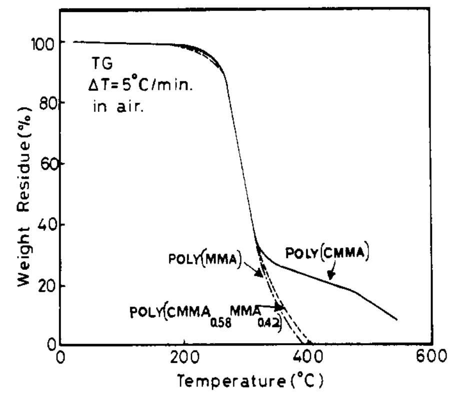


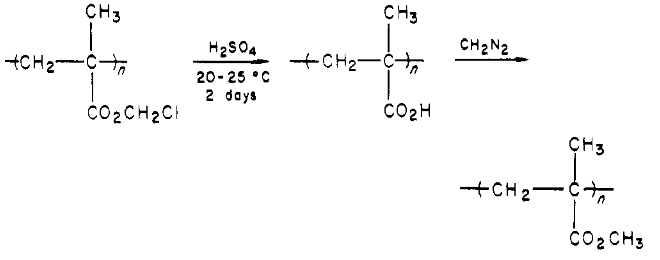
Figure 11. TG curves of poly(CMMA), poly(CMMA–MMA), and poly(MMA).

Table V
Thermal Characterization of Polymers

polymer	mole ratio $[M_1]/[M_2]$ in copolymer	degradation temp,[a] °C init wt loss in air	degradation temp,[a] °C 10% wt loss in air
poly(MMA) (M_1)		240	260
poly(CMMA) (M_2)		210	265
poly(MMA-CMMA)	77/23	200	275
poly(MMA-CMMA)	57/43	195	250
poly(MMA-CMMA)	42/58	180	265
poly(MMA-CMMA)	26/74	170	270

[a] Observed by TGA at a heating rate of 5 °C min^{-1}.

Thus, CMMA, like most other methacrylates, gave a syndiotactic polymer with radical initiators.



The glass transition temperature (T_g) of poly(CMMA) was observed at 75–80 °C by thermomechanical analysis (TMA). This may be compared to the reported T_g value of about 105 °C[14] for poly(MMA). No melting point was observed for poly(CMMA), in agreement with its X-ray diffraction pattern, which showed very little crystalline structure. Thermogravimetry (TG) was carried out in air at a heating rate of 5 °C/min on poly(CMMA) and on a 58:42 CMMA/MMA copolymer. Typical thermograms are shown in Figure 11, where a thermogram for poly(MMA) is included for comparison. The degradation temperature for a 10% weight loss was 265 °C for poly(CMMA). This is comparable to that of poly(MMA). However, a small amount of residue remained up to 550 °C after rapid degradation. This may be compared to the TG curve of poly(MMA), where no residue remained. In poly(CMMA-MMA) copolymers, the initial degradation temperature decreased with increasing CMMA content, but such trends were not observed in the degradation temperature for 10% weight loss of the copolymers. These results are summarized in Table V.

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Binding of Zinc Ions to Polymethacrylate Anions at Varying Charge Densities

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ABSTRACT: The interaction of zinc ions with partly neutralized poly(methacrylic acid) (PMA) has been studied by using conductance, potentiometric titration, and equilibrium dialysis techniques. Partially neutralized PMA was titrated with a solution of zinc nitrate so as to enable the polymer/zinc ion ratio to be varied over a wide range. The results from potentiometric and conductance titrations show the existence of two types of complexes, one existing at low concentration and the other at high concentration of metal ions. Results from dialysis studies confirm the above observations and reveal that only one type of complex is stable. Equations were developed to enable calculations of the binding constants.

