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INTERACTION OF DIVALENT IONS OF COPPER, MAGNESIUM AND ZINC WITH ISOTACTIC POLYMETHACRYLIC ACID

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Abstract—The interaction of divalent metal ions (Cu^{2+}, Mg^{2+} and Zn^{2+}) with isotactic poly(methacrylic acid) (PMAA) has been studied using potentiometric, equilibrium dialysis and viscometric techniques. Partially neutralized isotactic PMAA was titrated with solutions of metal ion so as to enable the polymer/metal ion ratio to be varied over a wide range. The results show the existence of two types of complexes, one at low and the other at high metal ion concentrations. Results from dialysis studies confirm the observations from potentiometric results, indicating the existence of two types of complexes in the solution. Viscometric titrations reveal that the presence of the bound metal ions on the polyelectrolyte imposes structural restrictions on the chain.

INTRODUCTION

It is known that divalent metal ions interact with isotatic polymethacrylic acid (PMAA) [1–3]. Of the divalent metal ions studied so far, Cu(II) has attracted most attention. There are few data available on the interaction of zinc and magnesium with these systems, although Loebl and O'Neill [1] suggested that Mg^{2+} will not show a great tendency to undergo complexation as expected.

Significance differences have also been found in the extent to which Na^+ ions bind to isotactic and syndiotactic PMAA [2] with the fraction of Na^+ ions bound to isotactic PMAA compared with syndiotactic PMAA. Morawetz *et al.* [4] using the method of dialysis equilibrium have shown that the affinities of isotactic PMAA and syndiotactic PMAA for Mg^{2+} are in the opposite order to those found for Cu^{2+}. Eldrige and Treloar [5] from u.v. studies showed that cobalt could bind three carboxylate groups on a single polymer chain. They also showed that Co unlike Cu could not force a redistribution of charges on the polyacrylic anion. Considerable differences were also observed in the binding strength of Co [5] and Cu [6], attributed to the strong covalent bonding between Cu(II) and polycarboxylate. From the protonation and Cu binding data for three maleic acid copolymers, Crescenzi *et al.* [7] attributed the high values of differential volumes of binding obtained to extensive desolvation of the interacting Cu^{2+} ions and the vicinal pairs of carboxylate groups which would also perturb the solvation layers of the neighbouring chain elements. It seems therefore, from the specificity observed in the binding with stereoregular PMAA that neighbouring carboxylate groups along the chain of the polymeric acid are involved in the complex formation.

The structural conformations of iPMAA in aqueous solutions have been investigated by many authors. Mandel and Leyte [8] first recognised the existence of two conformations of PMAA and said that it was responsible for its abnormal behaviour. Barone *et al.* [9] pointed out that the isotactic PMAA behaves as a weaker acid than the syndiotactic form. Similar results have been obtained by Nagasawa *et al.* [10] and an indication of this fact was earlier given by Loebl and O'Neill [1]. It is interesting to recall that there was no difference in the potentiometric behaviour of stereoisomeric samples of poly(acrylic acid). The various reasons for such anomalous behaviour could be summarized as follows. The isotactic form has a "locally" helical structure in solution whereas the syndiotactic form has a planar zig-zag conformation. The atactic form is known to be in compact conformation in the ionized and partially ionized state. The tightly coiled form of isotactic PMAA seems to be more stable at low degrees of dissociation as indicated by its insolubility at low α values ($\leqslant 0.3$). We found that isotactic PMAA becomes soluble only at an α value beyond the conformational transition region of syndiotactic and atatic PMAA.

In the present studies, potentiometric and viscometric titrations have been carried out by titrating partially ionized isotactic PMAA with solutions of metal ions at various constant ionic strengths.

Dialysis experiments have also been carried out on PMAA brought to the same degree of ionization and in the presence of a range of metal ion concentrations. From these results, the amounts of carboxylate ion bound per metal ion at different metal ion/PMAA ratios have been calculated.

It should be pointed out that there were experimental limitations in the techniques, resulting in limitation to the ionic strengths open to investigation. Dialysis measurements required high ionic strength while viscometric titrations required low ionic strength. There was no restriction of ionic strength in the range I = 0.1 to I = 0.01 for potentiometric titrations and the series of experiments show the effect of ionic strength on the resulting binding curves.

