

EXPANSION COEFFICIENTS IN POLYELECTROLYTES

**AN INVESTIGATION OF POLYMETHACRYLIC ACID
SOLUTIONS BY LIGHT SCATTERING AND VISCOSITY**

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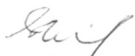
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CERTIFICATE

Certified that the work incorporated in the thesis entitled '**EXPANSION COEFFICIENTS IN POLYELECTROLYTES - An Investigation of Poly-methacrylic Acid Solutions by Light Scattering and Viscosity**' submitted by **Sivadasan Kuniyil**, was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.


(Dr. S. Gundiah)
Research Guide

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CHAPTER ONE

INTRODUCTION

General Introduction

Polyelectrolytes, macromolecules bearing ionizable groups, exhibit special properties of macromolecules as well as electrolytes. When dissolved in a polar solvent (usually water), the ionizable groups dissociate, resulting in macromolecule bearing electrostatic charges. Electrostatic and ionic interactions. The strong electrostatic interaction of the charges on the macromolecule results in several interesting phenomena.¹⁻³ For instance, the activity coefficient of macromolecules is greatly influenced by the charge density of the macromolecule. The magnitude of the like charges on the macromolecule greatly influences the conformation for the macromolecule. Relatively minor changes in the environmental conditions like the degree of ionization of the polyelectrolyte, the nature and concentration of added simple electrolyte bring about large variations in the dimensions of these charge bearing macromolecules.⁴

The conformational changes brought about by the progressive ionization of the ionizable groups in the polyelectrolyte have been the subject matter of several theoretical and experimental studies.^{1,2,5-7} Theoretical treatments of polyelectrolyte expansions eventually use

1.1 General Introduction

Polyelectrolytes, macromolecules bearing ionizable groups, exhibit typical properties of macromolecules as well as electrolytes. When dissolved in a polar solvent (usually water), the ionizable groups dissociate resulting in macromolecule bearing electrostatic charges (macroions) and mobile counterions. The strong electrostatic interaction of the charges on the macroion results in several interesting properties^{1,2,3}. For instance, the activity coefficient of mobile ion is greatly influenced by the charge density of the macroion. The repulsions of the like charges on the macroion result in greatly expanded conformation for the macroion. Relatively minor changes in the experimental conditions like the degree of ionization of the polyelectrolyte, the nature and concentration of added simple electrolyte bring about large variations in the dimensions of these charge bearing macromolecules⁴.

The conformational changes brought about by the progressive dissociation of the ionizable groups in the polyelectrolyte have been the subject matter of several theoretical and experimental studies^{1,3,4,5}. Theoretical treatments of polyelectrolyte expansions invariably use

idealized models which may not totally represent the complexity of the real systems³. Experimental investigations thus assume importance with a view to obtain better quantitative description of the polyelectrolyte conformations.

Theoretical treatments of the configurational properties of polyelectrolytes in solution have largely depended upon the theoretical developments of the configurational properties of neutral macromolecules in solution⁵. Linear macromolecules in solution are more commonly represented as random-coils wherein no long-range order exists between any two remotely connected statistical elements^{6,7}. At low degrees of ionization and with sufficient concentration of added simple electrolytes, polyelectrolytes in solution may be represented as random-coils^{3,5}. The time-averaged distribution of the chain elements about an internal reference point characterize random coil configuration⁸. Mean-square displacement of the chain ends or mean-square radius of gyration is used for this purpose.

Dimensions of random-coil neutral macromolecules in solution, in the context of the two parameter theory⁶, are expressed in terms of short-range effects characteristic of the chemical constitution of the macromolecule and the number of repeat units in it, and long-range interference effect resulting from volume exclusion and environmental factors like the nature of the solvent in which it is dissolved. The long-range interference effect is a function of the excluded volume parameter characteristic of the mutual volume of exclusion for one of the statistical elements due to the presence of the other^{7,8}.

Different molecular models and theoretical treatments have been employed to describe the configurational properties of polyelectrolytes in solution¹⁻⁵. However, the electrostatic expansions, i.e. the expansions brought about by the presence of electrostatic charges, according to various theories, can be expressed in terms of an electrostatic excluded volume parameter^{4,5,9}. It may be recollected that various two parameter theories of polymer solutions also express expansion as a function of the excluded volume parameter. The expressions derived for macroion expansions by the various theories widely differ.

Systematic investigations of the polyelectrolyte expansions in solutions are severely limited. In order to evaluate the expansions due to the presence of electrostatic charges alone, the dimension of the macromolecule identical to the polyelectrolyte but lacking electrostatic charges, is needed^{9,10}. This is an experimentally unrealizable condition. Nagasawa and his group of investigators have carried out^{4,9} the most significant investigations on the expansions of polyelectrolytes with varying charge density. For evaluating the electrostatic expansion coefficients, they used the model of the polyelectrolyte in the presence of infinite concentration of the added simple electrolyte as the reference state. The increasing concentration of the added salt brings about progressive screening of the charges on the macroion by the counterions and presumably total screening occurs at infinite concentration of the added salt. However, theta conditions are realized for many aqueous solutions of polyelectrolytes at finite concentrations of the added electrolyte⁴.

Hence, infinite concentration of the added salt to the polyelectrolyte solution is likely to correspond to an immiscible two-phase system. Thus it is doubtful that the dimension of the polyelectrolyte at infinite concentration of the added salt represents the dimension of the discharged state of the dissolved polyelectrolyte in solution.

Recently, an attempt has been made^{10,11} to evaluate the variation of the electrostatic expansion of the polyelectrolyte with charge density using hydrolysed polyacrylamide as polyelectrolyte and parent polyacrylamide as the reference molecule. It was observed that the steric factor hindering free rotation around the skeletal bonds for polyacrylamides and sodium polyacrylate are about equal and was cited as the justification for using parent polyacrylamide as reference molecule. It was observed that the electrostatic interactions being very large, total expansions with reference to the unperturbed state of the parent polyacrylamide could be ascribed to the presence of electrostatic charges alone. As closed expressions for the variation of expansion coefficient with charge density were not available in terms of number of ionizable groups present on the polyelectrolyte (the variable they used for bringing about varying charge density) according to various theories, the investigators assumed that i^2/c_s (where 'i' is the degree of ionization and c_s is the concentration of the added salt) is proportional to the number of ionizable groups present on the polyelectrolyte. No justification was cited for this assumption.

As pointed out earlier, the predicted variation of the expansion of polyelectrolytes in solution with varying charge density according

to different theories widely differ. The limited experimental data available in literature suffer from the shortcomings noted above. Extensive experimental investigations are needed for a more quantitative description of the configurational changes brought about by changes in experimental conditions which affect the charge density of the polyelectrolyte. The present investigation describes systematic studies by viscosity and light scattering techniques on the variation of the dimensions of fractionated samples of polymethacrylic acid at varying degrees of ionization and concentrations of the added salt. The expansions due to the presence of electrostatic charges were evaluated with respect to the unperturbed state of the undissociated polymethacrylic acid.

Polymethacrylic acid exhibits a conformational transition during the course of its ionization^{12,13}. It exists in a compact conformation at very low degrees of ionization but at a more expanded conformation at higher degrees of ionization. For evaluating the electrostatic expansions at higher degrees of ionization, unperturbed dimensions corresponding to the expanded conformation at higher degrees of ionization are needed. Unperturbed dimensions obtained for the undissociated polymethacrylic acid in aqueous solutions will not serve the purpose.

For several of polyelectrolytes possessing hydrophobic groups and exhibiting conformational transitions during the course of their ionization, higher unperturbed dimensions have been reported^{14,15} in organic solvents as compared to their unperturbed dimensions in aqueous solvents. Polymethacrylic acid is also observed to exhibit large increases in viscosities when a miscible organic solvent is added to its aqueous solution^{16,17}. Thus polymethacrylic acid is very likely to exist in a more expanded

configuration (conforming to that at higher degrees of ionization) in organic solvents. Total expansions have been, therefore, evaluated with reference to the unperturbed dimensions in an organic theta solvent. The computed expansion coefficients have been used to evaluate the relative applicability of the different macroion expansion theories.

The remaining sections of this introductory chapter, discuss the theories of configurational properties of neutral macromolecules and polyions in solution and the theoretical and experimental background of the experimental techniques used in this investigation. These topics are extensively covered in several books and monographs and only a brief outline relevant to the discussion is presented here.

1.2 Configurational Properties of Macromolecules in Solution

The configurational analysis of linear macromolecules has received great deal of attention and the subject has been treated in detail by Flory^{7,18}, Yamakawa⁶, Volkenstein⁸ and others. Linear macromolecules are commonly represented as random coils wherein two statistical segments distant from each other have no specific correlation with reference to their orientation in space. The macromolecule can assume a large number of configurations due to the rotation of one part of the molecule relative to another. The time-averaged distributions of chain elements about an internal reference point determines its configuration. The configurational characteristics of macromolecules are expressed in terms of their average dimensions. The dimensions generally employed are $\langle r^2 \rangle$, the mean-square end-to-end distance and $\langle s^2 \rangle$, the mean-square radius of gyration.

One of the earlier molecular models used to study the configuration

of the macromolecule is the random flight model. In the random flight chains, bonds can take up any position irrespective of the position of its neighbour. The statistical treatment of this freely-jointed chain model yields $\langle r^2 \rangle = nl^2$ when $r \ll r_{\max}$ and $n \gg 1$; $r_{\max}$ is the end-to-end distance of the fully stretched chain. The segment density distribution for the freely-jointed chain follows the Gaussian distribution,

$$W(r)dr = \left(\frac{3}{2\pi nl^2} \right)^{3/2} \exp \left(-\frac{3r^2}{2nl^2} \right) 4\pi r^2 dr$$

where $W(r)dr$ is the probability that the separation of ends lies between r and $r + dr$. For Gaussian chains, the relation between $\langle r^2 \rangle$ and $\langle s^2 \rangle$ is given by $\langle s^2 \rangle = \langle r^2 \rangle / 6$.

In the real molecules, the neighbouring bonds are forced to lie at fixed (bond) angles and only a few rotational isomeric states are possible. These restrictions, referred to as short range interactions, are disregarded in the above model for the sake of mathematical simplicity.

Introducing the valence angle restriction in to the random flight model, the dimension obtained for a vinyl chain is

$$\langle r^2 \rangle = nl^2 (1 - \cos \Theta / 1 + \cos \Theta)$$

where Θ is the valence angle. Similar expressions have been derived for linear chains having more than one type of bond angle in their skeletal structure. The freely rotating chain also follows Gaussian statistics.

In the hindered rotation model, it is assumed that the angle of rotation about each bond is independent of the rotation of the other,

and that the hindrances to rotations are governed by symmetric potentials. The mean-square end-to-end distance for this model of vinyl chains is given by the following expression,

$$\langle r^2 \rangle = nl^2 \frac{1 - \cos \Theta}{1 + \cos \Theta} \frac{1 + \overline{\cos \Phi}}{1 - \overline{\cos \Phi}}$$

where $\overline{\cos \Phi}$ is the average of cosine of the angles of rotations about the skeletal bonds.