Introduction

Considerable importance and interest exist in the study of binding of counterions to polycarboxylates. The interaction between di- and trivalent cations with polyelectrolytes has been widely regarded as chelation of cations by neighboring[1-3] or widely separated[4,5] anionic groups. Various techniques have been used. Of the cations studied so far, copper[3,6,7] and cobalt[8] have received the greatest attention. Eldridge and Treloar[8] showed from their UV studies that cobalt could bind three carboxylate groups on a single polymer chain. Cobalt, unlike copper, could not force a redistribution of the charges on the polyacrylate anion. Mandel and Leyte,[9] using a variety of techniques, have shown that zinc(II) forms complexes with polycarboxylates. Marinsky and Travers[10] have also shown that the dominant complex species in Zn(II)-poly(methacrylic acid) is an ion pair. Recently we[6] have shown that zinc can form a complex with polymethacrylate anion involving two carboxylate groups to one metal ion in such a manner that leads to dimerization of the molecules in solution. We now report the results of an extension of this work on samples of conventional PMA in which the number of carboxylate anions has been limited by partial KOH neutralization. We report the results obtained from conductance, potentiometric titration, and equilibrium dialysis measurements. Dialysis experiments have been carried out on PMA brought to the same degree of neutralization in the presence of a range of zinc ion concentrations. From the results the amount of metal ion bound to the carboxylate groups could be obtained. A comparison of the amounts of metal ion bound by the polycarboxylate should reveal the number of carboxylates binding per metal ion and thus provides a test of our earlier model.[6]

In the present work, however, there were experimental limitations in the techniques, resulting in limitations to the ionic strengths open to investigation. Equilibrium dialysis requires high ionic strength while conductance differences can only be measured in a medium of low ionic strength if reproducible results are to be obtained. There was no restriction of ionic strength in the range $I = 0.01$–0.1 for potentiometric titrations and the series of experiments reveals the effect of ionic strength on the resultant binding curves (Figure 4).

Experimental Section

(A) Materials. A sample of poly(methacrylic acid) was prepared from the monomer. The monomer was first purified by low-pressure distillation and stored over calcium hydride. It was then polymerized at 60 °C in water-methanol with 0.5% benzoyl peroxide as initiator. At the end of the polymerization the polymer obtained was purified. The polymer was then fractionated by the method of Flory.[11] The various fractions were dried in a vacuum oven at 110 °C. The molecular weight of the various fractions were determined by light scattering. The sample having a weight-average molecular weight ($\bar{M}_w$) of 4.81×10^5 was used for all measurements.

(B) Methods. Equilibrium Dialysis Measurements. Viskin cellophane tubing appropriate for the volume of acid (10.0 cm^3) was boiled for 1 h 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 h, 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 the PMA (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 concentration. The concentration of the metal ion initially and after attainment of equilibrium was determined by the method described in ref 12. Analysis showed that the time to reach equilibrium was 5 days and that the amount of zinc ions bound to the cellophane bag was negligible.

Potentiometric Titrations. The potentiometric titrations were carried out by using a Pye Unicam pH meter, Model 290, in conjunction with a combined glass and reference electrode for the pH determinations. The polymer solutions were pretitrated to varying degrees of ionization (α) and then titrated with zinc ion solutions in plastic beakers thermostated at 25 ± 0.1 °C. Titrations at constant ionic strengths were carried out by the method of Kolawole.[13]

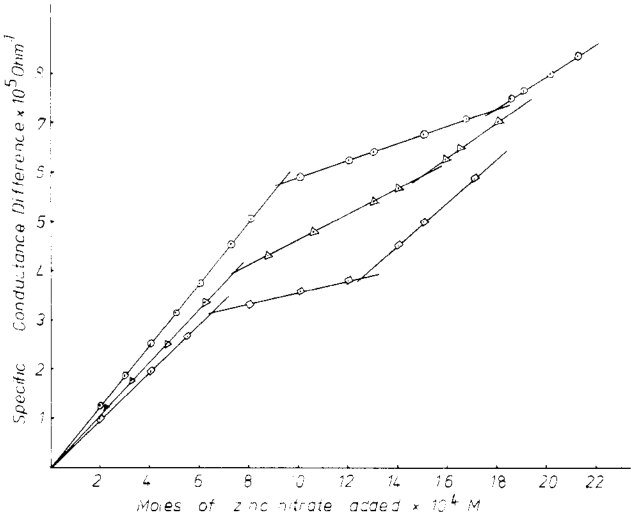

Figure 1. Conductance titration of poly(methacrylic acid) with Zn^{2+} ions at various degrees of ionization α at a constant ionic strength of 0.01 and a constant polymer concentration of 2.5×10^{-3} M at 25 °C. The abscissa denotes the concentration of added zinc ions. The ordinate gives the specific conductance difference in Ω^{-1}. (○) $\alpha = 0.70$; (△) $\alpha = 0.60$; (□) $\alpha = 0.50$.