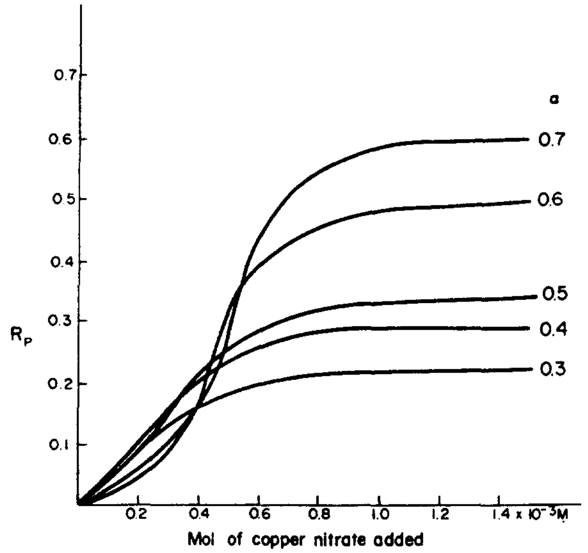

Fig. 1. Potentiometric titration of isotactic PMAA with Cu^{2+} ions at various degrees of dissociation, α, at constant ionic strength, 0.10, and polymer concentration, 2.5 × 10^{-3} M. at 25°. The abscissa denote concentration of added Cu^{2+}. The ordinate, R_p, gives the mole of complexed carboxylate groups per mol of the total polyacid.

EXPERIMENTAL

Materials

A sample of isotactic polymethylmethacrylate was prepared from the monomer. The monomer was first purified by low pressure distillation and stored over calcium hydride. It was then polymerised at 25° in dry toluene, with ethylmagnesium bromide as initiator. At the end of the polymerization, the polymer obtained was purified. The resulting fluffy precipitate was dried in a vacuum oven at 60°.

The polymethylmethacrylate was hydrolysed by dissolving 5 g in a solution of 3 g *p*-toluene sulphinic acid in 80% acetic acid and the solution then refluxed in an oil bath at 110° for 340 hr. The product isolated by precipitation in ether was purified and dried in a vacuum oven at 60°.

The molecular weight of the polymer was determined by viscometry [11] and the sample having viscosity-average molecular weight of 4.8 × 10^4 and a percentage isotacticity of 91.0 was used in all the measurements. The % isotacticity was determined from a knowledge of the coupling constant, J, obtained from the NMR spectra of the polymer.

Methods

Potentiometric titrations

Potentiometric titrations were carried out by using a Pye-Unicam pH meter model 200 in conjunction with a combined glass and reference electrode for the pH determination. Since the unionized isotactic PMAA was insoluble in water, the polymer solutions were pretitrated to varying degrees of ionization, α (α > 0.25), and titrated with metal ion solutions in plastic beakers thermostatted at 25 ± 0.1°. Titrations at constant ionic strength were carried out by the method of Kolawole [12].

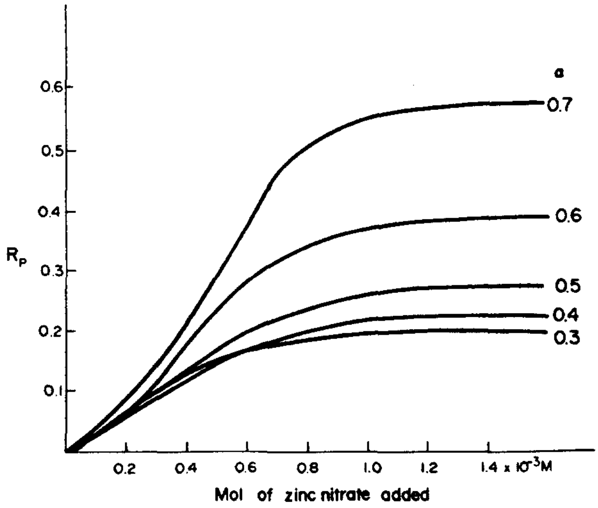

Fig. 2. As for Fig. 1, using Zn^{2+} in place of Cu^{2+}.