The rotation about the individual skeletal bonds are not independent but are influenced by the rotation about other skeletal bonds. Volkenstein and others⁸ have taken into consideration the effect of the rotation of the neighbouring bonds on the rotation of the skeletal bond under consideration. Similarly, the rotation about the skeletal bonds have discrete values as the trans, gauche-1 and gauche-2 positions in the lower hydrocarbons. In either case, the root-mean square end-to-end distance is given by

$$\langle r^2 \rangle = nl^2 \frac{1 - \cos \Theta}{1 + \cos \Theta} \sigma^2$$

where σ is a structural factor that accounts for the hindrances to rotation around the skeletal bonds due to steric effects of the substituents.

Rotational isomeric state theory¹⁸ has been advantageously used to calculate the dimensions of linear chain molecules. The basic assumption is that each bond in the linear chain has a small number of discrete rotational states, their relative probability being determined by the differences in the potential energy minima for the various rotational states.

The calculated results are in very good agreement with the experimentally determined values in several cases¹⁸.

The concept of Kuhn's 'equivalent chain model'⁷ can be used to show that the real chains with fixed valence angles and hindrances to free rotation also follow Gaussian statistics. In the equivalent chain model, the chain is divided into 'n' statistical segments each of 'm' arbitrarily chosen bonds. The fully extended length of the equivalent chain equals to that of the real chain. The hypothetical chain of n/m statistical elements of length l' (where l' is the root-mean square end-to-end distance of elements constituting 'm' bonds) replaces the real chain, removing the restrictions of fixed valence angle and hindrances to free rotation.

In all these mathematical models discussed above, it is assumed that the segments do not have any mutual energy of interaction with themselves or with the solvent surrounding it. Since no two segments can occupy the same space (due to their finite volumes), such configurations involving mutual overlap will be totally forbidden or excluded. Hence the actual chain will tend to be more extended than predicted by random flight statistics. In a thermodynamically good solvent, the energy of interaction for polymer-solvent is favourable and results in a larger dimension. Whereas in poor solvents, interaction between molecules of similar kind is preferred and the macromolecules will have configurations of smaller dimensions. In certain solvents at specific temperatures, the concentration of the macromolecule due to the unfavourable environment can compensate for its expansion due to the volume exclusion effects. The polymer molecule in such solvents (known as theta solvents) behaves as an idealized random flight chain. The temperature at which this

condition is satisfied is the Flory's theta temperature and the macromolecule is said to be in the unperturbed state. The unperturbed dimension is characteristic of the chemical constitution of the polymer and is also referred to as the short-range interference effect.

The expansion factors account for both the volume exclusion as well as environmental effects and are characterized in terms of the linear expansion coefficients (either α_r or α_s) defined as

$$\langle r^2 \rangle = \alpha_r^2 \langle r^2 \rangle_0 \quad \text{and} \quad \langle s^2 \rangle = \alpha_s^2 \langle s^2 \rangle_0$$

where $\langle r^2 \rangle_0$ and $\langle s^2 \rangle_0$ are the dimensions of the macromolecule in the absence of excluded volume effect. No simple relationship exists between α_r and α_s .

The first theoretical attempt to predict the dependence of the expansion coefficient on chain length was made by Flory⁷ with the help of a smoothed density model. In this model, polymer chain is regarded as a continuous cloud of unconnected segments whose concentration is spherically symmetrical. Considering the equilibrium expansion of macromolecule, the osmotic swelling force is in balance with the retractive force of the elastic chain. The model assumes a Gaussian distribution for the segment density. The equation for expansion factor obtained is

$$\alpha^5 - \alpha^3 = 2C_M \psi_1 (1 - \Theta/T) M^{1/2}$$

where ψ_1 is the entropy parameter and

$$C_M = \left(\frac{27}{2^{5/2} \pi^{3/2}} \right) \left(\frac{\bar{v}^2}{N_A V_1} \right) \left(\frac{M}{\langle r^2 \rangle_0} \right)^{3/2}$$

$\bar{v}$ and M are the partial specific volume and the molecular weight of the polymer, V_1 is the molar volume of the solvent and N_A is Avogadro number. At temperature $T = \Theta, \alpha = 1$; volume exclusion effects disappear and configurationally and thermodynamically the dissolved macromolecule is in the ideal state.

Zimm, Stockmayer, Fixman^{19,20} and others⁶ followed a rigorous statistical mechanical approach to the problem of excluded volume effects in real polymer molecules. In these theories, expansion of the polymer dimension due to excluded volume effect is treated in terms of an excluded volume parameter z ,

$$z = \left(\frac{3}{2\pi a^2} \right)^{3/2} \beta n^{1/2}$$

where n is the number of segments of effective bond length a and β , the binary cluster integral representing the effective volume excluded to one segment by the presence of the other, is given by

$$\beta = 4\pi \int_0^{\infty} [1 - \exp(-U(r)/kT)] r^2 \cdot dr$$

$U(r)$ is the interaction potential for a pair of segments at a distance ' r '.

There have been two approaches to the theory of the excluded volume effect; (i) deriving exact expression valid for small expansions based on the theory of imperfect gases and (ii) attempts to derive closed expression valid for intermittent and larger expansions which corresponds to the theory of condensed liquids at high densities.

Using the cluster expansion method, Fixman¹⁹ and Yamakawa-Tanaka²¹ derived

$$\alpha_r^2 = 1 + 1.333 z - 2.075 z^2 + 6.459 z^3 \dots\dots\dots$$

Pairwise decomposability of the interaction potential and its short range nature were assumed. The expression derived is valid for large chains at small expansions. Similarly, Yamakawa and Kurata²² obtained

$$\alpha_s^2 = 1 + 1.276 z - 2.082 z^2 + \dots\dots\dots$$

When z is zero, $\alpha = 1$ and the macromolecule is in the unperturbed state.

The above expressions for α_r and α_s are slowly convergent and are valid for low values of expansions very near the theta temperature. However, the series cannot describe the interesting good solvent regime.

In terms of the excluded volume parameter z , Flory's equation may be written as

$$\alpha^5 - \alpha^3 = 2.60 z$$

The expansion coefficient with reference to end-to-end distance and radius of gyration are not distinguished.

There have been several attempts⁶ to obtain closed expressions valid for realistic expansions. Various α - z relationships in the form

$$\lim_{z \rightarrow \infty} \alpha^y = \text{const. } z$$

have been obtained with exponent, ν ranging from 1 to 5. As pointed out by Fixman¹⁹, the assumption of a spherical segment distribution about the centre leads to a Flory's theory type fifth-power law and Flory's theory continues to be popular for describing the entire range of excluded volume. Stockmayer proposed²³ that the coefficient of z term in the Flory's fifth-power law may be substituted with the term valid for the exact first order perturbation theory. Fixman¹⁹, by a differential equation approach and applying an uniform expansion approximation, derived

$$\alpha_r^3 = 1 + 2z$$

$$\alpha_s^3 = 1 + 1.914z$$

Based on this third-power law the widely used Stockmayer-Fixman extrapolation method for obtaining the unperturbed dimensions from intrinsic viscosities in good solvent has been proposed. By a more elaborate treatment, Yamakawa-Tanaka have derived²¹

$$\alpha_r^2 = 0.572 + 0.428 (1 + 6.23z)^{1/2}$$

$$\alpha_s^2 = 0.541 + 0.459 (1 + 6.04z)^{0.46}$$

More recent calculations based on renormalization group theory²⁴ are in agreement with Yamakawa-Tanaka theory.

In the context of the perturbation theories, the average molecular dimensions of a random coil polymer are expressed in terms of n , a and β ,

the unperturbed dimension being given by na^2 and the increase in dimension by $n^2\beta$. For this reason, these are described as two parameter theories and other properties of dilute polymer solutions such as second-virial coefficients, intrinsic viscosities and critical phenomena may also be expressed in terms of these two parameters.

L.3 Expansion Coefficients of Polyelectrolytes

The electrostatic charges on the macroion lie in close vicinity of one another along the polymer backbone. Due to strong electrostatic repulsions, these cause the polyion to greatly expand. The increases in dimensions due to ionization are several fold higher than those that can be realised in non-ionic macromolecules by other means (like change of solvent, temperature, etc). Due to their polar nature the polyelectrolyte molecule in solution is likely to be in an expanded configuration as compared to its unperturbed state, even in the absence of dissociation. It is generally assumed that the expansions due to electrostatic and non-electrostatic interactions are additive¹. Several theoretical attempts aimed at predicting the electrostatic expansion with charge density have been published in literature^{1,3,4,5} over the years.

The theories of neutral macromolecules in solution have served as the model for the development of the macroion expansion theories. In many of the theories, the chain-like character is retained with the electrostatic charges suitably arranged either discretely or as a diffused cloud, the charge density and the dimension of the molecular model being identical with those of the real macroion. Macroion expansions have also been treated by the excluded volume method as in the case of neutral macromolecule.

Though several detailed theoretical treatments of macroion expansion have been published, they invariably ignore some of the complexities of the real systems. It is known that a polyion due to its high charge density, attracts a large proportion of the oppositely charged small ions to its vicinity³. The resulting charge density of the macroion is sizably lower than its value analytically calculated, due to 'ion binding' or 'ion pair' formation. Manning's theory²⁵ gave a quantitative interpretation of the phenomenon of ion binding. A critical charge density parameter (equal to the inverse of Bjerrum length) above which counter ion condensation occurs to keep the effective charge density below the critical value, was proposed. Most of the theories on macroion expansion do not take proper cognizance of ion binding and also suffer from idealized molecular models. The theories are briefly enumerated below.

In one of the earliest approaches to the problem of electrostatic expansion, Kuhn, Kunzle and Katchalsky considered²⁶ the equivalent chain model with electrostatic charges located at the junction points. They assumed Gaussian density distribution for the hypothetical equivalent chain. The electrostatic free energy change was calculated for the case of the macroion free of counter ions. The equilibrium value of the most probable end-to-end distance was evaluated by the free energy balance between the gain in entropy due to increase in the number of accessible conformation and the gain in energy due to polyion charges brought closer to each other. The predicted expansions are too high due to the neglect of the presence of the counter ions in the vicinity of macroions.

Katchalsky and Lifson²⁷ used the equivalent chain model with the charges located at the centre of the chain segments. The charges

were allowed to interact via screened Debye-Huckel potential and the electrostatic expansion was obtained from the electrostatic free energy. Rice and Harris²⁸ took into consideration the changes in the average angle between adjacent segments brought about by the presence of electrostatic charges, the charges being located at the centre of the chain elements. They argued that a lower value of the effective dielectric constant should be used due to the hydrocarbon nature of the backbone. In the expression thus obtained the dielectric constant is an adjustable parameter.

In another approach, Baily²⁹ modified the self consistent field formalism by assuming screened coulombic interactions between charges localized at the segment joints of the equivalent chain and the counter ion binding was taken into consideration.