Conductance Measurements. A Wyne Keer universal conductivity bridge, Model B221, with an attached adjustable voltage stabilizer giving 240 V was used for all conductivity measurements. The conductivity cell used was of the dipping type with platinum electrodes coated with platinum black. The experimental solutions were contained in a glass container capable of holding 50.0 cm^3 of solution thermostated at 25 ± 0.1 °C. Conductivity water having a conductance of 1.0×10^{-7} Ω^{-1} cm^{-1} was used for all solution preparations. Conductance titrations were carried out in 0.01 M KNO_3 and at various degrees of ionization of the polymer. Zinc nitrate solution was added in aliquots of 0.10 cm^3 to 25.0 cm^3 of 2.5×10^{-3} M PMA in 0.01 M KNO_3 pretitrated to the desired degree of neutralization. Solutions similar to the above but containing no PMA were also titrated.

Results and Discussion

Conductance Measurements. Figure 1 shows the conductance titration curves for PMA at different degrees of ionization and at an ionic strength of $I = 0.01$. Conductance values for PMA–Zn^{2+}–KNO_3 systems were subtracted from the values for Zn–KNO_3 systems to obtain the specific conductance difference. The points fall on straight lines intersecting at equivalence points. Each different segment has different slopes. Each change of slope has been associated with a change of the species present. It should also be noted that the maximum concentration of complex species should be that present when the ratio of the metal to ligand is that represented in the formula of the species; then the ratio of the metal ion to the initial concentration of the free carboxylate groups at the breaks in the curves will represent the probable major complex species present. Zinc is able to form two types of complex species with PMA, i.e., one at low and the other at high metal ion concentration, giving a 2:1 and 1:1 complex species. The results are given in Table I.

Potentiometric Titrations. The main types of equilibria that are occurring in the system under study are

$$-COOH \rightleftharpoons -COO^- + H^+ \quad (1)$$

$$-COO^- + Zn^{2+} \rightleftharpoons -COOZn]^+ \quad (2)$$

$$-COOZn]^+ + -COO^- \rightleftharpoons -COOZnOOC- \quad (3)$$

The binding of Zn^{2+} to $-COO^-$ appearing in eq 2 and 3 results from the dissociation of the carboxyl groups in eq

Table I
Analysis of Complex Species

α	$10^4[Zn^{2+}]$, M, at equiv point	no. of carboxylate groups per Zn^{2+} ion
0.50	6.25	2.00
	12.45	1.00
0.60	7.55	1.99
	15.00	1.00
0.70	8.70	2.01
	17.40	1.01

1. It is essential to calculate the concentration of carboxylate groups available for binding in order to obtain binding curves. This is necessary in order to identify the types of complexes formed during the reaction. We can easily relate apparent degree of dissociation α to the number of carboxylates [-COO$^-$] by

$$[\text{-COO}^-] = \alpha C \qquad (4)$$

where C is the original concentration of the -COOH present on the polyion. In a like manner, the pH of the system can readily be related to αC by

$$\text{pH} = \text{p}K_a^{\,1} + \log \frac{\alpha C}{(1-\alpha)C} \qquad (5)$$

$$\text{pH} = \log (1-\alpha)C + \log (\alpha C/K_a^{\,1}) \qquad (6)$$

$$\text{pH} = Q + \log (\alpha C)/K_a^{\,1} \qquad (7)$$

The value of -COOH at any time can be obtained from the difference between the original value and the value of H^+ released. In most cases [H^+] is so small as to be insignificant compared with the original [-COOH]. This means that the quantity Q remains virtually constant, as this comes from the original value of H^+ released. It is therefore concluded that the change in pH, (ΔpH) is some function dependent on the change in log ($\alpha C/K_a^{\,1}$). These equations have been derived by using the Henderson–Hasselbalch equation, where $K_a^{\,1}$ represents the mass action expression for the equations above plus all modifications to the Henderson–Hasselbalch equations. All other experimental artifacts have been taken into consideration in all calculations.

