INTERACTION OF DIVALENT METAL IONS WITH ISOTACTIC POLY(METHACRYLIC ACID).

Thesis

Presented to the Ahmadu Bello University
for the Degree of Master of Science
in the Faculty of Science.

BY

MOJI AFUSAT BELLO (MRS.)

Department of Chemistry
Ahmadu Bello University
Zaria, Nigeria.

JUNE, 1977

A C K N O W L E D G E M E N T S

I wish to express my greatest pleasure and gratitude to Dr. E. G. Kolawole who initiated and supervised this work. I am also greatly appreciative of his asistance, kindness and untiring encouragement and his useful suggestions throughout the course of this project. I thank him very much for being kind enough to read through the draft of the thesis and pointing out errors and omissions.

I wish to thank Professor A. R. Mathieson, Head of Chemistry Department and Dean of Science, for his keen interest in this research programme. I also thank him for making available for me all the facilities of the chemical laboratories.

I thank the technical and stores staff for their co-operation. My sincere thanks to Mr. J. O. Aina of Chemical Engineering Department for exercising patient in typing this thesis admirably.

I sincerely thank my children, Abiodun and Gboyega, for their co-operation, and most especially my husband Abdul Ganiyu for being a continual source of inspiration, encouragement, devotion and understanding in all matters.

Finally I thank the Ahmadu Bello University for providing grant for this research work.

June, 1977 M. A. Bello

A B S T R A C T

Isotactic polymethacrylic acid (PMA) has been prepared by hydrolysing the isotactic polymethylmethacrylate (PMMA) which was prepared from the monomer (MMA) using Grignard reagent initiator in toluene. The most suitable method of hydrolysis waa found to involve the use of glacial acetic acid with para-toluene sulphonic acid as catalyst. This method of hydrolysis resulted in complete hydrolysis.

The interaction between isotactic polymethacrylic acid (i-FMA) and divalent metal ions has been studied at 25°C and varying experimental conditions of ionic strength, degree of ionization, cation concentration using two different techniques. The experimental techniques used for these studies are equilibrium dialysis and potentiometric titration techniques.

Results from the two methods of studies reveal that copper and zinc interact quite strongly with preionized isotactic EMA while magnesium only binds weakly. The binding strength of the ions has been found to be $Cu^{+2} > Zn^{+2} > Mg^{+2}$.

Copper and zinc ions bind with i-PMA. to form complexes involving two carboxylate groups to one metal ion.

The isotaotic PMA exists in compactly coiled state when unneutralised and at very low degrees of ionization (alpha<0.25>). The unionized acid was also found to be insoluble• The ionized molecules undergo configurational transition in the range alpha= 0.5 to 0.7.

In chapter 4 the binding of divalent metal ions with isotactic PMA has been compared with that of conventional PMA using existing data. It was found that both copper and zinc bind more to the isotactic PMA than to conventional PMA,

C O N T E N T S

CHAPTER	
1	INTRODUCTION, PREVIOUS WORK, PREPARATION AND HYDROLYSIS OF PMMA AND THEORY OF BINDING.
2	DIALYSIS EQUILIBRIUM
3	POTENTIOMETRIC TITRATION
4	COMPARISON OF DATA AND CONCLUSIONS.

Chapter 1

INTRODUCTION, PREVIOUS WORK, PREPARATION AND HYDROLYSIS OF PMMA AND THEORY OF BINDING.

Contents

		Page
1.1	Introduction	1
1.2	Accounts of Previous Works Done	7
1.2.1	On Preparation of Isotactic Polymethyl-methacrylate and Isotactic Polymethacrylic acid	7
1.2.2	On Preparation and Ion binding of Stereoregular Polymethacrylic acid..	13
1.3	Preparation of Isotactic PMMA and its Hydrolysis	20
1.3.1	Experimental Details	20
1.3.1.1.1	Preparation of Isotactic Polymethlmethacrylate	20
1.3.1.1.1	Materials	20
1.3.1.1.2	Polymerization	21
1.3.2.	Results and Discussion	23
1.3.3	Hydrolysis of the Isotactic PMMA	25
1.3.3.1	Experimental	25
1.3.3.2	Results	25

1.4.	Theory of Binding	26
1.4.1	Binding by identical and independent sites with no interaction between them.. ..	28
1.4.2	Binding by identical and non-independent sites	30
1.4.3	Single set of sites with co-operative Interaction between them	31
1.5	R e f e r e n c e s	33

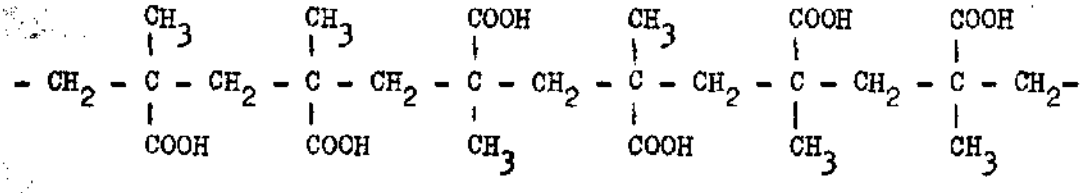
Chapter 1

1.1 INTRODUCTION

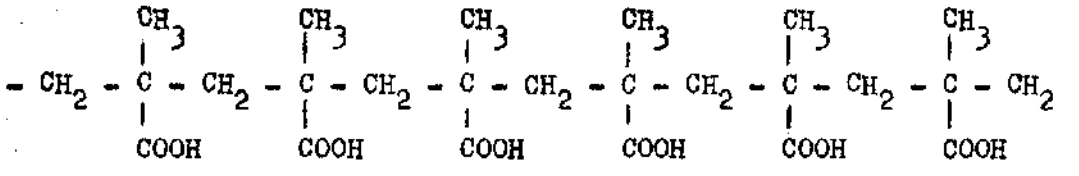
Polyelectrolytes are macromolecular compounds which carry many ionizable groups attached to their polymeric chains. The combination of large molecular weights with high charge densities leads to some unique physico-chemical properties which set polyelectrolytes apart from simple electrolytes and from uncharged polymers.

There are two distinct classes of polyelectrolytes namely: naturally occuring biologically important polymers (e.g. proteins, nucleic acid and pectins) and synthetic materials (e.g. polyacrylic acid, poly-methacrylic acid, polyvinyl pyrolidine and polyvinyl pyridinium halides). Further subdivisions exists depending on the chemical constitution (organic and inorganic), nature of the ionic groups attached to the polymeric chain (cationic, anionic and poly-ampholytes), and conformational structure (atactic, isotactic and syndiotactic polymers). Polymers with different steric order or configuration arise due to existence of stereoisomeric centres. The more important amongst such stereoisomeric centres are: (a) double bonds which can have cis- or trans- configurations and (b) tetrahedral stereoisomeric centres which have carbon atoms along the chain bonded to two different substituents. The latter give rise to stereoregular polymers. Thus one has eutactic polymer which is a regular polymer

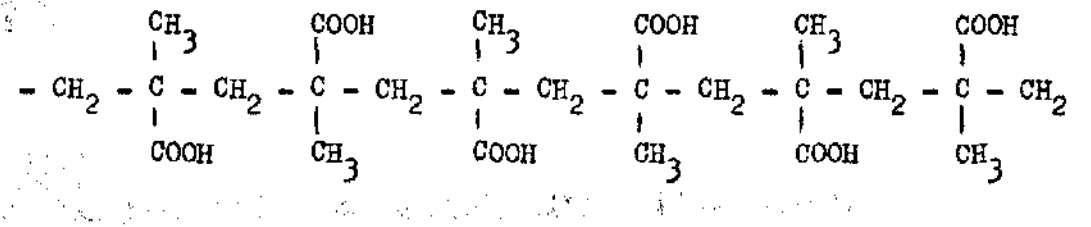
completely devoid of any element of structural disorder along its molecular chain, while atactic polymer has a completely random sequence of these centres. Isotactic polymer is that whose monomeric units are asymetric. The monomeric units are ordered in such a way that when passing from one monomeric unit to the other, one finds repetition of the unit configuration. In syndiotactic polymer, the position and structural arrangements are identical with those of isotactic polymer, but the unit configuration are arranged alternately. Examples are:



Atactic Polymethacrylic Acid.



Isotactic Polymethacrylic Acid.



Syndiotactic Polymethacrylic Acid.

The steric configuration becomes more complex when one has more than one stereoisomeric centres.

Some simple stereoregular polymers occur in nature and function as structural materials (e.g. chitin and rubber) and as reserved food materials in the cell (e.g. starch and cellulose). Much of the stimulation for the study of stereoregular macromolecules stems from the fact that, what had exclusively been in the power of nature, namely to join macromolecule with a predetermined steric order, and not at random is now also possible for man. Mankind since creation, has been unconsciously using macromolecules with preordered steric structure such as those occuring in clothing, building materials, food etc., but only about two decades ago did he get a clue to the synthesis.

Apart from synthesising these stereoregular polymers, studies carried out on their physico-chemical properties, in particular those of polyelectrolytes would serve as a useful guide to the behaviour of natural polyelectrolytes and biopolymers many of which are sterically ordered in structure. The very striking modification in the polymer produced by the attachment of large numbers of ionized groups (cationic, anionic and polyampholytes) to a macromolecular chain make studies of polyelectrolytes fascinating. The weakly cationic polymer has weakly basic group attached, while the anionic has acidic group attached, so that the charge density can be varied at will by changing the degree of neutralisation.

Polyelectrolytes are usually studied in aqueous solutions, and their properties in solution are greatly affected by such factors as molecular weight and molecular weight distribution, rigidity of the molecules, the conformation of the polymer molecule and addition of simple electrolytes. The polymer chain is in a coiled form, but can undergo extension in a solvent medium depending on the energetic interaction of the polymer segment with solvent molecules. An uncharged polymer chain, which is ionized by either titration or some other chemical modification, may undergo chain expansion due to mutual repulsion of the fixed charges. Thus the unionized molecule may be transformed from the coiled configuration into the extended configuration on complete ionization. However the ionic charges attached to the polymeric backbone not only affect the conformation of the polymer, but create a high local charge density which affects strongly the properties of simple ions in solution. Thus with ionized functional groups attached to the macromolecules, the forces between the charges are very much larger than the dispersion forces or the dipole - dipole interactions. Moreover these forces then act over relatively large distances. The polyion has a large effect in reducing the activities of counterions in solution but is without major influence on byions. Simple divalent cations in solution will also interact with polyanions thus causing a distribution of the ions which modifies the expansion

of the chain. On the other hand the polyanion will determine the interaction with cations. Such interaction with simple divalent cations will produce a shift in the titration curve of the polymeric acid. Therefore, there are various phenomena concerned in the understanding of this study. It is the author's intention to investigate the extent of expansion as a result of mutual repulsion, and the effect of such expansion on the solution properties. It is also intended to study the modification in the electrochemistry of the polyelectrolyte caused by the simple ions in solution, i.e. the effect of such complex forming cations on the stability of structure as well as the effect of isotacticity of the polymer on the properties outlined above.

There is a scarcity of data on the comparison of the behaviour of isotactic and conventional polymethacrylic acid (PMA). Though many workers have prepared and studied the degree of stereoregularity in PMA, little work has been done on the complex formation of isotactic PMA with divalent metal ions.

The present work involves, preparation of isotactic polymethacrylic acid and investigation of its affinity for metal ions, viz: Cu^{+2}, Mg^{+2} and Zn^{+2}, so as to be able to compare the stability of complexes formed with those of conventionally prepared PMA using existing data. Isotactic polymethacrylic acid was prepared by hydrolysing the corresponding polymethylmethacrylate prepared using Grignard reagent initiator in toluene. Various methods of hydrolysis were used including acid

and alkaline methods of hydrolysis and transesterification techniques. The polyacid produced was used in the studies of binding with metal ions. The techniques used in the physico-chemical studies were equilibrium dialysis and potentiometric titration methods.

From the equilibrium dialysis technique the amount of various metal ions bound can be obtained, while potentiometric titration gives the amount of carboxylate groups bound. From a combination of both results, the binding constants can be computed.

1.2 ACCOUNTS OF PREVIOUS WORKS DONE

1.2.1 On Preparation of Isotactic Polymethylmethacrylate and Isotactic Polymethacrylic acid:

Studies on the preparation of polymethylmethacrylate of various stereoregularities have been carried out more extensively than any other vinyl polymer. This is the author's view, is due to the fact that the properties of polymethlmethacrylate (PMMA) vary markedly with synthesis conditions due to very large variations in tacticity. The stereoregularity of the polymer chain is affected by such factors as, the nature of the innitiator, the types of solvents used in the reaction system, and the temperature at which the polymerisation is carried out.

The author will now very briefly review the available experimental evidence on the various factors affecting the stereoregularity of PMMA. The preparation of stereoregular PMMA was first reported in 1958 by various workers (1-3). Fox and co-workers(1) reported the synthesis of crystallizable PMMA, by free radical and anionic polymerisation. They obtained three different types of stereoregular polymers depending on reaction conditions: (a) isotactic polymer obtained with 9-fluorenyllithium at -60°C in hydrocarbons, for instance toluene (b) syndiotactic polymer obtained using the same initiator in

1,2-dimethoxyethane at -60°C and (c) a stereoblock co-polymer consisting of isotactic and syndiotactic blocks formed with 9-fluorenyllithium in toluene containing small amounts of dioxane. This was confirmed by Glusker and co-workers (4) in their polymerisation of methylmethacrylate using 9-fluorenyllithium in toluene, where predominantly isotactic polymer was obtained whereas in a mixture of toluene and tetrahydrofuran (THF) the fraction of isotactic links decreases rapidly with increasing concentration of THF. An extensive study of the effect of various Grignard reagents on stereoregularity of PMMA was carried out by Nishioka and co-workers (6). They found that the stereoregularity of PMMA can be controlled over a wide range, by selection of suitable alkyl groups in the Grignard reagents, and temperature for polymerisation. Isotactic polymer was produced by branched chain alkyl Grignard reagents, phenylmagnesium bromide in toluene above 0°C, and cyclohexyl magnesium bromide. Straight chain alkyl Grignard reagents in toluene produced stereoblock polymers. Increasing isotacticity is shown with increase in temperature from -70°C to +20°C, but pure isotactic polymer was difficult to attain with these sets of catalysts. This result is consistent with those of other workers (7;33,52) who assigned an isotactic configuration to polymer prepared using Grignard reagent in toluene. Goode and co-workers (8) observed that the nature of the solvent is of profound

influence on the course of the propagation reaction in their preparation of PMMA innitiated by organometallic compounds. In toluene and other weakly polar solvents isotactic linking predominates but with THF or dimethoxyethane, syndiotactic polymers were formed.

These various investigation using different initiator systems all showed that anionic polymerisation of methylmethacrylate (MMA) in non-polar solvents yields primarily isotactic polymer, whereas in polar solvents syndiotactic propagation is favoured. It was also observed (17) that stereospecificity of propagation not only depends on the extent of polarisation of carbon-metal bond, or on the solvation of the terminal ionic groups of the chain but is also influenced by the radius of metal ions of the initiator.

It is essential to have an efficient means of determining the tacticity of polymers. Infra-red spectra served as a useful means innitially (8, 11-13) but now nuclear magnetic resonance (NMR) has become the primary means for this purpose. Such determinations were fist carried out by Bovey and Tiers (18) and later many other workers have used NMR to examine steric isomerism in PMMA prepared under different conditions (17-22). This is because the absence of hydrogen atoms directly bonded to the α-carbon atom, and the adequate chemical shifts differences between the two methyl groups and the methylene group result in little complication of spin-spin coupling.

The creation of polymethacrylic acid (PMA) whose isotacticity approaches 100% has to proceed through the synthesis of a corresponding ester and its subsequent hydrolysis. In doing this methods would have to involve gradual hydrolysis without degrading the polymer, nor altering the tacticity. Several methods used by many workers to effect hydrolysis will now be reviewed.

Glavis (23) carried out alkaline hydrolysis in a heterogenous system containing PMMA, an organic solvent and aqueous base. As much as 75% hydrolysis was obtained if hydrolysis was allowed to run for 48 hours. The conventional polymer and the syndiotactic polymer were found to hydrolyse relatively slowly while isotactic PMMA was hydrolysed faster and to a higher final conversion than the other two. The greater ease of hydrolysis for isotactic PMMA was latter confirmed by Selegny (26) who worked with the same heterogenous system. Alkaline hydrolysis in homogenous phase i.e. reflux heating of a solution of polymer already 75-80% hydrolyzed, was found (26,53) to follow the same trend as above except that a new limit of 85% hydrolysis was attained.

Morawetz and Kandanian (25) obtained isotactic PMA by dissolving the isotactic PMMA in cold 96% sulphuric acid, and warming for 30 minutes at 60°C, precipitated in excess water and purified by prolonged dialysis. The unionised form of their polymeric acid was insoluble in water. This method of hydrolysis was later observed (26,27) to give

a degraded polymer at high conversion both in mass and tacticity. The isotactic polymer gave dark brown or black products even after several purifications, while the syndiotactic gave green, but the order of reactivity remained the same. The mechanism of hydrolysis of this polymer was studied by Semen and Lando (28). Their result on the order of reactivity was consistent with those of other workers (5,25-27, 42). They proposed that the mechanism of hydrolysis must proceed through anhydride formation. Another method of hydrolysis of isotactic PMMA reported (26) was that in which a mixture of hydriodic and acetic acid was used. About 90% hydrolysis was reported, and the technique was found to cause no alteration in molecular mass and tacticity. The results of the various workers on the order of reactivity were agreeable, however the limit of hydrolysis seems to depend on the method used and none seem to give a complete hydrolysis. The use of concentrated sulphuric acid is likely to give rise to degradation both in mass and tacticity.

None of the above methods were found suitable in the author's case, and the method used has been reported elsewhere in the thesis. The kinetics observed by several workers followed no simple behaviour and it has been proposed (29,30) that the rate of hydrolysis of a given ester group is affected by the configuration of the groups proximate to it. The great differences in chemical reactivity must therefore

arise from difference in backbone configuration of the polymers. The limit of hydrolysis of about 90% could be due (26) to the necessity of forming a six-membered ring anhydride cycles which are generally accepted in hydrolysis mechanism.

1.2.2 On Conformation and ion binding of Stereoregular Polymethacrylic acid:

Polymethacrylic acid (PMA) is the first example, in the author's opinion, in which the influence of chemical constitution and stereoregularity on the properties of vinyl polyelectrolytes in aqeous solution has generated a great interest. This might be due to the fact that its chain can undergo a pH-induced conformational transition, and also because polymethacrylic acid is available in different degrees and types of stereoregularity.

The author will now briefly review the various studies carried out on the conformation and ionbinding of PMA. Emphasis will however be layed on the stereoregular PMA.

In studying the physico-chemical properties of PMA in solution, so many techniques have been used by various authors, prominent amongst which are: equilibrium dialysis measurements, potentiometric titration, viscometric technique, electrophoretic, conductance, spectroscopic and polarographic methods. Various authors have used the potentiometric method to investigate the structural changes of PMA in solution. Mandel and Leyte (31) first recognised the existence of two conformations of PMA and reported that this was responsible for its abnormal behaviour. Crescenzi (32) showed that in the potentiometric titration of syndiotactic and isotactic PMA, the isotactic PMA was seen to behave as a weaker acid over the whole range of degree of

neutralisation (α). Similar results were obtained by Nagasawa and co-workers (33) who found that the pK_a values for the isotactic form were always higher than for syndiotactic, while the corresponding values for atactic and conventional PMA were intermediate. The differences between the stereoregular PMA were accounted for by assuming that the isotactic form has a locally helical structure, whereas the syndiotactic one has a planar zig-zag conformation. An indication of this possibility was earlier given by Loebl and O'neill (34) who reported that significant differences exist in the titration behaviour of isotactic and atactic PMA, their apparent dissociation constant differing by 0.3 pK_a units. In all these cases potentiometric plots reveal a clearly defined step between values of α = 0.1 to 0.3 which is found absent in the titration of other vinyl polyelectrolytes. These anomalies have been attributed (31) to a conformational transition of PMA chains taking place with a distinctly co-operative character in a narrow range of α values. Furthermore the phenomenon is largely independent of polymer molecular weight and concentration. From the peculiar trend of PMA viscosity against degree of neutralisation it was first argued (31) that the conformational transition of PMA can be visualized as an unwinding of a tightly coiled unionized polyacid, stable at low degrees of ionization. The tighly coiled form of isotactic PMA seems to be more stable at low degrees of neutralisation as indicated by its insolubility (33,34,39) at low α values up to α = 0.3. It is

interesting to note that isotactic PMA becomes soluble only at a pH beyond the conformational transition of conventional and syndiotactic PMA. This will be expected to confirm some specific properties of the isotactic PMA. This observation can be linked with the revelation from potentiometric plots where a fraction of the carboxyl groups would not be accessible in the compact PMA structure stable at low pH values, as these become only titratable only above the transition. Differences in the electrophoretic mobility of isotactic and syndiotactic PMA have been reported (38), indicating that the isotactic form is the slower moving one. A discontinuous dependence of neutralisation on α was observed, and again the effect has been consistently ascribed to the conformational transition of the polyelectrolyte. Hydrophobic interaction would play a major role on the stability of the tightly coiled PMA chains at low pHs as has been emphasized by Liquori and co-workers (35) whose views are essentially consistent with those of Birshtein (37).

Apart from the conformational changes in PMA, another interesting aspect of the influence of stereoregularity on physico-chemical properties is in its ion-binding. The association of both mono- and divalent cations with polyelectrolytes has been investigated by many workers. The various systems investigated include those containing sodium, zinc, cadmium, copper, nickel and magnesium with partially ionized conventional PMA (43-48). The divalent cations form more stable

complexes with polyanions than monovalent ions. Of the cations studied the chelation of Cu(II) with partially ionized PMA has received greater attention. In the PMA-Cu^{+2} system the ligand groups are evenly spaced along the polyion and the cation is capable of forming complexes with up to four carboxylate groups. Kotlair and Morawetz (42) studied the Cu(II)-binding with PMA from equilibrium dialysis measurements. Such measurements were carried out using large polymeric acid/Cu^{+2} ratios in the presence of high concentrations of potassium nitrate to swamp the Donnan effect and minimize the electrical free energy of complexation.

Various authors (40,43-48) have used potentiometric titration to demonstrate complex formation of PMA with copper and zinc. Pronounced shifts to lower pH values in the titration curves were obtained and these were attributed to complex formation. Similar concentrations of alkaline earth metal ions produce no shifts in the titration curves of PMA. Spectroscopic studies on PMA-Cu^{+2} system by Kotlair and Morawetz (43) and by Morawetz (45), indicated formation of copper-tetracarboxylate complex with PMA, which is in agreement with results from dialysis equilibrium (20). Mandel and Leyte (31) have also studied the binding of zinc, magnesium, cadmium, nickel and cobalt by PMA using potentiometric method. They showed that Cu^{+2} bound more strongly to PMA than any of these ions. It was noted that the order of binding was: $Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2} < Cd^{+2}$.

It has long been recognized by various authors that many of the properties of polyelectrolytes in solution cannot be adequately accounted for by the average electrostatic potential of the polyelectrolyte molecule. The question of whether, the formation of a chelate complex by a polyion with small cations involves ligands attached to neighbouring residues of the polymer chain has to be clarified. If such neighbouring ligands are involved then the steric configuration of the polymer chain should have an appreciable effect on the stability of the chelate.

Some striking and interesting results have been obtained on the influence of stereoregularity on the binding of counterions by PMA. O'neill and Loebl (34) did comparative studies of Cu^{+2} and Mg^{+2} ions binding with isotactic and syndiotactic PMA using equilibrium dialysis over a range of degrees of ionization of the polyacids. It was found that the isotactic PMA has higher affinity for Cu^{+2} while Mg^{+2} is bound more strongly to syndiotactic polymer, the difference becoming more pronounced as the degree of ionization increases. Significant differences have also been found in the extent to which Na^{+} ions bind to isotactic and syndiotactic PMA (48), with fraction of Na^{+} ions bound to syndiotactic PMA greater than that bound to isotactic PMA. The order of binding to both conventional and isotactic PMA were found to be the same in the ions: $Co^{+2} > Cu^{+2} \simeq Ni^{+2} > Mg^{+2}$ using turbidimetric techniques (48).

The binding of Mg^{+2} and bispyridinium bolaform cations to partially neutralised polyacrylic acid (PAA), isotactic and syndiotactic PMA was studied by Morawetz and co-workers (25) using dialysis equilibrium technique. The three polymeric acids differ from one another with the isotactic PMA less efficient, and the syndiotactic more efficient than PAA in the binding of bolaform cations. The characteristics of Mg^{+2} binding were found to have a surprisingly low sensitivity to the concentration of added salt (NaBr). At the higher degrees of ionization Mg^{+2} ion is bound much more strongly to the syndiotactic PMA. The affinity of isotactic PMA and syndiotactic PMA for Mg^{+2} is thus in an opposite order to that found for Cu^{+2}, which is consistent with the results of O'neill and Loebl (34). Very recently a study on the effect of chain tacticity on dye-binding (acridine-orange dye) to stereoregular PMA was carried out (49). It was found that the binding strength of the dye is higher and its stacking coefficient was lower in the presence of isotactic PMA. This was interpreted as due to the higher probability for the dye molecules to be located between couples of negatively charged groups arranged in helical sequences when bound to the isotactic polymer.

From the various results obtained the specificity observed in binding with stereoregular PMA, would indicate, in the author's opinion, that neighbouring carboxylate groups along the chain of the polymeric

acid are involved in the chelate formation. Only in this way can the pronounced effects of stereorregularity on chelate stability be accounted for.

1.3 Preparation of Isotactic PMMA and its hydrolysis:

In order to prepare isotactic polymethylmethacrylate (PMMA) a modification of the technique of Goode and co-workers (8) was used. The methylmethacrylate (MMA) monomer was polymerised using phenyl magnesium bromide and ethylmagnesium bromide in toluene as initiators at different temperatures, $-75^{\circ}C$, -25, $+4^{\circ}C$.

The hydrolysis of the isotactic PMMA was carried out using various methods. The alkaline hydrolysis in both heterogenous and homogenous phases (23-26), the acid hydrolysis using concentrated sulphuric acid (26, 28, 33,34,39) and hydrolysis using a mixture of hydroiodic acid and acetic acid (26) were used, but the results obtained were unsatisfactory. The method used by the author for effective hydrolysis of the polymer is reported in detail latter in this section. This method involves use of acetic acid with para toluene sulphonic acid as the catalyst.

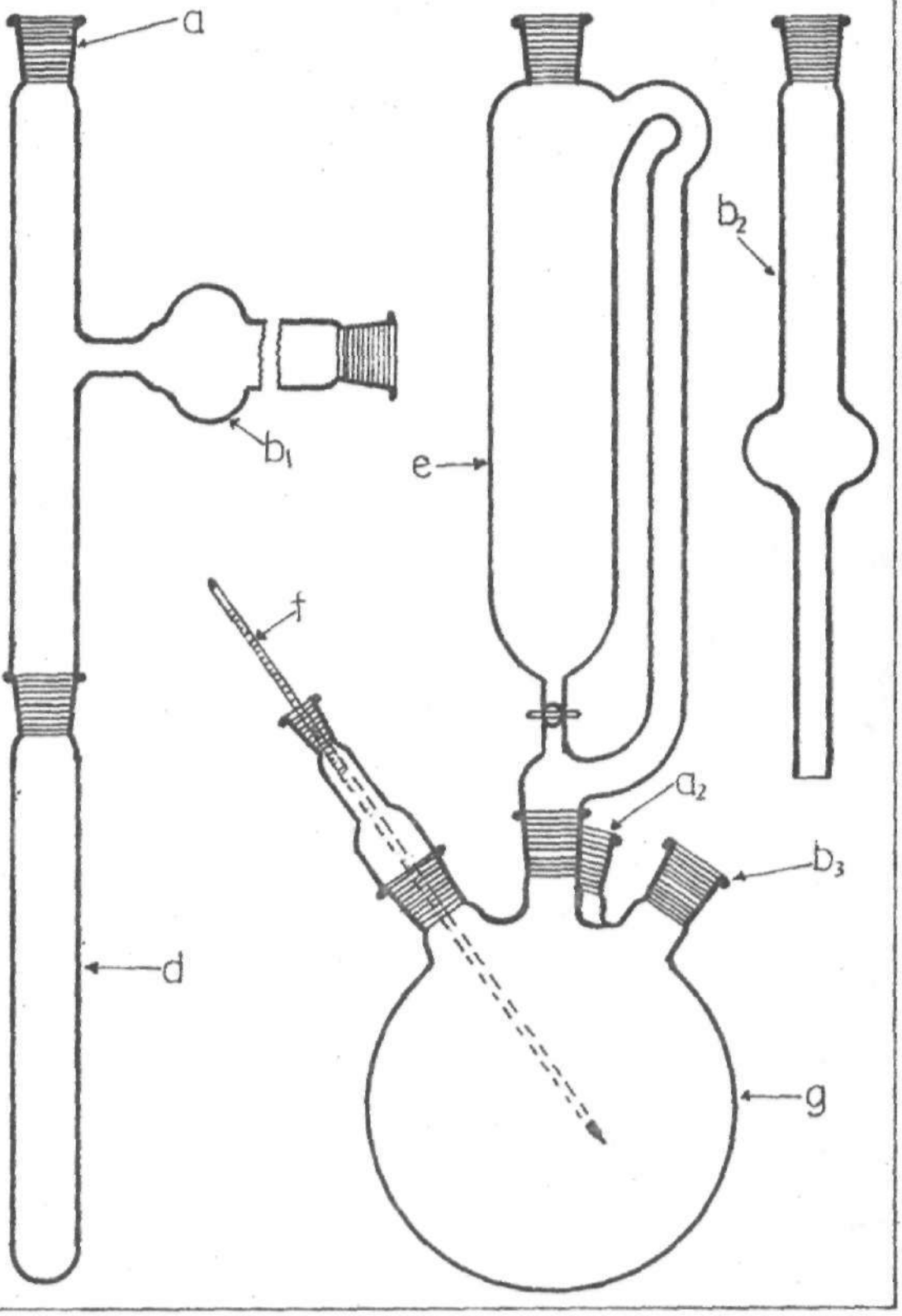
1.3.1 Experimental Details:

1.3.1.1 Preparation of Isotactic Polymethylmethacrylate:

1.3.1.1.1 Materials:

The methylmethacrylate monomer was obtained from Koch-light Laboratories, and was distilled freshly and stored over calcium hydride before use. The toluene used was distilled and stored over sodium wires. Purified dry nitrogen gas was used as the inert atmosphere for the reaction. The initiators used were ethylmagnesium

Fig. 1.4 Grignard generator and polymerization set up:



bromide and phenylmagnesium bromide prepared in anhydrous ether. All other reagents used were of analytical grade.