In the continuous charge distribution model, the polymer molecule is considered^{3,5} to be a spherically symmetrical charged cloud. The polymer expands as a result of the electrostatic repulsion of such cloud and modify the end-to-end distribution function. The hydrodynamic radius, R_s of the charged sphere and the total concentration of backbone charges are considered equivalent to that of the real polymer chain. In the presence of an excess simple electrolyte, an equation for the electrostatic potential and a suitable solution of the Poisson-Boltzmann equation can be obtained by making use of the charge density at any point.

Hermans and Overbeek³⁰ obtained a solution for the Poisson-Boltzmann equation by applying the Debye-Huckel approximation and obtained an approximate expression for the average repulsion energy.

They derived an expression in terms of the expansion factor,

$$\alpha_e^5 - \alpha_e^3 = 3\gamma^2/8(V_s)_0 C_s$$

where γ is the total charge per polymer molecule, V_s is the volume of the equivalent sphere and C_s is the concentration of the mobile electrolyte. The disadvantage of the method is that the Debye-Huckel approximation is valid only when the potentials within the charged spheres are low.

Assuming Donnan electroneutrality within the polymer coil, Lifson³¹ was able to derive an expression, which at sufficient added electrolyte concentration, becomes identical to that obtained by Hermans and Overbeek.

In an alternative approach, also based on the continuous charged sphere model, Flory³² evaluated the free energy of formation of the charged sphere as the sum of two terms : the free energy difference for the solvent molecules and the mobile small ions inside and outside the sphere (an osmotic term), and the excess free energy arising from the mixing of solvent and polyion segments (as in the case of non-ionic polymers). The sum of the ionic and non-ionic free energies is calculated and the expansive force is equated to the elastic retractive force. Assuming a Gaussian charge density distribution, Flory obtained an expression in terms of the expansion factor α ,

$$\alpha_e^5 - \alpha_e^3 = 2C_M (1 - \Theta/T) M^{1/2} + 2(C_1/C_s) M^{1/2}$$

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where C_M and C_1 are constants for any given polymer-solvent system.

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Ptitsyn, Kurata and Alexandrowicz made use of a modified approach of the excluded volume effect for the uncharged polymers in their theoretical treatments to describe the expansion of a polyion in solution. Kurata³³ obtained an expression for polyelectrolyte expansion employing an equivalent ellipsoid model. The Donnan assumption for electroneutrality was applied in solving the Poisson-Boltzmann equation and the charge distribution along each axis of the ellipsoid was treated as Gaussian.

In Alexandrowicz theory³⁴, the model is depicted as a coil in which the polymer filament is covered by a sheath from which other portions of the coil are excluded. The excluded volume is identified as the co-axial shell volume surrounding the polyelectrolyte segment and a general expression for expansion results for all but extremely low ionic strengths.

Kurata³⁵ and independently Alexandrowicz³⁶ provided another expression, in terms of excluded volume which employs an equivalent Gaussian chain. A similar general equation was also developed by Ptitsyn³⁷.

The polymer model used by Fixman³⁸ is the so called 'fuzzy sphere' model which superimposes a continuous distribution of polymer segments on a background cloud of charges. The assumption is that the segments in the spherical interior of the polyelectrolyte do not contribute to the expansion. The expansion is mainly due to the repulsion between segments outside and inside the background cloud.

Recently the model of worm-like chain has been extended³⁹ to polyelectrolytes. The persistence length of the polyelectrolyte has been treated as the sum of the persistence lengths due to electrostatic and non-electrostatic interactions. This approach is rather attractive as

there is experimental evidence that the unperturbed dimension of the polyelectrolyte is greatly affected by ionization⁴ (generally increases with ionization).

The Electrostatic Excluded Volume

The configurational properties of neutral polymers in solution have been developed by the use of excluded volume approach. The expansion is caused by the repulsive pair potential of the mean force between two remotely connected segments. The forces responsible for the expansion in macroion is repulsive electrostatic potential of the charges along the polymer backbone. The expansion of the macromolecule in concept is the same whether it arises from electrostatic or other interactions. Thus excluded volume approach can be used to describe the expansion of polyelectrolyte molecule in solution. This approach, to some extent overcomes the difficulties associated in evaluating ionic interactions.

Interactions causing expansions in neutral polymers are essentially short-range in nature and justifies the implicit assumption of the short-range nature of the interaction potential in the excluded volume theories of polymer solutions. In contrast, the electrostatic interactions are effective over sizable distances. It is therefore difficult to comprehend the extension of the excluded volume theories to macroion expansions. Probably in the presence of sufficient concentration of the added simple electrolyte, the short-range nature of the screened electrostatic interactions may be applicable and the excluded volume approach to macroion expansions may be justified.

Nagasawa⁹ first pointed out that the electrostatic expansion

coefficient obtained by various theoretical calculations can be expressed in terms of an 'electrostatic excluded volume parameter'. A more detailed account is given by Eisenberg⁵.

The excluded volume parameter used in the theory of polymer solutions is given by

$$z = \left(\frac{3}{2} \right)^{3/2} m_s^{-2} \left(\frac{M}{\bar{r}_0^2} \right)^{3/2} \beta M^{1/2}$$

where m_s is the molecular weight of the statistical segment, $\bar{r}_0^2$ is the unperturbed mean-square end-to-end distance and β is the excluded volume per segment. The excluded volume per segment is given by

$$\beta = 4 \pi \int_0^{\infty} [1 - \exp(-U(r)/kT)] r^2 dr$$

where $U(r)$ is the interaction potential for a pair of segments at a distance 'r'. β has the dimension of the volume. Replacing β by $10^3 i^2 / 2 N_A c_s$ (where i , is the degree of ionization; c_s , the concentration of the added salt and N_A , the Avogadro number) in the expression for z , the electrostatic excluded volume parameter z_{el} is obtained as,

$$z_{el} = (3/2)^{3/2} m_s^{-2} (M/\bar{r}_0^2)^{3/2} (10^3 i^2)/(2N_A c_s) M^{1/2}$$

The replaced value for β , $(10^3 i^2)/(2N_A c_s)$ has also the dimension of the volume.

The expansion coefficient according to various excluded volume

theories of neutral polymer can be expressed⁶ as

$$\alpha^y \propto z$$

Similarly, the final expression obtained in most of the macroion expansion theories can be expressed^{4,5} as

$$\alpha_e^y \propto z_{el}$$

The expression derived by Fixman for the polyelectrolyte expansion cannot be expressed in terms of z_{el} . However, by substituting

$$\left(\frac{1}{3} \right)^{3/2} \quad \left(\frac{i \epsilon_o}{\epsilon} \right) \quad \left(\frac{\bar{r}_o^2}{Nk} \right)$$

for β in the equation for z , the final equation can be given in terms of z'_{el} . The substituted term has also the dimension of volume.

The functional dependence of the electrostatic expansion coefficient obtained by different polyelectrolyte expansion theories are listed below.

$$(i) \quad \text{Katchalsky-Lifson}^{27} \quad \alpha_e - \frac{1}{\alpha_e} = 1.77 z_{el}$$

$$(ii) \quad \text{Kurata}^{33} \quad \alpha_e^3 - 1 \simeq 2 z_{el}$$

$$(iii) \quad \text{Ptitsyn}^{37} \quad \alpha_e^2 = (1/4.68)[3.68 + (1 + 9.36z_{el})^{2/3}]$$

- (iv) Alexandrowicz $\alpha_e^2 = 1.7(z_{el})^{1/2} + 0.35$ for $\alpha_e^2 \geq 2$
- (v) Hermans-Overbeek³⁰ $\alpha_e^5 - \alpha_e^3 = 7.0 z_{el}$
- (vi) Fixman³⁸ $\alpha_e^3 - 1 = 2 z_{el}'$
- (vii) Flory³² $\alpha_e^5 - \alpha_e^3 = 2.60 z_{el}$
- (viii) Odijk-Houwaart³⁹ $\alpha_{s,e}^2 = 0.541 + 0.459(1 + 6.04 z_{el})^{0.46}$

1.4 Light Scattering From Dilute Polymer Solutions

With all the complexity and time required for the use of light scattering technique, it remains one of the most useful absolute methods for the determination of molecular weights of macromolecules including polyelectrolytes and biological macromolecules. The dimension of the dissolved macromolecule as well as thermodynamic interaction parameter are also determined from light scattering measurements in solution. The development of the theory and practice of light scattering is due to Debye⁴⁰, Zimm^{41,42} and others. Many authors⁴³ have reviewed the application of light scattering to macromolecules including macroions.

When a particle is exposed to an electromagnetic field, an oscillating dipole is induced in it. This oscillating dipole itself is a source of secondary electromagnetic radiation known as scattered radiation. It was Rayleigh who applied the classical electromagnetic theory to the scattering of light by small isotropic particles. For incident unpolarized light of intensity I_0 , the light scattered from 'n' particles contained

in unit volume is given by

$$\frac{i_{\Theta} r^2}{I_o} = \frac{n^2 \lambda_o^4 \alpha^2}{\lambda_o^4} (1 + \cos^2 \Theta)$$

where i_{Θ} is the intensity of the scattered light at a distance r and at angle Θ , λ_o is the wave length of the incident light and α is the polarizability of the particle.

When a solute is dissolved in a solvent, the difference in polarizability is related to the change in refractive indices. Introducing this relationship for polarizability in the above equation, the expression obtained is

$$\frac{i_{\Theta}}{I_o} = n \frac{2 \lambda_o^2 (1 + \cos^2 \Theta)}{N_A \lambda_o^4 r^2} n_o^2 \left(\frac{dn}{dc} \right)^2 M^2$$

where n_o is the refractive index of the solvent, (dn/dc) is the refractive index increment and N_A the Avogadro number. Assuming that the total intensity of the light scattered is the sum of the contributions from the individual particles and with $n = N_A c/M$ the equation becomes

$$\frac{i_{\Theta}}{I_o} = \frac{2 \lambda_o^2 (1 + \cos^2 \Theta)}{N_A \lambda_o^4 r^2} n_o^2 \left(\frac{dn}{dc} \right)^2 Mc$$

This relationship is the basis for the determination of molecular weights from light scattering measurements. The quantity determined in the light scattering experiment is the Rayleigh ratio,

$$R_{\Theta} = i_{\Theta} r^2 / I_o (1 + \cos^2 \Theta)$$

which is independent of the scattering angle for very small particles. The final expression is

$$\frac{Kc}{R_{\Theta}} = \frac{1}{M}$$

In the above relationship K is an optical constant given by

$$K = \frac{2\pi^2 n_o^2 (dn/dc)^2}{N_A \lambda_o^4}$$

Smoluchowski⁴⁴ and Einstein⁴⁵ extended the treatment to the light scattered from solutions at finite concentrations. Scattering in pure liquids is due to the local thermal fluctuations which leads to inhomogeneity in structure. By dissolving a solute in pure liquids, fluctuations in concentrations lead to additional scattering. Though small, this increase in scattering is measurable and is related to the concentration and molecular weight of the solute. It is this relationship that forms the basis for the use of light scattering technique for dilute polymer solutions. By considering the dependence of the chemical potential of the solvent on the concentration of the dissolved solute, the excess chemical potential for low concentration solutions can be expressed in the form of a power series in concentration of the solute.

$$\frac{Kc}{R_{\Theta}} = \frac{1}{M} + 2 A_2 c + 3 A_3 c^2 + \dots$$

A_2 and A_3 are known as the second and third osmotic-virial coefficients.