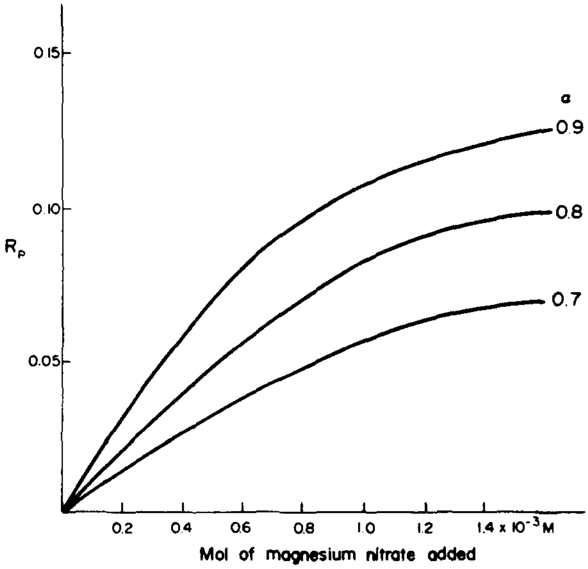

Fig. 3. As for Fig. 1, using Mg^{2+} in place of Cu^{2+}.

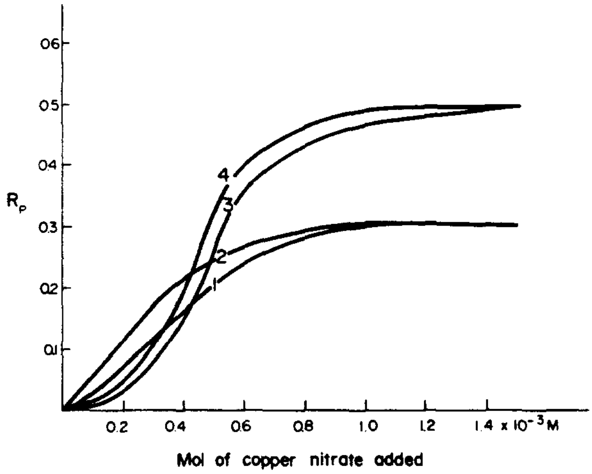

Fig. 4. Potentiometric titration data of iPMAA with Cu^{2+} showing the ionic strength effect on the binding of Cu to iPMAA at polymer concentration = 2.5×10^{-3} M. 1—$\alpha = 0.40$, $I = 0.10$; 2—$\alpha = 0.40$, $I = 0.05$; 3—$\alpha = 0.60$, $I = 0.10$; 4—$\alpha = 0.60$, $I = 0.05$.

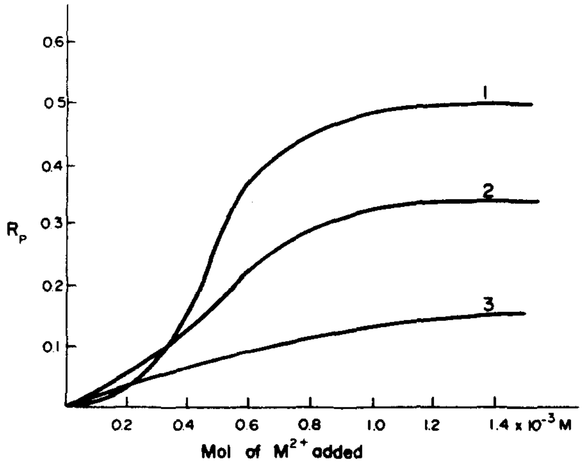

Fig. 5. Potentiometric titrations of iPMAA with divalent ions at $\alpha = 0.6$ at constant ionic strength $I = 0.10$ and polymer concentration = 2.5×10^{-3} M. The ordinate, R_p, denotes the extent to which the available sites have been occupied by M^{2+} and the abscissa gives the concentration of the added metal ions. (1)—Cu^{2+}; (2)—Zn^{2+}; (3)—Mg^{2+}.