1.3.1.1.2 Polymerization:

Figure (4) shows the diagrams for the Grignard generator and polymerization vessel. To prepare the Grignard reagent 2 grams of magnesium turnings were added to the T-test tube d, fitted with a straight vacuum take off adaptor. The apparatus was flame dried, and fitted with a serum stopper and drying tube containing calcium sulphate, before cooling. Using an hypodermic syringe previously stored in a desiccator, 12.8 cm^3 of ethyl bromide and 28 cm^3 of anhydrous ether were added to the T-test tube through the serum stopper a. The reaction was allowed to proceed, cooling at intervals, until effervescence was minimal.

The four necked flask g, was equiped with a magnetic stirrer , a predried addition funnel e, serum stopper, drying tube containing calcium sulphate, and a low temperature thermometer. 400 cm^3 of the toluene was added into the flask and 20 cm^3 of the monomer into the addition funnel e, in the diagram. The flask was cooled to $4^{\circ}C$ (+1) by immersing it in an ice bath. The nitrogen inlet tube was fixed into the addition funnel. After passing the nitrogen gas through a series of Fiesers' solutions, (to absorb any traces of oxygen) and drying tubes containing calcium sulphate, a slow stream was bubbled through the monomer (methylmethacrylate) and passed over the stirred toluene for

30 minutes. The nitrogen inlet tube was then removed and quickly replaced with a drying tube b_2 while the drying tube b_3 on the flask was then stoppered. With the temperature at $4^{\circ}C$, 12 cm^3 of the Grignard reagent was introduced through the serum stopper a_2 using the hypodermic syringe. The stopcock of the addition funnel was then opened and the monomer added dropwise at a rate sufficient to maintain the temperature at $4^{\circ}C$. The reaction was allowed to proceed for 4 hours.

At the end of the polymerisation period, the contents of the flask was poured into one litre of well stirred petroleum ether. The mixture was filtered and the filter cake was washed several times with distilled water acidified with dilute hydrochloric acid to dissolve the inorganic salts. The polymer obtained was dissolved in the minimum amount of tetrahydrofuran and extracted with petroleum other. This was repeated several times to make sure that the polymer was free from monomer and initiator. The fluffy precipitate was dried in the vacuum oven at $60^{\circ}C$, and weighed to determine the yield. The experiment was repeated at two other temperatures ($-75^{\circ}C$, $-25^{\circ}C$) using in turn ethyl- and phenylmagnesium bromide initiators.

The infra red and NMR spectra of the samples were taken. From the NMR spectra, the coupling constant, J, was determined. The molecular weight of the polymer samples were obtained from viscometric determinations in chloroform solution at $25 \pm 1^{\circ}C$ using the equation obtained by Evans (52). This relationship has been found to be valid for isotactic PMMA.

1.3.2 RESULTS AND DISCUSSION

Table I: Results of Polymerization innitiated by Grignard reagent initiators.

Initiator	Temp. °C	% Yield	Coupling constant J	$\bar{M}_v \times 10^{-4}$	% Isotacticity
Phenyl MgBr	+4	35.3	15.5	5.0	91.2
Ethyl MgBr	+4	60.0	15.5	4.8	91.2
Phenyl MgBr	-75	12.4	15.1	-	88.8
Ethyl MgBr	-75	15.1	15.0	10	88.2
Ethyl MgBr	-25	20.0	15.2	6.0	89.4

From the NMR spectra the PMMA obtained using ethylmagnesium bromide and phenylmagnesium bromide initiators have similar tacticity. At low temperature of -75°C the yield was very low, 12-15%. The yield was found to increase with increase in temperature of polymerization with the yield for ethylmagnesium bromide often higher than that for phenylmagnesium bromide. A maximum yield of 60% was obtained using ethylmagnesium bromide at 4°C whereas the yield for phenylmagnesium bromide was about 35% at that temperature.

The interesting aspect of the result was the fact that ethyl magnesium bromide initiator (i.e. a straight chain alkyl Grignard reagent initiator) gave a polymer of high isotacticity (about 91%) comparable with that obtained using phenylmagnesium bromide. This is different from what was reported by Nishioka (6) and other workers that ethyl magnesium bromide gave mainly stereoblock co-polymer. It was also observed that in the present work, the yield increases with temperature increase.

The infra red spectra fig.1·1 of the samples compare favourably well with those of other workers, with high isotacticity. The NMR of the sample determined in chloroform is shown in fig.1·2. The extreme right hand line belongs to the internal standard tetramethyl silane (TMS) while the position of other peaks are given in δ units with respect to the signal of TMS taken as $\delta = 0$. The signal of the ester group appears at 3.6δ. The signal for the two methylene protons appears as a quadruplet as a result of geminal spin-spin coupling between the magnetically non-equivalent protons. Three of the expected four peaks can be seen distinctly, the fourth is under the α-methyl resonance which appears at 1.2δ. The coupling constant J was found to be 15.5 cycles per second. This indicates an isotacticity of about 91%, which is comparable with that obtained by other workers (18, 25, 33). It is quite reasonable to say that even straight chain alkyl Grignard reagent initiators produce wholly isotactic PMMA contrary to the previous beliefs.

1.3.3 Hydrolysis of the Isotactic PMMA:

1.3.3.1 Experimental:

5 grams of the polymer was dissolved in a solution of 3 grams paratoluene sulphonic acid in 38.1 cm^3 acetic acid and 10 cm^3 of water. The solution obtained was refluxed at 110°C, using an oil bath, for 336 hours. The product was isolated by precipitation in ether. The precipitate was filtered, dissolved in methanol and reprecipitated in ether. This process was repeated several times to get rid of any acetic acid. The polyacid so obtained was dried in a vacuum oven at 60°C. The white dried sample was weighed and infra red spectrum was determined.

1.3.3.2 Results:

The sample obtained was white in colour and the unionised form of the polyacid was insoluble up to $\alpha = 0.25$, both with and without added potassium nitrate. The infra red spectra of the PMA (fig.1.3) showed absorption at 1700 cm^{-1} instead of 1730 cm^{-1}, indicating complete hydrolysis has taken place. From the colour of the sample, and the viscosity average molecular weight of the reesterified PMA, there was no evidence of degradation of the polymer both in isotacticity and molecular mass. These facts show that this method would be better than the methods previously used (26,28,33,34,39) for hydrolysing

isotactic PMMA. It is also interesting to note that the tacticity is unaffected.

1.4 Theory of Binding:

In the binding of ions or molecules to a macromolecule, a large number of combining sites is always available. Treatment of such binding must therefore take into account the fact that more than one ion or molecule can bind to the available sites.

The strength of the complex formed between a metal ion and ligand in solution is usually expressed in terms of the dissociation constant. The following equations define the equilibrium constants between a polymer P and metal ion M.

$$P + M \rightleftharpoons PM \qquad K_1 = \frac{[PM]}{[P][M]} \qquad \text{.....(1-1)}$$

$$PM + M \rightleftharpoons PM_2 \qquad K_2 = \frac{[PM_2]}{[PM][M]} \qquad \text{.....(1-2)}$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

$$PM_{n-1} + M \rightleftharpoons PM_n \qquad K_n = \frac{[PM_n]}{[PM_{n-1}][M]} \qquad \text{.....(1-3)}$$

where P denotes the concentration of free polymer molecules and M denotes the concentration of free metal ion that can be bound. The concentration of individual species are usually not obtainable experimentally. However a more useful quantity in describing the

metal-polymer interaction is r, which is defined by

$$r = \frac{\text{Moles of M bound}}{\text{Total moles of polymer present}} \quad \ldots\ldots\ldots(1\text{-}4)$$

The methods for determining r have been described in appropriate sections in this thesis. r can be expressed in terms of the association constants using the equations (1-1, 1-2, 1-3).

$$\left.\begin{aligned} [PM] &= K_1[M][P] \\ [PM_2] &= K_2[M][PM] = K_1K_2[P][M]^2 \\ [PM_n] &= K_n[PM_{n-1}][M] = K_1K_2 \ldots\ldots K_n[P][M]^n \end{aligned}\right\} \quad \ldots\ldots\ldots(1\text{-}5)$$

so that the equation for r becomes

$$r = \frac{[PM] + 2[PM] + \ldots\ldots\ldots {}_n[PM]}{[P] + [PM] + \ldots\ldots\ldots [PM_n]} \quad \ldots\ldots\ldots\ldots(1\text{-}6)$$

Substituting from equations (1-1, - 1-3) for the concentrations of each species of complex in equation (1-6) in terms of the free metal, free polymer and equilibrium constants

$$r = \frac{K_1[M] + 2K_1K_2[M] + \ldots\ldots\ldots {}_nK_1K_2\ldots\ldots K_n[M]^n}{1 + K_1[M] + K_1K_2[M]^2 + \ldots\ldots\ldots K_1K_2\ldots\ldots K_n[M]^n} \quad \ldots\ldots(1\text{-}7)$$

Equation (1-7) is a general equation and the only assumption made is that the interaction is reversible and that the polymer has a fixed

number of sites for binding the metal ion.

1.4.1 Binding by identical and independent Sites with no Interaction between them:

The situation for binding by identical and completely independent sites will now be considered. Let P denote a polymer having n sites for binding to ligand M. Consider the simplest case in which the polymeric molecule P combines with only one molecule of M to form complex PM i.e.

$$P + M \rightleftharpoons PM \quad \text{.....(1-8)}$$

The association constant K is defined as

$$K = \frac{[PM]}{[P][M]} \quad \text{.....(1-9)}$$

where square brackets denote the concentration of the respective species. From equation (1-9) above

$$[PM] = K[P][M] \quad \text{.....(1-10)}$$

If $[P_t]$ is the total polymer concentration then

$$[P_t] = [PM] + [P] \quad \text{.....(1-11)}$$

Combining equations (1-10) and (1-11)

$$[PM] = K\{[P_t] - [PM]\}[M] \quad \text{....(1-12)}$$

Rearranging equation (1-12) equation (1-13) is obtained.

$$[PM] = K[M][PM] = K[M][P_t] \quad \text{.....(1-13)}$$

$$\text{of} \quad \frac{[PM]}{[P_t]} = \frac{K[M]}{1 + K[M]} \quad \text{.....(1-14)}$$

where $\frac{[PM]}{[P_t]}$ is the number of moles of M bound per mole of total polymer.

$$\text{Thus} \quad r = \frac{[PM]}{[P_t]} = \frac{K[M]}{1 + K[M]} \quad \text{.....(1-15)}$$

Many alternative forms of equation (1-15) are useful in fitting equations to data. For such purposes a linear equivalent is more desirable. Rearrangement of equation (1-15) leads to

$$\frac{[M]}{r} = \frac{1}{K} + M \quad \text{.....(1-16)}$$

$$\text{or} \quad \frac{1}{r} = \frac{1}{K}\cdot\frac{1}{M} + 1 \quad \text{.....(1-17)}$$

$$\text{or} \quad 1-r = \frac{1-K[M]}{1+K[M]} = \frac{1}{1+K[M]} \quad \text{.....(1-18)}$$

From equation (1-18) it follows that $\frac{r}{1-r} = K[M]$

Therefore if a graph of $\frac{1}{r}$ is plotted against $\frac{1}{M}$ then K is obtained from slope and the intercept is 1.

1.4.2 Binding by identical and non-independent sites:

Suppose a macromolecule has n identical electrostatically charged sites which interact with one another in such a way that the binding at any site affects the binding affinity at other sites. Consider for example the aliphatic dibasic acid $HOOC-(CH_2)_n-COOH$, it can be seen that the affinity of the species $\bar{O}OC-(CH_2)_2-COO^-$ for H^+ ions will be greater than the affinity of $HOOC-(CH_2)_n-COO^-$. This is because the extra COO^- on the former species provides extra electrostatic attraction for the H^+ ions, than the latter. This electrostatic attraction will therefore make the first association constant K_1, greater than the second association constant K_2. If n is large then mutual interaction of the COO^- groups is reduced and K_1 and K_2 approach each other. It is possible to allow for the former effect without in any way altering equation (1-18) simply by allowing K and ΔF° (standard free energy of complexation) to vary as $\bar{r}$ varies. The intrinsic association constant K_{int} can be defined as the limiting value of K_{ass} when r = 0 i.e. before any interaction due to binding takes place. Corresponding to K_{int} there is ΔF°_{int} which is standard free energy when electrostatic factors are taken into account and is given by

$$\Delta F^\circ = \Delta F^\circ_{int.} + RT\,\phi(\bar{r}) \quad \ldots\ldots(1\text{-}19)$$

where $\phi(\bar{r})$ is some function of r such that $\phi(\bar{r}) = 0$ when $\bar{r} = 0$ and $\phi(\bar{r})$ is a completely unrestricted function.

If $\phi(\bar{r})$ is an increasing function of $\bar{r}$, binding at some sites makes binding at other sites difficult, but if $\phi(\bar{r})$ is a decreasing function of $\bar{r}$, then there is co-operative interaction between sites i.e. occupation of some sites facilitates binding at other sites.

1.4.3 Single Set of Sites with co-operative Interaction between them:

There are some examples of polymer complexes where the uptake of the first metal ion makes it easier for the second metal ion to approach the charged sites on the macromolecule. In such co-operative interactions the second association constant will never be reduced, compared to the first, as much as would be expected from statistical considerations.

Infact the second association constant may even be larger than the first. The ratio of successive association constants, corrected for statistical factors, may be defined as an interaction constant. It has been shown (53) that for n sites with independent intrinsic affinities

$$\frac{\bar{r}}{n} = \frac{K[\bar{M}]^a}{1+K[\bar{M}]^a} \quad 0 \leq a \leq 1 \quad \ldots\ldots\ldots(1\text{-}20)$$

where a is a constant for interaction between a pair of species. When a = 1 all sites possess the same intrinsic free energy of association,

and the above equation reduces to equation (1-21)

$$\frac{r}{M} = K_n - K_r \quad \text{.....(1-21)}$$

which for a single binding site reduces to equation (1-16)

$$\frac{[M]}{r} = \frac{1}{K} + M$$

However it must be pointed out that when electrostatic intereaction do occur the exponent a in equation (1-20) is always greater than unity.

$$\frac{r}{n} = \frac{K[M]^a}{1+K[M]^a} \qquad a > 1 \quad \text{.....(1-22).}$$

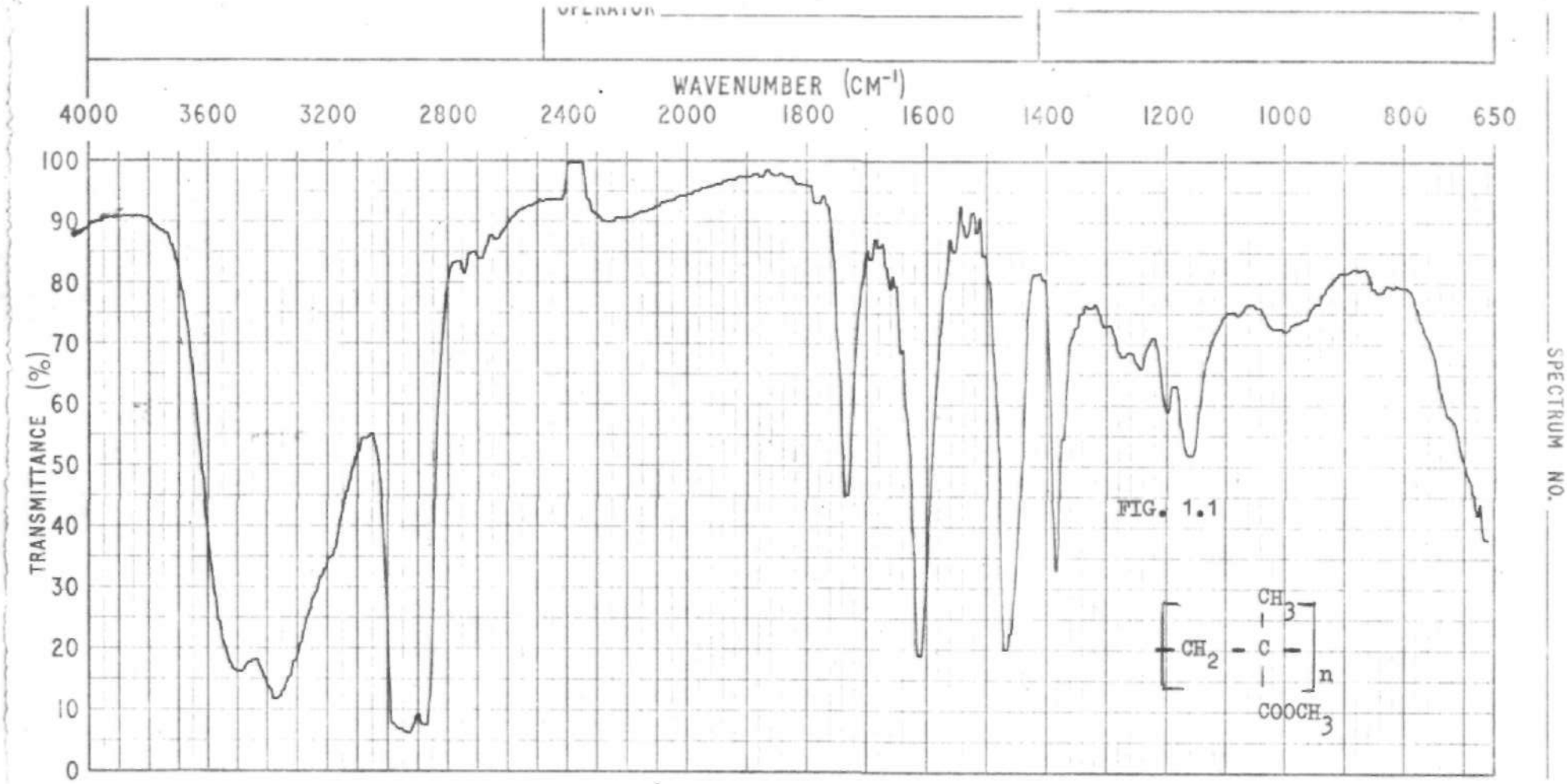


FIG. 1.1

$$\left[CH_2 - \underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} \right]_n$$

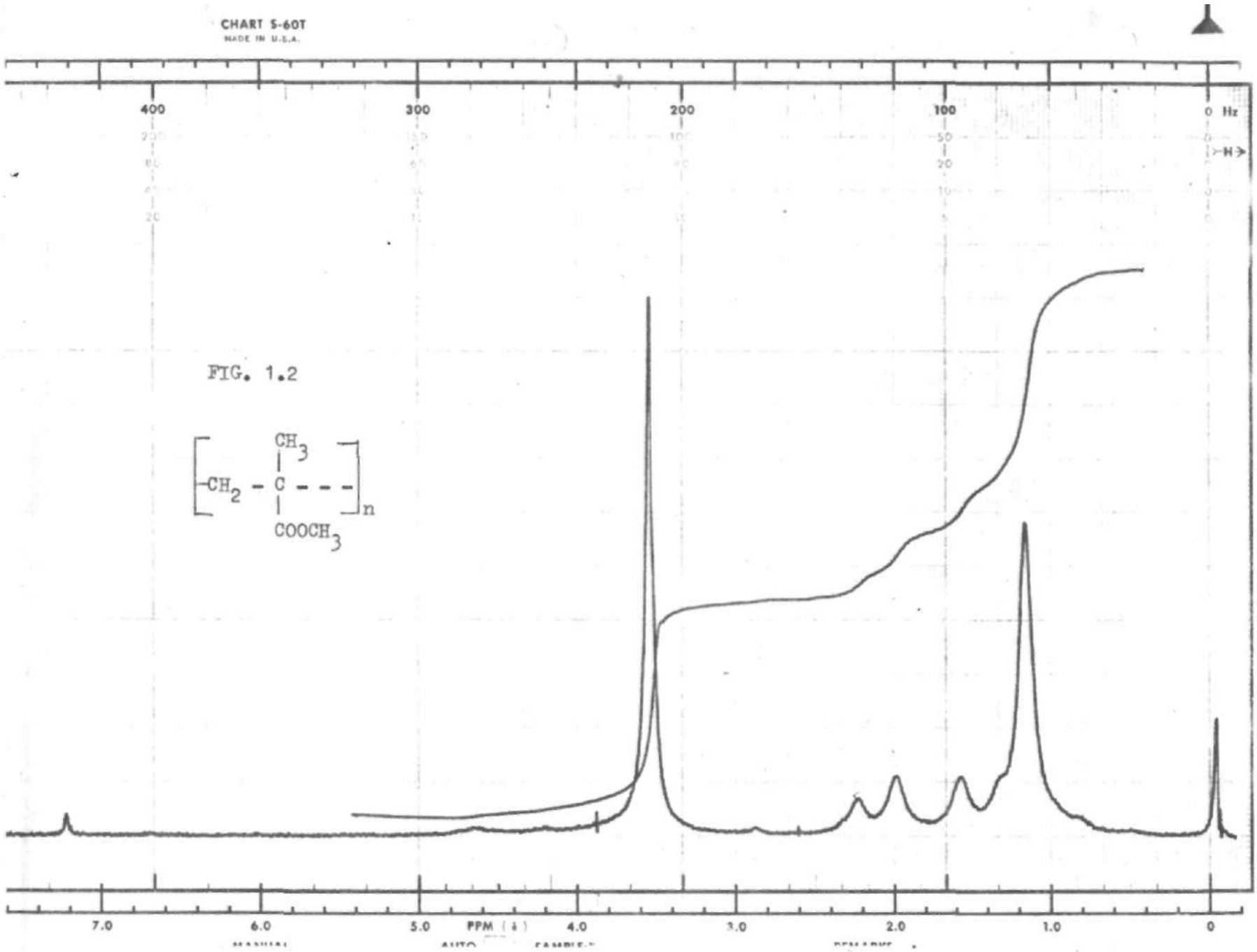
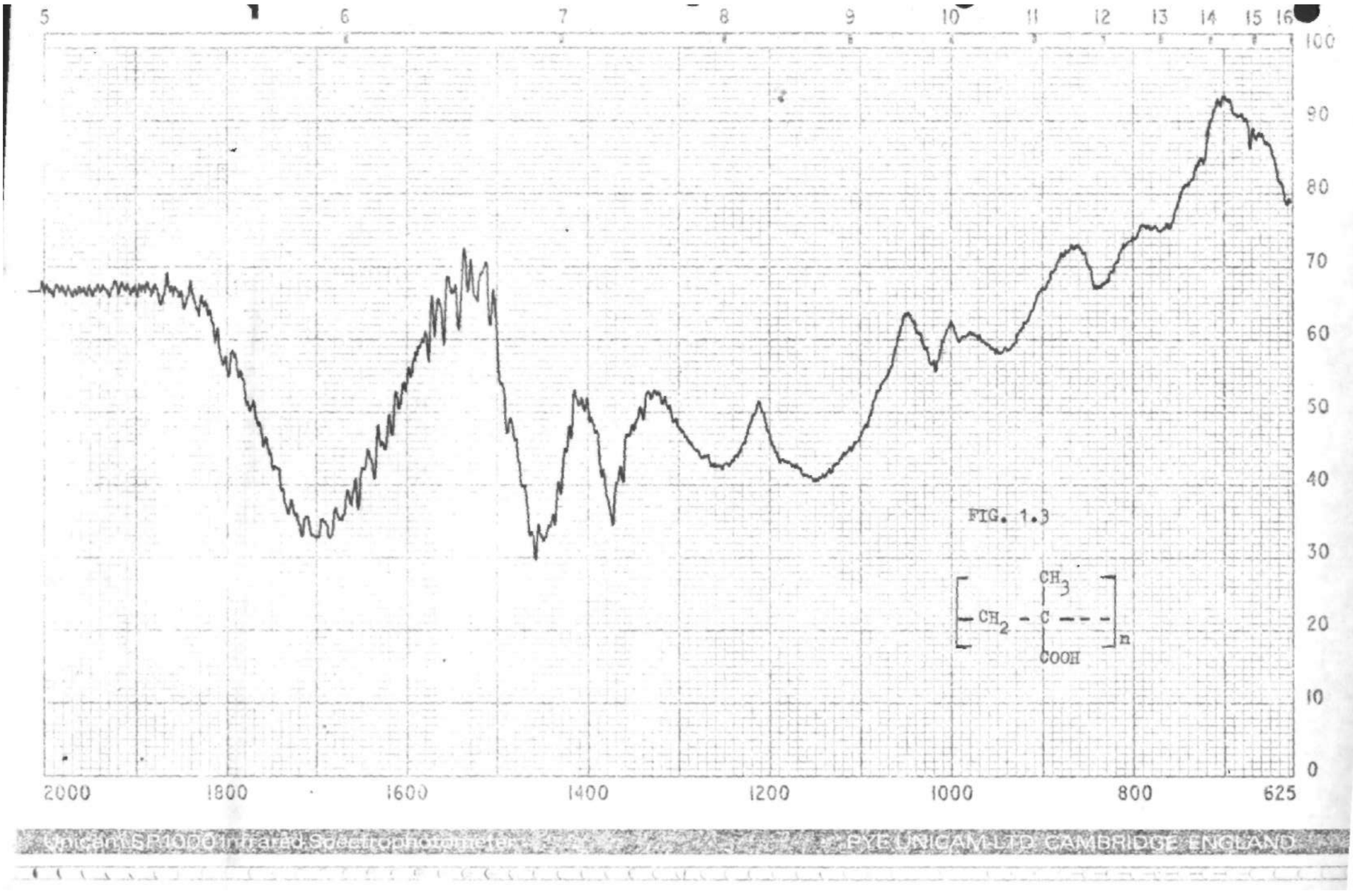


FIG. 1.2

$$\left[-CH_2 - \underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - - - \right]_n$$


5
6
7
8
9
10
11
12
13
14
15
16
100
90
80
70
60
50
40
30
20
10
0
2000
1800
1600
1400
1200
1000
800
625
FIG. 1.3
CH3
CH2 - C - - -
n
COOH
Unicam SP1000 Infrared Spectrophotometer
PYE UNICAM LTD CAMBRIDGE ENGLAND

1.5 REFERENCES

1. Fox T. G., Garett B.S., Goode W.E., Gratch S., Kincaid J., Spell A., and Stroupe J.D. J. Amer. Chem. Soc. 80, 2341, (1958).

2. Miller R.G.J., Mills B., Small P.A., Turner-Jones A., and Wood D.G.M., Chem. and Ind. (London) 1323, (1958).

3. Watanabe H., and Sono Y., paper presented at meeting of Chem. Soc. of Japan Nagoya November 1958.

4. Glusker D.E., Stiles E., and Toncoskie B. J. Polymer Sci. 49, 297, (1961).

5. Smets G., and Deloecker W. J. Polymer Sci. 45, 461, (1960).

6. Nishioka A., Watanabe H., Abe K., and Sono Y. J. Polymer Sci. 48, 241, (1960).

7. Matsuzaki K., Okamoto T., Ishida A. J. Polymer Sci. A(2), 1105, (1964).

8. Goode W.E.F., Owens H., Fellman R.P., Snyder W.H., and Moore J.E. J. Polymer Sci. 46, 317, (1960).

9. Wiles D.M., and Bywater S. Polymer 3, 175, (1962).

10. Wiles D.M., and Bywater S., ACS Div. Polymer Chem. 4(2), 317, (1963).

11. Bauman U., Schreiber H., and Tessmar K. Makromol. Chem. 36, 81, (1960).

12. Kawasaki A., Furukawa J., Tsuruta T., Inone S., and Ito K., Makromol. Chem. 36, 260, (1960).

13. Watanabe H., Sono Y., Abe K., paper presented at annual meeting of the Chem. Soc. Japan Tokyo April (1960).

14. Bacskai R. and Pohl H., J. Polymer Sci. 42, 151, (1960).

15. Dryefuss M. P., and Dryefuss P., J. Polymer Sci., 6, 93, (1965).

16. Higashimura T., Watanabe H., Sutuoki K., and Okamura S., J. Polymer Sci., C-4, 361, (1964).

17. Braun D., Herner M., Johnsen U., and Kern W., Makromol. Chem. 51, 15, (1962).

18. Bovey F. A. and Tiers G. V. D., J. Polymer Sci., 44, 173, (1960).

19. Bovey F. A., Pure Appl. Chem. 12(1-4), 525 (1966) and J. Phys. Chem. 45, 1565, (1966).

20. Furukawa J., Polymer Reprints 8(1), 39, (1967).

21. Coleman B. D., Fox T. G., and Reinmoller M., J. Polymer Sci. B4, 1029, (1966).

22. Nagasawa M., Murase T., and Kondo K., J. Phys. Chem. 69, 4005, (1965).

23. Glavis F. J., J. Polymer Sci. 36, 547, (1959).

24. Smets G., and Deloecker, J. Polymer Sci. 45, 538, (1960).

25. Morawetz H., and Kandanian A. Y., J. Phys. Chem. 70, 2995, (1966).

26. Selegny E., and Segain P., J. Macromol. Sci. Chem. A5(3), 603, (1971).

27. Tsuruta T., Makimoto T., and Kanai H., J. Macromol. Chem. 1, 31, (1966).

28. Semen J., and Lando J. B., Macromolecules 2(6), 570, (1969).

29. Morawetz M., and Zimmering P-E., J. Phys. Chem. 50, 753, (1954).

30. Morawetz H., and Gatjaens E., J. Polymer Sci. 32, 526, (1958).

31. Mandel M., and Leyte J. C., J. Polymer Sci. A2, 1879, (1964).

32. Crescenzi V., Adv. Polymer Sci. 5, 538, (1968)

33. Nagasawa M., Murase T., Kondo K., J. Phys. Chem. 69, 4005, (1965).

34. Loebl E. M., and O'neill J. J., J. Polymer Sci. 45, 538, (1960).

35. Liquori A. M., Barone B., Crescenzi, V., Quadrifoglio F., and Vitagliano V., J. Macromol. Chem. 1, 287, (1966).

36. Arnold and Overbeck J., Th. G. Rev. Trav. Chim. 68, 879, (1949).

37. Birshtein T. M., Anufrieva E. V., Nekrasova T. N., Ptitsyn O. B., and Sheveleva T. V., Vysolcomolekul. Soedin 1, 372, (1965).