For poly disperse polymers,

$$\frac{Kc}{R_{\Theta}} = \frac{1}{\bar{M}_w} + 2A_2c + 3A_3c^2 + \dots$$

$\bar{M}_w$ is the weight-average molecular weight defined as

$$\bar{M}_w = \sum M_i N_i^2 / \sum M_i N_i$$

When the dissolved particle dimensions are comparable to that of the wave length of the incident light, the scattering envelope no more remains symmetrical and differs from the expected as a consequence of the interference effects. As the distance between two scattering centres on the same particle increases, destructive interference increases. The scattering intensity is unaffected when the viewing angle is zero and decreases as the angle changes from forward to backward direction. This effect due to the large size of the particle can be described by the function $P(\Theta)$ which will also depend on the shape of the scattering particle;

$$P(\Theta) = \frac{i_s(\Theta) \text{ with interference}}{i_s(\Theta) \text{ without interference}} = \frac{R_{\Theta}}{R_0}$$

$P(\Theta)$ becomes independent of the particle shape as Θ , the angle of observation, approaches zero and under this limiting condition

$$\lim_{\Theta \rightarrow 0} \frac{1}{P(\Theta)} = 1 + \frac{16\pi^2}{3\lambda^2} \langle s^2 \rangle \sin^2 \Theta/2$$

which gives a measure of the radius of gyration of the scattering particle. Hence introducing the particle scattering factor $1/P(\Theta)$, the equation for light scattering for monodisperse polymers becomes,

$$Kc/R_{\Theta} = 1/M P(\Theta) + 2A_2c + 3A_3c^2 + \dots$$

and

$$\lim_{c \rightarrow 0} [Kc/R_{\Theta}] = \frac{1}{M} + \frac{16\pi^2}{3\lambda^2 M} \langle s^2 \rangle \sin^2 \Theta/2$$

where $\langle s^2 \rangle$ is the mean-square radius of gyration and λ is the wave length of the light in solution. For polydispersed polymers, the dimensions obtained from light scattering is the z-average mean-square radius of gyration.

Theoretical treatments based on excluded volume theories have also been extended⁶ to the osmotic second virial coefficient A_2 , given in the above equation. The binary cluster integral is related to the thermodynamic parameters by,

$$\beta = 2 V_0^{-1} V_s^2 \psi (1 - \Theta/T)$$

where V_s is the volume of the segment; V_0 is the molar volume of the solvent; ψ is the entropy parameter and Θ is the theta temperature. The osmotic second-virial coefficient A_2 , in the context of perturbation theories, is related to the excluded volume parameter z , as;

$$A_2 = (N_A n^2 \beta / 2M^2) \text{ ho } (z)$$

where n is the number of segments, N_A is the Avogadro number, M is the molecular weight of the solute, β is the binary cluster integral (discussed in section I.2) and $h(z)$ is a function of z , the excluded volume parameter. For small values of z , $h(z)$ may be expressed as,

$$h(z) = 1 - C_1 z + C_2 z^2 - \dots$$

The constant terms C_1 and C_2 have been derived by Zimm⁴², Albrecht⁴⁶ and others.

For larger values of z , $h(z)$ may be replaced by $h(z)$ in the above equation. The behaviour of $h(z)$ over a wide range of z has been examined by Flory-Krigbaum⁴⁷, Orofino-Flory⁴⁸ and others⁴⁹ using a smoothed density model. The expression obtained is

$$h(z) = 1 - C_1 z + C_2 z^2 - \dots$$

where $h(z) = h_0(z)$ with $z = z/(\alpha^*)^3$. The expansion factor α^* is due to the expansion of one polymer molecule in contact with another. As $h(z)$ is a decreasing function of z , the equation correctly predicts the decrease in A_2 with increasing molecular weight. Similarly, at $T = \Theta$, both β and z are zero and for the theta temperature, zero value of A_2 is predicted.

From the above equations, it may be shown that

$$A_2 = \frac{4\pi^{3/2} N_A \langle s^2 \rangle^{3/2}}{M^2} \Psi$$

where $\Psi = \bar{z} h(\bar{z})$

Ψ approaches a constant value as $\bar{z}$ tends to infinity and A_2 becomes proportional to $\frac{\langle s^2 \rangle^{3/2}}{M^2}$ in the limit of $z = \infty$. Therefore polymer chains in very good solvents are noninterpenetrating, whereas they are completely interpenetratable at theta temperature. Hence, Ψ is sometimes called the penetration factor⁵⁰ or penetration function²⁴.

The second virial coefficients of linear polyelectrolytes have been investigated⁴ in some detail. Treating the polyelectrolyte as a spherically colloidal particle, the predicted second virial coefficient for a polyion containing added salt of concentration c_s and Z charges is given by

$$A_2^0 = 10^3 Z^2 / 4M^2 c_s$$

This expression is called the ideal Donnan term. Several investigators have tried to improve the theory by taking the chain like character of the polyion in to consideration. The expression obtained has the form

$$A_2 = A_2^0 T_2'(\alpha)$$

A_2^0 is the ideal Donnan term and $T_2'(\alpha)$, due to the chain like character of the polyion, is a function of the expansion coefficient α . Nagasawa and Takahashi propose⁴ that an equation of the form $A_2 = A_2^0 T_1' T_2'(\alpha)$ is valid for most of the polyelectrolyte systems. Here A_2^0 represents the salt concentration dependence of A_2 , T_1' a constant nearly independent of the molecular weight and ionic strength but depends on the charge density of the polyion and $T_2'(\alpha)$ the correction factor for the chain like character of the polyion and a function of expansion coefficient.

The determination of molecular weight, osmotic second virial coefficient and the radius of gyration from light scattering technique involves measurements and the extrapolation of the measured scattering intensities to zero concentration and zero angle. This is achieved more conveniently making use of Zimm⁴¹ method. The excess scattering intensities due to the dissolved macromolecule is measured at varying concentrations of the solution and at different scattering angles. Kc/R_θ is plotted against $\sin^2 \Theta/2 + kc$ where Θ is the scattering angle and k is a suitably chosen constant to give a satisfactory spread of the data. The plot obtained is in the form of a grid and the data are simultaneously extrapolated to zero scattering angle and zero concentration. The zero angle and zero concentration lines are further extrapolated to a common intercept whose inverse gives the weight-average molecular weight. The slope of the zero angle line gives the osmotic second-virial coefficient. From the limiting slope of the zero concentration line and the intercept, the mean-square radius of gyration, $\langle s^2 \rangle$ is calculated.

The light scattering method so far discussed is applicable only to dilute solutions consisting of polymers dissolved in a single solvent. When systems such as those consisting of a mixture of two solvents and polyelectrolytes in presence of added salt, etc. are considered, the equations derived for the binary systems are not valid. This is because, the addition of the third component introduces microinhomogeneity in refractive indices within the macromolecular domain and outside. In the mixed solvent system, it is due to the preferential adsorption of one of the solvent component on to the polymer, whereas in the polyelectrolyte-water-salt solution it is due to the differences in chemical potential of

the mobile ions in the macroion domain and macroion-free domain.

The theory of light scattering in multicomponent systems has been developed by Vrij-Overbeek⁵¹, Casassa-Eisenberg⁵² and others^{53,54}. These are based on the theory of light scattering from linear polymers in mixed solvents which was first investigated by Ewart et al⁵⁵. It can be shown that the excess scattering at a concentration c for a polymer in a mixed solvent is given by

$$\lim_{c \rightarrow 0} \frac{K^* c}{R_\Theta} = \frac{1}{\bar{M}_w P(\Theta)}$$

$$K^* = \frac{2\pi^2 n_o^2}{N_A \lambda_o^4} \left[\frac{dn}{dc} + \alpha_a \frac{dn}{d\phi} \right]$$

where $(dn/d\phi)$ is the variation of the refractive index of the solution with the composition of the solvent and α_a the variation of the composition of the solvent surrounding the polymer due to preferential adsorption. When the refractive indices of the solvents in the mixture are identical $(dn/d\phi) = 0$, and the expression for K^* reduces to that applicable to the solution of the polymer in a single solvent.

The theoretical treatment applicable for mixed solvents has been extended⁵¹⁻⁵⁴ to the multicomponent system consisting of polyelectrolyte-water-added salt. The expression obtained for the optical constant K^* is given as

$$K^* = \frac{2\pi^2 n_o^2}{N_A \lambda_o^4} \left[\left(\frac{\partial n}{\partial c} \right)_{c_s, p} + \left(\frac{\partial n}{\partial c_s} \right)_{c, p} \left(\frac{\partial c_s}{\partial c} \right)_{p, s} \right]$$

where $(\partial n / \partial c)_{c_s, p}$ and $(\partial n / \partial c'_s)_{c, p}$ are the values of the refractive index increments with c , c'_s representing the concentration (g/mL) of the dissolved polyelectrolyte and the added salt respectively, and p the pressure; $(\partial c'_s / \partial c)_{\mu_s}$ is the variation of the concentration of the added salt with the concentration of the polymer at constant chemical potential of the added salt. If the compressibility of the partial molar volume is neglected,

$$K^* = \frac{2 \pi^2 n_o^2}{N_A \lambda_o^4} \left[\left(\frac{dn}{dc} \right)_{\mu_s} \right]^2$$

where $(dn/dc)_{\mu_s}$ is the specific refractive index increment of the polymer in the salt solution at constant chemical potential of the added salt. Hence the molecular weights and osmotic second-virial coefficients can be evaluated⁴ for the polyelectrolytes in the aqueous salt solutions by using the values of the specific refractive index increments determined for the solutions in dialysis equilibrium with the salt solution used as solvent.

Though by the use of the values of (dn/dc) for the dialysed solutions the calculation of the weight-averaged molecular weight and osmotic second-virial coefficient is theoretically sound, the calculation of the dimension of the polyelectrolyte from the light scattering measurements is some what uncertain. The study of counterion distribution within the macroion domain and its effects on the dimension of polyelectrolyte has not been carried out so far. It is generally believed that the errors are not very serious. The dimension of the polyelectrolyte obtained from light scattering, however, may be in considerable error.

1.5 Intrinsic Viscosities of Polymers

The ability of a dissolved macromolecule to greatly alter the flow characteristics for the solution was well recognized early. The fact that this effect is characteristic of the chemical constitution, molecular weight of the dissolved macromolecule and its concentration has been made use of for the determination of molecular weights and dimensions of the dissolved solute macromolecules by solution viscosity measurements^{7,56}. The equipmental set up is rather simple, requires less skill and relatively high accuracy is obtained.