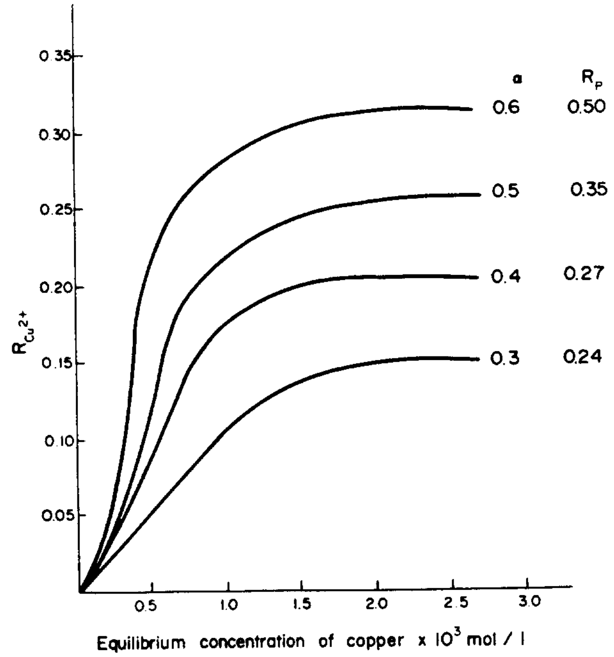

Fig. 6. Equilibrium dialysis data at various degrees of dissociation, α, ionic strength I = 0.1 and polymer concentration = 2.5×10^{-3} M at 25°. The ordinate, $R_{Cu^{2+}}$, denotes the moles of added Cu^{2+} bound per mol of total polyacid. The abscissa gives the equilibrium concentration, $[Cu^{2+}]_f$, of the added Cu^{2+}.

Equilibrium dialysis measurements

Visking Cellophane tubing appropriate to the volume of acid used ($10.0\,cm^3$) were boiled for 1 hr and thoroughly rinsed in glass-distilled water. The tubes were soaked in distilled water for a few hours and then soaked in 0.1 M KNO_3 for another 24 hr, adjusting the pH occasionally to the desired value. These tubes were used for dialysis inside a stoppered Pyrex tube at 25 ± 0.1°. The solution of iPMAA (2.5×10^{-3} M) in 0.1 M KNO_3 at the desired degree of ionization was put inside the bag. The solution outside the bag contained the chosen concentration of metal ion under investigation and the same concentration of KNO_3 as inside the bag.

The time to reach equilibrium was determined for each metal ion. The concentrations of the metal ion initially and after the attainment of equilibrium were determined by the method described in Beckman Technical Bulletin [13]. Analysis showed that the time required for attainment of equilibrium was five days and that the amount of metal ion bound to the cellophane bag was negligible in each case.

Viscometric titrations

Viscosities were measured at 25 ± 0.1° in an Ubbelohde (suspended-level dilution) viscometer. The viscosity of $5\,cm^3$ of iPMAA solutions at a particular degree of ionization containing various concentrations of metal ion were measured. The procedure was repeated for iPMAA solutions with α between 0.3 and 0.8.

RESULTS AND DISCUSSION

Potentiometric titrations

In the binding results presented below, three equilibria are considered:

$$\text{—COOH} \rightleftharpoons \text{—COO}^- + H^+ \qquad (1)$$

$$\text{—COO}^- + M^{2+} \rightleftharpoons \text{—COOM]}^+ \qquad (2)$$

$$\text{—COOM]}^+ + \text{—COO}^- \rightleftharpoons \text{—COOM OCC—}. \qquad (3)$$

The binding of M^{2+} to —COO^- (Eqns 2 and 3) results from the dissociation of the carboxyl groups in Eqn (1); M^{2+} represents the free cation. To obtain the binding curves in order to identify the types of complexes formed as reactions take place, it is essential to calculate the concentration of the carboxylates available for binding. The apparent degree of dissociation, α, is related to the number of carboxylates $[\text{—COO}^-]$ by $[\text{—COO}^-] = \alpha C$ where C = original concentration of the —COOH present on the polyion. Similarly the pH of the solution is related to αC by

$$\begin{aligned} pH &= pK_a^1 + \log \frac{\alpha C}{1 - \alpha C} \\ &= -\log(1 - \alpha C) + \log \frac{\alpha C}{K_a^1} \\ &= Q + \log \frac{\alpha C}{K_a^1}. \end{aligned}$$