38. Anzuino G., Constantino L., Gallo R., and Vitagliano V., J. Polymer Sci. B4, 459, (1966).

39. O'neill J. J., Loebl E, M., Kandanian A. Y., and Morawetz H., J. Polymer Sci. A3, 4201, (1965).

40. Kern E. E., and Anderson, D. K., J. Polymer Sci. A1, 2765, (1968).

41. Bywater, Adv. Polymer Sci. 4, 66, (1965).

42. Jaffe J., Bricman G., and Berliner C., J. Polymer Sci. B5(2), 153, (1967).

43. Kotlair M., and Morawetz H., J. Amer. Chem. Soc. 77, 3692, (1965).

44. Gregor H. P., Luttinger B., and Loebl E. M., J. Phys. Chem. 59, 34, (1965).

45. Morawetz H., J. Polymer Sci. 17, 442, (1955).

46. Mande M., and Leyte J. C., J. Polymer Sci. A2, 2883, 3771, (1964).

47. Bolewski K., and Lubina M., Roc. Chem. Ann. Soc. Chim. 44, 647, (1970).

48. Constantino L., Crescenzi,V., Quadrifoglio F., and Vitagliano V., J. Polymer Sci. A-2(5), 771, (1967).

49. Vitagliano V., Constantino L., and Sartorio R., J. Phys. Chem. 80(9), 959, (1976).

50. Smets G., Angew Chem. 1, 306, (1961).

51. Wiles D. M., and Bywater S., J. Phys. Chem. 68, 1983, (1964).

52. Baxendale, J. H. Bywater S., and Evans M. G., J. Polymer Sci. 1, 237, (1946).

53. Valko E., Kolloid Z. 51, 130, (1930).

Chapter 2

DIALYSIS EQUILIBRIUM

Contents

		Page
2.1	Introduction	36
2.2	Brief Theory of Donnan's Equilibrium	36
2.3	Experimental Details	41
2.3.1	Materials	41
2.3.2	Method	42
2.3.2.1	Preparation of Membrane and Filling of Dialysis Tubing	42
2.3.2.2	Analysis of Solution at Equilibrium	43
2.3.2.3.	Calibration Curve	43
2.4	Results and Discussion	45
2.4.1	Results	51
2.4.2	Discussion	51
2.4.2.1	Effect of binding on Polyion Configuration ..	53
2.4.2.2	Stability of M^{2+}-i-PMA Complexes	56
2.5	R e f e r e n c e s	58

Chapter 2

DIALYSIS EQUILIBRIUM

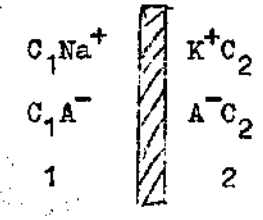
2.1 Introduction:

The use of equilibrium dialysis technique permits the gathering of precise quantitative data on polyelectrolyte-metal equilibria in solution. The technique has been used by many workers to obtain information on the polyelectrolyte-metal interaction. In principle the technique consists of a vessel divided into two compartments by a specially prepared membrane which is permeable to the small molecules and ions but impermeable to the macromolecules. If the macromolecules are confined to one compartment, and if they bind some of the small ions in the macromolecule - containing chamber, then the number of small ions in this chamber will exceed that in the macromolecule-free chamber. The difference between the two concentrations is a measure of the amount of bound ions, provided the Donnan effect has been suppressed or accounted for.

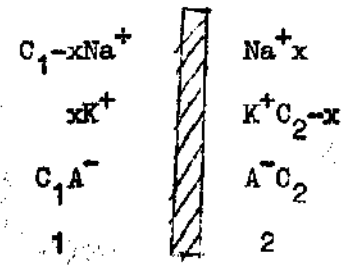
2.2 Brief Theory of Donnan's Equilibrium:

Some peculiar electrical and other effects have been observed (1,2) in a system where two solutions containing electrolytes are separated by a membrane which is freely permeable to most of the ions but

impermeable to one specie. To understand this a very simple case may be considered. Suppose that a membrane M separates two solutions 1 and 2 of equal constant volume containing only the salts NaA and KA respectively. The membrane is permeable to Na^+ and K^+ but not A^- ions. The cation can therefore exchange places by diffusion across the membrane but this is subject to the restraint condition of equimolar quantities. At first one might be inclined to think that the interchange of Na^+ and K^+ ions would continue until they are equally distributed throughout the whole system. This would occur if the system were permeable to A^- ion also, but that it will not occur readily in present case can be seen in the following illustration. Assuming complete ionization, the initial and final states can be represented as follows:



Initial state



Equilibrium state

If F denotes the free energy of the system then the equilibrium state is characterised by the condition $(dF)_{P,T} = 0$ If the following variation is considered, dn Moles $Na^+ \rightarrow 2$

dn Moles $K^+ \rightarrow 1$

then the electrical work terms vanish and we get

$$dF = RT\left\{dn \log \frac{[Na^+]_1}{[Na^+]_2} + dn \log \frac{[K^+]_2}{[K^+]_1}\right\} = 0$$

So that $\frac{[Na^+]_1}{[K^+]_2} = \frac{[Na^+]_2}{[K^+]_2} = \frac{C_1}{C_2}$

Thus only when $C_1 = C_2$ is it true that for equilibrium

$$[Na^+]_1 = [K^+]_1 = [K^+]_2$$

Let the above simple consideration be applied to a polyelectrolyte of high molecular weight separated by a semi permeable membrane from water. Although the polyelectrolyte contains mobile counterions which can pass through the membrane no such passage will be possible, since this will result into a rapid build up of very large electrostatic changes of opposite sign in the two portions of the system. However, if a uni-univalent salt such as KNO_3 is added on either side of the membrane, its anions and cations may diffuse together. Such distribution of the salt between the two portions of the system must satisfy two conditions according to Donnan (1, 3). The first condition requires that the solution on either side of the membrane must be electroneutral. Thus if m_f is the molarity of the fixed charges in solution containing the polyelectrolyte, and m_s is the molarity of the added uni-univalent salt,

then molarity of the byion will be $m_b = m_s$ and molarity of counterion $m_c = m_f + m_s$. In the dialyzate both ions will be at the same molarity $m'_b = m'_c = m'_s$. The second condition is that at equilibrium the diffusible electrolyte must have the same thermodynamic activity on both sides of the dialysis membrane.

$$m_b m_c \gamma_{\pm}^2 = m'_b m'_c (\gamma'_{\pm})^2.$$

$$(m_f + m_s) m_s \gamma_{\pm}^2 = (m'_s)^2 (\gamma'_{\pm})^2 \quad \text{.....(2-1)}$$

where $\gamma'_{\pm}$ and $\gamma_{\pm}$ are the mean ionic activity coefficients in the absence and presence of polyelectrolyte respectively.

Consider first, the result which would be obtained if the activity coefficients could be neglected. Equation (2-1) then gives for a relation between m_s and m'_s

$$m_s = \frac{-m_f}{2} + \sqrt{m_f 2)^2 + (m'_s)^2} \quad \text{.....(2-2)}$$

If $m'_s / m_f \ll 1$ then $m_s = m_s \ (m_s / m_f)$ i.e. the added salt is excluded from the polyelectrolyte solution. In the other extreme case when $\frac{m'_s}{m_f} \gg 1$, and expansion of (2-2) yields:

$$m_s = m'_s - \frac{m_f}{2} + \frac{m_f^2}{8 m'_s} \quad \text{.....(2-3)}$$

so that the difference in the total molarity of mobile ions m_i on the two sides of the membrane is

$$m_i = m_c + m_b - m'_c - m'_b = m_p^2/4m'_s \quad \ldots\ldots(4)$$

Equation (4) shows that the value of m_i, which contributed to the osmotic pressure of the polyelectrolyte solution, is minimised with increase in concentration of the added salt.

In the system studied, partially ionized PMA of concentration P on one side of the semi-permeable membrane is brought to equilibrium with the cation solution of concentration M in the same solvent as is on the other side. The low molecular weight cation passes freely across the membrane such that its activity on both sides of the membrane is reached. The solutions on the two sides were made sufficiently similar by addition of simple electrolyte - KNO_3 so that activity coefficients should also be the same on both sides. This was necessary because both P and M are ionic and Donnan's effect must be suppressed.

The theory of dialysis equilibrium just discussed has an interesting bearing on the ionic and other exchanges which take place in living cells or tissues and their circumnatant fluids. In these cases, however, the phenomena may be complicated by the variable permeability of the cell membranes and by many other factors, so that the extremely simple relationships which result from ideal membrane equilibria as

presented in the foregoing sections will represent only a very small part of the associated complex of phenomena which make up the reaction of the cell towards variation of its environment. However the complexity in living matter can only be understood by analysing it into its simplest constituents and ascertaining, one by one, the laws which govern the operation - the action and the equilibrium - of these constituents.

2.3 Experimental Details

2.3.1 Materials

Semi-permeable membrane (viskintubing 24/32 inch) which is permeable to water, small molecules and ions, but impermeable to PMA molecules. Pyrex test tubes, low temperature bath, buffer solution pH=10. The buffer solution used was prepared by adding 142 cm^3 of concentrated ammonia solution to 17.5 g of analar ammonium chloride and diluting to 250 cm^3 with distilled water. Eriochrome black T indicator (4), used for the determination of both zinc and magnesium ions, was prepared by dissolving the dye in triethanolamine and absolute alcohol. 0.5 percent solution of Fast Sulphon Black F indicator (4) was used for estimation of copper. 0.1M stock solution of EDTA was prepared by dissolving 37.23 g of analar disodium dihydrogen ethylenediamine tetra-acetate dihydrate in distilled water and diluting to one litre with distilled water.

2.3.2 Method

2.3.2.1 Preparation of Membrane and Filling of Dialysis Tubing

Appropriate lengths of the viskin tubings to be used were put in distilled water and heated for one hour. The tubings were transfered to fresh water and reheated for another one hour. The tubings were next soaked in water for a few hours and then in 0.1M KNO_3 for another 24 hours, adjusting the pH occasionally to the required one. A piece of dialysis tubing was removed from the KNO_3 solution and a knot was tied at one end of it. 5 cm^3 of PMA solution at a given degree of ionization α, and enough KNO_3 was added to give the desired ionic strength of 0.10 in a total acid volume of 10 cm^3. The other end of the tubing was closed and tied using a nylon thread. The membrane bag was suspended in a test tube containing polymer-free solution. The polymer-free solution contained 5 cm^3 of zinc ion of varicus concentrations, and enough KNO_3 solution to give the desired ionic strength of 0.1 in a total volume of 10 cm^3. In all the experiments 2.5×10^{-3} base molar PMA solution was used and the studies were carried out at varying degrees of neutralisation.

Adequate mixing was necessary to attain equilibrium in the minimum possible time. The dialysis bag was made taut and had an air space provided in the bag. The dialysis was carried out at $25 \pm 0.1^{\circ}C$. The time required for equilibration was determined for each metal ion, and

minimum time was found to be five days. It was also necessary to determine that an appreciable amount of Zn^{+2} ion did not bind to the dialysis bag within the time required for equilibration. The amount of Zn^{+2} ions bound to the membrane was negligible.

The above procedure was repeated for Cu^{+2} and Mg^{+2} ions, and the amounts of Cu^{+2} or Mg^{+2} bound to membrane were negligible.

2.3.2.2 Analysis of Solution at Equilibrium

The analysis of the PMA-free solution was carried out using an adaptation of the volumetric analysis, where 2 cm^3 of the polymer-free solution was used for titration. In principle the solution was buffered to pH = 10 and titrated against 25 x 10^{-3}M EDTA solution in the presence of Eriochrome black T indicator. The metal ions form chelate complexes with the EDTA where the absence of zinc ions is indicated by a colour change from wine-red to blue. The unknown concentration of zinc ion can be determined, by reading from the calibration curve, once the volume of EDTA used was known.

2.3.2.3 Calibration Curve

A calibration curve has to be prepared for the zinc ion. To do this 2 cm^3 of $Zn(NO_3)_2$ solution of known concentrations ranging from 0 to 20 x 10^{-3}M was titrated against 25 x 10^{-3}M EDTA solution. A plot of concentration of zinc ion against volume of EDTA used was made.

The unknown concentration of zinc ion can thus be determined.

The amount of zinc ion bound can be determined, and is the difference between the amount of zinc ion put in and the amount of free zinc ion found from titration.

The analysis of other ions were similarly carried out except that the buffer solution used for Cu^{+2} was concentrated ammonia solution, and the indicator was Sulphon Black F, but buffer and indicator used for Mg^{+2} were the same as for zinc ion. The whole equilibrium dialysis measurement was repeated at least thrice for each degree of neutralisation studied.

The average number of metal ions bound per base molar PMA molecule r, is equal to the molar concentration of bound metal ion divided by the molar concentration of the polymer present.

2.4 RESULTS AND DISCUSSIONS

A lot of work has been done to determine the co-ordination numbers and stability constants of chelate complexes formed between macromolecules and metallic ions. Bolewski and Lublina (5) have applied the theory of multiple equilibria to study the interaction between conventional PMA (c-PMA) and Zn^{+2}, Cd^{+2} and Cu^{+2} ions using polarographic techniques. Other analytical methods such as potentiometric titration (8) spectrophotometric (6, 8) and equilibrium dialysis (7, 8, 9) techniques have been used to determine the co-ordination numbers and stability constants of Cu(II) - PMA complexes. Kolawole (8) in his studies of Zn-c-PMA and Cu-c-PMA complexes considered two types of reactions to be taking place. The reaction between M^{2+} and c-PMA has been considered as (a) straight forward chelation and (b) as chelation leading to dimerization of the macromolecules.

In the first case the reaction

$$M^{2+} + (COO^-) \rightleftharpoons M(COO)_2$$

giving $K_1 = \dfrac{[M(COO)_2]}{[M][COO^-]_2}$, has been considered. From the above reaction it has been shown (8) that $\dfrac{1}{r} = \dfrac{2}{K_1[M_f]} + 2$ .....(2-5)

$$\text{where} \quad r = \frac{[(COO)_2]_{total}}{[M^{+2}]_{bound.}}$$

If $\frac{1}{r}$ is plotted against $\frac{1}{M_f}$ the slope is $\frac{2}{K_1}$ and the intercept is 2.

In the second case (b) if the co-ordination number is assumed to 2 i.e. n = 2, one can either have bi-co-ordinate complex or dimerization involving two COO^- groups. i.e. $M^{2+} + 2COO^- \rightleftharpoons M(COO)_2$

$$\text{giving} \quad K_2 = \frac{[M(COO)_2]}{[M^{2+}][COO^-]^2} \qquad \ldots\ldots\ldots\ldots(2\text{-}6)$$

From this equation it has been shown that

$$\left\{L^2/M_b - 4(I-M_b)\right\} = \frac{1}{K_2 M_f} \qquad \ldots\ldots\ldots(2\text{-}7)$$

where $L = [COO^-]$

M_b = Concentration of the metal ion bound

M_f = Concentration of free metal ions.

The above equation also applies to an equilibrium involving a tetra-co-ordinate complex

$$M^{2+} + 2(COO^-) \rightleftharpoons M(COO^-)_4$$

where L is here the original concentration of $(COO^-)_2$ resulting in the tetra-co-ordinate complex. Both equations (2-5) and (2-7) have been tested in the present study and the results have been reported later in this chapter.

Summary of results obtained from dialysis equilibrium studies showing the amount of the metal ion bound and the amount of metal ion added at various degress of ionization of i-PMA in 0.10 M KNO_3 at 25 ± 0.1°C. All concentrations are in moles/litre.

Table 2-I

$\alpha = 0.3$

$[Zn^{+2}]_{added} \times 10^4$	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0
$[Zn^{+2}]_{bound} \times 10^4$	0.92	1.80	2.25	2.90	3.35	3.65	3.85	3.90

$\alpha = 0.4$

$[Zn^{+2}]_{added} \times 10^4$	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0
$[Zn^{+2}]_{bound} \times 10^4$	1.20	2.20	3.15	3.87	4.40	4.75	4.90	5.00

$\alpha = 0.5$

$[Zn^{+2}]_{added} \times 10^4$	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0
$[Zn^{+2}]_{bound} \times 10^4$	1.55	2.60	3.65	4.60	5.12	5.43	5.60	5.80

$\alpha = 0.6$

$[Zn^{+2}]_{added} \times 10^4$	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0
$[Zn^{+2}]_{bound} \times 10^4$	2.30	3.45	4.33	5.00	5.45	5.80	6.02	6.27

Table 2-II

$\bar{\nu} = 0.3$

$[Cu^{+2}]_{added} \times 10^4$	5.0	6.0	7.0	8.0	10.0	12.0	14.0	16.0
$[Cu^{+2}]_{bound} \times 10^4$	1.075	1.30	1.50	1.68	2.10	2.51	2.88	3.18

$\bar{\nu} = 0.4$

$[Cu^{+2}]_{added} \times 10^4$	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0
$[Cu^{+2}]_{bound} \times 10^4$	1.40	2.30	3.20	4.00	4.53	4.80	4.95	5.00

$\bar{\nu} = 0.5$

$[Cu^{+2}]_{added} \times 10^4$	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0
$[Cu^{+2}]_{bound} \times 10^4$	1.65	2.82	3.98	4.83	5.35	5.75	6.03	6.30

$\bar{\nu} = 0.6$

$[Cu^{+2}]_{added} \times 10^4$	5.0	7.5	10.0	12.5	15.0	17.5	20.0	25.0
$[Cu^{+2}]_{bound} \times 10^4$	2.05	3.75	5.20	6.15	6.75	7.14	7.40	7.65

Table 2-III

$\alpha = 0.7$

$[Mg^{+2}]_{added} \times 10^4$	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0
$[Mg^{+2}]_{bound} \times 10^4$	0.12	0.30	0.40	0.50	0.71	1.06	1.40	1.56	1.60

$\alpha = 0.8$

$[Mg^{+2}]_{added} \times 10^4$	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0
$[Mg^{+2}]_{bound} \times 10^4$	0.23	0.46	0.60	0.69	0.90	1.31	1.63	1.79	1.81

$\alpha = 0.9$

$[Mg^{+2}]_{added} \times 10^4$		10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0
$[Mg^{+2}]_{bound} \times 10^4$		0.61	0.72	0.84	1.08	1.48	1.80	1.92	1.94

Table 2-IV

α	$[Zn^{2+}]_{max.}$	COO^-/Zn^{+2}_b
0.3	3.90	1.92
0.4	5.15	1.94
0.5	5.80	2.15
0.6	6.90	2.17

Table 2-V

α	$[Cu^{+2}]_{max.}$	COO^-/Cu^{+2}_b
0.3	3.75	2.00
0.4	5.0	2.00
0.5	6.45	1.94
0.6	7.65	1.96

2.4.1 Results:

Figures 2.1-7 show the plots from equilibrium dialysis studies. Figures 2.1, 2.4 and 2.7 are the plots of the amount of metal ion bound against the total amount of divalent metal ion added. Tables 2-I, 2-II and 2-III show the amount of metal ion bound and the amount of metal ion added at various degrees of ionization, while tables 2-IV and 2-V show the co-ordination number n $\left[= \frac{COO^-}{M^{+2}} \right]_b$ i.e. maximum number of carboxylate group bound per metal ion when the maximum amount of metal ion is bound.

2.4.2 Discussion:

Figures 2.1 and 2.4 show a gradual increase in the amount of Zn^{+2} and Cu^{+2} ion bound respectively, indicating a gradual build up of the complex which finally levels off for each degree of ionization studied. As the amount of metal ions added increases the amount bound increases as the concentration of the metal-i-PMA complex builds up, until finally a levelling off in the curves is observed. The levelling off indicates that beyond a certain concentration, no matter how much of the metal ion is added, the amount of metal bound remains the same. This means that all the available binding sites at any particular degree of neutralisation (α) have been taken up and no further binding is possible. The amount of metal ion bound is found in all cases (figures 2.1 and 2.4) to increase with increase in the value of α. This is to be

expected since the net charge on the polyanion increases with degree of neutralisation. From the values of $\left[M_b^{2+}\right]$ when levelling off occured, the co-ordination number n(= $\frac{COO^-}{M_b^{2+}}$) was obtained and was found to be 2 for both copper and zinc as seen from tables 2-IV and 2-V. The ratio COO_b^-/M_b^{2+} decreases as binding takes place probaly due to decrease in the amount of free COO^- groups available as metal ion binding takes place. When maximum binding has occured the ratio stays constant.

A situation more difficult to analyse is observed in the case of Mg^{2+}-PMA complex. The shapes of the curves in figure 2.7 show two types of equilibria. There is a gradual rise in the amount of Mg^{2+} ion bound followed by an almost flat region where little rise in Mg_b^{2+} is observed with increase in the amount of Mg^{2+} added. This portion is then followed by a moderately sharp rise in Mg_b^{2+} which eventually levels off. There is obviously a gradual build up of some sort of association between Mg^{2+} and i-PMA, which because of the build up in electrostatic energy (high α) is unstable, and so breaks down to form a new type of association. As expected the amount of Mg^{2+} bound increases with increase in the degree of neutralisation.

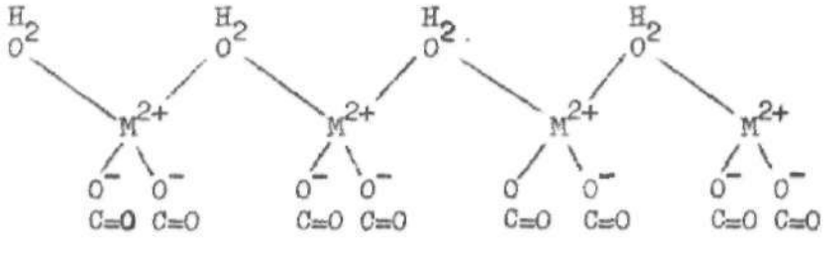
Figure 2.8 shows a plot of maximum metal ion bound against degree of ionization for the three metal ions studied. The figure shows that

when the amount of M^{2+} bound at the same $\bar{\nu}$-value is compared, Cu^{+2} binds more to the i-PMA than Zn^{+2} which in turn binds much more than Mg^{+2}. These findings suggest the order of binding as $Cu^{+2} > Zn^{+2} > Mg^{+2}$. This order is expected since the binding of the metal ions to the polymer proceeds through oxygen; i.e. the greater the $M^{2+} \rightarrow O$ attraction the stronger the binding of the M^{2+} to the macromolecule. The order of electronegativity is infact $Cu^{+2} > Zn^{+2} > Mg^{+2}$ which will be the order for $M^{+2} \rightarrow O$ attraction. In the binding between M^{2+} and the carboxylate groups some water molecules are being replaced from the hydrated M^{2+} by the COO^- groups. Since the greater the hydration energy the more difficult it is for water molecules to be displaced, then the greater the hydration energy of the M^{2+} the less effective the binding of the macromolecule. It follows that Mg^{+2} with greater hydration energy will bind less to the macromolecule.

2.4.2.1 Effect of binding on polyion configuration:

The high concentration of K^+ ions (0.1M) will provide a shielding of the fixed charges of the polyion, and so the expansion of the chain backbone, resulting from mutual electrostatic repulsion of the fixed charges will be greatly reduced i.e. the molecule would still exist in the coiled form. Under these conditions and from the data presented in tables 2-IV and 2-V, two ways in which the interaction of metal ion

with polymer are suggested. One can either have (a) intrachain interaction which involves binding within a polymer chain or (b) interchain interaction which involves two chains alligned together, such that the M^{+2} ion forms a sort of bridge between the two chains. (a) In the intrachain interactions binding of a cation to a polymer will involve carboxylate groups from the same polymer chain i.e. two neighbouring carboxylate groups would be involved. This mode of interaction is likely to lead to coiling of the molecules at low degrees of neutralisation. Intrachain chain interaction in which more than two neighbouring carboxylate groups (e.g. 4) are involved would be very difficult on account of steric strain. If more than two carboxylate groups are bound, then interchain interaction is more favoured. For isotactic polymethacrylic acid, the following arrangement may be found for intrachin interaction.



This mode of interaction can either involve two carboxylate groups within helix where an inter-calated type of bridging is formed or involves bridging between adjacent turns of the helix. Since both copper and zinc form tetrahedral complexes then the above type of representation is favoured. However the tetrahedral complex of copper is more stable than that of zinc, since the d^9 orbital in copper allows for distortion which further stabilises the structure.

In interchain interaction, two chains will be alligned in such a way that either (a) the two remaining water molecules bonded to M^{2+} are replaced by two carboxylate groups from the other polymer chain or (b) the M^{2+} ion forms a bridge between two carboxylate groups one from each i-PMA chain. The former will involve four carboxylate groups to one metal ion , which has not been observed in the present study. The latter will involve two carboxylate groups to one metal ion i.e. a sort of dimerization of the macromolecules. This is unlikely because two highly charged macromolecules will find it very difficult to approach each other because of the strong electrostatic repulsive forces. The closeness of the COO^- groups (in helical structure) of isotactic PMA will reinforce this effect and make such coming together of two chains for interchain interaction almost impossible. Thus the intrachain interaction is more likely to take place. This conclusion seems to

agree with Kolawole's recent result in viscometric studies (10) that the binding of M^{2+} to i-PMA is likely to be intramolecular rather than intermolecular binding.

2.4.2.2 Stability of M^{2+}-i-PMA Complexes:

In calculating the binding constant for Cu-c-PMA and Zn-c-PMA complexes Kolawole (8) obtained equations (2-5) and (2-7). From a plot of $\frac{1}{r}$ against $\frac{1}{M_f}$, the reciprocal slope gives the binding constant while the intercept gives n (= co-ordination number). These equations have also been employed in the present study. It was not clear from the derivation the type of interaction assumed before deriving these equations, but from the study of the equations it would appear that equation (2-5) assumes intramolecular binding mechanism whilst equation (2-7) assumes intermolecular binding mechanism.

Figures 2.2 and 2.5 show the plot of $\frac{1}{r}$ versus $\frac{1}{M_f}$ when equation (2-5) is used, and figures 2.3 and 2.6 are obtained when equation (2-7) is used. Figures 2.2 and 2.5 give straight line graphs while 2.3 and 2.6 do not. Thus it is reasonable to conclude that from the shape of these curves, the likely mode of binding is intramolecular binding. It is also clear that intermolecular binding would probably involve more than two COO^- groups. The straight line obtained in figures 2.2 and 2.5 would rather suggest one type of complex for both copper and zinc.

The equation 2-5 also predicts one binding constant which would support the reaction

$$M^{2+} + (COO^-)_2 \rightleftharpoons M(COO^-)_2$$

The binding constant was found to be 1.98×10^3 for zinc while for copper it was 2.62×10^3 (at $25 \pm 0.1^{\circ}C$). This shows again that Cu^{+2} forms a more stable complex with i-PMA than zinc does.

The binding constant for zinc-c-PMA was reported (8) to be 1.844×10^3, which indicates that zinc forms more stable complex with isotactic PMA than it does with conventional PMA. However, for copper the binding with c-PMA was reported by Kolawole (8) to result in more than one complex formation. Some of the results obtained in the present work is in agreement with those of previous workers (11, 12) who reported that Cu^{+2} binds more than Mg^{+2} to i-PMA.

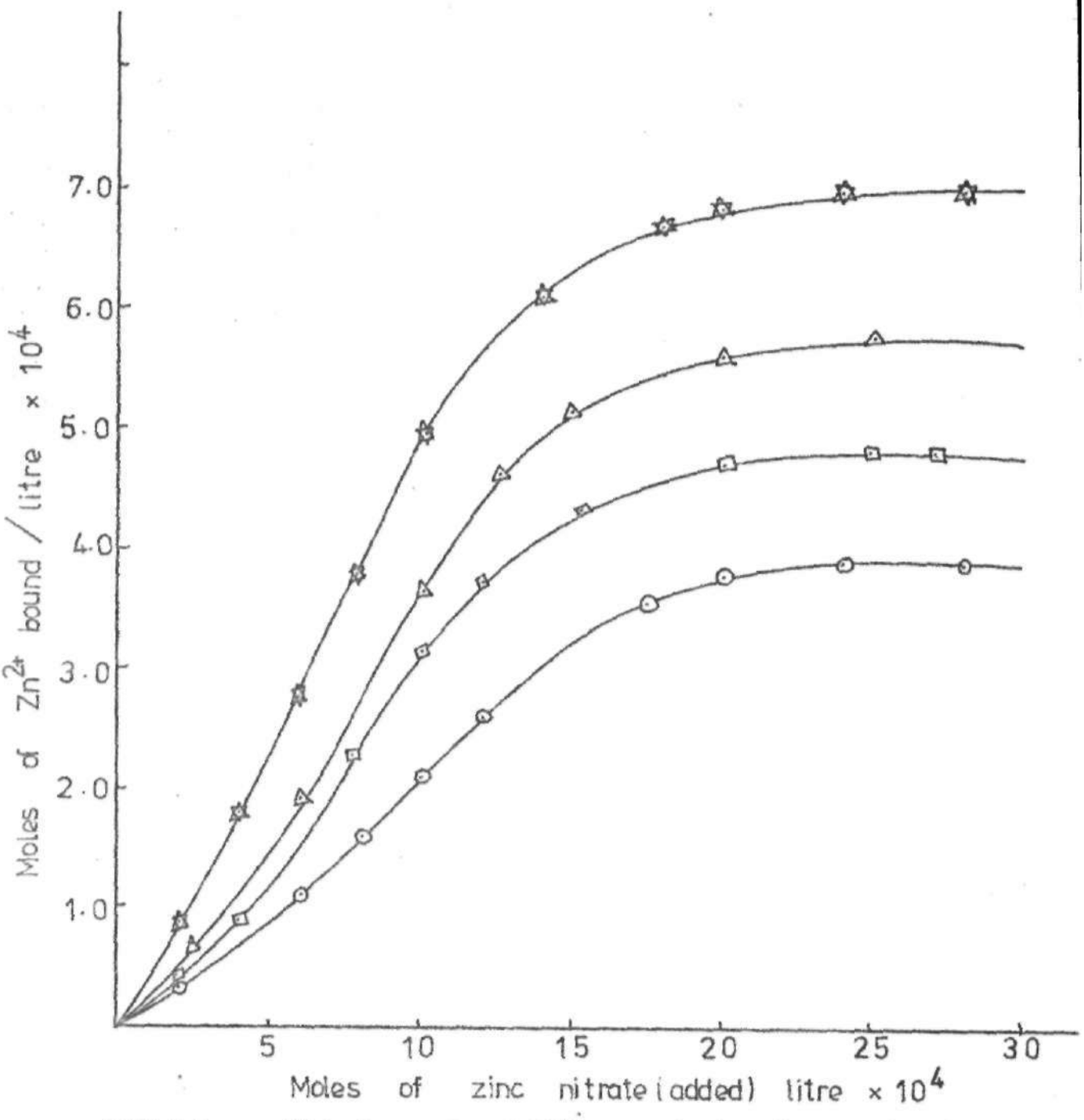


FIG. 2.1 Dialysis of i-PMA against zinc at four degrees of ionisation. [i-PMA] = 2.5×10^{-3}; I = 0.10
(⊙) 0.30 (⊡) 0.40 (△) 0.50 (⛛) 0.60

