson-Hasselbalch equation

Acid	$\text{p}K_a$	n
P4A	4.95	2.76
P2A	5.22	2.03
4A	3.22	1.00

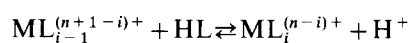
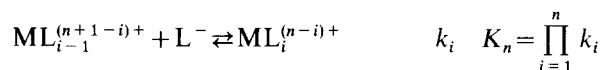
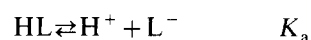
Table 2 Overall complexation constants (K_2) of divalent metal ions

Metal ion	$\log K_2$		
	P4A	P2A	4A
Copper(II)	8.17	7.91	5.61
Cadmium(II)	6.77	7.49	5.61
Nickel(II)	6.26	6.06	5.56
Cobalt(II)	6.13	5.96	5.59
Zinc(II)	6.10	6.34	5.54
Manganese(II)	6.06	6.08	5.44

Generally, n is considered to be a parameter which represents interaction between neighbouring groups in the chain, with values near 2 for polymers and near 1 for low-molecular-weight compounds.

A variety of $\text{p}K_a$ values for P2A have been reported. The $\text{p}K_a$ value varies with experimental conditions such as temperature, ion strength, and salt used for controlling ion strength⁶. Gregor *et al.*⁸ and Kavanov *et al.*⁹ have found $\text{p}K_a = 4.30$ and 6.4 for P2A, respectively. An intermediate value was obtained in this work. The $\text{p}K_a$ for P4A is larger than that for 4A and smaller than that for P2A. It is the general tendency that the $\text{p}K_a$ value of a polyacid is larger than that of its monomeric compound.

Complexation constants of P4A, P2A and 4A with six kinds of divalent transition metal ion and P4A with nine kinds of rare earth metal ion were determined by the modified Bjerrum method. Figure 2 shows two examples of the modified Bjerrum plot, where \bar{n} is the degree of formation, and $[\text{HL}]$ and $[\text{H}^+]$ represent total concentration of ligand and hydrogen ion concentration, respectively. The value of \bar{n} increases with decrease in $p([\text{HL}]/[\text{H}^+])$, and the curves break in the vicinity of $\bar{n} = 2$ or $\bar{n} = 3$. These findings suggest that the maximum coordination number is 2 for Cu(II) ion and 3 for La(III) ion. The overall complexation constants (K_2) ($=k_1k_2$) were calculated from the values of B_n and K_a . Symbols correspond to the following reactions:



$$b_i, \quad B_n = \prod_{i=1}^n b_i = K_n^n K_a$$

where HL, H^+ and M^{n+} represent ligand, proton and metal with ionic valence n , and k_i and K_n are referred to as successive and overall complexation constants, respectively. Only overall complexation constants for divalent metal ions are shown in Table 2 (the k_1 values are larger than k_2 values in all the systems).

The following conclusions may be derived from the data shown in Table 2. (1) P4A and P2A have superior complexation ability with Cu(II) and Cd(II) ions, while

overall complexation constants of 4A are independent of metal ions. (2) There was no difference between the complexing abilities of P4A and P2A, even though the additive effect of acetyl and carboxyl groups was expected on complexation. (3) The complexation constants of the polymer (P4A) are larger than those of the monomer (4A). (4) Metal ion selectivity of P4A follows the Irving-Williams series¹⁰.

The overall complexation constants (K_3) ($=k_1k_2k_3$) of trivalent rare earth metal ions with P4A are shown in Figure 3, together with the published data^{11,12} on ethylenediaminetetraacetic acid (EDTA) and iminodiacetic acid (IMDA) complexes. The magnitude of successive complexation constants is in the order $k_1 > k_2 > k_3$. The K_3 values of P4A lie in the region between those of EDTA and IMDA. P4A exhibits excellent properties as a complexing agent for rare earth metal ions except for low selectivity.

Interaction of 4A and P4A with divalent metal ions

The interaction of poly(γ -glutamic acid) (PGA) with Cu(II) and Mn(II) ions has been discussed on the basis of the relationship between the concentration of the metal ion added to aqueous solution of PGA and the height of ¹³C n.m.r. peaks¹³. P4A is similar in chemical structure to PGA. Therefore, the structure of metal complexes of 4A and P4A can be assumed by using broadening of ¹³C n.m.r. signals.