The value of —COOH at any time can be obtained from the difference between the original value and the value of hydrogen ion released. In most cases $[H^+]$ is so small as to be insignificant compared with the original [—COOH]. This means the quantity Q remains virtually constant as this comes from the original value of H^+ released. Therefore, the change in pH is proportional to the change in $\log \alpha C/K_a^1$ i.e.

$$\Delta pH \propto \Delta \log \frac{\alpha C}{K_a^1}.$$

The above equation is derived using the Handerson–Hasselbalch equation where all modifications are represented by the variable value of K_a^1. This relation-

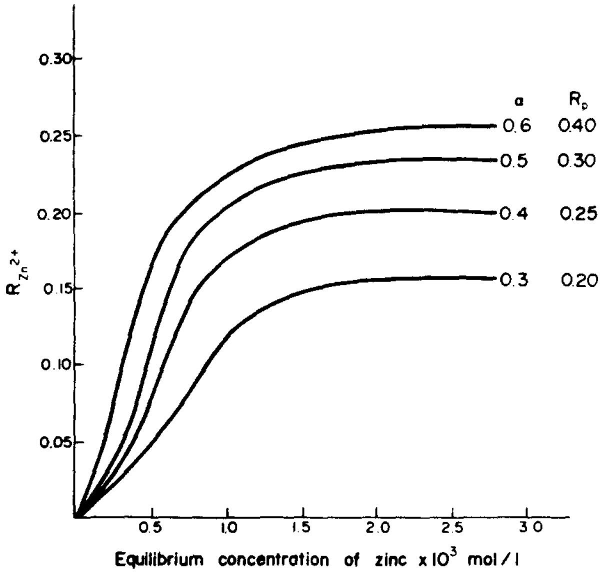

Fig. 7. As for Fig. 6, using Zn^{2+} in place of Cu^{2+}.

ship is now developed to enable calculation of the amount of bound carboxylate. The method used for the determination of the number of unbound carboxylate groups present was similar to that of Mandel and Leyte [14]. Titration of isotactic PMAA at appropriate constant ionic strength gave reference curve of pH + log(1 − α)C vs log C at constant polymer concentration (2.5 × 10^{-3} M). In the present work, we have used the general term C and (1 − α)C to enable use of the reference curves over a very small range of concentration differences which resulted from the titration of the preionized polymer with concentrated metal ion solutions. Using the reference curves and from a knowledge of pH + log [COOH] = pH + log(1 − α)C after the addition of different amounts of metal ion, log αC and hence the free carboxylate groups present could be estimated. Previous workers [14] assumed that pK_a is dependent solely on the number of free carboxylate groups on the polyion and unaffected by conformational changes brought about by intra- and intermolecular binding. We object to these assumptions and feel that the present method of estimating free carboxylate groups gives a more consistent picture than methods based chiefly on the calculation of electrostatic potentials.

When the procedure outlined above for calculating the amount of free carboxylate concentration was employed, the amounts of carboxylate ions bound to the metal ions were calculated. The binding curves for the equilibrium reactions (2) and (3) above are plotted in terms of the binding ratio R_p i.e. the ratio of the concentration of the carboxylate groups bound to the total concentration of the carboxyl groups on the polymer.

Figures 1–3 show the plot of R_p as a function of total concentration of M^{2+} added, $[M^{2+}]_T$ for five degrees of dissociation at constant ionic strength I = 0.1. The figures show that nearly 90% of $[Cu^{2+}]_T$, 70% of $[Zn^{2+}]_T$ and about 26% $[Mg^{2+}]_T$ were bound

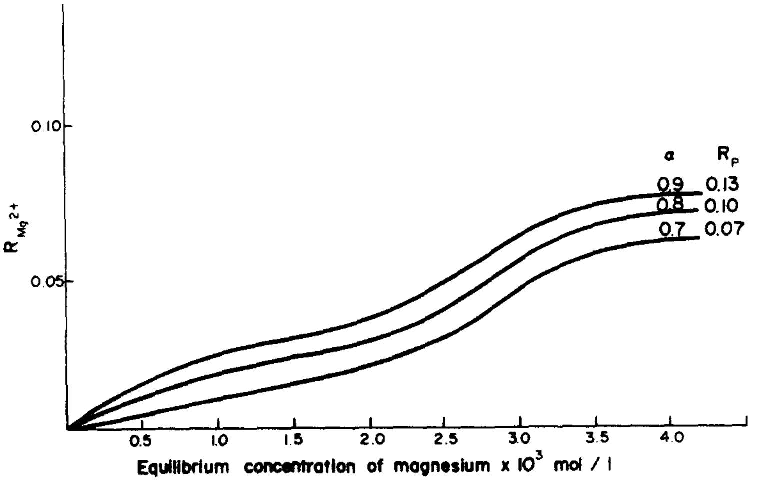

Fig. 8. As for Fig. 6, using Mg^{2+} in place of Cu^{2+}.