The quantity of interest is the intrinsic viscosity $[\eta]$, defined as

$$[\eta_{sp}/c]_{c \rightarrow 0} \text{ or } [\ln \eta_r/c]_{c \rightarrow 0}$$

where η_r is the relative viscosity with respect to solvent and $\eta_{sp} = \eta_r - 1$. The concentration dependence of dilute solution viscosities of macromolecules follow Huggins' or Kraemer's equation

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \text{ or}$$

$$\ln \eta_r/c = [\eta] - k'' [\eta]^2 c$$

where k' and k'' are the slope constants which are complex functions of thermodynamic and hydrodynamic solute-solute and solute-solvent interactions. Intrinsic viscosities are obtained by the use of one of the above relationships.

Intrinsic viscosities are related to molecular weights by the Mark-Houwink-Kuhn (MHK) equation

$$[\eta] = KM^a$$

The values of exponent 'a' for flexible linear macromolecules lie in the range $0.5 < a < 0.8$. Extensive data exist⁵⁷ for the values of 'K' and 'a' for various polymer-solvent systems at different temperatures.

Theoretical consideration of the intrinsic viscosity of a flexible macromolecule involves⁶ the consideration of the motion of the macromolecule in a viscous medium where the viscous forces and the Brownian motion are simultaneously operative. The velocity field in the fluid and its flow is perturbed by the hydrodynamic resistance offered by the polymer segments. The change in flow is the sum of the perturbations due to each of the segment and the perturbations are cooperative in that the effect by one segment is felt by the others also. The most commonly used molecular model is the 'pearl string model'. The elements or the segments are considered as the centres of the hydrodynamic resistance and the connecting links are considered to offer no resistance. Kirkwood and Riseman⁵⁸ obtained an approximate analytical solution of the Navier-Stokes equation by the Fourier series method. Intrinsic viscosity was correlated to the frictional coefficient of the segment, its molecular weight and the number of segments. The final expression obtained is

$$[\eta] = \Phi_0 \langle r^2 \rangle_0^{3/2} / M \quad \text{where} \quad \Phi_0 = (\pi/6)^{3/2} N_A [Xf(X)]$$

$\chi F(X)$ is a function dependent on the frictional coefficient of the segment, its molecular weight and the number of segments. The asymptotic value of Φ_0 obtained at $X = \infty$ was 2.87×10^{21} .

Flory⁵⁹ proposed that the effect of the excluded volume on the dimensions of the macromolecules may be incorporated to the above equation

$$[\eta] = \Phi \langle r^2 \rangle^{3/2} / M = \Phi [\langle r^2 \rangle_0 / M]^{3/2} M^{1/2} \alpha^3$$

where $\langle r^2 \rangle_0$ is the root-mean-square end-to-end distance and α is the linear expansion coefficient. At $T = \Theta$, $\alpha = 1$ and the excluded volume effects are absent. Intrinsic viscosity at theta temperature varies as the square-root of the molecular weight. The values of MHK exponent 'a' > 0.5 obtained for linear polymers in good solvent are accounted to be due to the molecular weight dependence of the linear expansion coefficient α .

The relationship given above, based on spherical segment density distribution, shows that the expansion coefficient is related to intrinsic viscosities as $[\eta]/[\eta]_\Theta = \alpha^3$. Other investigators have proposed different functional relationship taking the differences in the linear expansion coefficient and the hydrodynamic expansion coefficient in to consideration. For example, Kurata and Yamakawa⁶⁰ proposed

$$[\eta]/[\eta]_\Theta = \alpha_s^{2.43}$$

The asymptotic value of Φ_0 , for the unperturbed random-coil macromolecule obtained by Kirkwood-Riseman⁵⁸, Auer-Gardner⁶¹, Zimm⁶²

and others are in the range of $(2.82 \text{ to } 2.87) \times 10^{21}$. Theoretical calculations of Φ for the polymer coil with excluded volume by Kurata-Yamakawa,⁶⁰ Ptitsyn-Eizner⁶³ and Fixman⁶⁴ show that Φ decreases with increasing solvent power. The experimental values obtained for Φ for nonionic polymers in good solvents⁷ are in the range of $(2.1 \pm 0.2) \times 10^{21}$. However, low values have been reported for solutions of copolymers and polyelectrolytes^{4,65}.

It is not always possible to select a suitable solvent with theta temperature in a convenient range owing to experimental difficulties. In such cases several extrapolation methods which utilize the viscosity data in thermodynamically good solvents are suggested to estimate the characteristic short-range interference effects. The Stockmayer-Fixman⁶⁶ equation

$$[\eta]/M^{1/2} = K_0 + 0.51 \Phi B M^{1/2}$$

based on Fixman's third power α - z relationship¹⁹ is generally in agreement⁴ with experiment. Here $K_0 = \Phi [\langle r^2 \rangle_0 / M]^{3/2}$ and B is the polymer-solvent interaction parameter related to its second-virial coefficient.

The viscosity behaviour of polyelectrolyte solution have additional complications^{3-5,7}. In the absence of sufficient quantity of added salts, the dilution of a polyelectrolyte solution brings about an increase in the value of their reduced viscosity due to the progressive migration of the counterions from within the macromolecular domain to its outside. With sufficient concentration of the added electrolyte, reduced viscosity

decreases linearly with concentration and obeys Huggins' relationship as in the case of nonionic polymer solutions. In the absence of sufficient concentration of added salt, the viscosity measurements may be carried out by diluting the solutions in such a way that the ionic atmosphere surrounding the polyion is unchanged during dilution (isoionic dilution). In the absence of an added electrolyte or in the presence of insufficient quantities of added salt, the viscosities of the aqueous polyelectrolyte solutions follow the Fuoss⁶⁷ empirical relationship,

$$\eta_{sp}/c = A/(1 + B\sqrt{c})$$

The intrinsic viscosities of polyelectrolyte solutions decrease with increase in concentrations of the added salt. Many investigators^{4,9,68} observed that intrinsic viscosity is inversely proportional to the square-root of the concentration of the added salt. The dependence of intrinsic viscosity on molecular weight is exactly similar to that of the nonionic polymers and satisfy MHK relationship^{3,5}. Theta temperatures have been determined for several polyelectrolytes and their intrinsic viscosities at theta temperature also vary as square-root of molecular weight^{3,5}. At relatively low values of expansion coefficients ($\alpha_{\eta}^2 < 2$), the Stockmayer-Fixman relation is found to be valid for polyelectrolyte solutions also⁴. However, at high degrees of ionization and low concentrations of added salt, polyelectrolyte solutions exhibit curvature in the Stockmayer-Fixman plots⁴. Generally, values of Flory viscosity constant Φ for polyelectrolytes are lower than the values reported for the neutral polymers⁴.

CHAPTER TWO

EXPERIMENTAL

2.1 Polymerization

2.1.1 Monomer purification

Acrylonitrile and monomer obtained from JCI Ltd., India, was purified by distilling under reduced nitrogen pressure. During the distillation, ferrous sulphate was added to decompose peroxides, and hydroquinone added to inhibit the polymerization. The column was packed with copper helices to ensure the complete oxidation of the hydroquinone during distillation. The fraction boiling at 74-76°C and 10-12 mm Hg was collected and stored in the dark under nitrogen in bottles.

2.1.2 Solvents

Water and 1,4-dioxane used as solvents for polymerization were purified as described below.⁶⁹

Laboratory distilled water (3 L) was refluxed over alk. KMnO₄ (2 g/l) for 15-12 h and distilled. The colourless colourless liquid (under reduced pressure) was collected and used.

1,4-Dioxane (Laboratory reagent grade, 50% Pure Chemicals Ltd., Bombay) was purified by the following method. 1,4-Dioxane (1 L) was refluxed with concentrated HCl (18 vol% aq. soln) (100 mL) for 6-12 h. The mixture was cooled and poured into 100 mL of water. The organic

II.1 Polymerization

II.1.a Monomer purification

Methacrylic acid monomer obtained from ICI Ltd., U.K., was purified by distilling under reduced nitrogen pressure. During the distillation ferrous sulphate was added to decompose peroxides, and monomethyl ether hydroquinone to inhibit the polymerization. The column was packed with copper helices to ensure the complete inhibition of the polymerization during distillation. The fraction boiling at 54-56°C and 11-12 m bar was collected and stored in the dark under nitrogen blanket.

II.1.b Solvents

Water and 1,4-dioxane used as solvents for polymerization were purified as described below⁶⁹.

Laboratory distilled water (5 L) was refluxed over alk. KMnO_4 (5 g) for 10-12 h and distilled. The constant boiling fraction (bp. 97.5-98°C ambient pressure) was collected and used.

1,4-Dioxane (Laboratory reagent grade, S.D. Fine Chemicals Ltd., Bombay) was purified by the following method. 1,4-Dioxane (1 L) was refluxed with concentrated HCl (14 mL) and water (100 mL) for 6-12 h.

A slow stream of nitrogen was simultaneously bubbled through it to remove the aldehyde formed. The solution was cooled and the acid was neutralized by adding KOH pellets till some pellets remained undissolved even after repeated shaking. The organic layer was separated and allowed to stand over KOH pellets for 24 h. The solvent thus freed from most of the residual water was refluxed over freshly cut sodium for about 10 h and fractionally distilled. The middle cut boiling at 99.5°C at ambient pressure was collected and stored over sodium in amber coloured bottles.

Methanol, acetone and diethyl ether used for the purification of the polymer and for polymer fractional precipitation were middle cut fractions of distilled commercial grade solvents.

II.1.c Polymerization procedure

Solution polymerization experiments were carried out at 65°C in water in the presence and absence of added salts and in 1,4-dioxane using potassium peroxodisulphate ($K_2S_2O_8$) as initiator. It was observed that the molecular weights and conversions obtained in aqueous solution were higher than those desired. In pure 1,4-dioxane, heterogeneous polymerization (with the polymer insoluble in reaction medium) and lower molecular weights than desired were obtained. Polymerizations were therefore carried out in mixtures of 1,4-dioxane/water as solvent and the composition of 1,4-dioxane/water mixture yielding polymer with desired molecular weight range was determined. Polymerizations in 1,4-dioxane/water mixtures showed very good reproducibility with respect to the conversion and molecular weight of the polymer. The polymer used in this investigation was prepared in 1,4-dioxane/water mixture (25/75, v/v) at 65°C using 0.2% (w/v) $K_2S_2O_8$ as initiator.

Freshly distilled methacrylic acid monomer (40 mL) 1,4-dioxane (100 mL) and water (280 mL) were taken in a 1 L round-bottomed flask mounted in a thermostatic water bath. Nitrogen freed from oxygen bubbled through the reaction mixture for 15 to 20 min. The temperature of the thermostatic bath was raised to $65 \pm 1^\circ\text{C}$ and the solution was gently stirred. When the reaction contents attained the set temperature, the polymerization reaction was initiated by introducing aqueous Na_2SO_3 solution (10 mL, 0.1 g in 50 mL) followed by $\text{K}_2\text{S}_2\text{O}_8$ solution (10 mL, 0.4 g in 50 mL). The addition of Na_2SO_3 was essentially aimed as an oxygen scavenger. The thickening of the reaction mixture was observed in about 5-10 min from the time of the addition of the initiator. The reaction was allowed to continue at constant temperature under a nitrogen blanket. The polymerization reaction was stopped after 3 h by cooling the flask and its contents in a bath of ice-water. The monomer-polymer conversion determined by bromate-bromide analysis⁷⁰ and gravimetrically from the final weight of the polymer was 75%.