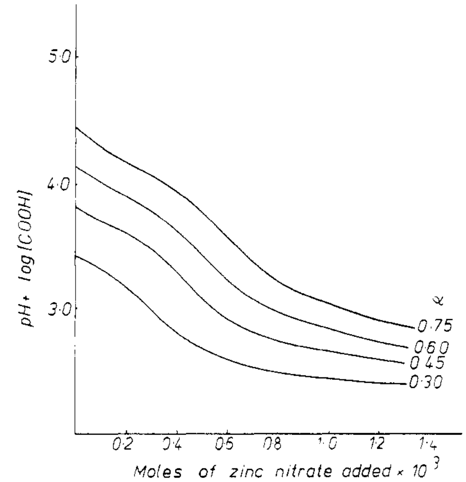

Figure 2. Potentiometric titrations of PMA with zinc ions at varying degrees of ionization α at a constant ionic strength of 0.10 and a constant polymer concentration of 2.5×10^{-3} M at 25 °C. The ordinate denotes pH + log [COOH] while the abscissa denotes the moles of added zinc nitrate.

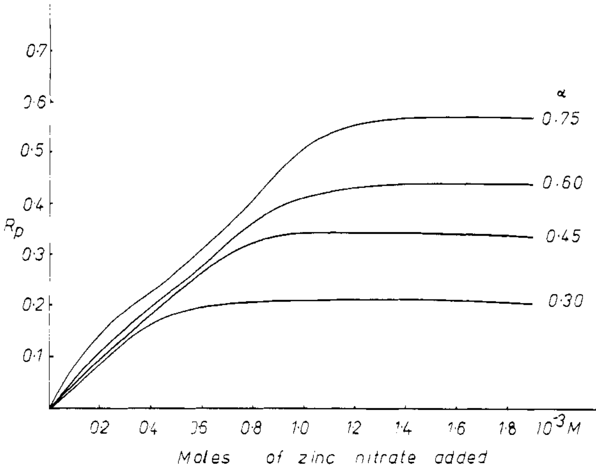

Figure 3. Complex formation curves. Potentiometric titration of PMA with Zn^{2+} ions at various degrees of ionization α at a constant ionic strength of 0.10 and a polymer concentration 2.5 $\times 10^{-3}$ M at 25 °C. The abscissa denotes the concentration of added Zn^{2+}. The ordinate, R_p, gives the moles of complexed carboxylate groups per mole of total polyacid.

Transformation of Titration Curves to Complex Formation Curves. The above equation is now developed to enable calculation of the amount of bound carboxylates. Titration curves were obtained for Zn(II) at various ionic strengths between $I = 0.1$ and $I = 0.01$. Titration of unionized PMA and fully ionized PMA at appropriate constant ionic strengths gave a reference curve of pH + log $(1-\alpha)C$ vs. log C at constant polymer concentration (2.5×10^{-3} M). The general terms C and $(1-\alpha)C$ have been used 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 zinc ion solutions. Corrections for dilution and other experimental artifacts have been taken into consideration. Now with the calibration curve and from a knowledge of pH + log [COOH] = pH + log $(1-\alpha)C$ after the addition of different amounts of metal ion, log (αC) and hence free carboxylate groups present could be estimated. When the procedure outlined above is now employed for calculating the amount of free carboxylate concentration, the amount of carboxylate groups bound to zinc ions is readily calculated. The binding curves for the equilibrium reactions shown in eq 1–3 have been plotted in terms of the binding ratio R_p, i.e., the ratio of the number (concentration) of the groups or ions bound to the total number (concentration) of carboxyl groups (un-ionized and ionized) on the polymer. Taking p to be the total concentration of the monomer units, we define R_p to be the carboxyl group binding ratio

$$R_p = [\text{complexed carboxyl groups}]/p$$

Figure 2 shows a plot of pH + log [COOH] vs. [Zn^{2+}] added for $I = 0.10$. The values of -COOH can be obtained from the difference between the original value and the amount of [H^+] released. This gives a family of curves, each showing a region of rapid change in pH with metal ion added. This region occurs at a higher total metal ion concentration as the degree of ionization increases. Again at higher degree of ionization there appears to be another dissociation at low zinc concentration. A similar series of curves is obtained at other ionic strengths.