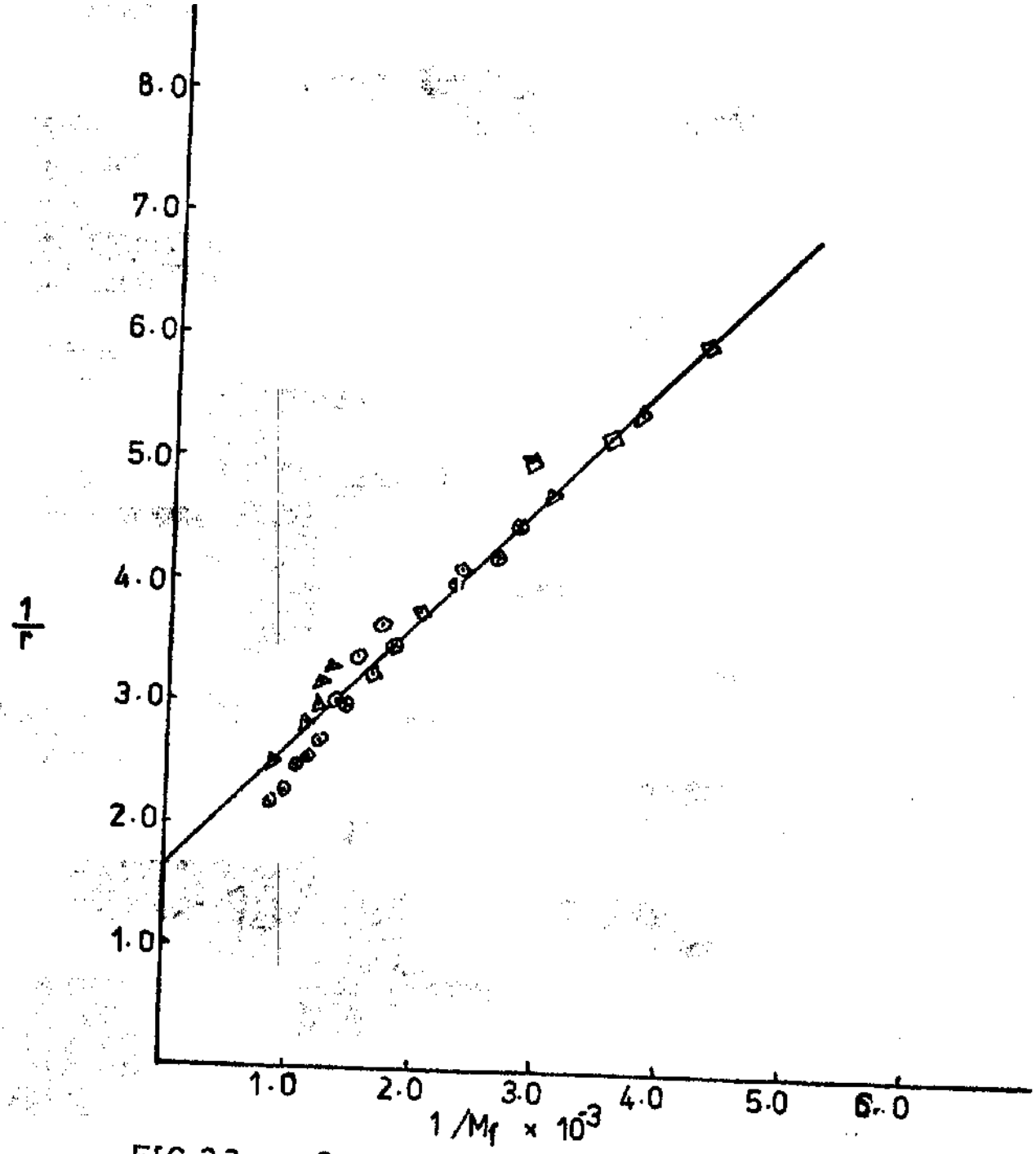
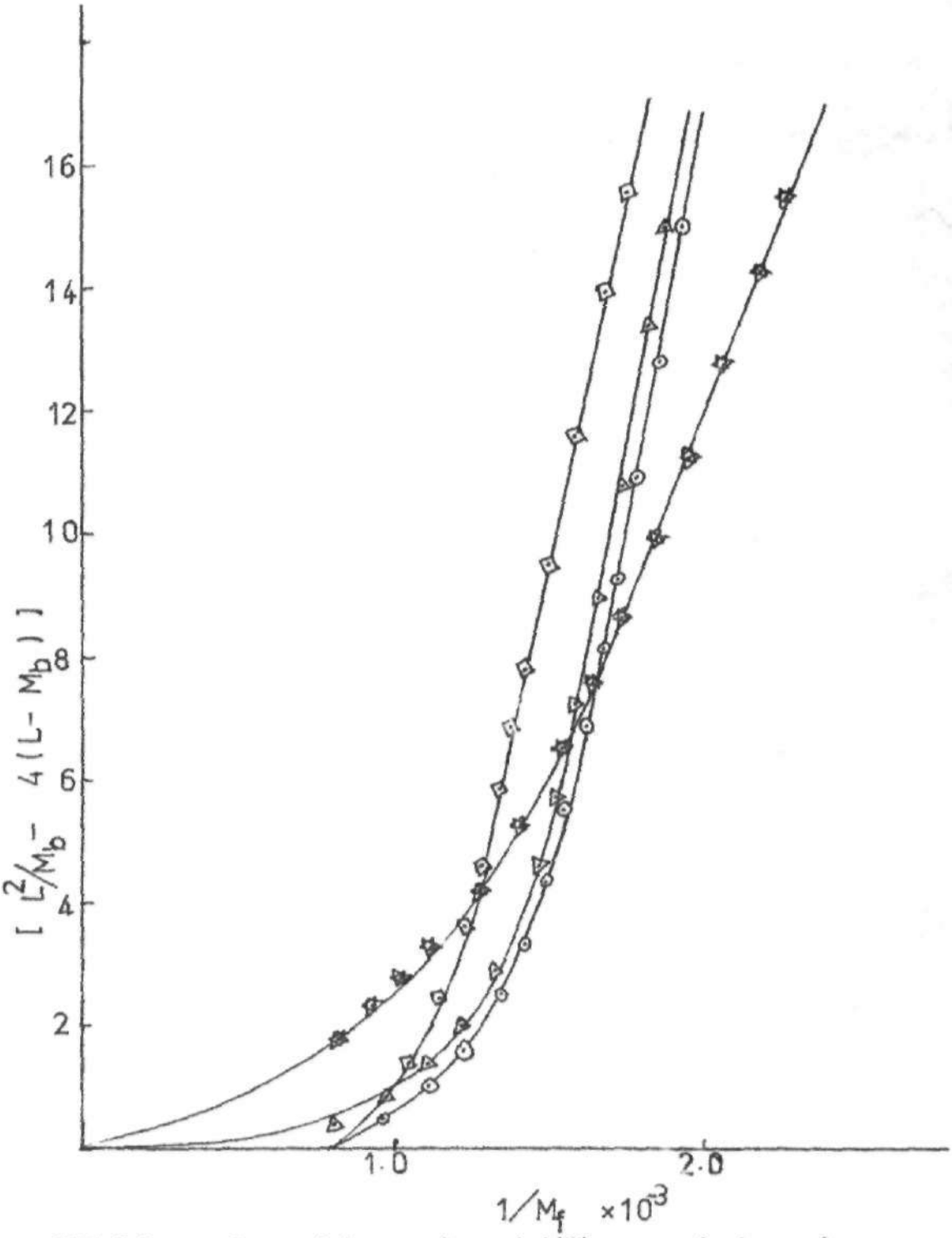
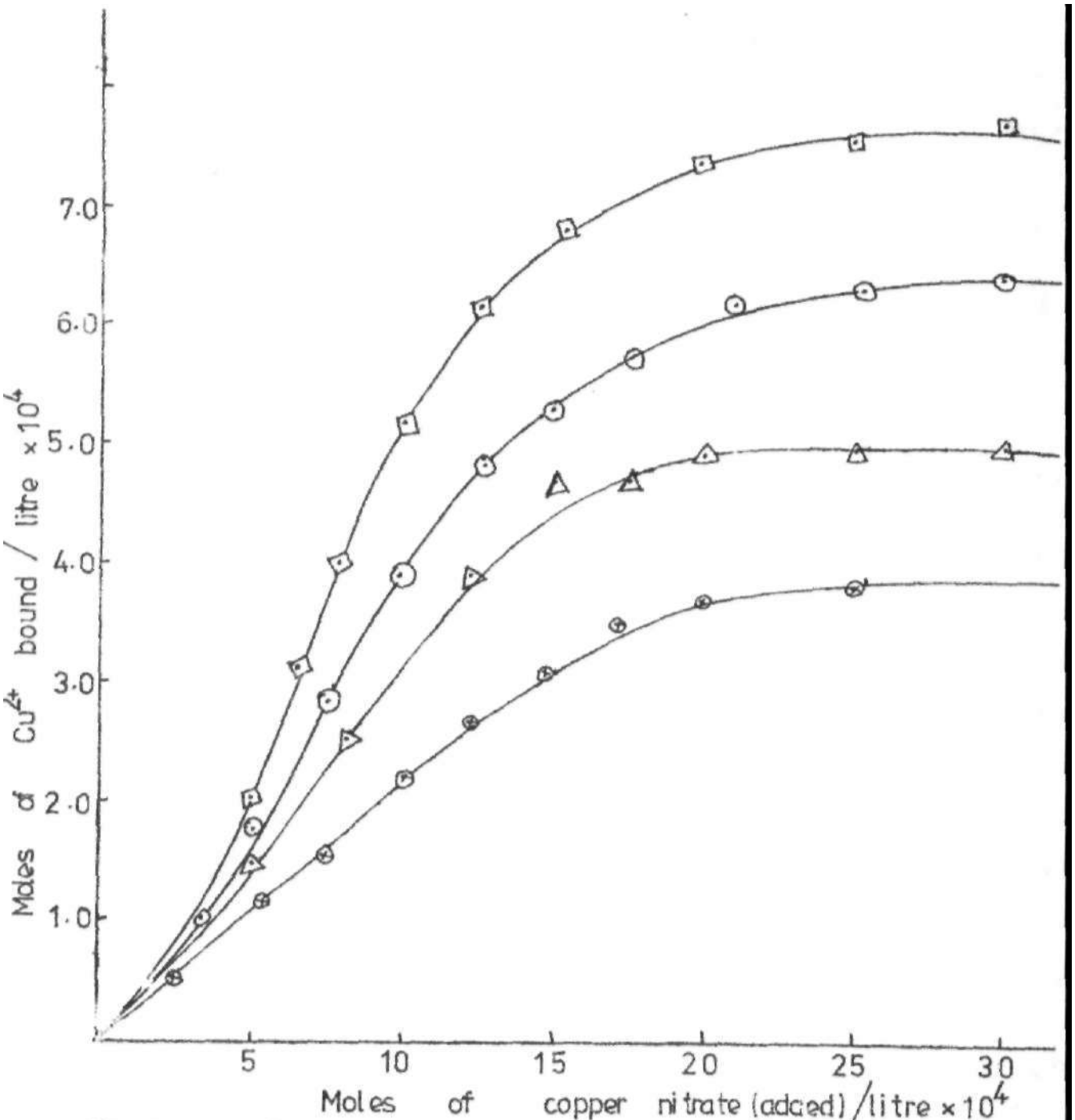


FIG. 2.2 Computation of stability constants and co-ordination number of Zn-PMA complexes. [i-PMA] = 2.5×10^{-3} M; I=0.10
α: (△) 0.30, (□) 0.40, (○) 0.50; (⊗) 0.60.



FIG·2·3 Computation of stability constants of Zn-PMA complexes.
[i-PMA] = 2.5×10^{-3} M; I = 0·10
α: (⊙) 0·30; (⊡) 0·40; (△) 0·50; (⊠) 0·60.



FIG·2·4 Dialysis of i-PMA against copper at four degrees of ionisation

[i-PMA] = $2 \cdot 5 \times 10^{-3}$M ; I = 0·10

(⊗) 0·30 ; (△) 0·40 ; (⊙) 0·50 ; (□) 0·60 .

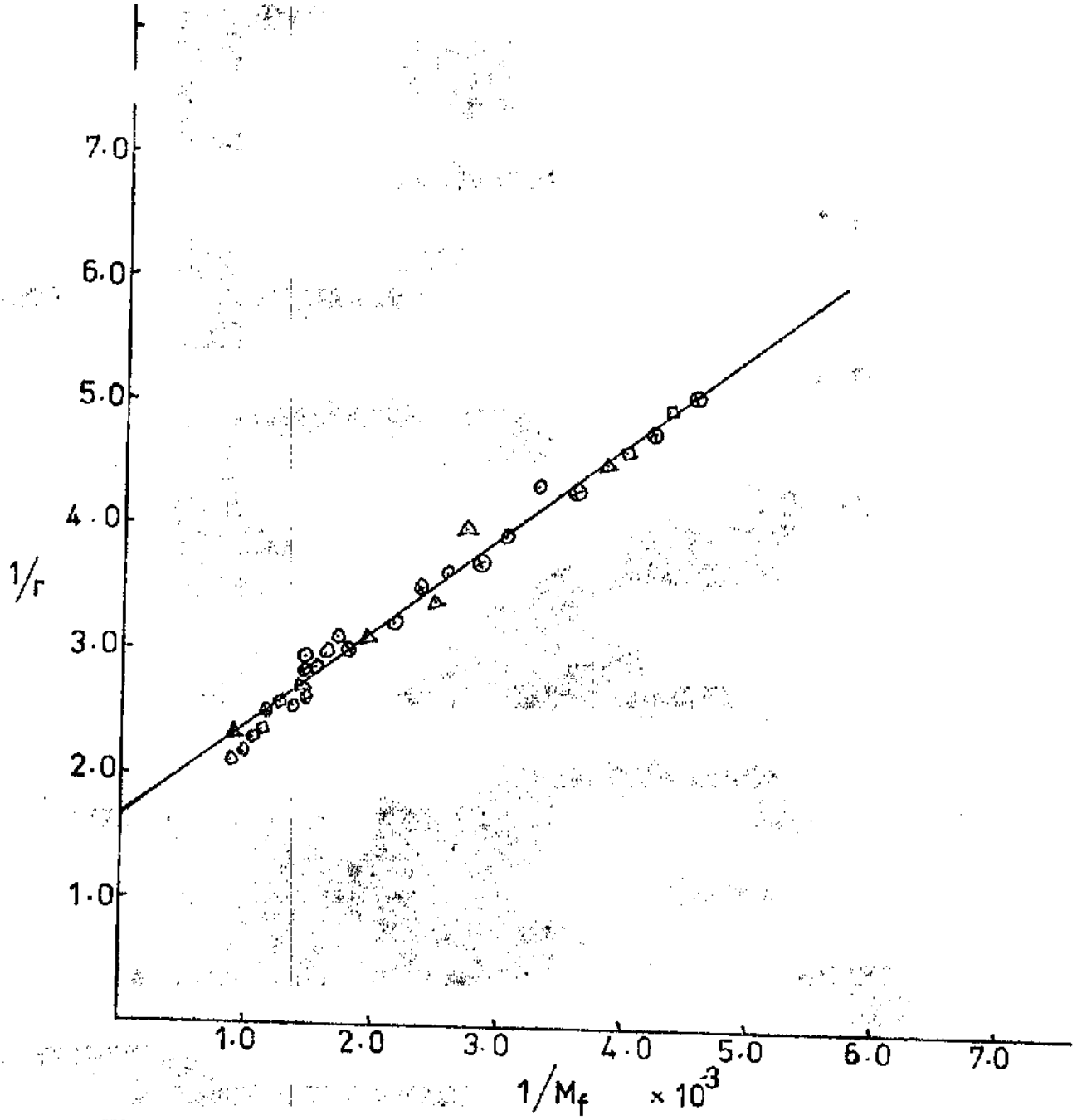
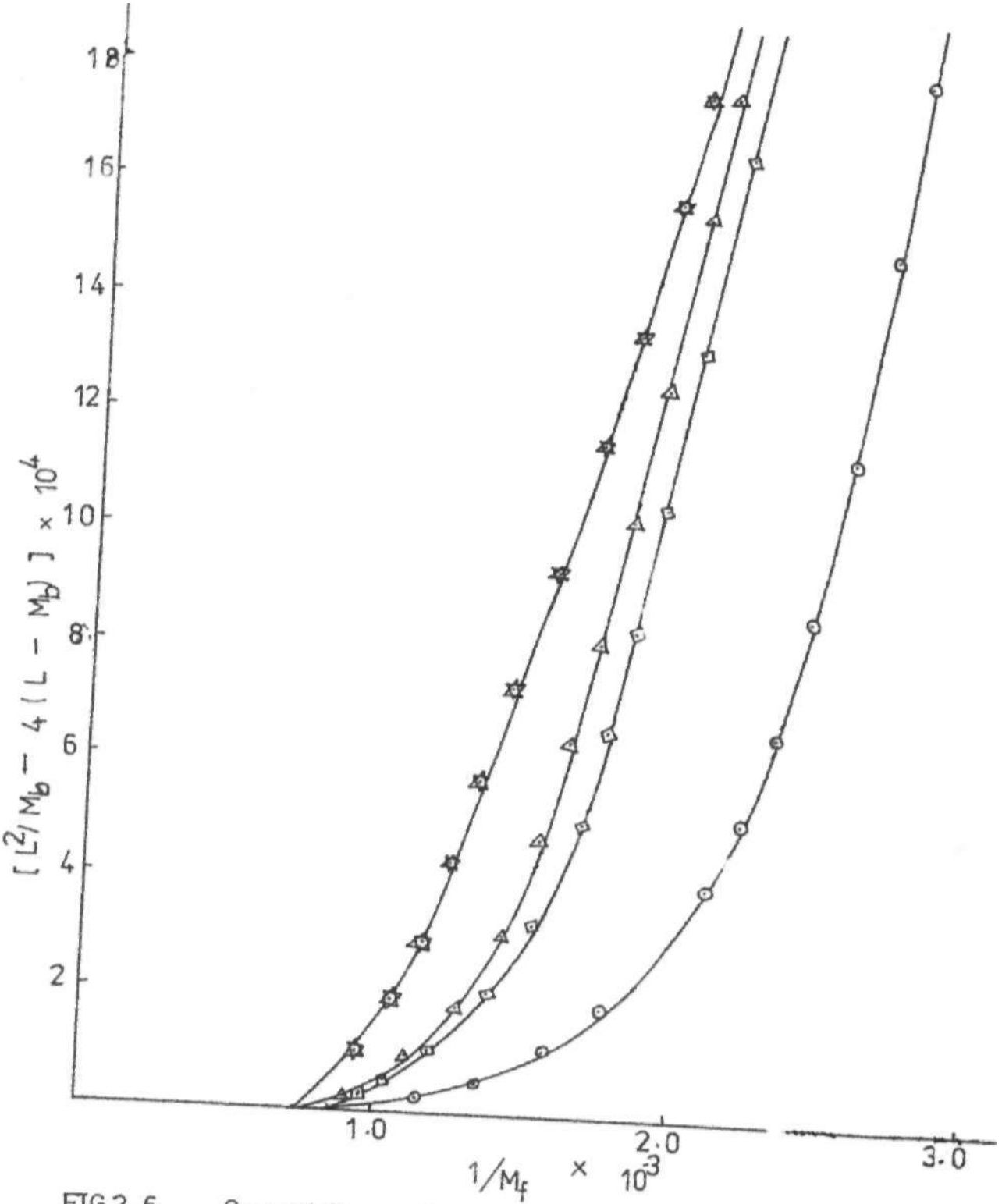


FIG 2.5 Computation of stability constants and co ordination number of Cu-PMA complexes. [i-PMA] = 2.5 10^{3} I 0.10 (△) 0.30; (⊡) 0.40; (⊙) 0.50; (⊛) 0.60.



FIG·2·6 Computation of stability constants for Zn-PMA complexes. [i-PMA] = 2.5×10^{-3} M ; I = 0·10 .
α : (✲) 0·30 ; (△) 0·40 ; (□) 0·50 ; (○) 0·60 .

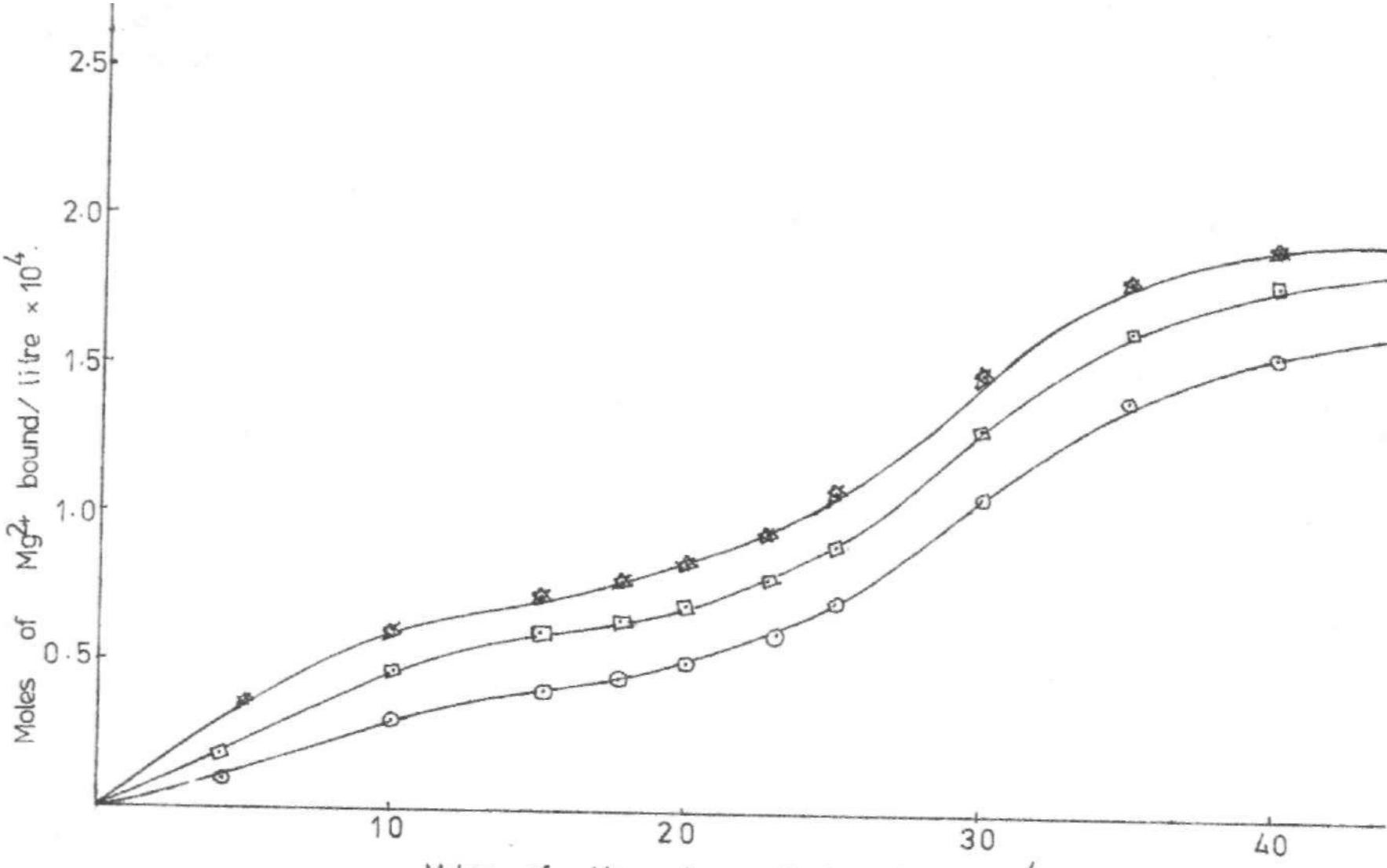


FIG 2·7 Dialysis of i-PMA with magnesium at three degrees of ionisation [i-PMA] $= 2.5 \times 10^{-3}$ M ; I = 0.10. α : (⊙) 0.70 ; (⊡) 0.80 ; (⊠) 0.90.

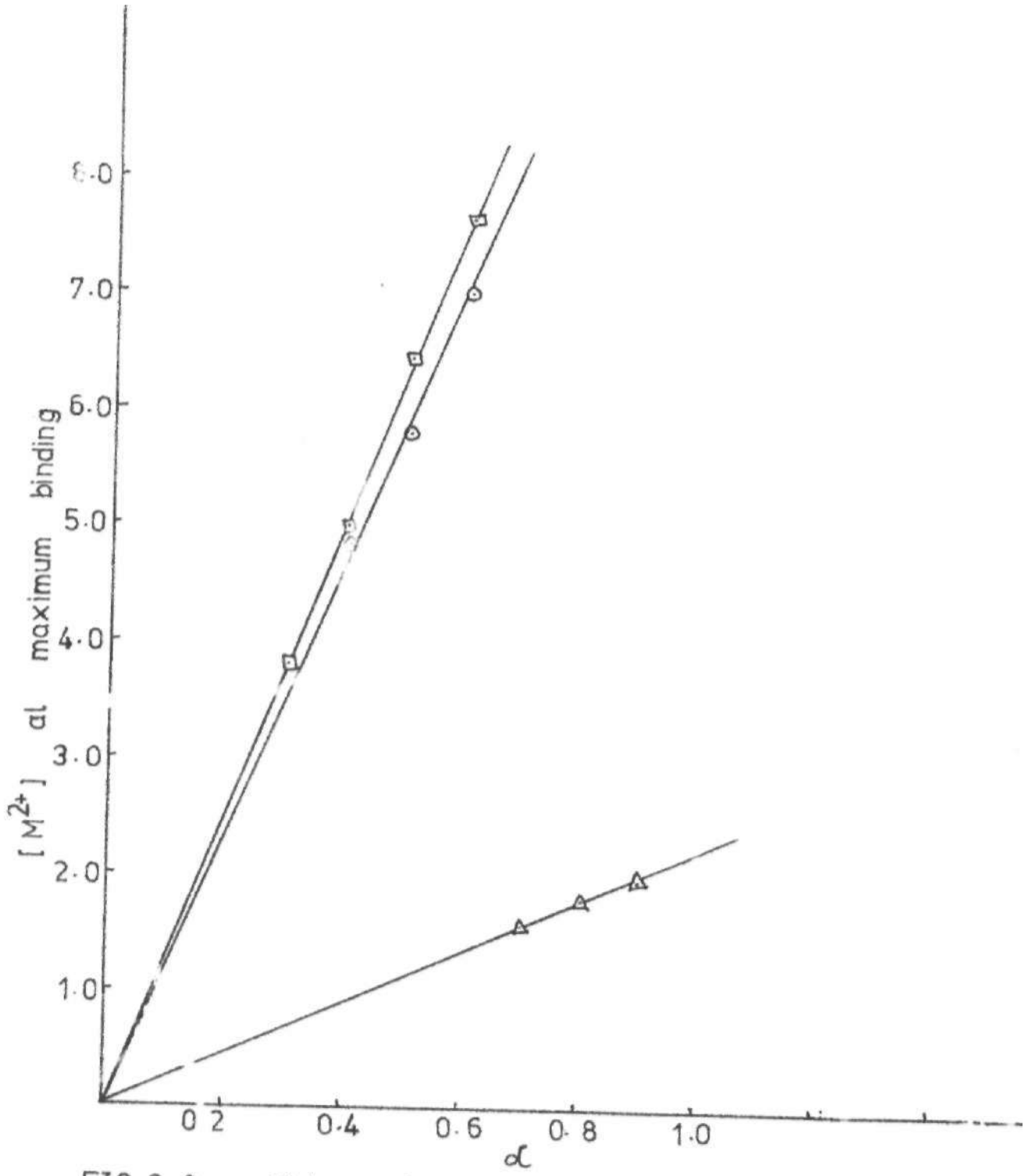


FIG.2.8 Plots for three metal ions at maximum binding.
(□) Cu^{2+} ; (⊙) Zn^{2+} , (△) Mg^{2+}.

2.5 REFERENCES

1. Donnan, G. F.; Chemical Reviews 1, 73, (1924)

2. Ostwalt, W.; Address to Sterling Chemistry Laboratory (189).

3. Donnan, G. F. and Guggenheim, E. A.; Z. Physik, Chem. (Leipzig) 162, 346, (1932).

4. Beckman Instrument Inc. Technical Bulletin No. 6071 C, (1960).

5. Bolewski, K., and Lublina M., Roczniki Chem. Ann. Soc. Chim. 44, 647, (1970).

6. Morawetz, H., J., Polymer Sci., 17, 442, (1955).

7. Kotlair, A. M., and Morawetz H., J. Am. Chem. Soc. 77, 3692, (1955).

8. Kolawole, E. G., Ph.D. thesis (1974).

9. Morawetz, H., and Kandanian, A. Y., J. Phys. Chem. 70, 2995, (1966).

10. Kolawole, E. G., Unpublished Results.

11. Constantino, L., Crescenzi, V., Quadrifoglio, F., and Vitalgliano, V. J. Polymer Sci. A-2(5), 771, (1967).

12. O'neill J. J., Loebl, E. M., Kandanian, A. Y., and Morawetz, H., J. Polymer Sci. A3(9-12), 4201, (1965).

Chapter 3

POTENTIOMETRIC TITRATION

Contents

		Page
3.1	Theory	59
3.2	Experimental Details	64
3.3.	Results and Discussion	66
3.3.1	Results	67
3.3.2	Discussion	67
3.3.2.1	Potentiometric behaviour of aqueous Solutions of i-PMA	67
3.3.2.2	Potentiometric behaviour of aqueous Solutions of i-PMA in the presence of Copper, Zinc and Magnesium nitrate Solutions	69
3.3.2.3	Transformation of Titration Curves to Complex formation Curves	76
3.3.2.4	Effect of Ionic Strength	80
3.4	R e f e r e n c e s	82

Chapter 3

POTENTIOMETRIC TITRATION

3.1 Theory:

The potentiometric titration technique can be most useful for obtaining information about the chemical nature of bound ionic groups, and the sites and the shapes of macromolecules. It can also provide an insight into the mechanism of conformational changes which occur as a consequence of ionizations and yield information about the forces which play a part in the stabilization of macromolecule-metal complex structures.

A carboxylic acid in aqueous solution dissociates as follows

$$-COOH \rightleftharpoons -COO^- + H^+ \quad \text{.....(3-1)}$$

The conventional dissociation constant k_o is defined by

$$K_o = \frac{[-COO^-][H^+]}{[-COOH]} \quad \text{.....(3-2)}$$

Equation (3-2) can be rewritten to give

$$pH = pK_o - \log\left[\frac{(1-\alpha)}{\alpha}\right] \quad \text{.....(3-3)}$$

Where the degree of ionization α is defined as:

$$\alpha = \frac{[-COO^-]}{[COO^-] + [COOH]} \quad \text{.....(3-4)}$$

The ionization equilibria in a dibasic acid may be represented by:

$$\begin{array}{l} \text{COOH} \quad \text{COOH} \rightleftharpoons \text{COOH} \quad \text{COO}^- \\ H_2A \rightleftharpoons HA^- + H^+ \end{array} \qquad \text{.....(3-5)}$$

$$\begin{array}{l} \text{COOH} \quad \text{COO}^- \rightleftharpoons \text{COO}^- \quad \text{COO}^- \\ HA^- \rightleftharpoons A^{-2} + H^+ \end{array} \qquad \text{.....(3-6)}$$

The ionization constants k_1 and k_2 are defined as

$$k_1 = \frac{[HA^-]}{[H_2A]} a_{H^+} \qquad \text{.....(3-7)}$$

$$k_2 = \frac{[H^{-2}]}{[HA^-]} a_{H^+} \qquad \text{.....(3-8)}$$

and the degree of ionization is given by

$$\alpha = \frac{[HA^-] + 2[A^-]}{Cn} = \left[\frac{\frac{k_1}{a_H} + \frac{k_1 k_2}{(a_{H^+})^2}}{1 + \frac{k_1}{a_{H^+}} + \frac{k_1 k_2}{(a_{H^+})^2}} \right] \qquad \text{.....(3-9)}$$

where a_{H^+} is the activity of the hydrogen ion and Cn is the concentration of the dicarboxylic acid. If the ionizable groups are far from each other, the ease of ionization of each of the carboxyl groups will be independent of the state of ionization of the other. The titration curve will then be the same as that for monocarboxylic acid treated above.