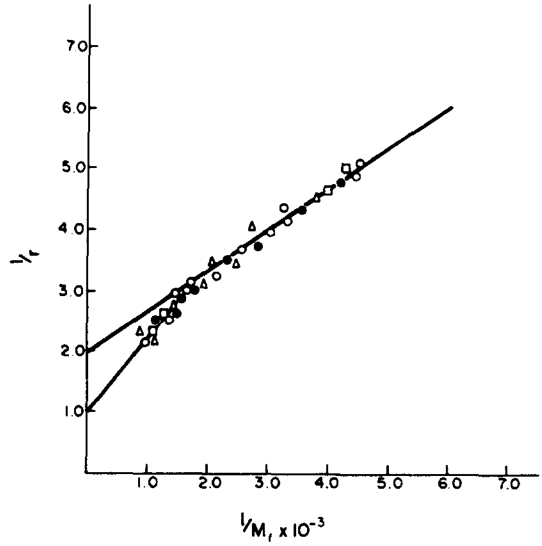

Fig. 9. Determination of stability constants and coordination numbers for Cu–PMAA complexes. Polymer concentration = 2.5 × 10^{-3} M, I = 0.10. α: (○) 0.30; (△) 0.40; (□) 0.50; (●) 0.60.

to the polyelectrolyte. All three figures show that, as the charge density on the polyion falls, the limiting binding ratio reduces. In Figs 1 and 2 at higher degrees of dissociation the curves exhibit sigmoid shapes. The shapes of the curves suggest that there are two types of complexes, one existing at low and the other at high metal ion concentration. It can be seen that R_p continuously varies as the amount of M^{2+} being linked to the polyelectrolyte chain increases until a limiting value of R_p is obtained.

In the case of Cu (Fig. 1), the extent to which the available sites have been occupied at high α and low $[Cu^{2+}]_T$ is lower than at low α and low $[Cu^{2+}]_T$. However for Zn and Mg (Figs 2 and 3), R_p values at low $[M^{2+}]_T$ and low α are lower than R_p values at low $[M^{2+}]_T$ and high α. This observation is true for all ionic strengths studied. A possible explanation for the behaviour of Cu under these conditions might be that, at low metal ion concentration and high charged density, the highly extended configuration hinders complex formation compared with the coiled form of the molecule. In the presence of Cu^{2+} ions, the extended configuration of iPMAA imposes structural restrictions whereas, in the presence of Zn^{2+} and Mg^{2+} ions, no structural restrictions are imposed.

Figure 4 reveals that ionic strength has a considerable effect on the extent of binding at low metal ion concentrations but not at high metal ion concentration. Similar observations have been made for Zn and Mg. Using Fig. 4 for the Cu plot, the observation is explained thus. It is assumed that only the M^{2+} ions which reach the ionic atmosphere of $—COO^-$ will be able to bind to the available sites. This means that, if the ionic strength is high, the K^+ ions in the ionic atmosphere will shield the M^{2+} ions from $—COO^-$ and will cause a reduction in the extent of binding. At high metal ion concentration, binding can be regarded as a competition between the divalent and univalent cations for binding sites.

In Fig. 5, the R_p values for equal metal ion concentrations are compared for the same $\alpha = 0.6$ for all the metal ions studied. The figure shows that the extent to which the available sites are bound is the order Cu > Zn > Mg in the ratio (85:60:26%) of the total available sites. This observation agrees with results obtained using the equilibrium dialysis technique. Similar observations have been made at other α values.