Figure 3 shows a plot of R_p as a function of total concentration of Zn^{2+} added, $[Zn^{2+}]_T$, for four degrees of ionization at a constant ionic strength of $I = 0.1$. This figure reveals that about 76% of the available sites on the polyelectrolyte have been occupied by Zn^{2+}. As the charge density on the polyion decreases, the limiting binding ratio

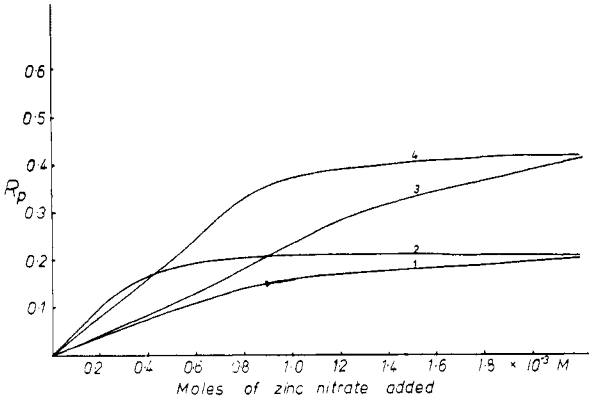

Figure 4. Potentiometric titration data of PMA with Zn^{2+} showing the ionic strength effect on the binding of Zn to PMA at 2.5 × 10^{-3} M polymer concentration: (1) $\alpha = 0.30$, $I = 0.10$; (2) $\alpha = 0.30$, $I = 0.01$; (3) $\alpha = 0.60$, $I = 0.10$; (4) $\alpha = 0.60$, $I = 0.01$.

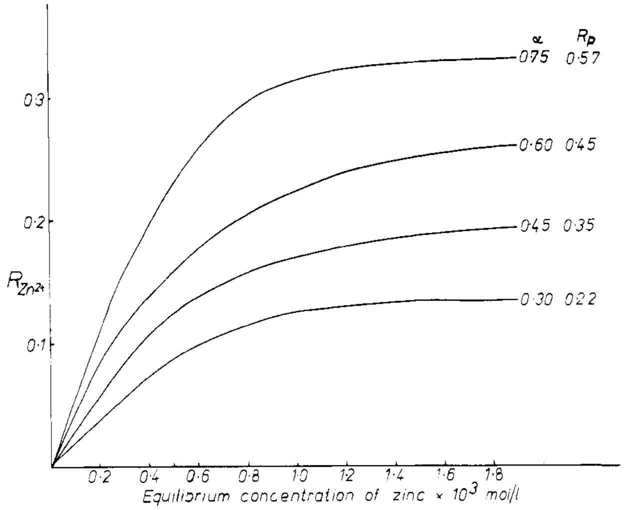

Figure 5. Equilibrium dialysis data at various degrees of ionization α, ionic strength $I = 0.10$, and 2.5 × 10^{-3} M polymer concentration at 25 °C. The ordinate, $R_{Zn^{2+}}$ denotes the moles of added Zn^{2+} bound per mole of total polyacid. The abscissa gives the equilibrium concentration $[Zn^{2+}]_f$ of the added Zn^{2+}.

also decreases. The second dissociation apparent in Figure 2 is now reflected in the complex formation curves at higher degrees of dissociation. This may suggest that there are two types of complexes, one existing at low zinc ion concentration and the other at high zinc ion concentration. This supports the finding from conductance measurements. R_p continuously varies as the amount of the Zn^{2+} complexing the polyelectrolyte chain increases until a limiting value of R_p is obtained.