If the carboxyls are sufficiently close to one another, the removal of the proton will be impeded by the electrostatic attraction of the neighbouring carboxylate group. In order to overcome this, an additional amount of work is required. Thus the molar free energy for the second ionization step will have to be increased by "electrostatic free energy of ionization" ΔG^i_{el} given by

$$\Delta G^i_{el} = N\int_{r=r_e}^{r=\infty} -\frac{e^2}{Dr^2}\,dr = \frac{Ne^2}{Dr_e} \qquad \text{.....(3-10)}$$

where r_e is the distance between the two ionizable groups, and the ratio of the first and second ionization constants becomes then

$$\frac{k_2}{k_1} = \frac{1}{4}\exp\left(\frac{-\Delta G^i_{el}}{RT}\right) \qquad \text{.....(3-11)}$$

For a polymeric acid having p monomer units per polymer molecule, the apparent stepwise dissociation constant is defined by

$$k_1 = \frac{\left[H_{p-1}\,A\right]a_{H^+}}{\left[H_pA\right]} \qquad \text{.....(3-12)}$$

$$k_n = \frac{\left[H_{p-n+1}\,A\right]a_{H^+}}{\left[H_{p-n+1}\,A\right]} \qquad \text{.....(3-13)}$$

Hence the degree of ionization is given by α

$$\alpha = \sum n \frac{[H_{p-n+1} A]}{Cn} \qquad \text{.....(3-14)}$$

$$\text{i.e. } \alpha = \frac{\sum_{n=o}^{n=p} \frac{n}{(a_{H^+})^n} \pi_i k_i}{\sum_{n=o}^{n=p} \frac{1}{a_{H^+}} \pi_i k_i} \qquad \text{.....(3-15)}$$

where C_n is the concentration of the acid in moles per litre. In the above expressions the hydrogen ion activity has been used rather than hydrogen ion concentration. The hydrogen ion activity is considered to be pH = -log a_{H^+} in all the work done.

The constants k_i which appear in equation (3 - 15) above are stepwise apparent dissociation constant for a reaction such as

$-COOH \rightarrow -COO^- + H^+$ at single sites.

The apparent dissociation k_i is a function of the pH or degree of ionization. The values of the k_i for each dissociation is practically impossible to determine, and so many authors (1-4) have developed empirical formulae which relate the potentiometric behaviour of polymeric acids to a single dissociation constant. Kern (4) and Katchalsky and Spitnik (5) found that a single titration curve of polymeric acid may be described emperically by constants pK and n according to the following

equations:

$$pH = pK^* + BpH \quad \text{.....(3-16)}$$

and

$$pH = pK_a - n \log \frac{1-\alpha}{\alpha} \quad \text{.....(3-17)}$$

Equation (3 - 16) was that obtained by Kern and equation (3 - 17) by Katchalsky and Spitnik. This is a modified form of the Henderson-Hasselbach's equation (3 - 2) above, where pK^*, B, pK_a and n are constants for a given titration.

Attempts by many other workers to analyse the potentiometric behaviour of polyelectrolytes (6, 7) can be summarised by the following equation:

$$pH = pK_o - \log \frac{1-\alpha}{\alpha} + \frac{0.4343}{KT}\left(\frac{\delta Fe}{\delta V}\right)k \quad \text{.....(3-18)}$$

where pK_o is an intrinsic dissociation constant charadteristic of the ionizable group of the polymer and independent of ionic strength, Fe is the electrostatic free energy of the ionized polyelectrolyte molecule carrying V negatively charged groups and k is the inverse Debye radius determined by the concentration of the small ions in the solution.

Katchalsky and Lifson (8) proposed the following expression for randomly linked polycarboxylic acid

$$\left(\frac{\delta Fe}{\delta V}\right)k = \frac{2V\epsilon^2}{Dh}\left[\lambda n\left(1 + \frac{6h}{kh_o^2}\right) - \alpha\frac{(Si - So)}{2S}\,\frac{6h/kh_o^2}{1 + 6h/kh_o^2}\right] \quad \text{..(3-19)}$$

Here h is the end to end distance of the ionized polymolecule, stretched

by the electrostatic repulsion of the V charges spread over the molecule. If this equation is now introduced into equation (3-18) for potentiometric titration of polymeric acid one gets

$$pH = pK_o - \log \frac{1-\alpha}{\alpha} + \frac{2V\epsilon^2}{KhKT}\left[\log \frac{(Kh_o 2 + 6h)}{Kh_o{}^2} - \frac{0.4343\alpha(S_i - S_o)}{2S} \cdot \frac{6h}{Kh_o{}^2 + 6h}\right] \quad \ldots\ldots\ldots(3-20)$$

where $h = Zb$ and b = hydro dynamic length of the monomer and Z the degree of polymerization. According to Kuhn (9)

$$h_o{}^2 = 2Sb^2$$

where S is the number of monomers per statistical element. The value of S depends on steric factors and on solute-solvent interaction. When the polyacid is highly soluble, S is independent of α. When the polyacid is only slightly soluble at low degrees of ionization and becoming highly solvated with increasing α, then S becomes markedly dependent on the degree of ionization.

3.2 Experimental Details:

A Pye-Unicam pH meter model 290 was used for these titrations at $25 \pm 0.1^{\circ}C$. The model 290 pH meter has a combined glass and reference electrode for the pH determination.

Solutions at 5×10^{-3} base molar PMA at various degrees of neutralisation were made. 2.5×10^{-3} base molar solution was used throughout for the potentiometric titrations. The general procedure for the titration was as follows:

Since the unionised form of the isotactic PMA was insoluble in water, solution of PMA at various degrees of neutralisation were always made, that is, the polymer was pretitrated to varying degrees of neutralisation α. (0.3 - 1.0). This was done by dissolving a known weight of the PMA in a calculated quantity of 0.05M KOH to give the desired value of α, and a final concentration of 5.0×10^{-3} base molar PMA when diluted to 250 cm^3. Such solutions were prepared fresh each time they were required. 10 cm^3 of the 5.0×10^{-3} base molar PMA was pipetted into the titrating vessel and enough KNO_3 was added to give the desired ionic strength when the solution was diluted to 20 mls. The solution was then titrated against 0.01M $Zn(NO_3)_2$ solution and the pH of the solution read from the pH meter after the addition and after stirring for about two minutes. The volume added each time was noted. Two concentrations of added salt were used (0.1, 0.05)M KNO_3. A blank titration was carried out for each titration, in order to find out the effect of dilution on metal-polymer interaction. The titration procedure was repeated using two other metal ions viz; Cu^{+2} and Mg^{+2}.

3.3 RESULTS AND DISCUSSIONS

The potentiometric titration of isotactic polymethacrylic acid (i-PMA) has been studied by some workers (1-3). The experimental results for a single titration have been expressed by the modified form of Handerson-Hasselbach's equation.

$$pH = pK_a + n \log \frac{\alpha}{1-\alpha} \quad \text{.....(3-21)}$$

Differences in behaviour between isotactic, syndiotactic and conventional PMA have been reported (10, 11, 13, 15). It has been proposed by Nagasawa and co-workers (2) on the basis of their potentiometric titration data that isotactic PMA has a locally helical conformation which has a higher charge density than the presumed planar zig-zag structure of the syndiotactic PMA. Various investigators (15, 16) have also shown that i-PMA forms more stable complexes with Cu^{+2} ions than it does with Mg^{+2} ions. However none seem to have determined the co-ordination number of the metal-polymer complexes for i-PMA, nor have they studied the effect of binding of metal ion, on the electrochemistry of the system.

The potentiometric behaviour of isotactic polymethacrylic acid (i-PMA) has been studied in the present work. The pH behaviour of the i-PMA pretitrated to various degrees of neutralisation followed by titration with divalent metals at various constant ionic strengths has been reported here.

3.3.1 Results:

The results reported in this section were obtained by the method of potentiometric titration at constant ionic strengths and constant polymer concentration. Figures 3.1-18 are the various plots obtained from potentiometric titrations of isotactic PMA with and without divalent metal ions and in the presence of varying ionic strengths. Figures 3.1 and 3.2 are obtained from potentiometric titrations of i-PMA with KOH at constant PMA concentration (2.5×10^{-3}M) and two different ionic strengths (I = 0.05, 0.10) at 25°C. The plots are designed to show the solution properties of isotactic PMA and were obtained from the results of the above titration using equation (3-21). Figure 3.1 is a plot of pH against $\log \frac{\alpha}{1-\alpha}$ while figure 3.2 is a plot of $pK_a = (pH - \log \frac{\alpha}{1-\alpha})$ against α. Figures 3.3 and 3.4, figures 3.7 and 3.8 and figures 3.11 and 3.12 are the various plots of pH + log COOH against Cu^{+2}, Zn^{+2} and Mg^{+2} ion concentrations respectively. Figures 3.15-18 are comparison plots. Figure 3.1 is a comparison plot of i-PMA and c-PMA.

3.3.2 Discussion

3.3.2.1 Potentiometric behaviour of aqueous solution of i-PMA:

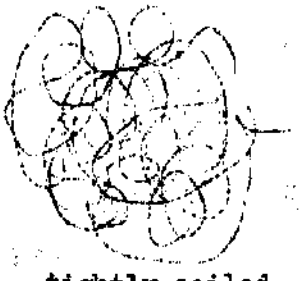
According to some previous workers (19), the plot of pH against $\log \frac{\alpha}{1-\alpha}$ for a polyacid should give a straight line corresponding to equation (3-21). Kolawole (17) in his studies with conventional PMA (c-PMA) obtained some curves. Fig. 3.1 is a plot of pH against $\log \frac{\alpha}{1-\alpha}$,

for i-PMA, which is not a straight line and is strikingly different from the curve obtained for c-PMA as is seen from the plot in figure 3.1. There is an inflection point which occurs at the same value of α for the two ionic strengths in the case of isotactic PMA. Figure 3.2 shows the plot of pK_a against α at the two ionic strengths studied. The figure reveals that the dissociation constant defined as

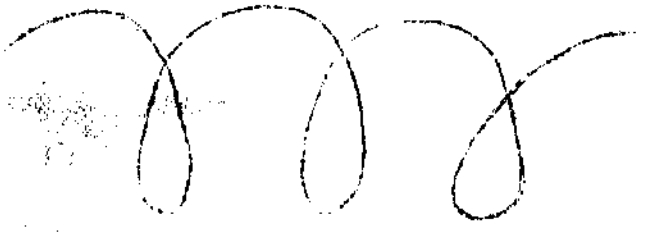
$$K_a = \frac{[H^+][COO^-]}{[COOH]} \quad \text{.....(3-22)}$$

is infact not a constant but varies with the degree of ionization. Some of the previous workers (11, 12) reported that i-PMA was insoluble at α below 0.3, while some said (4) that i-PMA was soluble at all α values (0 - 1.0). The findings in the present work are contrary to these views. Here it is found that i-PMA was insoluble below α = 0.25 and from α = 0.25 it became soluble. At low α values the molecules are presumably largely impenetrable to solvent and unless the hydroxyl groups (OH^-) are present up to a certain minimum concentration there will be no effect on the solubility. The shape of the curve in figure 3.2 shows a gradual increase in pK_a from 0.3 to 0.5 which marks the onset of the i-PMA conformational transition, and then the tight coil rapidly unwinds into a stretched helical structure between α = 0.5 and 0.7. The situation at α = 0.3 to 0.5 can be visualized as an intermediate state

between the tightly coiled structure, which does not allow solvent penetration and the open helical structure where the COOH groups are exposed for easy access. The process of unwinding of the polymer molecule can be represented thus:



tightly coiled structure



helical structure

At low α values the amount of available charged sites is small, so electrostatic repulsion by the neighbouring COO^- will be small, and therefore the expansion will be small. As the degree of neutralisation increases, the electrostatic repulsion increases. Between $\alpha = 0.5$ and 0.8 the number of carboxylate groups available for effective near neighbour interaction increases and therefore electrostatic repulsion between the charged groups becomes much greater.

3.3.2.2 Potentiometric behaviour of aqueous solutions of i-PMA in the presence of Copper, Zinc and Magnesium nitrate Solutions:

For this study the hydrogen ion concentration $[H^+]$, was measured against the concentration of metal ion. It was observed that as the

M^{+2} ion was added to the pretitrated PMA solution at constant ionic strength, the pH of the solution decreased. The pH changes can thus be used as a measure of the amount of M^{+2} (M^{+2} = Cu^{+2}, Zn^{+2}, Mg^{+2}) which has been bound to the polyion. The reaction may be represented as:

$$COO^-H^+ + M^{+2} \rightleftharpoons \underbrace{COO^- + M^{+2}}_{\text{associated}} + \underbrace{H^+}_{\text{measured in solution}}$$

The magnitude in the fall of pH of the solution can be used to estimate quantitatively the affinity of M^{+2} for polyion. Figures 3.3 and 3.4, figures 3.7 and 3.8 and figures 3.11 and 3.12 are plots of pH + log[COOH] for the Cu^{+2}-PMA, Zn^{+2}-PMA and Mg^{+2}-PMA complexes respectively. The plots were obtained from plots of pH against metal ion concentrations. The curves can be divided into two sections, first a region of sharp decrease in pH + log [COOH] followed by a moderate fall which then levels off at high concentration of metal ion. The two sections are more prominent in the case of Cu^{+2} and at higher ϕ values for both Cu^{+2} and Zn^{+2}. This observation is true at the two ionic strengths studied.

The amount of hydrogen ions produced in solution $[H^+]_p$ is due to the binding by counterion M^{+2}. If the amount of $[H^+]_p$ is known then the amount of free carboxylate groups available for binding can be determined. The pH behaviour and therefore $[H^+]_p$ is dependent on the

degree of netralisation (α), which is related to the number of COO^- groups in solution as follows:

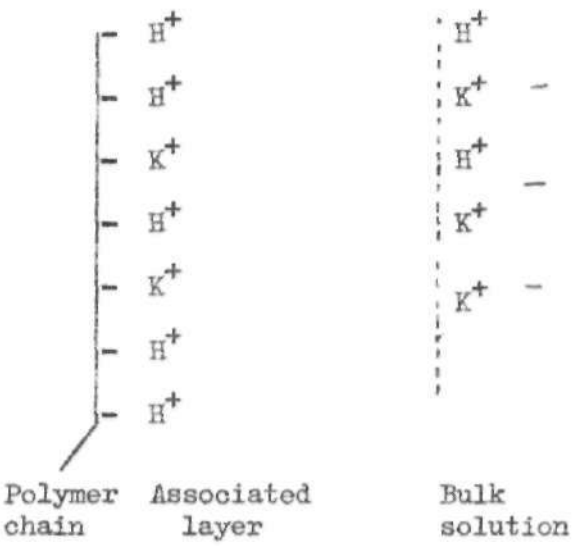
$$[COO^-] = \alpha C$$

where C is the concentration of COOH in moles/l initially present. Similarly the pH of the solution is related to C by the relation.

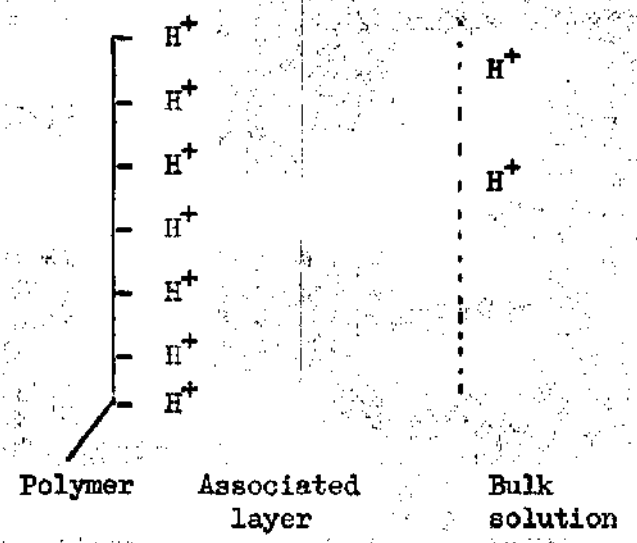
$$pH = pK_a' + \log \frac{\alpha C}{1-\alpha C} \qquad \ldots\ldots\ldots(3\text{-}23)$$

This equation is a modification of Handerson-Hasselbach's equation. The observed changes in pH in figures 3.3 and 3.4, figures 3.7 and 3.8 and figures 3.11 and 3.12 may be attributed to changes in concentration of COO^- as cations are bound which cause the release of H^+ ions into the solution. With the above relationship one can calculate the amount of COO^- bound as M^{+2} ions are added.

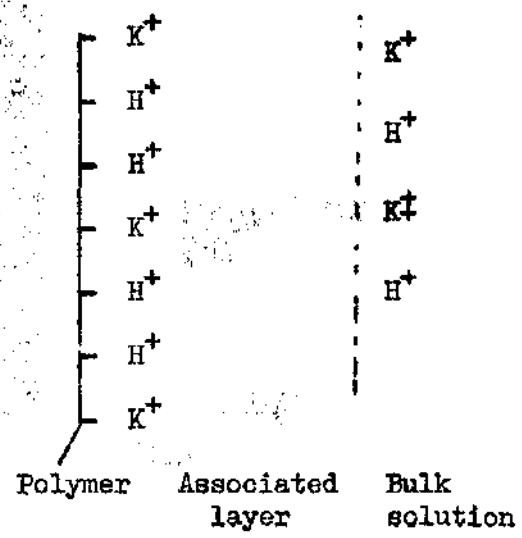
The experimental data might be understood better if a sort of double layer effect is considred, to see the effect of polymer environment on measured pH.



The picture presented above shows a polymer chain carrying negative charges. These fixed charges are surrounded by H^+, K^+ with some negatively charged byions, so that a sort of double layer is obtained. Now assuming that a hypothetical situation exists where the double layer (associated layer) is separated by a membrane from the bulk solution. When electrodes are dipped into the solution the $[H^+]$ in the bulk of the solution is being measured. If there are in addition to H^+ and K^+ ions in the associated layer, the cations M^{+2}, then three situations can now be considered.

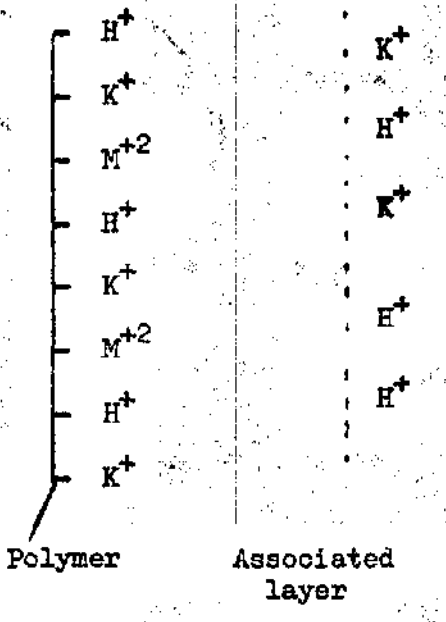


(i) $I = 0$ $M^{+2} = 0$



(ii) $I = X$ $M^{+2} = 0$

same α as in (i)



(iii) $I = X$ $M^{+2} = Y$

same α as in (i) and (ii)

The binding mechanism has been postulated to be a sort of competition between the H^+, K^+ and M^{+2} ions for the charged sites. Diagram (i) represents the charged polymer surrounded by H^+ ions which are in close proximity to it. This situation is observed in the absence of supporting electrolyte and divalent metal ions ($I = 0$, $M^{+2} = 0$). Due to the strong electrostatic attraction of COO^- for H^+, very little of H^+ ions is released into the bulk solution. However with addition of supporting electrolyte in (ii) the K^+ ions, which bind stronger than H^+ ions, now displace H^+ ions into the solution, which results in observed fall in pH. In (iii) addition of M^{+2} will displace K^+ and H^+ ions into the bulk solution. Since M^{+2} binds stronger than either K^+ or H^+ ions to i-PMA, a further lowering in pH of solution occurs. It has also been observed that K^+ binds more strongly to i-PMA than to c-PMA (18). The binding equilibrium which exists between the polymer and the ions in the associated layer will depend on a number of factors. The amount of M^{+2} in the double layer will be affected by the amount of K^+ ions. At higher ionic strength (i.e. more K^+) more shielding of the charged sites by K^+ will take place, and this will decrease the amount of H^+ and M^{+2} in the double layer. That means that at higher ionic strength and low $[M^{+2}]$ there will be decrease in binding of M^{+2} to the polymer. However in the presence of excess $[M^{+2}]$, since M^{+2} ion is a stronger binder, it will be able to penetrate the double layer to bind unto the charged sites.

This means that no decreased binding will be observed at higher ionic strength and higher metal ion concentration, in other words binding will be independent of ionic strength at high metal ion concentration.

The movement of ions across the hypothetical membrane leads to two types of equilibria,(a) an equilibrium exists between the double layer and the polymer and this equilibrium depends on the concentration of the ions in the double layer, (b) an equilibrium exists between the double layer and the bulk solution.

From point of view of Donnan's equilibrium treated in chapter 1, the concentration of ions in the double layer will be affected by the concentration of ions in the bulk solution. One would expect then that if the concentration of H^+ in the double layer is decreased, more will be produced by further ionization of the polymer molecule to maintain the equilibrium

$$COOH \rightleftharpoons COO^- + H^+$$

Such a decrease in H^+ will result from binding of M^{+2} to COO^-. This binding of M^{+2} to some COO^- will facilitate near neighbour interaction, and make adjacent COOH groups to ionize more and so release more H^+ into the solution.

3.3.2.3 Transformation of Titration Curves to Complex Formation Curves:

The approach used by Kolawole (17) in the calculation of formation curves has been employed here by the author. It has been stated earlier that COO^- groups will give a better measure of amount of M^{+2} bound. It is therefore necessary to calculate the amount of bound COO^- groups. In order to do this a reference plot of pH + $\log[COOH]$ against $\log[COO^-]$ is made for PMA = 2.5×10^{-3} base molar at two ionic strengths (I = 0.05, 0.10). The relationship between pH and α-C has also been stated in equation (3-3). After correcting for dilution, then pH + $\log[COOH]$ will correspond to a certain value of $\log[COO^-]$. It follows that the amount of COO^-_{free} and therefore the amount of COO^-_{bound} can be obtained using this plot.

When the above procedure is followed figures 3.5 and 3.6, figures 3.9 and 3.10 and figures 3.13 and 3.14 are obtained for Cu^{+2} - i-PMA, Zn^{+2} - i-PMA and Mg^{+2} - i-PMA complexes respectively. All the curves show a gradual build up of the complex with increase in metal ion concentration, and these finally level off at high metal ion concentration. The levelling can be interpreted as a saturation of available charged sites with metal ions, and this would depict formation of a stable complex. For Cu^{+2} and Zn^{+2} at low α values the maximum number of

carboxylate bound increases gradually with α up to $\alpha = 0.5$, but beyond $\alpha = 0.5$ a sudden increase in maximum amount of carboxylate bound is observed. This might be connected with a change in mode of binding. This is expected since it is in this region of α that the unwinding of the coiled polymer to the open helical structure was earlier observed. Between $\alpha = 0.3$ and 0.5 (the intermediate state), most of the binding of M^{+2} will involve only the COO^- on the periphery of the structure, while some buried COO^- might be inaccessible. However at higher α value (beyond $\alpha = 0.5$) the open helical structure allows for easy access by M^{+2} into the COO^- groups. For this reason the amount of COO^-_b at low α values ($\alpha = 0.3, - 0.5$) where little uncoiling has taken place, will be less than that at higher α values. The unusual increase in COO^-_b can also be attributed to chelation by neighbouring COOH groups. The binding of M^{+2} to COO^- groups will make ionization of neighbouring COOH group easier as predicted earlier. These near neighbour COOH groups can also enter into chelation with more M^{+2} ions. At low degrees of neutralisation, the coiled structure will not allow such near neighbour interaction to take place. However with the open helical structure more COOH groups are able to interact.

Figures 3.13 and 3.14 show the complex formation curves for Mg^{+2} - i-PMA system at two different ionic strengths. As observed for

Cu^{+2} - i-PMA and Zn^{+2} - i-PMA curves there is a gradual rise in the amount of COO^-_b but the maximum COO^-_b, is quite small. If the amount of COO^-_b is a measure of complex formation, then the amount of complex formed with Mg^{+2} is very small. At low α values (0.3 - 0.5) the amounts of COO^-_b obtained with Mg^{+2} were not measurable i.e. the amounts of COO^-_b were very small, and this could mean that little binding is taking place at low α values. The binding strength of Cu^{+2}, Zn^{+2} and Mg^{+2} are proportional to their various effective free energy changes. There are two types of free energy changes to reckon with in complex formation.

(a) $\Delta G_{chem} = \Delta G$ for M^{+2} + $\begin{matrix} COO^- \\ \vert \\ COO^- \end{matrix}$ or M^{+2} + COO^- i.e. the free energy change due to chelation or free energy change due to binding of M^{+2} to monomer respectively.

(b) $\Delta G_{elec.}$ is the electrostatic free energy change which can be favourable or unfavourable for metal ion binding.

When α increases there will be more COO^- groups and this would mean increased attraction of metal ion to the vicinity of the charged molecules which would enhance binding i.e. $\Delta G_{elec.}$ is favourable. $\Delta G_{elec.}$ can be unfavourable when α is high enough for electrostatic repulsive forces between the charged groups to stop either (i) chelation, which will require bringing together of many COO^- groups or (ii) alignment of two highly charged molecules. The two conditions under which $\Delta G_{elec.}$ operate act

opposite each other. It is the effective ΔG_{elec} together with ΔG_{chem}, which determines the free energy change of complexation. The smaller this quantity the more stable the complex obtained. In the helical structure of i-PMA, where there is high charge density, electrostatic free energy of repulsion will be quite prominent. Where the tendency of M^{+2} to be attracted to the charged sites is quite small, then this second effect will be more dominant and hence the free energy of complexation will be quite high i.e. the complex is unstable. The free energy due to attraction of metal ion to the vicinity of the charged molecule, and also the free energy due to bringing together of COO^- caused by metal binding PMA is less favourable in the case of Mg^{+2} than in the cases of Zn^{+2} and Cu^{+2}.

Figures 3.5 and 3.6 and figures 3.9 and 3.10 show some inflections at low metal ion concentration and higher α values. This suggests two types of equilibria which indicates two types of complexes or a change in stereochemistry of the complex. The amount of $[COO^-]$ at inflection can be seen to be about half of the total COO^-_b. The inflection point can also be interpreted as an indication of breakdown of the complex to a new form of association. The inflection is seen to be more pronounced for Cu^{+2} and is observed for both ionic strengths.

In figures 3.15 and 3.16 the amount of carboxylates bound for the same metal ion concentration are compared for the three metal ions

Cu^{+2}, Zn^{+2} and Mg^{+2} at α = 0.6. The figures show that in all, more COO^- groups are bound for Cu^{+2} and least bound to Mg^{+2} ion. This shows that copper binds strongest to i-PMA, followed by zinc while magnesium binds the least.

3.3.2.4 Effect of Ionic Strength:

Figure 3.17 is a plot of COO^-_b against $[Cu^{+2}]$ added at α = 0.6 and α = 0.4 and at two different ionic strengths (0.05, 0.10). Figure 3.18 is a similar plot for Zn^{+2} at α = 0.6, and α = 0.3 and at ionic strengths (0.05, 0.10). In the case of figure 3.17 for copper, it can be seen that the amount of complex formed is dependent on the ionic strength almost throughout the whole range of metal concentration. However at very high $[Cu^{+2}]$ the curves seem to converge. This will give an indication that at high metal ion concentration the amount of complex formed is independent of ionic strength which is in agreement with the earlier prediction that in presence of excess $[Cu^{+2}]$ the copper ions will be able to penetrate the double layer to bind the charged sites. The converging of the curves is observed at both values of α. At low α value and low $[Cu^{+2}]$ the effect of ionic strength is greater than at high α value. As can be seen from the graph, the amount of COO^-_b at I = 0.05 ionic strength is greater than the amount of COO^-_b at I = 0.10, at low metal ion concentration up to the middle portion. In high ionic

strength medium there appears to be a decrease in the binding efficiency of copper in this region. This is due to the screening effect of K^+ ions, which is greater at low values of α.

In figure 3.18 for zinc, it is seen that the amount of complex formed depends on the ionic strength both at low and high metal ion concentration, for $\alpha = 0.6$. However for low value of α, the amount of complex formed depends only on the $[COO^-]$ at low zinc concentration i.e. curves of the same α and different ionic strength converge to the same point in this region. In Zn^{+2} - i-PMA complex the effect of ionic strength is more pronounced at high α values than in Cu^{+2} - i-PMA complex. Also the ionic strength effect in the middle portion of the curve is more pronounced for Zn^{+2} - PMA system than for Cu^{+2} - PMA complex at both α values. These observations can be associated with the fact that copper has a greater penetrating power than zinc. So that copper can penetrate the double layer to bind the charged sites than zinc in presence of excess metal ion concentration, and therefore the binding will be independent of ionic strength for copper and still be dependent on ionic strength for zinc even at high metal ion concentration. The figures show that the complex formation with divalent metal ions is more favoured in low ionic strength medium than in high ionic strength medium.