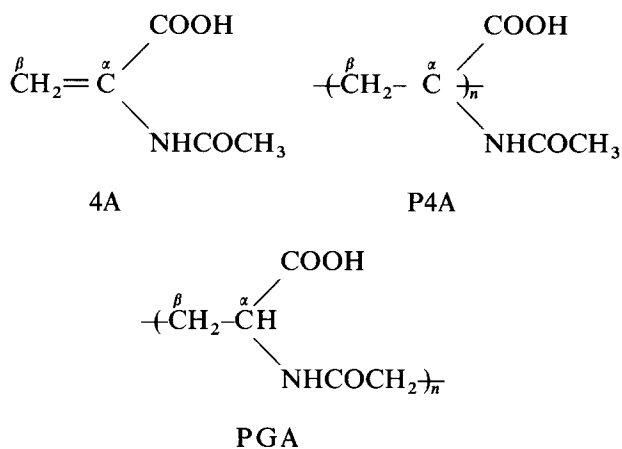


Figure 4 shows ¹³C n.m.r. spectra of 4A at various Cu(II) concentrations. The mixed solvent of D₂O and CD₃OD was used because of the slight solubility of 4A in water. The peak of CD₃OD as the internal standard is omitted in the figure. The signal of α -carbon appears at $\delta=133.2$ ppm, and carboxyl and acetyl carbons resonate at $\delta=165.8$ and 171.7 ppm, respectively. The assignments were made by selective ¹H decoupling. The carboxyl carbon and α -carbon resonances broaden remarkably with increasing concentration of Cu(II) ion. This observation suggests that the oxygen atom of the carboxyl group and the nitrogen atom of the acetyl group of 4A are bound to the Cu(II) ion, and rapid chemical exchange occurs between bound and free states. That is to say, 4A and Cu(II) ion appear to bind to form a five-membered ring.

Figure 5 shows ¹³C n.m.r. spectra of 4A in various Mn(II) concentrations. On adding Mn(II) salt to 4A solution, the carbonyl carbon resonances increase in linewidth as in the case of Cu(II). Furthermore, broadening of the resonance signal of acetyl carbon is

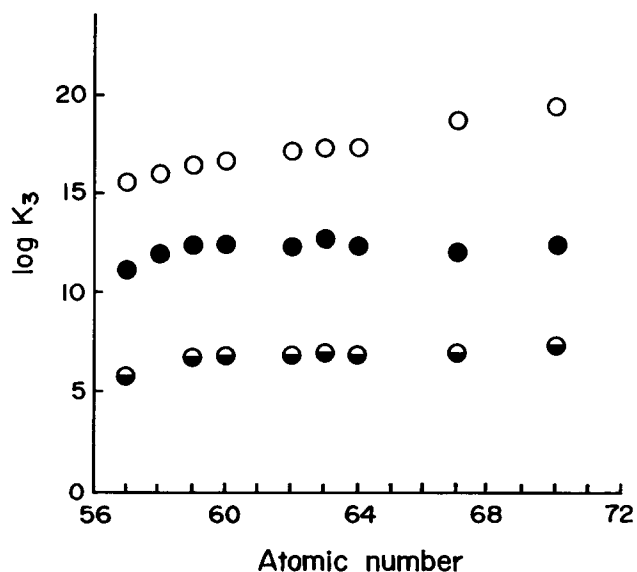


Figure 3 Complexation constants of rare earth metal ions with P4A. ●, P4A; ○, EDTA; ◐, IMDA