II.1.d Purification of polymer

Polymethacrylic acid was isolated from the polymerization medium by precipitation. A mixture of acetone/diethyl ether (1:1, v/v) was found very efficient in precipitating the polymer completely. The polymer was once again dissolved in distilled water and reprecipitated to remove water soluble ionic impurities. Finally the polymer was totally freed of water by repeated dissolution in methanol and reprecipitation using diethyl ether as the nonsolvent. The polymer thus purified was dried for 4-6 h at 60°C under vacuum.

II.2 Fractionation

Polymethacrylic acid was fractionated by fractional precipitation technique using methanol as solvent and diethyl ether as non-solvent. Polymer solution (1%, w/v) was used and the low molecular weight tail in the precipitated fraction was separated by refractionation for the sake of achieving homogeneous molecular weight fraction. In fractional precipitation method the precipitated polymer, after the addition of the non-solvent, is usually redissolved in the solvent/non-solvent mixture by raising the temperature and subsequently equilibrated at the fractionation temperature to achieve efficient fractionation. The system, polymethacrylic acid-methanol-diethyl ether, is anomalous in that the solubility is lowered by increasing temperature. Hence, homogenizing the solution after the addition of diethyl ether was achieved by suitably lowering the temperature of the precipitation medium⁷¹. The detailed procedure of the fractional precipitation method employed is described below.

A dilute solution of polymethacrylic acid (20 g in 2 L methanol) was taken in a 5 L, three necked fractionation flask. The fractionation flask along with a glass stirrer and mercury seal (to prevent evaporation of the low volatile solvents) was placed in a thermostatic water bath adjusted to $25 \pm 0.02^\circ\text{C}$. Diethyl ether, the non-solvent used for precipitation, was added dropwise from a graduated dropping funnel to the well-stirred solution. On appearance of permanent turbidity (that did not disappear with agitation), a further aliquot of non-solvent was added until the solution turned sufficiently milky. The solution was then cooled till it was clear and allowed to come up gradually to the original set

thermostatic temperature with continuous agitation. Once the solution attained the fractionation temperature the stirrer and the dropping funnel were removed, stoppered and left undisturbed at constant temperature. After 15-18 h the precipitated polymer fraction was withdrawn in to a 100 mL round/bottomed flask through the stopcock at the bottom. The precipitated polymer was redissolved in methanol and subfractionated from a dilute solution (about 1%, w/v) by slow additions of diethyl ether to the constantly stirred solution. The supernatant layer in the subfractionation step was concentrated and added to the original solution before the isolation of the next fraction. The precipitate obtained from subfractionation was taken as the intended fraction. Fractionation was continued till about 80% of the polymer was recovered. Eight fractions varying in weight from 0.8 to 4.0 g were collected. The low molecular weight polymer remaining in the methanol/diethyl ether mixture after about 80% polymer recovery was discarded. The fractions were thoroughly washed with diethyl ether and dried in a vacuum oven under reduced pressure at 60°C, to constant weight (4-6 h).

II.3 Light Scattering Measurements

II.3.a Solvents for light scattering measurements

Solvents used for light scattering measurements were rigorously purified according to the following methods.

Laboratory distilled water, refluxed over alk. KMnO_4 and distilled, was subjected to two further slow distillations in an all glass assembly. The middle cut fraction collected was stored in stoppered flat-bottomed flasks.

1,4-Dioxane was purified as given in section II.2.a.

N,N-Dimethyl formamide (laboratory reagent grade, S.D. Fine Chemicals Ltd., Bombay) was left over anhydrous MgSO_4 for 10-12 h to remove water. Further, to eliminate the traces of water it was decanted and again stored overnight over P_2O_5 . It was then distilled over P_2O_5 under reduced pressure and the distillate was stored in dry condition in amber coloured bottles over molecular sieve ($4\text{\AA}^\circ$). The purified solvent was used over a period of 5-6 days, otherwise it was redistilled over P_2O_5 before use. The purity of the solvent checked by gas chromatography was better than 99.8%.

Methanol (C.P. grade) was distilled and the middle cut fraction was collected for further purification. About 50-75 mL methanol was taken in a 2 L round bottomed-flask along with 5 g of clean dry magnesium turnings and 0.5 g of resublimed iodine. A double surfaced condenser was fitted and the mixture warmed over a water-bath until the magnesium was converted into its methoxide. About 900 mL methanol was added to this and the mixture was boiled for 30 min under reflux. The product was then distilled and stored under dry conditions.

Benzene used as a secondary standard for calibration in the light scattering measurements was purified as follows. Benzene (L.R. grade) repeatedly washed with sulphuric acid, distilled water, dilute sodium carbonate solution and finally distilled water (in that order) was dried over anhydrous CaCl_2 . It was fractionally distilled and the middle cut fraction boiling at 77°C (ambient pressure) was used.

II.3.b Preparation of solutions

Polymer solutions used for physical measurements were prepared

less than 24 h before use. Accurately weighed polymer was allowed to swell in 5-10 mL solvent for about 10-12 h in 25 mL volumetric flask. The solution was gradually diluted with the solvent and homogenized simultaneously. The solution volume was made upto the graduation mark. Predetermined quantities of standard sodium hydroxide solution in finite concentration NaCl solution was added to the aqueous solution of polymethacrylic acid to achieve desired extents of neutralization before diluting to the graduation mark.

Dissolution of the unneutralized polymethacrylic acid in the DMF/1,4-dioxane mixture, used as the theta solvent, was found to be difficult and needed 3-4 days for obtaining homogeneous solution. Hence the polymer was dissolved first in DMF and requisite volume of 1,4-dioxane was added to achieve the desired DMF/1,4-dioxane ratio. The polymer solutions prepared in the mixture were cooled five degrees below the precipitation temperature and slowly warmed up to 27.1°C (experimental theta temperature). Homogeneous solutions were obtained by this method which remained stable up to 72 h. Dilutions of the solutions were carried out with the solvent of the same composition for achieving varying polymer concentration.

Weighed quantity (~20 g) of sodium hydroxide (B.D.H., A.R. grade) was dissolved in carbonate-free boiled distilled water, in a 500 mL volumetric flask, for preparing standard sodium hydroxide solutions. The solutions were standardised against potassium hydrogen phthalate using phenolphthalein as indicator.

Sodium chloride (B.D.H., A.R. grade) was dried in vacuum for 4-6 h at 80°C. Weighed quantity (29.22 ± 0.02 g) was transferred

to a 500 mL volumetric flask and dissolved by adding aliquots of carbonate-free freshly boiled distilled water. The flask was shaken intermittently and volume was made up to the graduation mark. Pipetted quantities from this stock solution were diluted in volumetric flasks to prepare differing salt concentration solutions for dilutions. Predetermined quantities of standard NaOH and NaCl solutions were pipetted, mixed and diluted with distilled water in 100 mL volumetric flasks. Standard sodium hydroxide solutions with finite molarity NaCl concentrations were prepared in this method. These solutions were employed for neutralizing polymethacrylic acid solutions to varying extents at finite concentrations of added salt.

Potassium chloride solutions were used for calibrating differential refractometer. KCl was dried in vacuum oven for 4 to 6 h at 80°C. Solutions were prepared by dissolving accurately weighed KCl in distilled water in the volumetric flasks and making up the volumes.

11.3.c Instrument and measurements

The instrument used was a 3000-series Brice-Phoenix light scattering photometer located in a low humidity dark room. It consists of a mercury vapour lamp source, interference filters for isolating the monochromatic light of wave length 436 nm and 546 nm, a cell table and a photomultiplier detector which may be rotated about an axis passing through the centre of the cell table. The photomultiplier output is fed to a digimeter. The greatly varying intensities of the incident and the scattered light are monitored by the use of working standard and neutral filters which may be imposed in or withdrawn from the path of the incident light.

The photometer was calibrated by determining the transmission values of the neutral filters and the working standard constant 'a' with reference to the calibrated opal reference standard, as recommended by the manufacturer. The calibration was checked by using benzene as a secondary standard assuming a value of $48.4 \times 10^{-6} \text{ cm}^{-1}$ for the Rayleigh's scattering ratio R_{90} for benzene⁷².

All the solvents (except DMF) were clarified by filtration through $0.45 \mu\text{m}$ Millipore filters using a Water's solvent clarification kit. DMF was clarified by filtration through candle type sintered disc filters. It was observed that solution clarification by filtration through selected sintered disc filters and Millipore filters yielded almost identical results. Filtration through sintered disc was opted in view that the larger volume of the solution needed to be filtered. Filtered solvents had dissymmetries in the range $1.02 < Z < 1.05$.

The cylindrical light scattering cell was scrubbed with a wet cotton swab dipped in nonionic detergent and washed under running water for 30 to 45 min, rinsed several times with distilled water followed by filtered water. The cell was kept inverted for drying. The outside cell surface was rubbed with a soft tissue paper to remove adhering specks of dust.

Filtered solvent (30 mL) was pipetted in to the cell and the cell was placed on the cell table. The scattering intensities at various pre-selected angles in the range 35 to 135° were determined after allowing 10 to 15 min for thermal equilibrium. Finite aliquots of filtered solutions were added into the cell, gently stirred with a clean glass rod and the scattering intensities at different angles were noted. Further aliquots of filtered solution were added and the procedure was repeated for five to

seven concentration solutions in the concentration range $0.01 < c < 0.15 \text{ g dL}^{-1}$.

Experimentally determined digimeter readings along with neutral filters and filter combination transmission values, working standard constant, scattering angle, correction factor for residual refraction, etc. were input to a desk model Hewlett Packard calculator (model 9830 A) and the values of c/R_Θ at various scattering angles and concentrations of the solutions were calculated using a Basic Computer Program. Zimm plots were constructed by plotting c/R_Θ against $\sin^2(\Theta/2) + kc$ where k was an arbitrarily chosen constant to give a good spread of the experimental data. The data at constant angles and constant concentrations were extrapolated to zero concentrations and zero angles, respectively. The two lines obtained from these extrapolated points were further extrapolated to a common intercept. The weight-average molecular weight was obtained from the inverse of the common intercept. The dimension of the polymer molecule and the osmotic second-virial coefficient were calculated from the initial slopes of the zero concentration line and zero angle line, respectively.

11.3.d Refractive index increment measurements

The specific refractive index increment measurements were carried out using a Brice-Phoenix 2000-V series differential refractometer. The refractometer consists of a lamp housing equipped with a mercury vapour lamp and a filter turret for isolating monochromatic light of wave lengths 436 nm and 546 nm, a jacketed cell housing and telescope fitted with a micrometer eyepiece. The refractometer cell used had 1.5 cm path length with a thin diagonal glass partition which divides the

cell in to two equal compartments, one for solvent and the other for solution, and ground stoppers for preventing evaporation of the volatile solvents. The difference in refractive indices of the two liquids on either side of the partition in the cell causes deviation of the light beam emerging from the differential refractometer cell. This deviation is proportional to the difference in refractive indices and measured with the help of the micrometer which was calibrated using liquids of known refractive indices. Temperature of the measurements can be controlled by circulating constant temperature liquid through the cell-jacket.