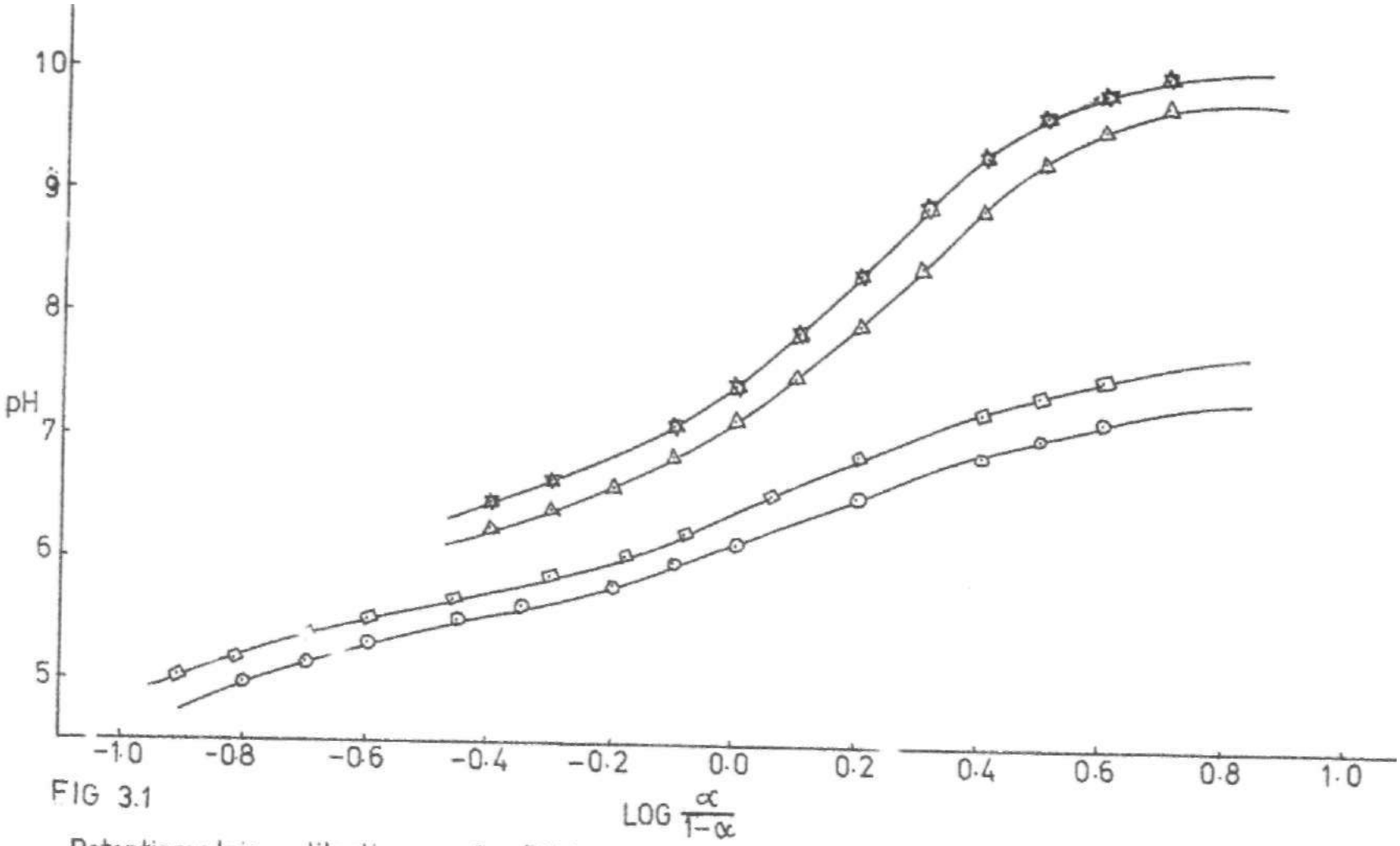


FIG 3.1

Potentiometric titration of PMA solutions with KOH at various constant ionic strengths and constant polymer concentrations

Isotactic PMA (✡), I = 0·05, (△), I = 0·10

Conventional PMA (⊡), I = 0·05; (⊙), I = 0·10

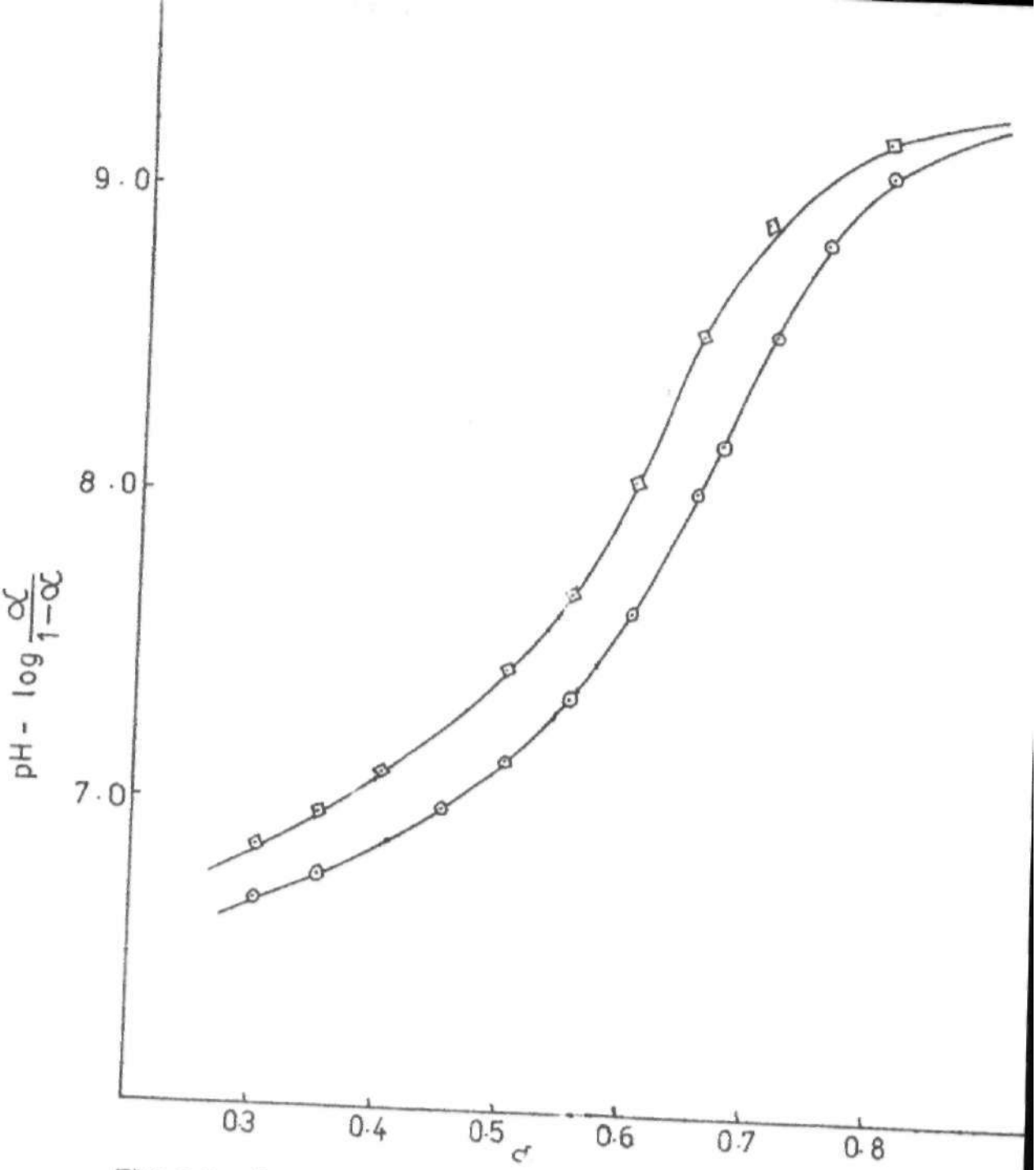
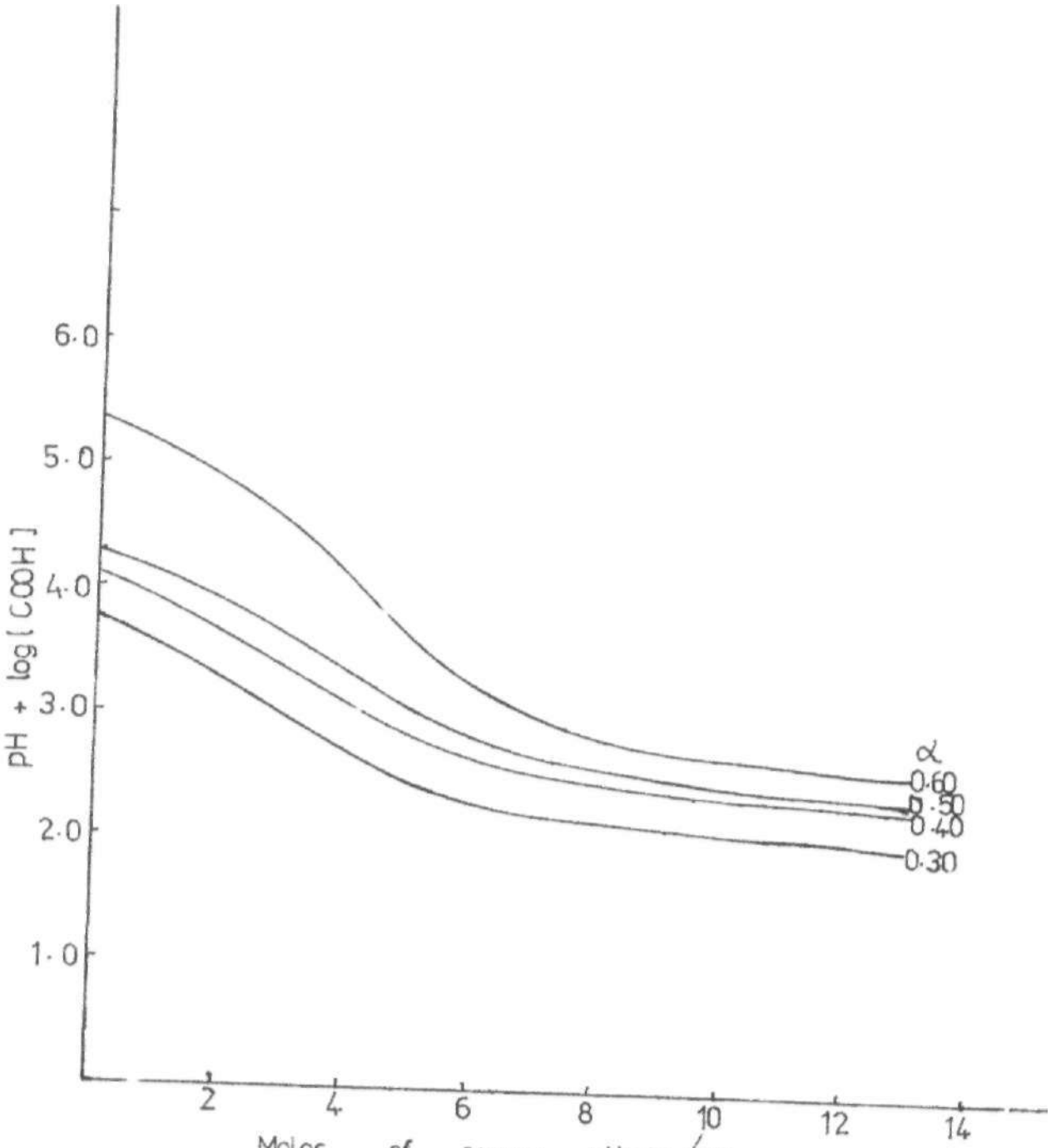


FIG. 3.2 Potentiometric titration of i - PMA with KOH at constant ionic strength and polymer concentration
[PMA] = 2.5×10^{-3}; (□) I = 0.05 ; (◎) I = 0.10 .



FIG·3·3 Potentiometric titration of partially ionised i-PMA with copper nitrate solution at constant ionic strength and varying α [i-PMA] = 2.5×10^{-3}M; I = 0.05.

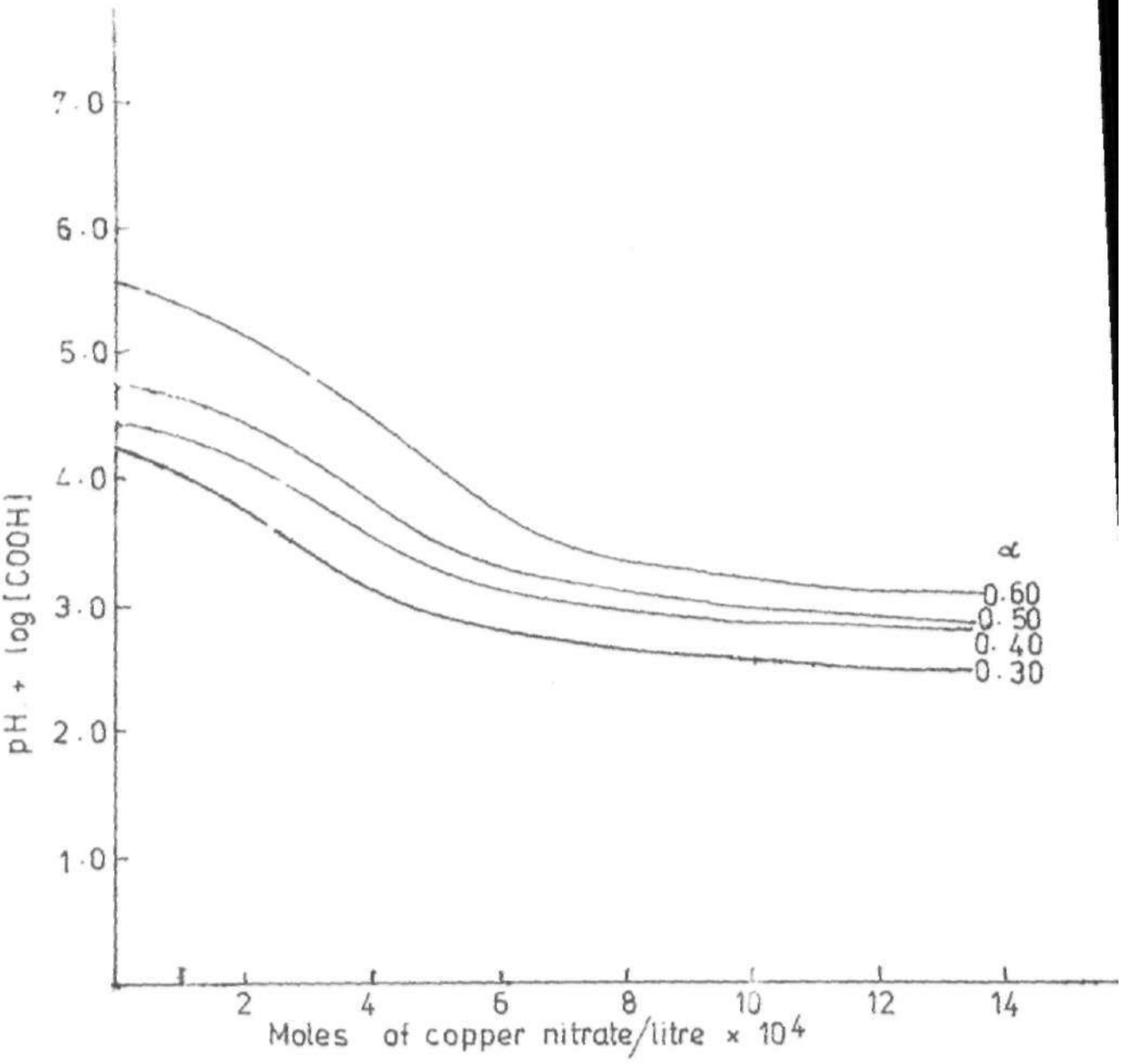


FIG 3·4 Potentiometric titration of partially ionised HPMA with copper nitrate solution at various degrees of neutralisation and constant ionic strength
[PMA] = 2.5×10^{-3}M I = 0·10

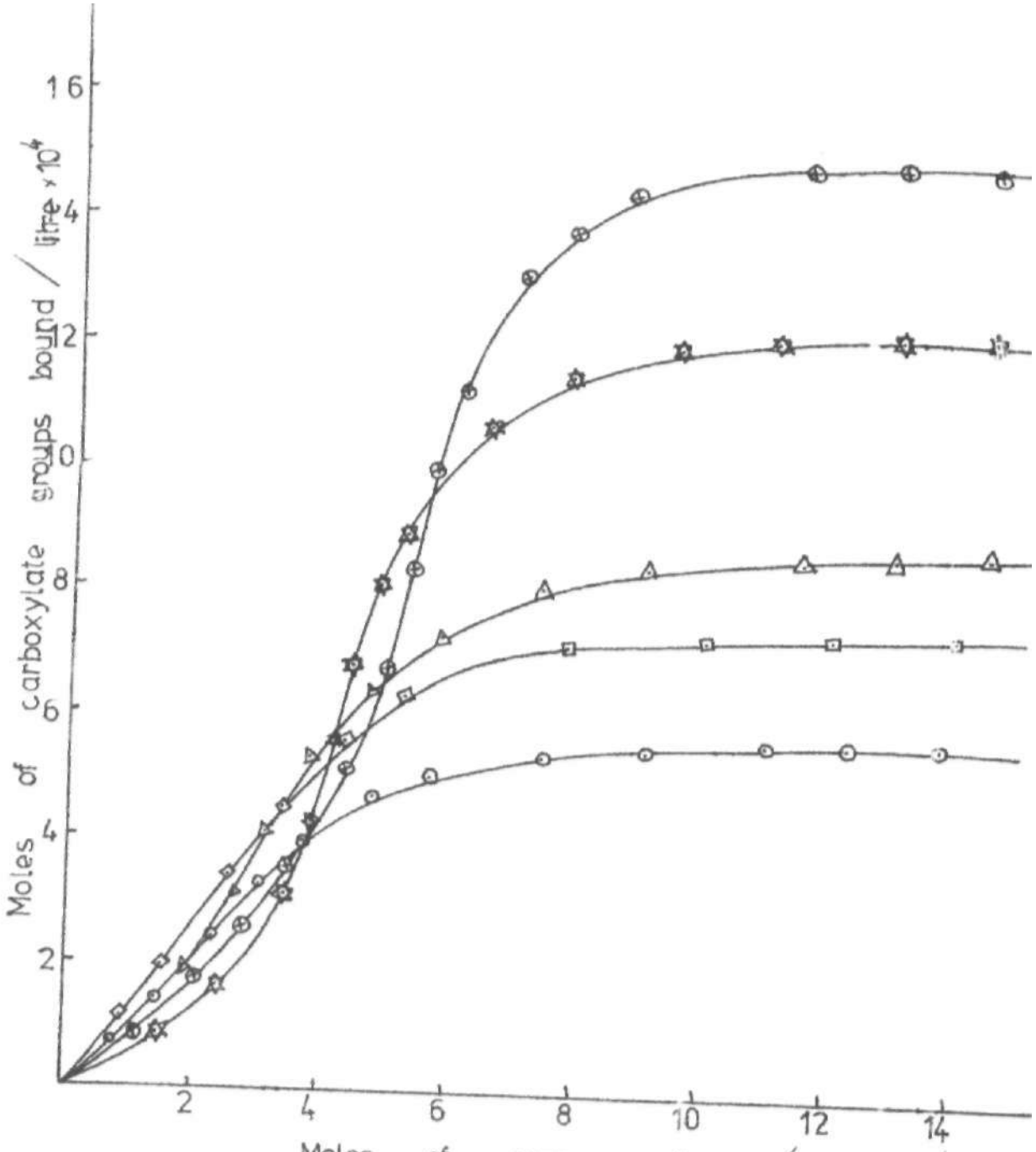


FIG. 3.5 Complex formation curves of Cu-PMA at constant ionic strength and varying α

[i-PMA] = 2.5×10^{-3}, I = 0.05

α: (⊙) 0.30; (⊡) 0.40; (△) 0.50; (⊠) 0.60. (⊗) 0.70.

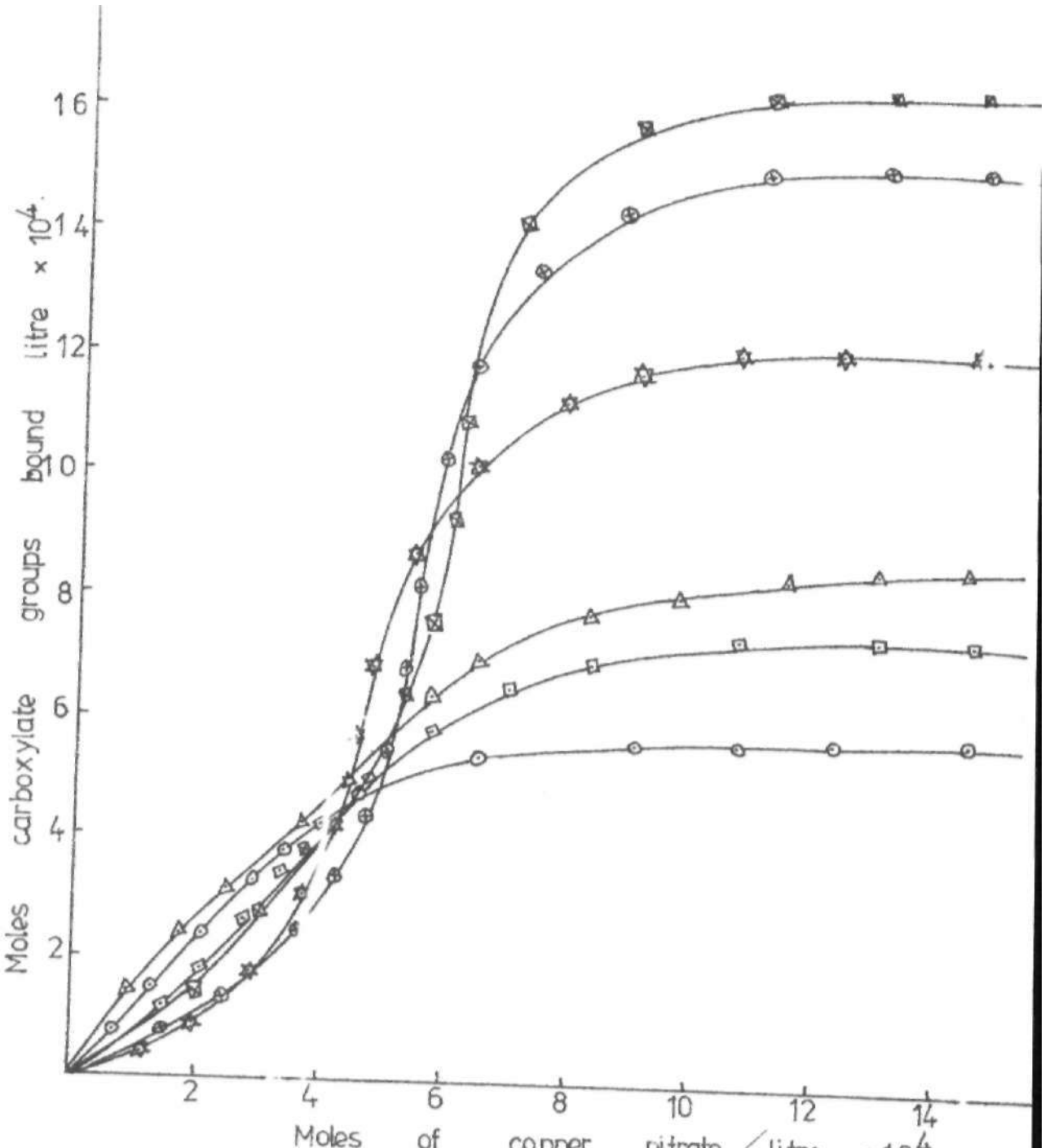


FIG. 3.6 Complex formation curves of Cu-PMA at constant ionic strength and varying degrees of neutralisation (α) ; [i-PMA] = 2.5×10^{-3}M; I = 0.10

α : (⊙) 0.30; (⊡) 0.40; (△) 0.50; (⊠) 0.60; (⊗) 0.70; (▣) 0.80 .

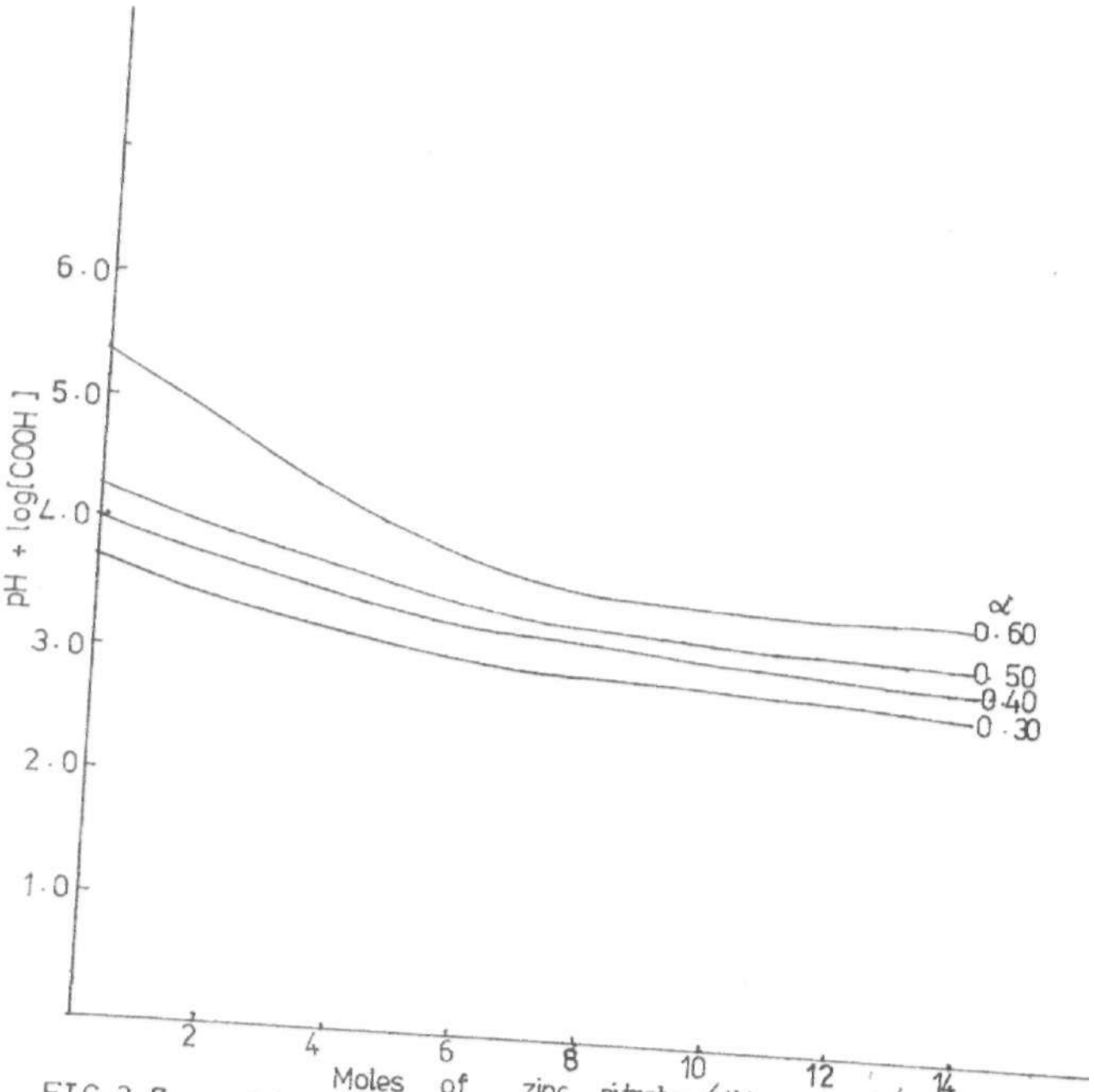


FIG. 3.7 Potentiometric titration of partially ionised PMA solutions with zinc nitrate solution at constant ionic strength and varying α. $I = 0.05$; $[i\text{-PMA}] = 2.5 \times 10^{-3}$ M

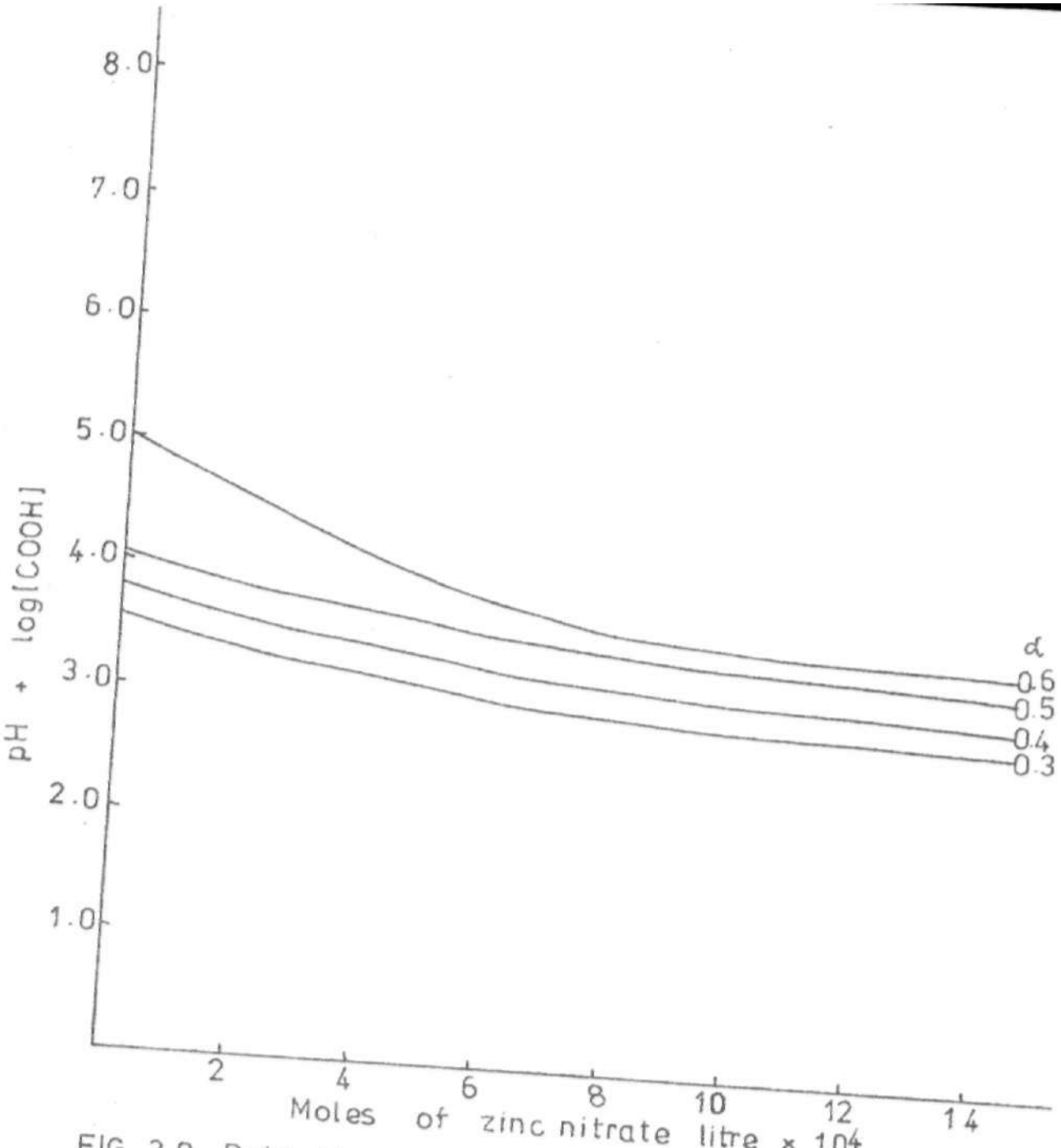


FIG 3.8 Potentiometric titration of partially ionised PMA solutions with zinc nitrate solution at constant ionic strength and at varying α. [PMA] = 2.5×10^{-3}M ; I = 0.10.