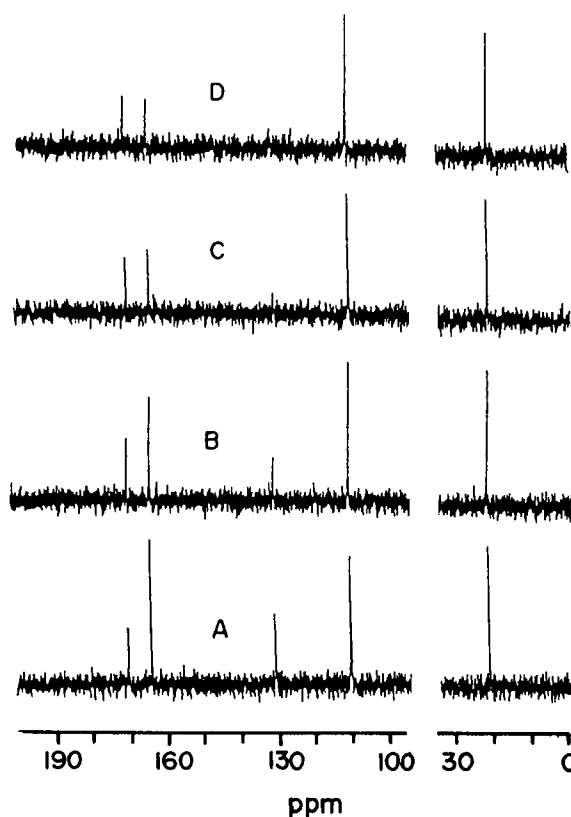


Figure 4 ¹³C n.m.r. spectra of 4A in mixed solvent of D₂O and CD₃OD at various Cu(II) concentrations. [Cu(II)]/[4A] = 0 (A), 1 × 10⁻⁴ (B), 5 × 10⁻⁴ (C) and 1 × 10⁻³ (D)

induced and the α -carbon signal remains unchanged in contrast to the system of Cu(II). These findings reveal that both oxygen atoms of carboxyl and acetyl groups are bound to the Mn(II) ion. The 4A-Mn(II) complexes are considered to be in the form of a seven-membered ring.

Figure 6 shows ¹³C n.m.r. spectra of P4A in D₂O in the absence or presence of copper(II) nitrate. The signal of dioxane as the internal standard is omitted. Two carbonyl carbons (acetyl and carboxyl) resonate at lower magnetic fields than those of 4A, and have the same

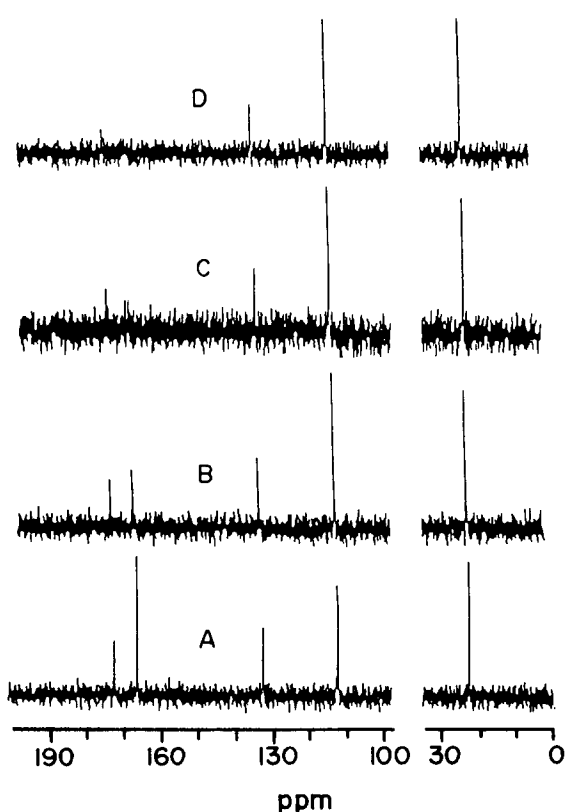


Figure 5 ^{13}C n.m.r. spectra of 4A in mixed solvent of D_2O and CD_3OD at various Mn(II) concentrations. $[\text{Mn(II)}]/[\text{4A}] = 0$ (A), 1×10^{-4} (B), 5×10^{-4} (C) and 1×10^{-3} (D)