Dialysis

Figures 6–11 show the results obtained from equilibrium dialysis studies. Figures 6–8 show the plots of R_M as a function of the equilibrium concentration of the metal ions $[M^{2+}]_f$, where M^{2+} is Cu^{2+}, Zn^{2+} or M_g^{2+} and R_M (the binding ratio) is the ratio of moles of M^{2+} bound mol of the polyelectrolyte.

The shapes of the curves support the potentiometric titrations showing an increase in the extent of binding as $[M^{2+}]_f$ increases. There is initially a small extent of binding at low $[M^{2+}]_f$ to give a final stable complex involving two carboxylate groups to one metal ion. It has also been found that $[M^{2+}]_b$ at any α value was proportional to α (Fig. 11). Extrapolation of the lines to $\alpha = 1$ gives the value corresponding to a 2:1 complex (Table 1), agreeing with the expected values for Cu^{2+} and Zn^{2+}. For Mg^{2+}, at low α, values are not given because they were not sufficiently reproducible but the figure reveals that Mg^{2+} is a very weak binder, less than 30% of the available sites being occupied.

It has been suggested for potentiometric titration studies that two types of equilibria exist indicating a change in stoichiometry i.e. one type of complex exists at low and another type at high metal ion concentrations. Attempts have been made to find support for this suggestion from dialysis studies.

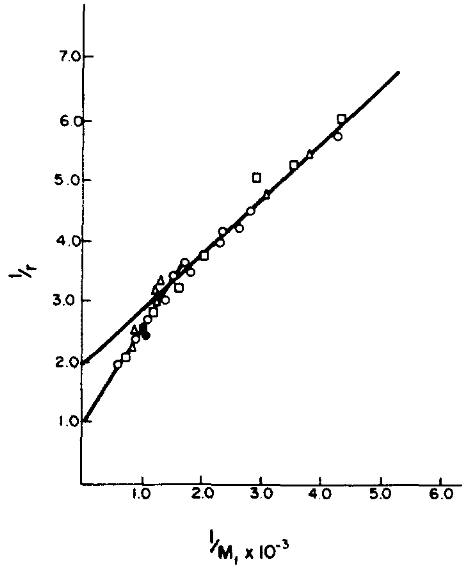

Fig. 10. Determination of stability constants and coordination numbers for Zn–PMAA complexes. Polymer concentration = 2.5 × 10^{-3} M, I = 0.10. α: (○) 0.30; (△) 0.40; (□) 0.50; (●) 0.60.

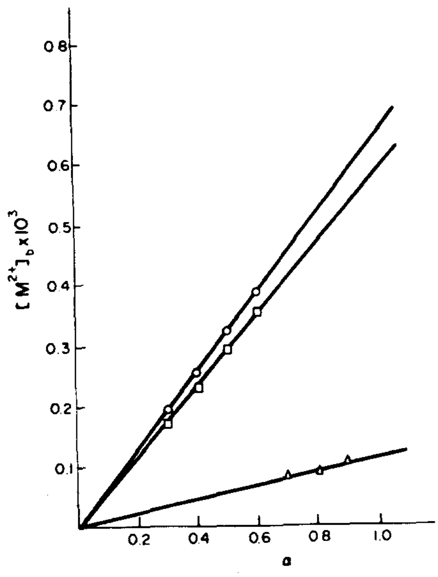

Fig. 11. Plot of maximum amount of metal ions bound $(M^{2+})_b$ at various values of as a function of degree of dissociation, α. Polymer concentration = 2.5×10^{-3}, I = 0.10. ○—Cu^{2+}; □—Zn^{2+}; △—Mg^{2+}.

Using the general multiple equilibrium theory and considering the following equilibria

$$—COO^- + M^{2+} \overset{k_1}{\rightleftharpoons} —COOM]^+ \quad \text{at high } [M^{2+}]_f \tag{2}$$

and

$$—COOM]^+ + —COO^- \overset{k_2}{\rightleftharpoons} —COOMOOC— \quad \text{at low } [M^{2+}]_f \tag{3}$$