The cell was repeatedly washed with solvent using a syringe. Solvent (1 mL) was introduced on either sides of the partition in the cell. Tap water was circulated through the cell-jacket. After 15 min, the centre of the slit image was brought to coincide with the cross wires in the eyepiece by moving the micrometer screw. The micrometer reading was recorded. The cell was rotated through 180° and again the centre of the slit image was brought to coincide with the cross wire. With both the compartments filled with the solvent the micrometer readings were almost identical. The solvent in the solution compartment was withdrawn and rinsed with the polymer solution of known concentration, two-three times. The solution compartment was filled with the solution and stoppered. After 15 min, the micrometer readings were taken both in the original position of the cell and by rotating the cell through 180° . The difference in these readings, corrected for solvent readings, is proportional to the difference in the refractive indices of the solution and solvent.

The solutions of polymethacrylic acid, neutralized to different extents, were dialysed using the spectrapore membrane tubing No.3787-D32,

7/8" dia (M/s. Arthur H. Thomas and Co., USA) dialysis bags in the following manner. Polymer solution (10 mL) was placed in a dialysis bag of 10" length and the bag was sealed. The dialysis bag containing the polymer solution was put into a long glass cylinder, containing the solvent. The solvent was gently stirred occasionally. The solvent was replaced every 12 h with a fresh lot and the dialysis was continued for 72 h. The dialysed solution in the bag was withdrawn with a syringe and the (dn/dc) was measured against the dialysate in the solvent compartment.

Potassium chloride solutions of known refractive indices were used to calibrate the refractometer. The values of refractive index increments of polymethacrylic acid in methanol and DMF/1,4-dioxane were determined in the usual way. For the neutralized samples, (dn/dc) measurements were carried out in sodium chloride solutions of different concentrations for both undialysed solutions as well as solutions dialysed against the solvent.

II.4 Viscosity Measurements

Dilute solution viscosities were measured in Ubbelohde dilution type viscometers having a precision bore capillary (0.4 mm dia, 11.0 ± 0.5 cm length) and the efflux times 120.1 ± 0.1 and 123.9 ± 0.1 sec. for water at 30°C . Kinetic energy corrections were not applied as it was found negligible. Shear-rate corrections were also not applied. Viscosity measurements for polymethacrylic acid, neutralized to different extents, were carried out in a thermostat maintained at $30 \pm 0.01^\circ\text{C}$. Viscosities in theta solvent and in methanol were obtained at $27.1 \pm 0.01^\circ\text{C}$ and $26.1 \pm 0.01^\circ\text{C}$ respectively.

Polymer solutions were prepared and clarified as described in

section II.c. Filtered solution (10 mL) was pipetted into the viscometer clamped vertically in the thermostat. After allowing 15 min for thermal equilibrium, the efflux times were recorded till the last two readings agreed within ± 0.1 sec. An aliquot of solvent (2 mL) was added to the solution mixed by blowing a gentle stream of air through the capillary arm of the viscometer and the flow times were recorded. Further dilutions with aliquots of solvent (2 mL, 4 mL & 7 mL) and efflux time determinations were carried out in the same way. The concentrations of the solutions were calculated from the known volume and concentration of the original solution and the volumes of the solvent added for dilution. Corresponding values of η_{sp}/c at varying concentrations were evaluated as $\eta_{sp}/c = (t - t_0)/t_0 c$ where t and t_0 are the efflux times for the solution of concentration c (g/dL) and for the solvent, respectively. Intrinsic viscosities and Huggins' slope constant, k' were determined using linear η_{sp}/c vs c plots.

II.5 Determination of Theta Temperature

Choice of organic solvents for polymethacrylic acid is severely limited. Dimethyl formamide is a good solvent and no polymer precipitation is observed in the temperature range 15 to 40°C. Polymethacrylic acid is insoluble in pure dioxane but dissolves in moist 1,4-dioxane (containing about 5% water). The refractive indices (n_D^{25}) of DMF and 1,4-dioxane are⁷³ 1.4269 and 1.4203, respectively. Mixtures of DMF/1,4-dioxane were selected for use as theta solvent in view that the refractive indices are very close and preferential adsorption will not cause any serious problem⁶ in the determination of the unperturbed dimensions from light scattering measurements.

Preliminary experimentations were carried out with DMF/1,4-dioxane mixtures of varying compositions using the highest molecular weight fraction to determine the composition of the DMF/1,4-dioxane mixture yielding precipitation temperature in a convenient range. DMF/1,4-dioxane ratio of 5:7 was selected for phase separation studies. The procedure followed was identical to the one used by Flory and Osterheld⁷⁴ for the determination of the theta temperature for partially neutralized polyacrylic acid in 1.245 M NaCl.

Stock solution of the polymer was prepared by dissolving an accurately weighed quantity of polymer in the solvent mixture and varying concentration solutions were prepared by dilution of the stock solution. Precipitation temperatures were determined by observing a graduated scale through the transversely illuminated solution held in a water-bath, the temperature of the water-bath being gradually increased or decreased at the rate of 0.5°C/min. The blurring of the graduated scale viewed through the solution was taken as the precipitation temperature and clear sighting of the graduation mark during the heating cycle as the dissolution temperature. The average of the two temperatures taken as the temperature of precipitation generally agreed within $\pm 0.2^\circ\text{C}$.

The precipitation temperatures were plotted against the concentration of the solutions and the precipitation temperatures at finite polymer concentrations were read off from these plots. The precipitation temperatures thus obtained were linearly extrapolated to infinite molecular weights by constructing $1/T_p$ vs $[1/x^{1/2} + 1/2x]$ plots, where x is the degree of polymerization. The extrapolated temperatures were plotted against the polymer concentrations and further extrapolated to infinite dilution. The temperature thus obtained was taken as the theta temperature.

CHAPTER THREE

3.1 Conformational Transition

RESULTS AND DISCUSSION

Polymers and macromolecules which possess ionizable functional groups undergo a conformational transition during ionization¹². Polyvinylacrylic acid (PVA), in fact, was the first macromolecule in which such conformational transition was observed. The variation of the apparent dissociation constant with degree of ionization for these polymeric acids differ from the behaviour expected for a simple acid. The differences in the apparent dissociation constant observed and those expected occur over a narrow range of ionization. The conformational transition occurs over the same ionization range. The polymer exists in a more compact form at low degrees of ionization and in a more extended conformation at higher degrees of ionization. The conformational transition is also reflected in several of the physical properties and can be demonstrated by experimental techniques like solvent viscosity^{12,13}, hydrodynamic volume^{14,17}, light scattering^{15,17} (anisotropy of the light scattered), micro-calorimetry¹⁶⁻²⁰ (changes in heats of neutralization), titrimetry^{21,22} (changes in volume during neutralization), NMR²³ etc.

Biological macromolecules undergo conformational transition either during ionization or by changes in solvent and/or temperature¹³. The two conformational states in biological macromolecules are well defined,

III.1 Conformational Transition

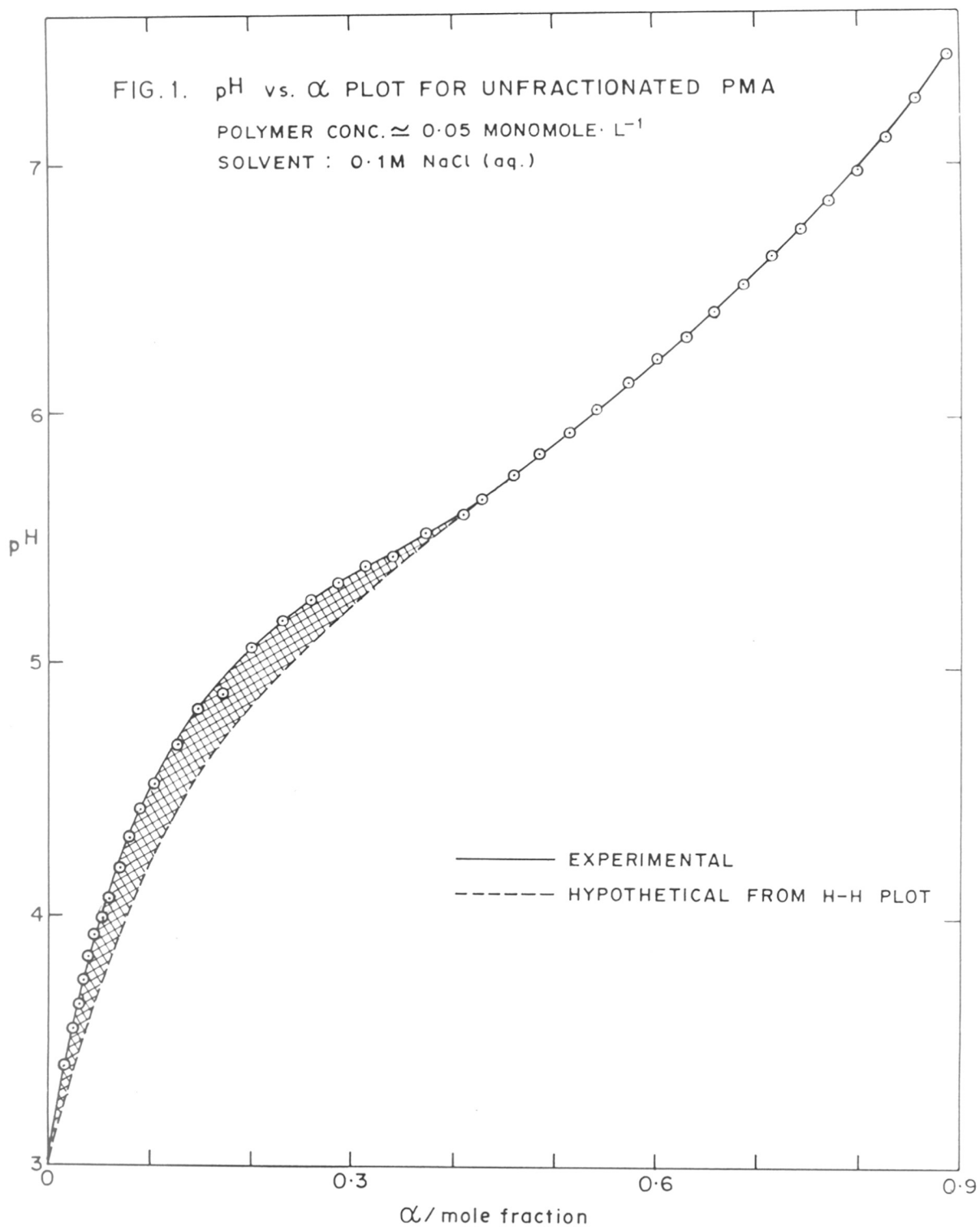
Several of the synthetic linear polyelectrolytes possessing pendant hydrophobic groups undergo a conformational transition during their ionization¹². Polymethacrylic acid (PMA), in fact, was the first polyelectrolyte in which such conformational transition was observed. The variation of the apparent dissociation constant with degree of ionization for these polymeric acids differ from the behaviour expected for a polyacid. The differences in the apparent dissociation constant obtained and those expected occurs over a narrow range of ionization. The conformational transition occurs over the same ionization range. The polymer exists in a more compact form at low degrees of ionization and in a more expanded conformation at higher degrees of ionization. The conformational transition is also reflected in several of the physical properties and can be demonstrated by experimental techniques like solution viscosity^{12,17,75-77} (hydrodynamic volume), light scattering^{75,77} (dissymmetry of the light scattered), micro calorimetry⁷⁸⁻⁸⁰ (changes in heats of neutralization), dilatometry^{78,79} (changes in volume during neutralization), NMR⁷⁶ etc.