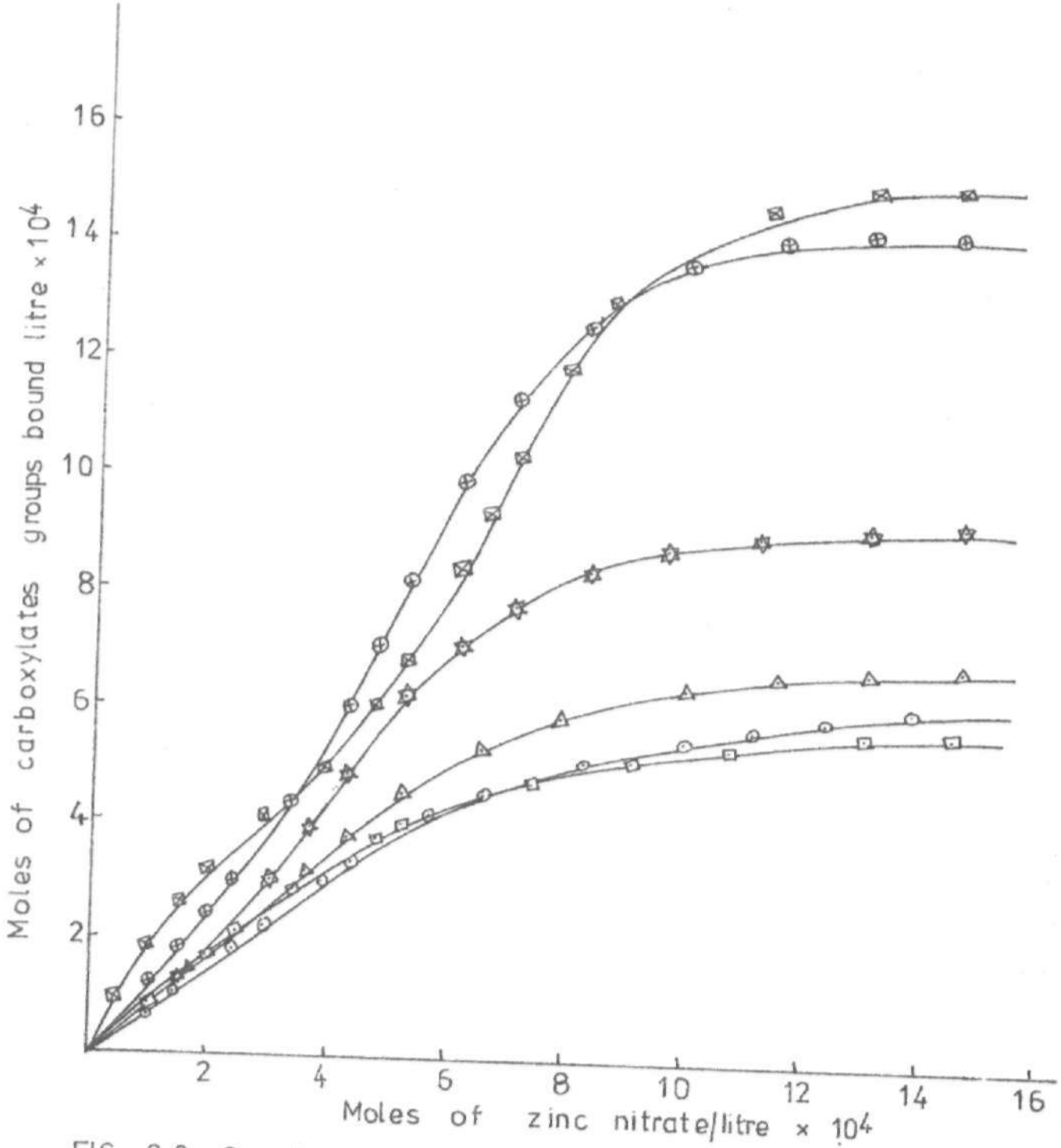


FIG 3.9 Complex formation curves of Zn-PMA at constant ionic strength and at varying α.
[PMA] = 2.5×10^{-3} M; I = 0.05
α :- (⊠) 0.80; (⊕) 0.70; (✲) 0.60; (△) 0.50; (⊙) 0.40; (□) 0.30.

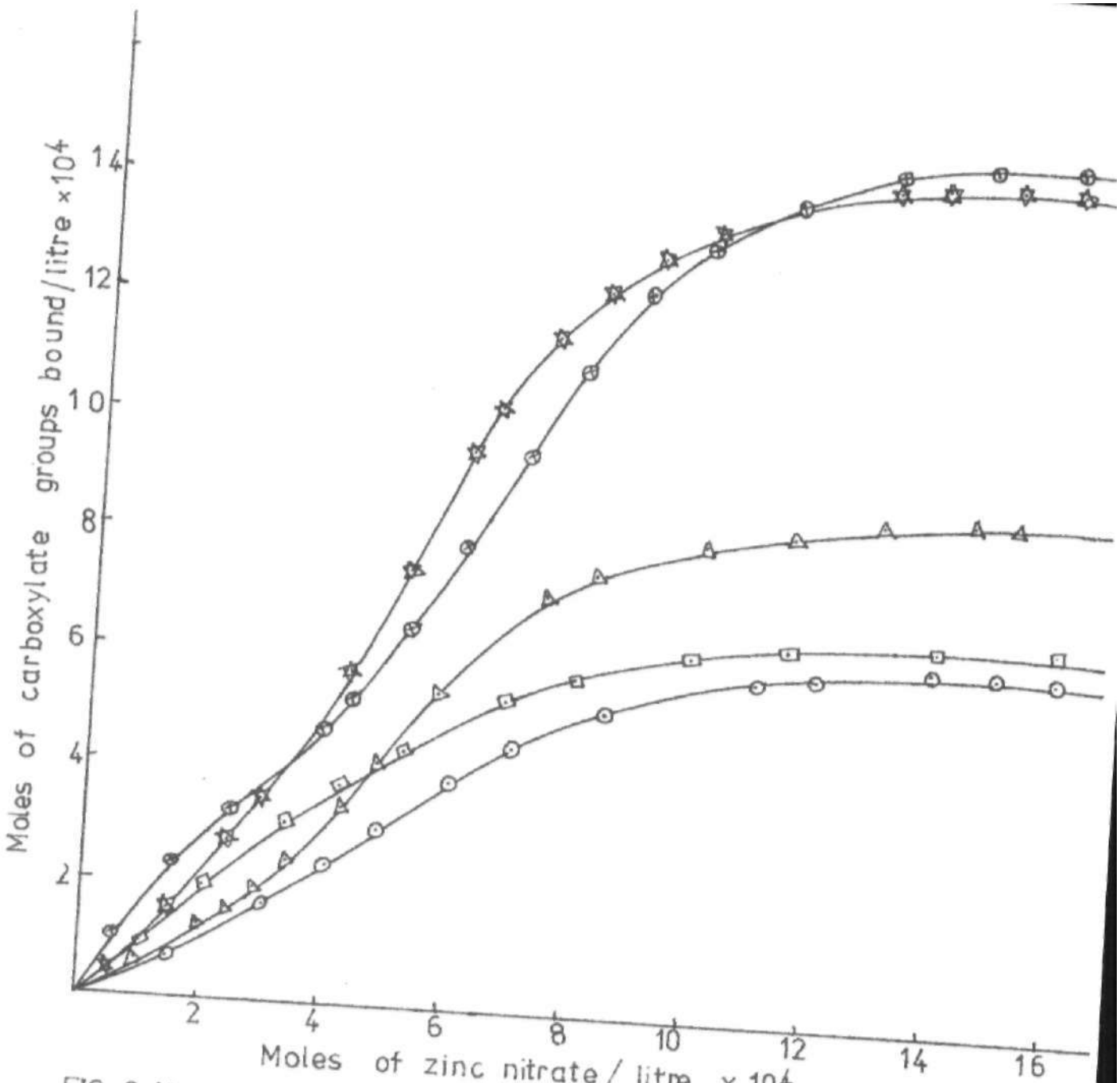


FIG 3.10 Complex formation curves of Zn - PMA at constant ionic strength and at various degrees of neutralisation. I = 0.10, [PMA] = 2.5×10^{-3}M. α :- (⊕) 0.80, (✡) 0.70; (△) 0.60; (□) 0.40; (⊙) 0.30.

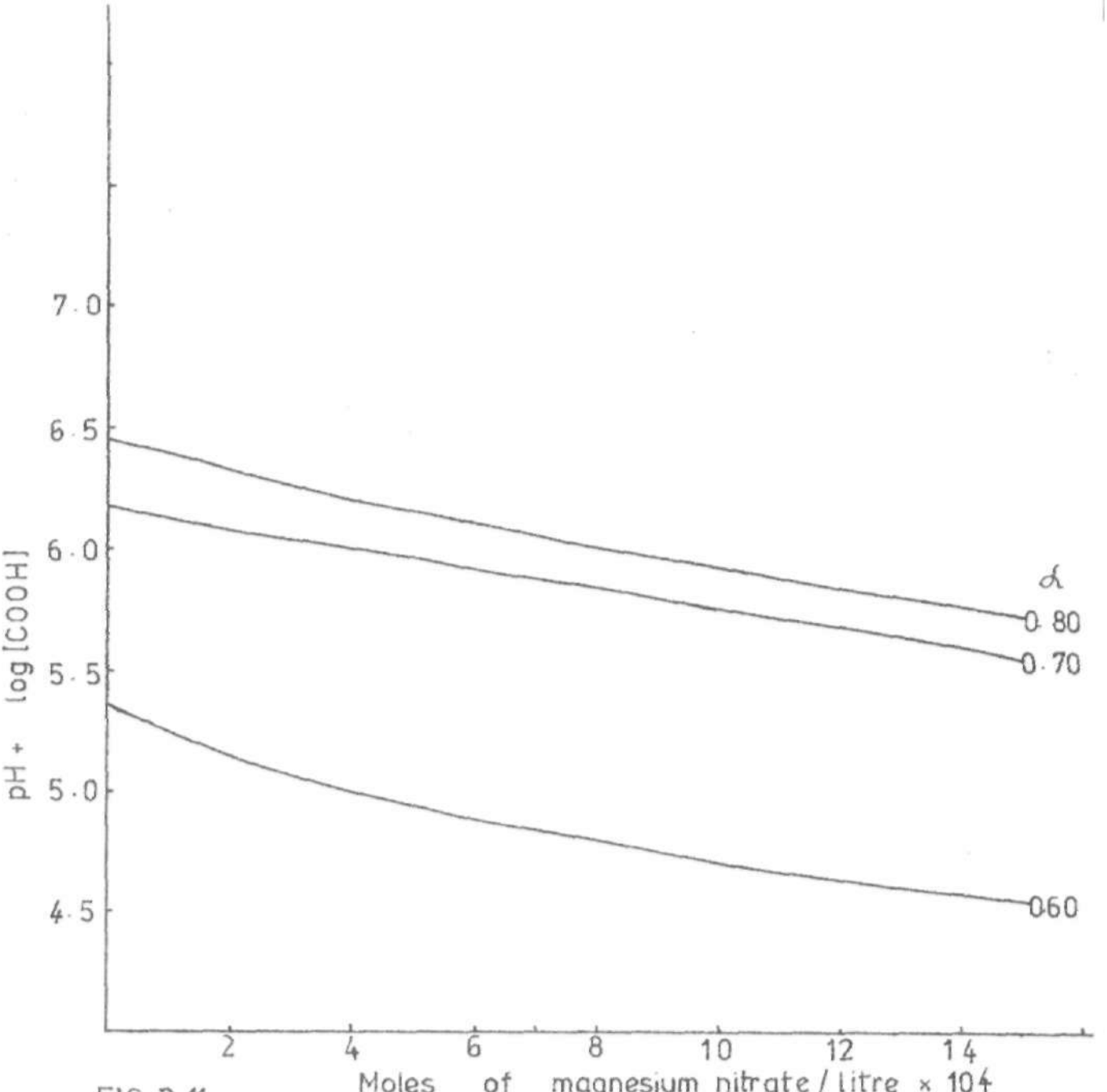


FIG 3.11 Polentiometric titration of partially ionised i-PMA with magnesium nitrate solution at constant ionic strength and various degrees of neutralisation (α).
[PMA] = 2.5×10^{-3}M I = 0·05

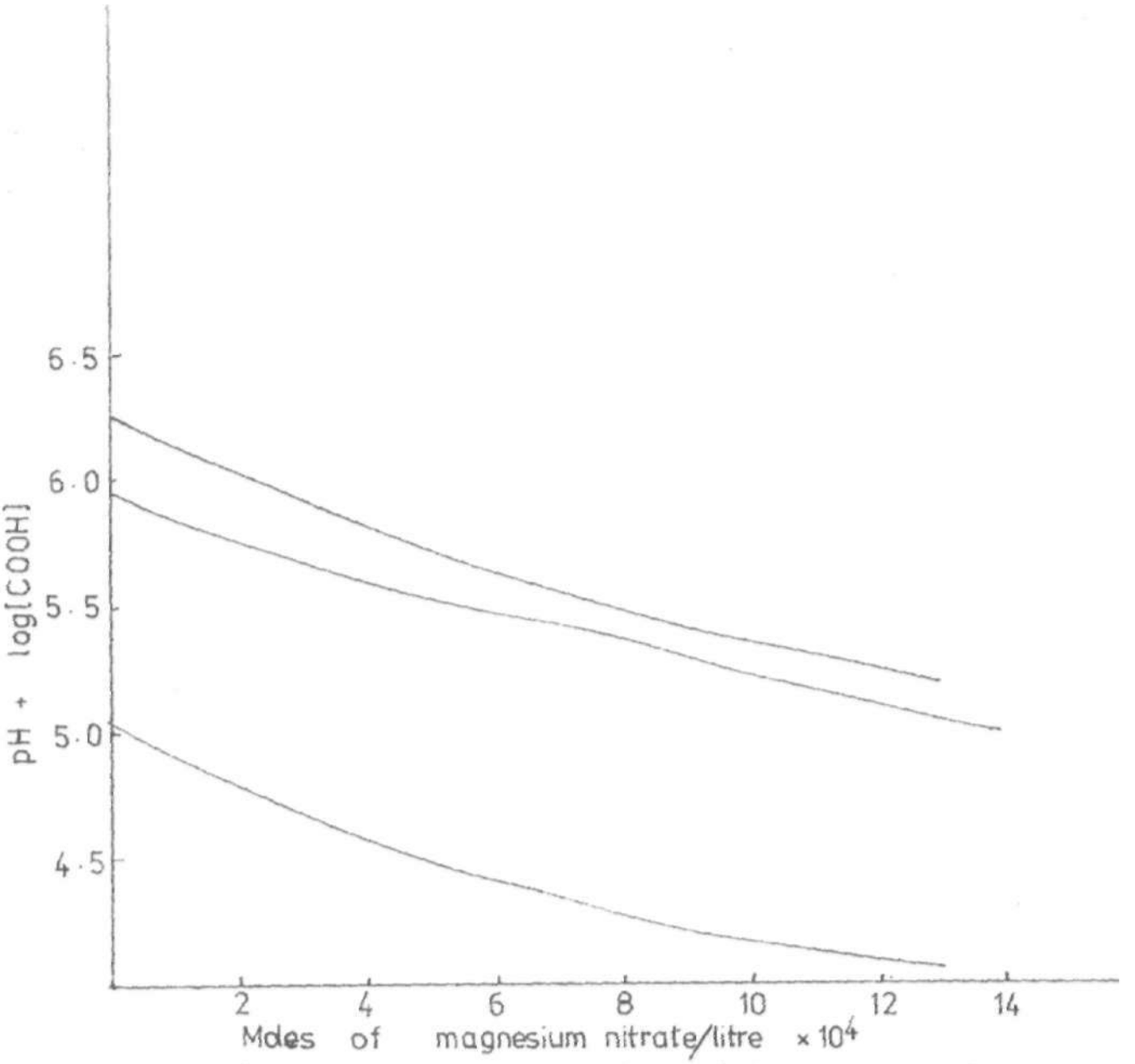


FIG 3.12 Potentiometric titration of partially ionised i-PMA with magnesium nitrate solution at constant ionic strength and various degrees of neutralisation, (α).
[PMA] = $2 \cdot 5 \times 10^{-3}$, I = 0·10

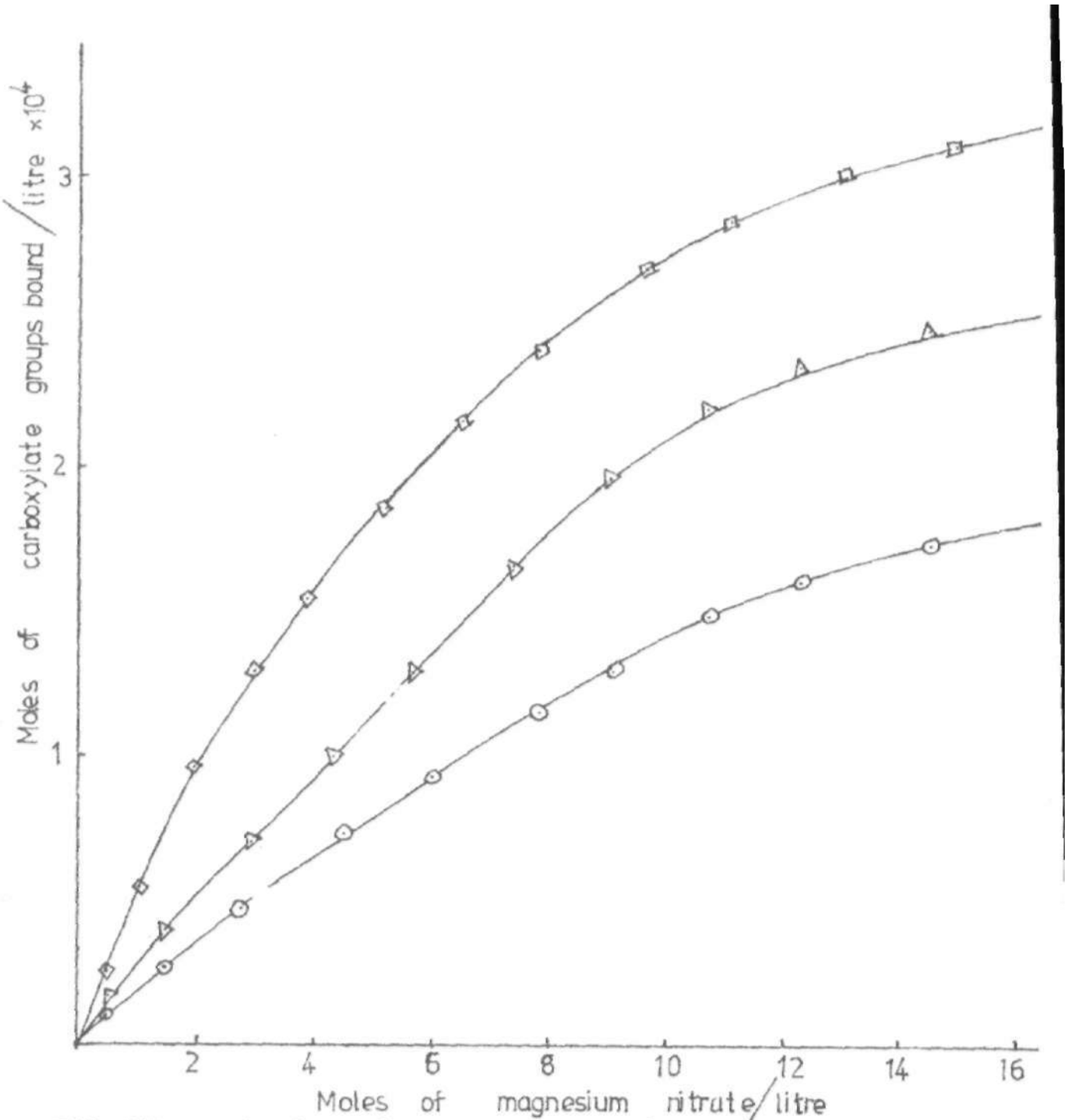


FIG. 3.13 Complex formation curves of Mg – PMA at constant ionic strength and varying degrees of neutralisation (α). [i-PMA] = 2.5×10^{-3} M, I = 0.05.
α: (⊙) 0.60 (△) 0.70 (□) 0.80

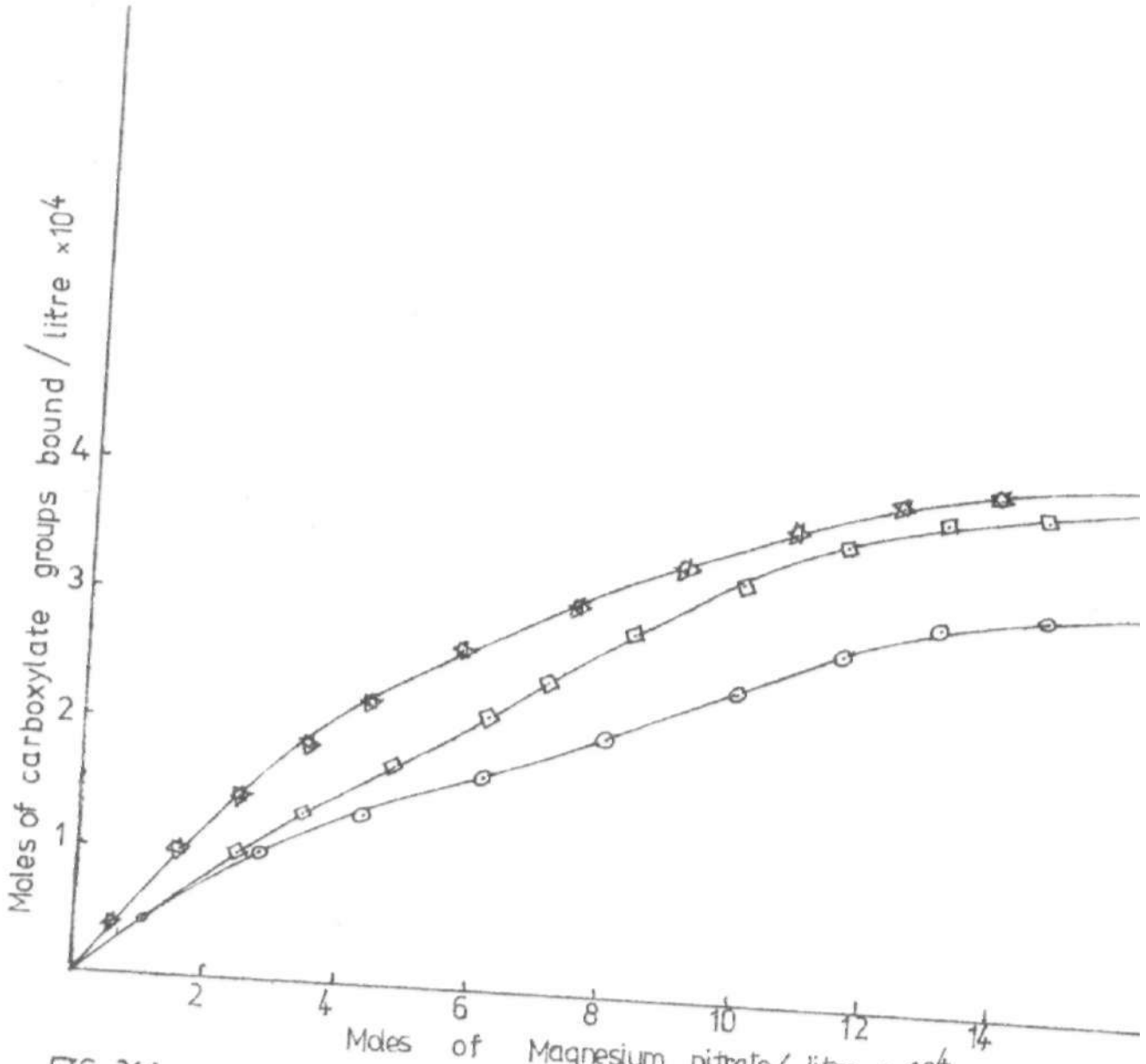


FIG. 3.14 Complex formation curves of Mg-PMA at constant ionic strength and various degrees of neutralisation (α). $I = 0.10$ [PMA] = 2.5×10^{-3} M; α :- (o) 0.60, (⊡) 0.70, (✡) 0.80.

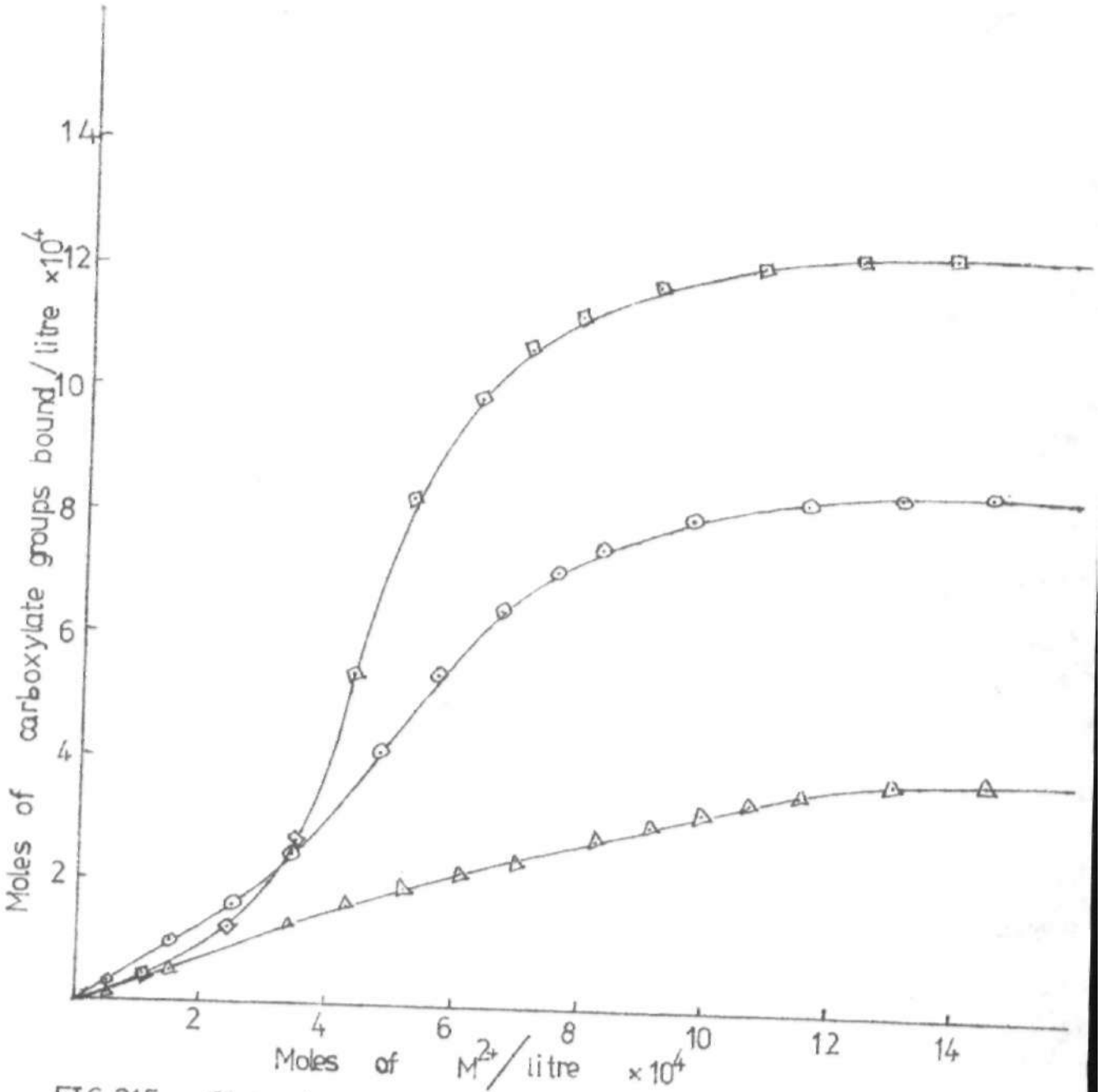


FIG.3.15 Comparison of the amounts of carboxylate groups bound for the same amount of copper zinc and magnesium at α = 0.6 and I = 0.10
[i-PMA] = 2.5×10^{-3} M ; (⊡) Cu^{2+}; (⊙) Zn^{2+}; (△) Mg^{2+}

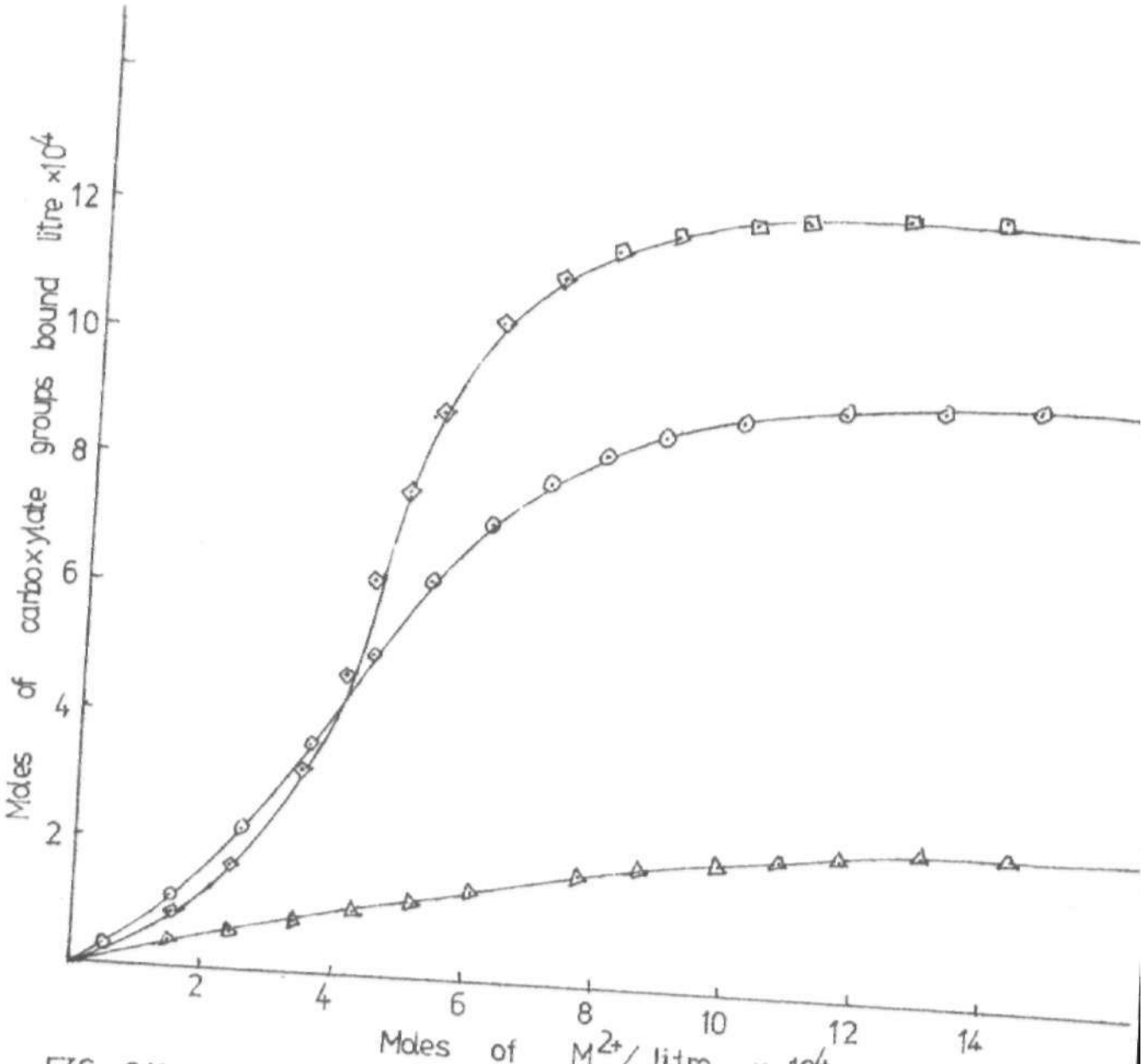


FIG. 3.16 Comparison of the amounts of carboxylate groups bound for the same amount of Copper, Zinc and Mugnesium at $\alpha = 0.6$
$I = 0.05$; $[i\text{-PMA}] = 2.5 \times 10^{-3}$ M
(⊡) Cu^{2+}; (⊙) Zn^{2+}; (△) Mg^{2+}