it can be shown that

$$\frac{1}{r} = \frac{n}{k}\frac{1}{[M^{2+}]_f} + n \tag{4}$$

where n is the number of carboxylate groups combining with the metal ion, r is the ratio of the carboxylate concentration in the solution to the concentration of the combining metal ion, K the apparent equilibrium constant. From Eqn (4) the values of K can be obtained once the value of n is obtained from the intercept on the ordinate. Plots of $1/r$ against $1/[M^{2+}]_f$ are shown in Figs 9 and 10 for Cu and Zn respectively. It is seen that $1/r$ rises linearly with $1|[M^{2+}]_f$ but with two distinct slopes for low and high concentration of metal ion. If the assumption is made that the binding constant of hydrogen ion of the polyelectrolyte varies with electrostatic potential and molecular configuration, so may the binding constant of the metal ions. It is therefore reasonable to conclude that these figures reveal the existence of complexes having different binding constants (Table 1). The intercept gave values of 2 and 1 respectively corresponding to an initial formation of a 2:1 complex at low $[M^{2+}]_f$ and then breaking down to the final formation of a 1:1 complex at high $[M^{2+}]_f$. The measurement of the amount of Mg^{2+} was not sufficiently reproducible to permit such a calculation.

Table 1. Equilibrium constants for Cu^{2+}–iPMAA and Zn–iPMAA complexes

M^{2+}	k_1	k_2	$[COO^-]_T/[M^{2+}]_b$ at $\alpha = 1$
Cu^{2+}	830	3000	2
Zn	630	1100	2

Thus from the values of the stability constants, it is seen that Cu^{2+} is a stronger binder than Zn^{2+}.

Viscometric titrations

It has been suggested from potentiometric titration data that binding of Cu^{2+} to isotactic PMAA imposed greater structural restrictions on the extended configuration of the polyacid than did Zn^{2+} or Mg^{2+}. To support this suggestion, viscometric titrations have been carried out in the presence of these ions at varying degrees of dissociation α. The data are represented graphically in Fig. 12 where $[\eta]$, the intrinsic viscosity, has been plotted as a function of α for a series of solutions containing 2.0×10^{-3} M of M^{2+} at I = 0.02. The curve for isotactic PMAA containing no metal ions has been included for comparison. At other metal ion concentrations, similar series of curves have been obtained. It can be seen that the presence of divalent metal ions causes a reduction in $[\eta]$ at any degree of dissociation. The binding of metal ions to the polyelectrolyte causes a reduction in the interaction between the carboxylate groups. Consequently this leads to a reduction in the repulsive electrostatic potential of the COO^- groups respon-

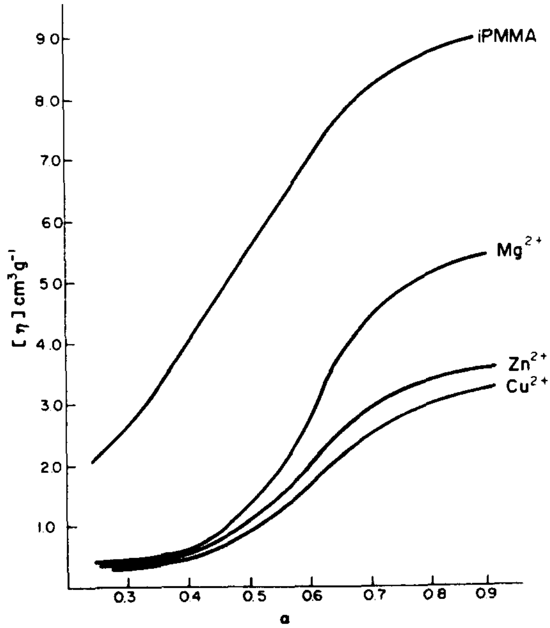

Fig. 12. Viscometric titration data for isotactic PMAA in the presence of Cu^{2+}, Zn^{2+} and Mg^{2+} at polymer concentration = 2.5×10^{-3} M, I = 0.02 at 25°. The ordinate, $[\eta]$ cm^3 gm^{-1}, gives the intrinsic viscosity. The abscissa, α, denotes the state of dissociation of the polymer.

sible for chain expansion. The reduction in $[\eta]$ may also be due to cross-linking of polymer chains by the cations; when this occurs, there will be conformational shrinkage. The shrinkage is greatest for Cu and least for Mg. These results reveal the effectiveness with which these cations bind isotactic PMAA. The order of binding $Mg^{2+} < Zn^{2+} < Cu^{2+}$ follows their binding strengths.

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