Figure 4 shows that more carboxylate is bound at $I = 0.01$ than at $I = 0.1$ for any given α until the maximum amount of carboxylate is bound, which appears to be virtually independent of the ionic strength. It is seen that R_p values at the same α in different ionic strengths converge to the same final value. The figure also shows that ionic strength has a considerable effect on the extent of binding at low metal ion concentration but no effect at high metal ion concentration. An explanation for this is based on the assumption that only the Zn^{2+} ions which reach the ionic sphere of $-COO^-$ will be able to bind the available sites. This means that at high ionic strength, K^+ ions will shield the Zn^{2+} ions from $-COO^-$ and will cause a reduction in the extent of binding. At high metal ion concentration, the binding is regarded as a competition between the Zn^{2+} and the univalent cations for the binding sites, and, since the forces of attraction between Zn^{2+} and $-COO^-$ are greater than between K^+ and $-COO^-$, the shielding effect seems to be nullified.

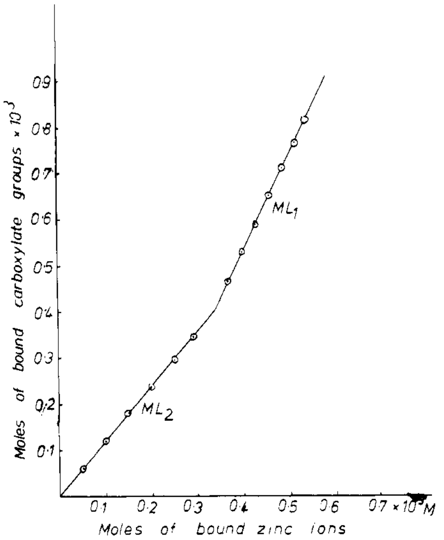

Figure 6. Stoichiometry of the complex species. Combination of potentiometric titration and equilibrium dialysis data. The ordinate denotes the moles of bound carboxylate groups, $[COO^-]_b$, while the abscissa denotes the moles of bound zinc ions, $[Zn^{2+}]_b$.

Table II
Analysis of Complex Species

α	$10^4[Zn^{2+}]$, M, at max binding	$[COO^-]_b/[Zn^{2+}]_b$
0.3	3.69	2.03
0.45	5.36	2.10
0.60	6.75	2.20
0.75	9.38	2.00

Equilibrium Dialysis Measurement. Figures 5 and 6 show the results obtained from equilibrium dialysis studies. Figure 5 shows a plot of $R_{Zn^{2+}}$ as a function of the equilibrium concentration of the zinc ion, $[Zn^{2+}]_f$. $R_{Zn^{2+}}$ (the zinc ion binding ratio) is defined as $R_{Zn^{2+}} = [\text{bound } Zn^{2+}]/p$, where p is the total concentration of the monomer units.

The shapes of the curve show an increase in the extent of binding as $[Zn^{2+}]_f$ increases. There is initially a small extent of binding at low $[Zn^{2+}]_f$ but a final stable complex involving two carboxylate groups to one metal ion. This is shown in Table II. It was found that $[Zn^{2+}]_b$ at any α value was proportional to α.

Figure 5 also shows that about 75% of the added zinc ions are bound to the polyelectrolyte. From the shapes of the curves, there is no indication of existence of two equilibria as found in the cases of conductance and potentiometric titrations. It may be that the dialysis technique may not be sensitive enough to reveal the existence of a 1:1 binding or that the 2:1 binding is the most stable complex species formed. The suggestion here is that the complex involving two carboxylate groups to one metal ion is the predominant species. This agrees with our earlier findings.[6]

Combination of dialysis and potentiometric titration results at the same ionic strength yielded Figure 6, showing the amount of carboxylates bound as a function of bound metal ions. This shows that there is an initial formation of a 2:1 complex followed by the formation at maximum binding of some 1:1 complex, but the 2:1 complex remains the predominant form. This is again in agreement with the results shown in Table II. Thus the results obtained from a combination of dialysis and potentiometric titra-

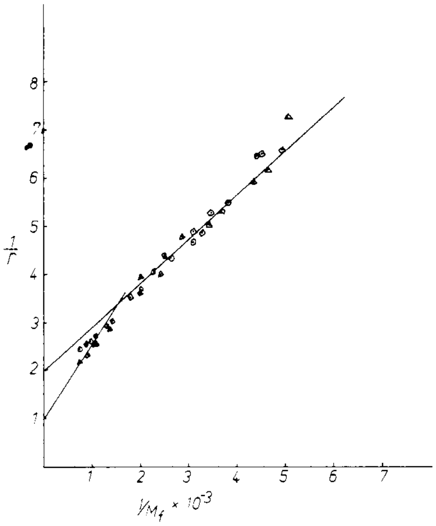

Figure 7. Determination of stability constants and coordination numbers for Zn–PMA complexes (2.5×10^{-3} M polymer concentration, $I = 0.10$). α: (○) 0.45; (△) 0.60; (□) 0.75.

tions are in perfect agreement with the results obtained from conductance titrations.