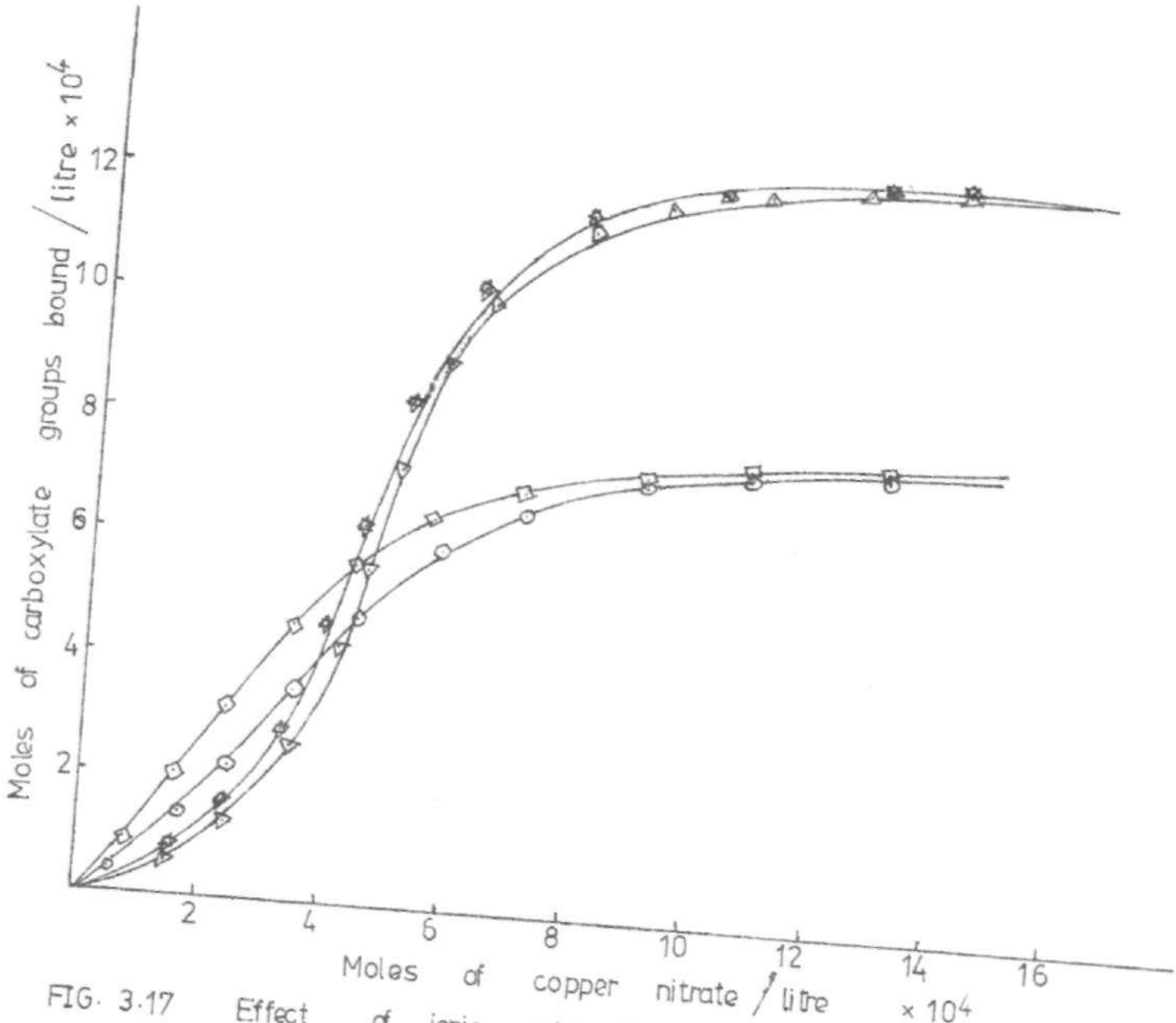


FIG. 3.17 Effect of ionic strength on binding of copper to i-PMA at [i-PMA] = 2.5×10^{-3}

(⊠) $\alpha = 0.60, I = 0.05$; (△) $\alpha = 0.60, I = 0.10$

(□) $\alpha = 0.40, I = 0.05$; (○) $\alpha = 0.40, I = 0.10$

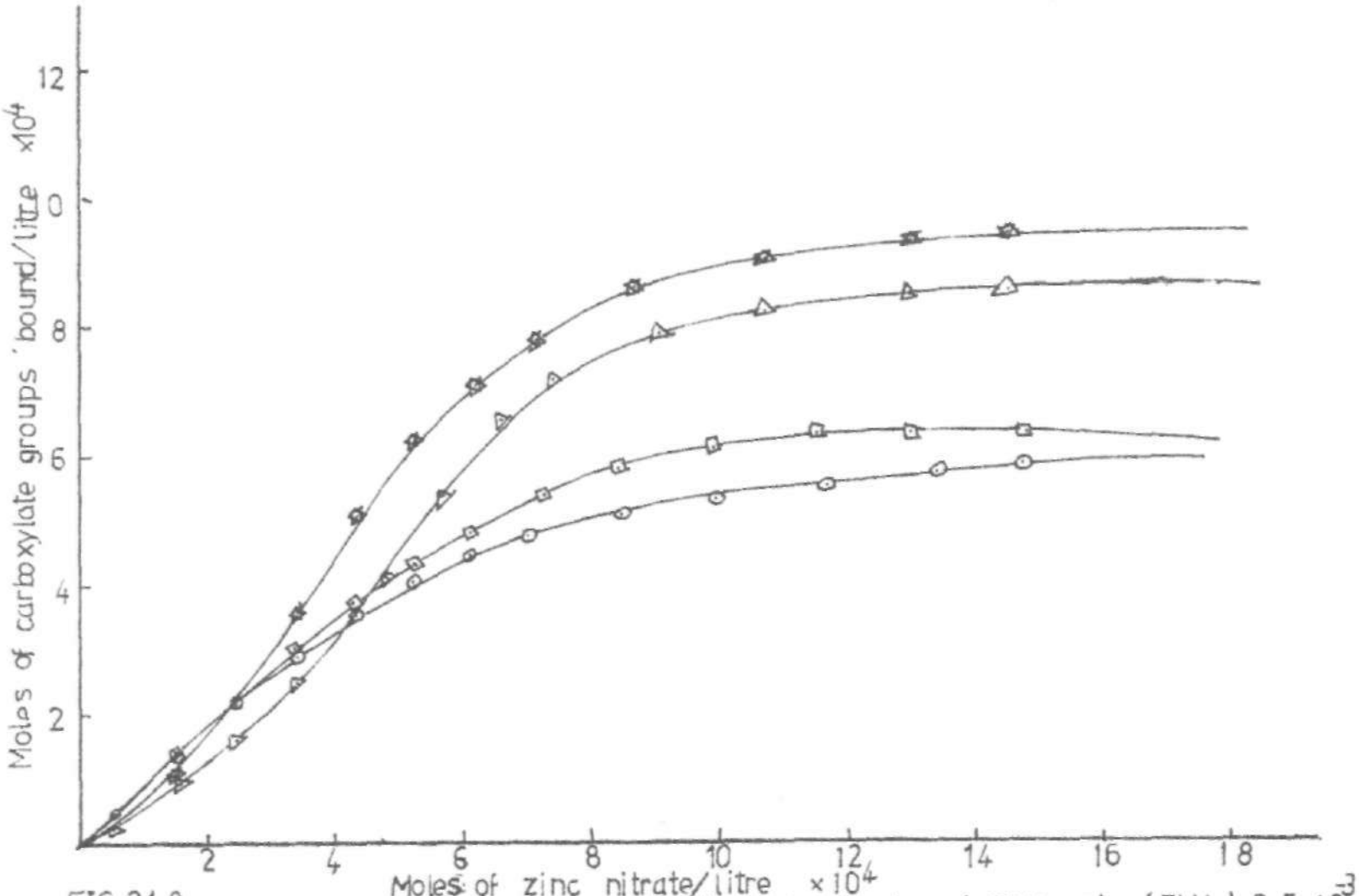


FIG. 3.1 8 Effect of ionic strength on binding of zinc to i-PMA at [PMA]=2·5×10⁻³

(o) α =0·6, I=0·05; (⊡) α=0·6, I=0·10; (⊠) α=0·3, I=0·05; (⊗) α=0·3, I=0·10

3.4 REFERENCES

1. Linderstrom-Lang K., Compt. Rend. Trav. 15, 17, (1924).
2. Cohn E. J., Cold Spring Habour Symposia, Quant. Biol. 6, 8, (1938).
3. Cohn E. J. et al J. Amer. Chem. Soc. 59, 509, (1937).
4. Kern W., Z. Physik Chem. 181, 249, (1938).
5. Katchalsky A. and Spitnik P., J. Polyer Sci. 2, 432, (1947).
6. Katchalsky A., and Gill J., Rev. Trav. Chim. 67, 761, (1948).
7. Arnold A., and Overbeek J. G. Rev. Trav. Chim. 69, 192, (1950).
8. Katchalsky A., and Lifson S., J. Polymer Sci. 13, 43, (1954).
9. Kuhn W., and Kuhn H., Helv. Chim. Acta. 26, 1394, (1943).
10. Barone G., Crescenzi V., and Quadrifoglio F., Ric. Sci. 35 (11A), 1069, (1965).
11. Nagasawa M., Murase T., and Konde K., J. Phys. Chem. 69, 4005, (1965).
12. Loebl E. M., and O'neill J. J., J. Polymer Sci. 45, 538, (1960).
13. Liquor A.M., Barone G., Crescenzi V., Quadrifoglio F., and Vitagliano V.,J. Macromol. Chem. 1, 287, (1966).
14. Anzuino G., Constantino L., Gallo R., and Vitagliano V., J. Polymer Sci. B4, 459, (1966).
15. O'neill J. J., Loebl E. M., Kandanian A. Y., and Morawetz H., J. Polymer Sci. A3, 4201, (1965).

16. Morawetz H., and Kandanian A. Y., J. Phys. Chem. 70, 2995, (1966).

17. Kolawole E. G., Ph.D. Thesis, (1974).

18. Kolawole E. G., Unpublished work.

19. Katchalsky A., and Spitnik P., J. Polymer Sci., 2, 432, (1947).

Chapter 4

Contents

		Page
4.1	Comparison of Data and Conclusions	84
4.2	Comparison of Data on Binding of Metal ions with Isotactic and Conventional polymethacrylic acid	85
4.3	R e f e r e n c e s	90

Chapter 4

4.1 COMPARISON OF DATA AND CONCLUSIONS

The data presented in table 2-IV show that both zinc and copper can form co-ordinate complexes involving only two carboxylate groups with isotactic PMA. This co-ordination number (n) has been evaluated from the ratio of total carboxylate groups initially present to the total amount of metal ion bound. These observations and how they affect the structure of the complex formed have been discussed in chapter 2. It should be noted however that the amount of carboxylate bound when maximum complexation occured cannot be obtained with this method, but it is possible to link the amount of metal ion bound here to the observations made in chapter 3. It has also been possible from the data to postulate a mechanism of interaction between metal ion and polymer molecule.

In chapter 2 figures 2.1, 2.4 and 2.7 are plots of M^{2+} added against M^{2+} bound for zinc, copper and magnesium respectively at varying degrees of ionization of the polymer and at I = 0.10. The great importance of these curves in relation to other types of measurement lies in the fact that at any stage, the amount of M^{2+}_{bound} could then be related to the amount of M^{+2}_{added} in other experiments provided that the

experiments are done under the same conditions of ionic strength, polymer concentration and degree of ionization. Figures 2.2 and 2.5 show that only one type of complex is formed between zinc and i-PMA and between copper and isotactic PMA. The order of binding suggested from these results is $Cu^{+2} > Zn^{+2} > Mg^{+2}$.

The results presented in chapter 3 dealt with potentiometric titrations under various conditions already mentioned. From figures 3.1 and 3.2 it was possible to suggest the type of transition occuring in the polymer. It has been pointed out in chapter 3 that the mode of binding for Cu^{+2} and Zn^{+2} at low degrees of ionization is different from that at higher degrees of ionization. Figures 3.15 and 3.16 show that the order of binding is in good agreement with the results of chapter 2, ($Cu^{+2} > Zn^{+2} > Mg^{+2}$). The effect of ionic strength on the efficiency of binding is also seen clearly in figures 3.17 and 3.18.

4.2 Comparison of Data on Binding of Metal ion with Isotactic and Conventional Polymethacrylic acid:

The data on c-PMA used was obtained from Kolawole's work (1). The isotactic PMA was found to be insoluble at low degrees of neutralisation (0-0.2) while the c-PMA is soluble at all values of α. This difference in solubility might be attributed to the regular arrangement of the COOH groups in i-PMA, which allows for a more compact structure than

in c-PMA where the COOH groups are arranged randomly along the macromolecular chain.

Figure 3.1 shows the plot of pH versus log $\frac{\alpha}{1-\alpha}$ for both i-PMA and c-PMA at two ionic strengths. This plot is to monitor the solution properties of PMA. It is very interesting to note that the i-PMA behaves as a weaker acid over the whole range of degree of ionization studied at the two ionic strengths. Instead of the sharp inflection observed in i-PMA, there is the gradual rise in pH for c-PMA, which can be associated with gradual transition from the coiled structure to the expanded chain. The sharp inflection might be related to the sudden unwinding of the more compact structure of i-PMA which makes way for solvent penetration. The transition in c-PMA takes place at lower α values (between α = 0.2 and 0.3) as reported by Kolawole (1) and some other workers (2, 3), but the transition of i-PMA has been suggested in section 3.3.2.1 to occur around α = 0.5 to 0.7. This result is also in agreement with recent results on i-PMA using viscometric technique (4).

Figure 4.1 compares the plots of potentiometric titration with copper for both isotactic and conventional PMA. The plot shows that at any metal ion concentration the value of pH + log COOH for any value of α is always higher for i-PMA than for c-PMA. This would indicate that the i-PMA has more of the COO^- groups at any given α, and so more COO^- groups are bound to the metal ion for i-PMA than for c-PMA. The plot also reveals two types of equilibria for c-PMA. This double equilibria

has been interpreted to monitor changes in the co-ordination number. It has also been observed (1, 3) from both conductance studies and equilibrium dialysis studies with c-PMA that a four co-ordinate complex exists as well as a two co-ordinate complex for copper. From both methods used in the present study it has been found that both copper and zinc form only a two - co-ordinate complex with i-PMA.

Figures 4.2 and 4.3 show the comparison plots of maximum metal ions bound against the degree of ionization. The figure shows that in all cases the amount of metal bound is proportional to α. Figure 4.2 shows that when the amount of Zn^{+2} bound for i-PMA and c-PMA is compared, more zinc is bound to i-PMA than to c-PMA. These findings suggest that zinc shows a greater affinity to bind unto i-PMA than to c-PMA. However for copper at very low α values the affinity of copper for charged sites seems to be the same in both i-PMA and c-PMA as can be seen from the converging of the two curves at low degrees of ionization. However at high values of α copper binds more to the i-PMA than to c-PMA. The difference in binding is not as much as for zinc. The higher charge density on the proposed helical structure of the i-PMA can be used to explain the greater affinity of the metal ions to it than to c-PMA. The closeness of COO^- groups in the i-PMA will allow very much for near neighbour participation which will make binding more efficient.

The mechanism suggested for the binding of Cu^{+2} and Zn^{+2} to conventional PMA was intermolecular interaction. However the results obtained for i-PMA seem to favour intramolecular interaction. This is not surprising because the closeness of the regularly arranged COO^- groups, of isotactic PMA, results in high electrostatic repulsion which would make approach of two highly charged macromolecules difficult even at high ionic strength. High concentration of KNO_3 has little effect on near neighbour COO^- groups but has a screening effect on the long-range interaction with the result that the long-range electrostatic field of the polyion is minimized. This near neighbour group effect is not as prominent in conventional PMA where the COO^- groups are randomly arranged.

To lend further support to the findings in the present work, a look has been taken at Kolawole's (4) recent work on isotactic and conventional PMA using viscometric methods. The end - end distances $\bar{r}$ was measured for various PMA solutions at various degrees of ionization and in the presence and absence of metal ions. For conventional PMA Cu^{+2} and Zn^{+2} were used, while for isotactic PMA Cu^{+2}, Zn^{+2} and Mg^{+2} ions were used in the studies. It has been shown that for conventional PMA (c-PMA) $\bar{r}$ reaches a constant value at α = 0.70 in the presence of Cu^{+2} ions whereas $\bar{r}$ continues to increase even beyond α = 0.7 for i-PMA to attain the same value for a metal free PMA solution. However in his

studies with isotactic PMA $\bar{r}$ was found to reach a constant value in the presence of Cu^{+2}, Zn^{+2} and Mg^{+2} ions at about $\alpha = 0.70$. These findings may suggest that in both conventional and isotactic PMA, Cu^{+2} ions form more stable complexes than Zn^{+2} ions or that the observed differences were only structural configurations. It is also suggested that in the two types of PMA, copper restricts further expansion of the polymer beyond that obtainable in salt solutions whereas Zn^{+2} ions seem to have no effect on the expansion of conventional PMA chains as it does on isotactic PMA. In the i-PMA, all the ions studied impose restriction on the expansion of the polymer chain because in all cases $\bar{r}$ became constant at $\bar{r} = 0.70$. Also if the magnitude of $\bar{r}$ could be used as a measure of the binding strength when maximum expansion has taken place, Kolawole(4) has shown that the binding strength of the ions is of the order $Cu^{+2} > Zn^{+2} > Mg^{+2}$. This same order has been found for c-PMA. These findings strongly support the order obtained in the present work, where potentiometric and dialysis methods have been used to deduce the strength of binding of these ions to isotactic PMA.

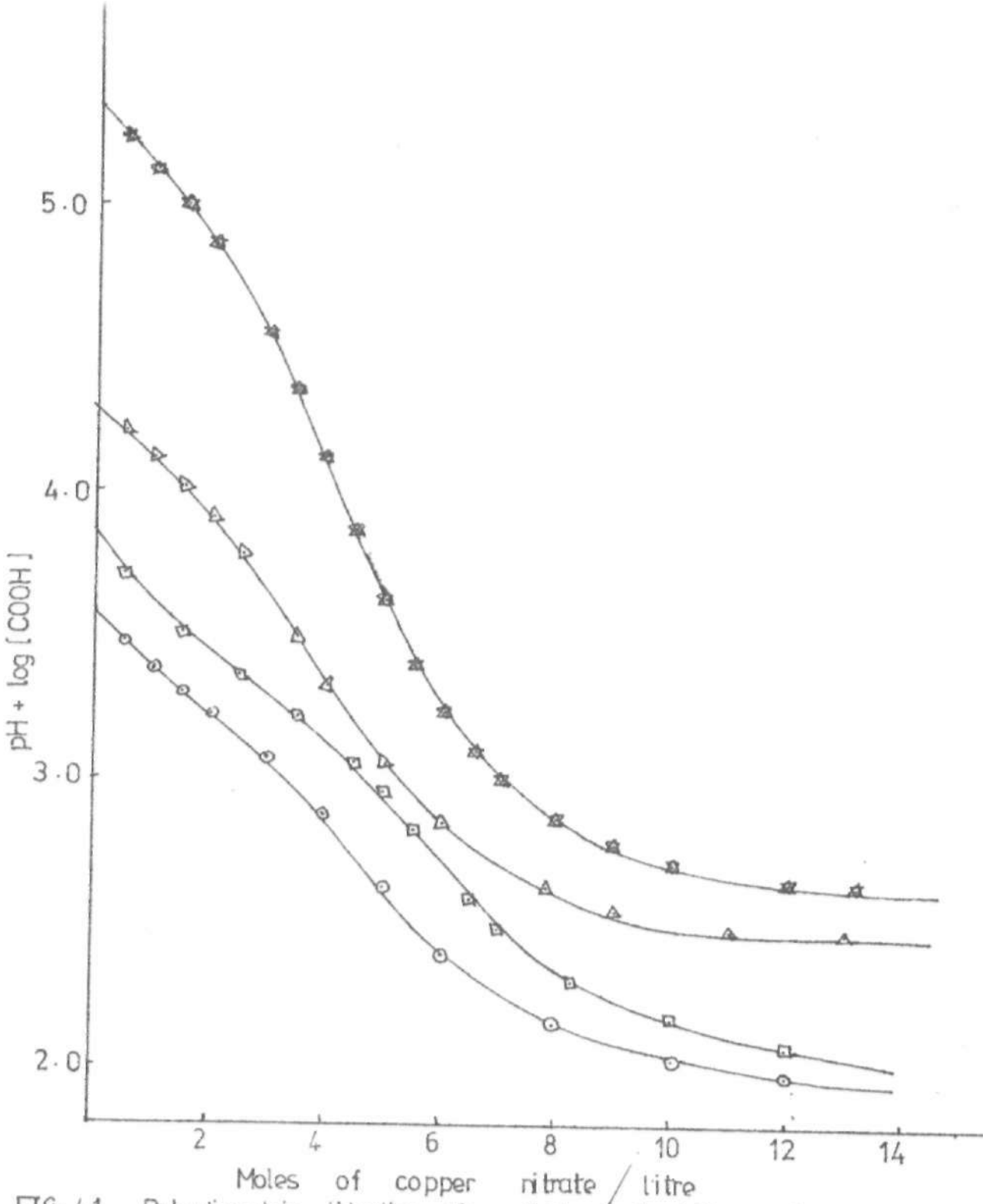


FIG. 4-1 Potentiometric titration of partially ionised PMA with copper nitrate solution at constant ionic strength and varying α. I = 0·10 , [PMA] = 2.5×10^{-3}. c-PMA, α: (⊙) 0·5 (⊡) 0·6
i-PMA, α: (△) 0·5 (✡) 0·6

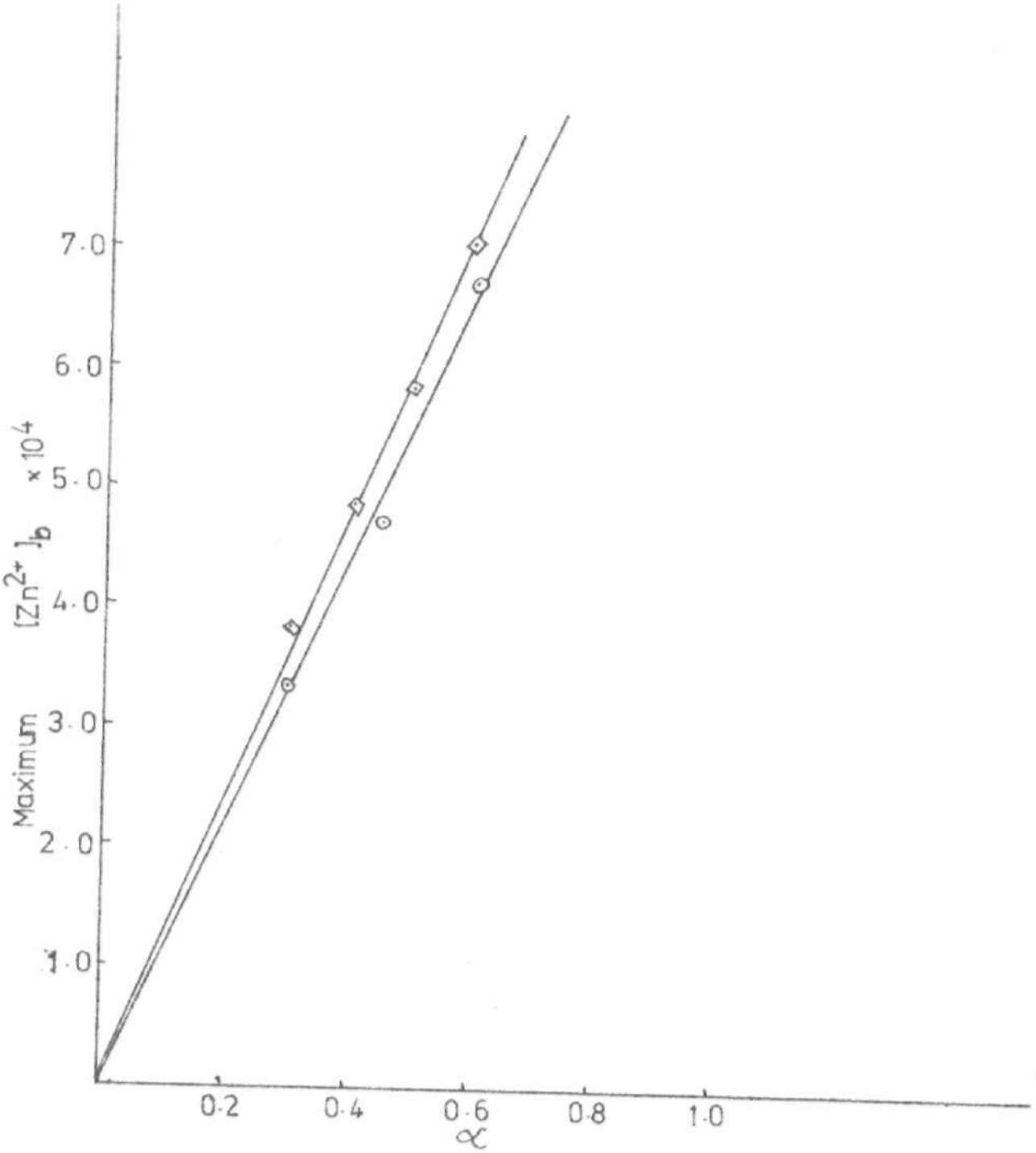
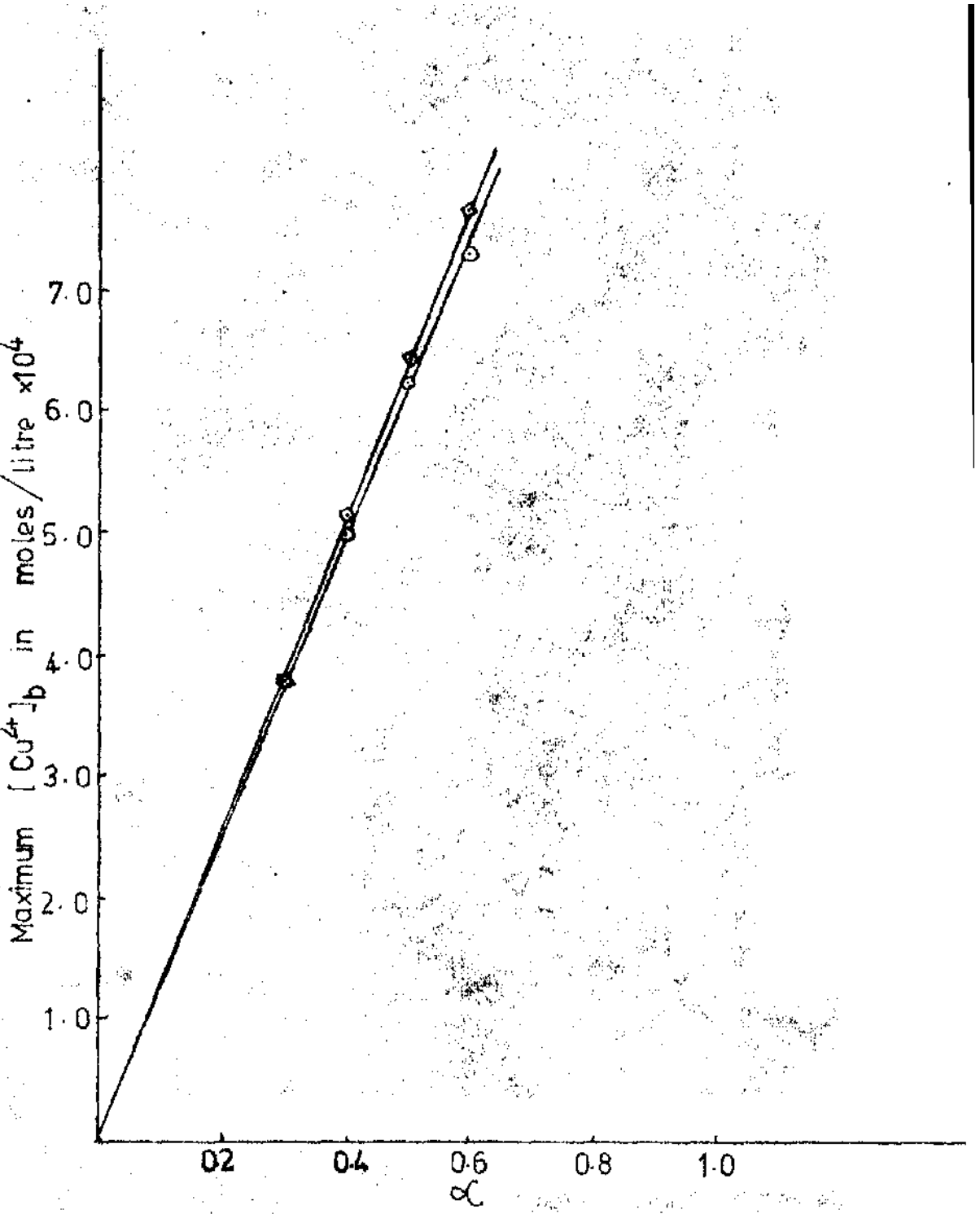


FIG. 4.2 Comparison of the amounts of zinc bound for isotactic and conventional PMA at I=0.10 ; [PMA] = 2.5×10^{-3}M (⊙) c-PMA ; (⊡) i-PMA



FIG·4·3 Comparison of maximum amounts of copper bound for isotactic and conventional PMA at I = 0·10, [PMA] = 2.5×10^{-3} M
(⊙) c-PMA, (⊡) i-PMA

4.2 REFERENCES

1. Kolawole E. G., Ph.D. Thesis (1974).

2. Leyte J. C., and Mandel M., J. Polymer Sci. A2, 1879, (1964).

3. Barone G., Crescenzi V., Quadrifoglio F., and Vitagliano V., Ric. Sci. 36, 477, (1966).

4. Kolawole E. G., Unpublished work.