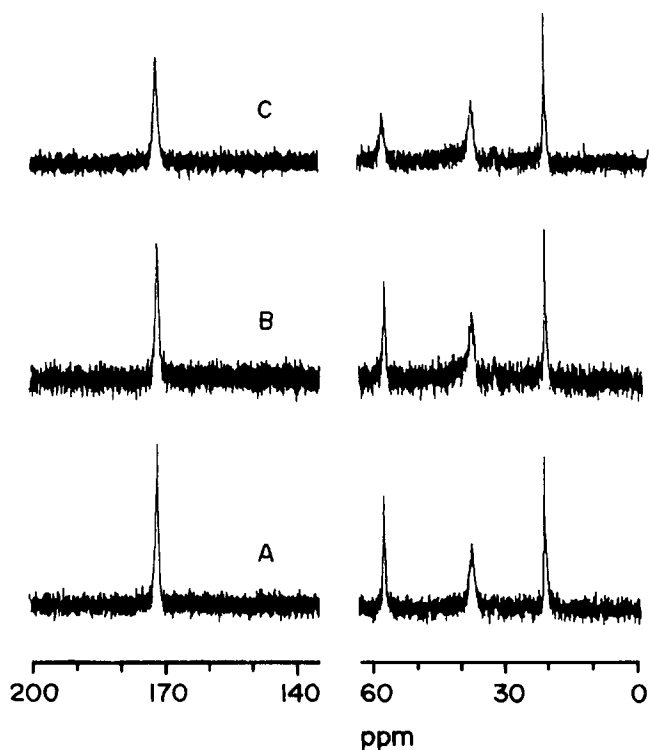


Figure 6 ^{13}C n.m.r. spectra of P4A in D_2O at various Cu(II) concentrations. $[\text{Cu(II)}]/[\text{P4A}] = 0$ (A), 1×10^{-4} (B) and 1×10^{-3} (C)

chemical shift ($\delta = 173.2$ ppm). The addition of a small amount of NaOH solution results in the appearance of a new resonance peak at 176.5 ppm. This peak may be assigned to the carbon of the carboxyl anion.

As can be seen from Figure 6, linewidth and peak height of carbonyl carbons and α -carbon resonances

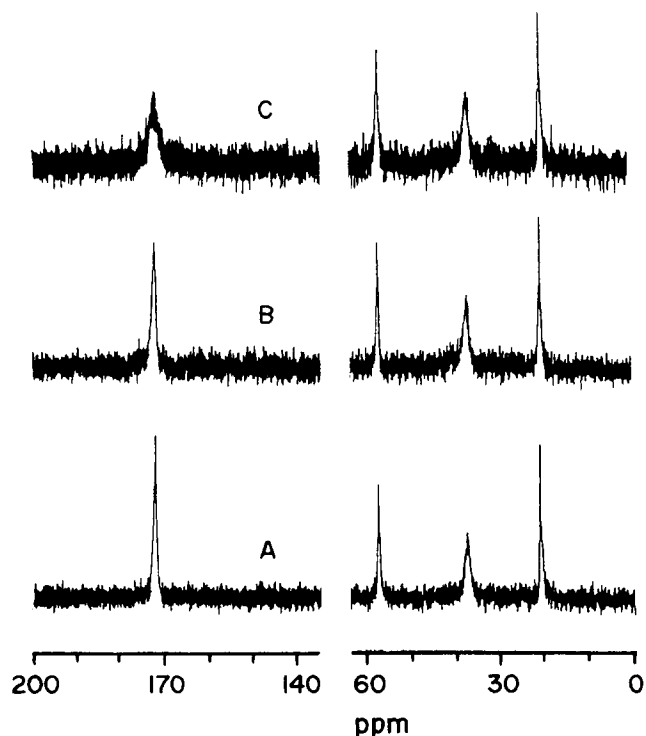


Figure 7 ^{13}C n.m.r. spectra of P4A in D_2O at various Mn(II) concentrations. $[\text{Mn(II)}]/[\text{P4A}] = 0$ (A), 1×10^{-4} (B) and 1×10^{-3} (C)

increase and decrease, respectively, with increasing concentration of copper(II) nitrate. It is thought with reference to the results for the 4A-Cu(II) system that the broadening of carbonyl carbon resonances results from the increase in the peak width of carboxyl carbon. Therefore, it may be concluded that P4A and Cu(II) ion bind to form the five-membered ring as in the case of the 4A-Cu(II) system.

Figure 7 shows ^{13}C n.m.r. spectra of P4A in the absence or presence of manganese(II) nitrate. Addition of manganese(II) nitrate to P4A solution causes only the peak of carbonyl carbons to broaden, and the other peaks remain unchanged. This finding suggests that both oxygen atoms of acetyl and carboxyl groups are bound to the Mn(II) ion. Therefore, it may be concluded that P4A and Mn(II) ion bind to form a seven-membered ring as in the case of the 4A-Mn(II) system.

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