Leading from the above suggestions further, we have attempted to find support for the above suggestions from dialysis studies. In this respect, we apply the general multiple equilibrium theory to the following equilibria:

$$\text{-COO}^- + \text{Zn}^{2+} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{-COOZn]}^+ \qquad (2)$$

(at high $[\text{Zn}^{2+}]_f$)

$$\text{-COOZn]}^+ + \text{-COO}^- \underset{}{\overset{K_2}{\rightleftharpoons}} \text{-COOZnOOC-} \qquad (3)$$

(at low and medium $[\text{Zn}^{2+}]_f$)

It can be shown that

$$\frac{1}{r} = \frac{n}{k}\,\frac{1}{[\text{Zn}^{2+}]_f} + n \qquad (8)$$

where n is the number of carboxylate groups combining with the zinc ion, r is the ratio of carboxylate concentration in the solution to the concentration of the combining zinc ions, and k is the apparent equilibrium constant. n should have more than one value if more than one type of complex is formed in the system. From eq 8 the value of k can be obtained once the value of n is obtained from the intercept on the ordinate. A plot of $1/r$ against $1/[\text{Zn}^{2+}]_f$ is shown in Figure 7. $1/r$ rises linearly with $1/[\text{Zn}^{2+}]_f$, but with two distinct segments. This reveals the existence of two complexes having different binding constants. The intercept gave values of 2 and 1, respectively, corresponding to an initial formation of a 2:1 complex at low and medium $[\text{Zn}^{2+}]_f$ and then some 1:1 complex at high $[\text{Zn}^{2+}]_f$. But, as can be seen from Figure 7, the 2:1 complex predominates. Values of $K_1 = 625$ and $K_2 = 2.183 \times 10^3$ have been obtained, confirming that the 2:1 complex is the more stable complex species present.

In addition, a plot of the maximum amount of $[\text{-COO}^-]_b$ against the maximum amount of $[\text{Zn}^{2+}]_b$ at varying degrees of ionization gave a slope of 2, showing clearly that the only stable complex formed is a 2:1 complex and that such a complex would lead to dimerization of the molecules in solution.[6]

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Hydrophobic Interaction between Alkyl Side Chains of Polyions and Alkyl Quaternary Ammonium Ions

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ABSTRACT: The degree of hydrophobic interaction between the alkyl side chain of polyion and alkyl quaternary ammonium ion was investigated by conductivity, potentiometric titration, and viscosity measurements. Alternating maleic acid–ethylene, –methyl vinyl ether, –ethyl vinyl ether, –butyl vinyl ether, and –isobutyl vinyl ether copolymers were used as specific polyions and $(\text{CH}_3)_4\text{N}^+$, $(\text{C}_2\text{H}_5)_4\text{N}^+$, $(\text{C}_3\text{H}_7)_4\text{N}^+$, and $(\text{C}_4\text{H}_9)_4\text{N}^+$ were employed as hydrophobic counterions. According to conductivity measurements, the larger the alkyl side chain, the more effective the hydrophobic interaction at full neutralization.

Introduction

The hydrophobic interaction remains one of the most important unsolved problems in understanding biological functions and the molecular structure of biological systems.

For example, for the ordering of lipid molecules in the biomembrane and the regulation of protein association and dissociation, it is well-known that hydrophobic interactions play an important role.[1,2] In the study of these subjects polyelectrolytes having both hydrophobic side chains and ionizable groups are believed to be good models of biopolymers. In this work, alternating copolymers of maleic acid and various alkyl vinyl ethers were used as polye-

0024-9297/81/2214-1054$01.25/0