Biological macromolecules undergo conformational transition either during ionization or by changes of solvent and/or temperature¹³. The two conformational states in biological macromolecules are well defined,

(i) a helical conformation stabilized by intramolecular hydrogen bonds and (ii) a random coil conformation. In the case of synthetic polyelectrolytes, the two conformational states before and after the transition are illdefined. These have been designated⁷⁵ as 'a' and 'b' states. While the more expanded form is likely to be the random coil conformation, the tightly coiled conformation has not been well understood.

Intramolecular hydrogen bonding, hydrophobic interactions with the water in which it is dissolved resulting in the 'structuring of water' and hydrophobic interactions of the substituent groups have been suggested as the causes for the tightly coiled conformation⁸¹. Intramolecular hydrogen bonding as the cause has been overruled^{12,82}, since similar conformational transition is not observed in polyacrylic acid (subject to hydrogen bonding as in the case of PMA) and partial esterification of PMA does not overcome the conformational transition. The question whether the cause is due to the hydrophobic interaction with the surrounding solvent or the hydrophobic interaction of the substituent groups on the polymer is unsettled.

Fig. 1 shows the variation of the p^H with degree of ionization, α , for the unfractionated sample of PMA ($\bar{M}_w = 6.51 \times 10^5$) in 0.1M NaCl at 25°C. The experimental curve obtained is depicted continuous. The data were obtained using a Mettler automatic titrator (Model DV-210) equipped with a Mettler DK-10 amplifier and a glass combination electrode. The electrode potentials were calibrated against freshly prepared standard aqueous buffers. Polymethacrylic acid solution (20 mL; ca 0.05 monomole L^{-1}) was titrated against 0.5M NaOH. The titrant was added in 0.01 mL increments under constant stirring and the electrode potentials were recorded after allowing 10 min.



The variation of the apparent dissociation constant (p^{K_a}) for polymeric acid can be represented⁸³ by the Henderson-Hasselbalch (H-H) equation; $p^{K_a} = p^H + \log \left(\frac{1-\alpha}{\alpha} \right)$. The plots of p^H vs $\log \left(\frac{1-\alpha}{\alpha} \right)$ result in straight lines. Even for synthetic polyelectrolytes, which do not exhibit conformational transition during the course of their ionization, the H-H plots result in straight lines and satisfy the equation.

$$p^{K_a} = p^H + n \log \left(\frac{1-\alpha}{\alpha} \right)$$

For polyelectrolytes exhibiting conformational transition, the H-H plots consist of two linear sections, the change over from one to the other occurring in the ranges of ionization in which the conformational transition takes place⁷⁵. The expected values of p^H in the absence of conformational transition can be evaluated by extrapolating the linear sections of the H-H plot prior to or after the conformational transition. The variation of the hypothetical values of p^H (in the absence of conformational transition) obtained from H-H plots, with the degree of ionization is shown as the dashed curve in Fig. 1.

The conformational free energy change, ΔF_c , during the ionization is given by

$$\Delta F_c = RT/0.434 \int_0^1 (p^{K_a} - p^{K_b}) d\alpha$$

or

$$\Delta F_c = RT/0.434 \int_0^1 (p^H_a - p^H_b) d\alpha$$

where p^{K_a} , p^{K_b} and p^H_a , p^H_b are the apparent dissociation constants

and p^H in conformational states 'a' and 'b', respectively. The values of ΔF_{α} can be calculated from the area enclosed between the observed variation of p^H with α and the hypothetical variation of p^H with α (shaded area in Fig. 1). The value obtained here is 427 J mole^{-1} in agreement with the values of 452 and 465 J mole^{-1} reported by Nekrasova et al⁸⁴ for the conformational transition of PMA in 0.10M NaCl at 5 and 25°C, respectively.

The helical conformation in biological macromolecules is stabilized through intermolecular hydrogen bonds¹³. Electrostatic charges are formed during ionization and increasing electrostatic repulsions of the like charges along the backbone overcomes the stabilization of the helix. The macromolecule thus undergoes a conformational transition during ionization. On adding a solvent (capable of breaking the hydrogen bonds) to the aqueous solution of a polypeptide, conformational transition can also be affected. In the case of synthetic polyelectrolytes, the compact form is stabilized by hydrophobic interactions. Addition of a miscible organic solvent (of low polarity) to the aqueous solution should help in overcoming the stabilizing forces of the compact form and bring about conformational transition. Reports of conformational transitions in hydrophobic group containing synthetic polyelectrolytes brought about by the addition of an organic solvent have not been published. Selegney et al⁸⁵, however, noted that in aqueous solutions containing 40% methanol conformational transitions were not observed for PMA. But Mandel et al⁸², on the basis of the spectroscopic studies, observed conformational transition in PMA in methanol-water mixture containing 40% (v/v) methanol in about the same ionization range.

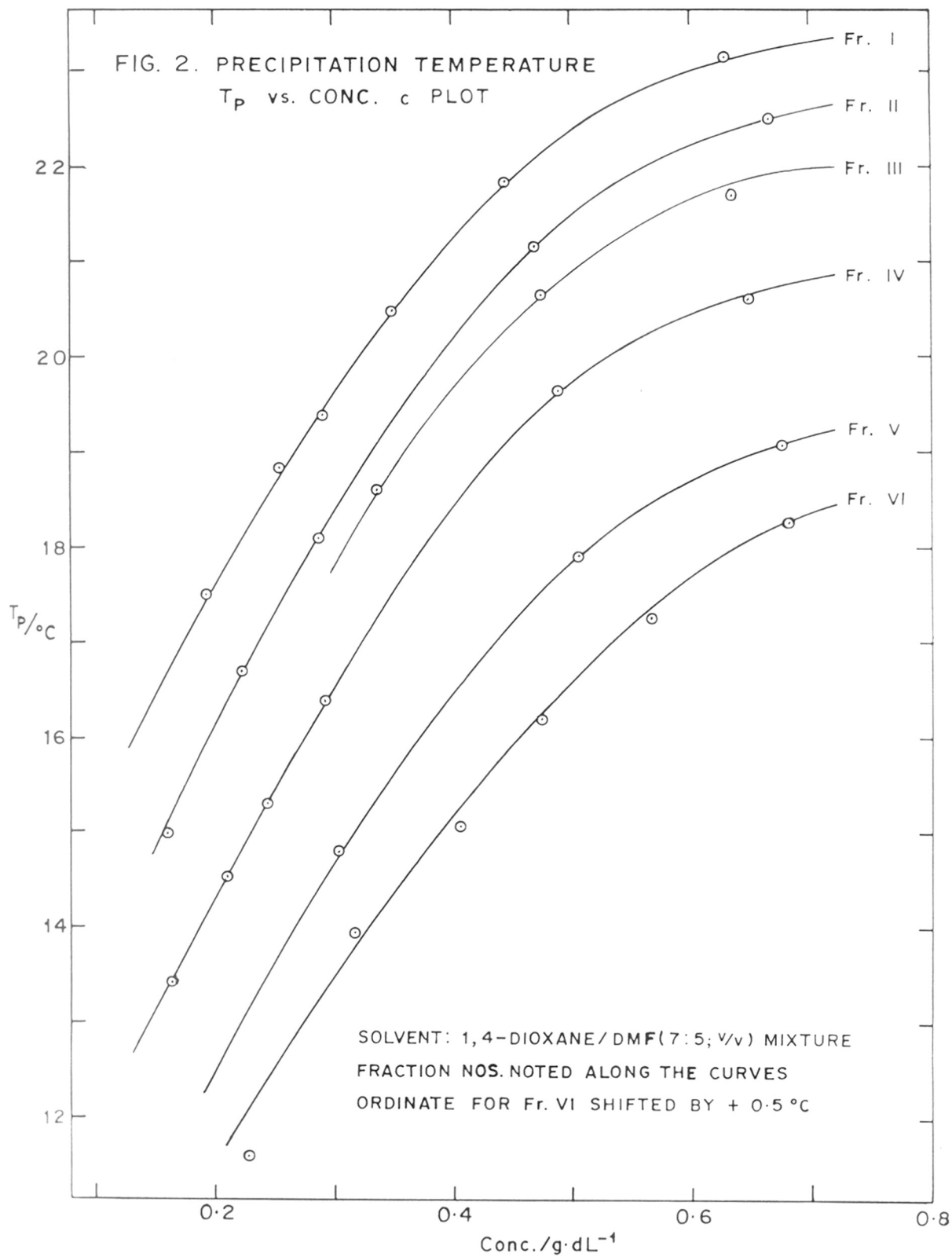
Recently, it has been reported¹⁶ that on the addition of 1,4-dioxane to the aqueous solution of PMA, the free energy change due to conformational transition gradually decreases and conformational transitions are not observed when the solvent contained about 20% 1,4-dioxane. Large increase in intrinsic viscosity is also observed by the addition of 1,4-dioxane to the aqueous solutions of PMA. Similar increase in viscosities have been reported¹⁷ by the addition of N,N-dimethyl formamide (DMF) to the aqueous solutions of PMA. These experimental findings lead to the conclusion that the incorporation of a water miscible organic solvent overcomes its hydrophobic interactions and the hydrophobic group containing polyelectrolytes in organic solvents exist in a more expanded form corresponding to the conformational state at higher degrees of ionization. The recently reported^{14,15} higher unperturbed dimensions in organic solvents as compared to those in aqueous solutions for some of the synthetic polyelectrolytes (exhibiting conformational transition during ionization) is in conformity with the above conclusion.

The purpose of the present investigation is to examine the expansions of polyelectrolytes attributable to their effective charge density. Therefore, it is essential that the conformational form in the reference state corresponds to the conformational state at the degrees of ionization employed. As inferred above, the conformational state of these hydrophobic group containing polyelectrolytes in organic solvents corresponds to the conformation obtainable at higher degrees of ionization. Hence, we employed DMF/1,4-dioxane mixtures as the theta solvent for computing the total expansions of PMA at different degrees of ionization and varying concentrations of added simple electrolyte.

III.2 Theta Solvent

The reported theta solvent for unionized PMA is 0.002N HCl at 30°C⁷¹. As discussed in the previous section, unionized PMA in aqueous solutions exists in a more compact form. In order to evaluate the expansion coefficients at higher degrees of ionization, a theta solvent in which the polymer exists in the more expanded conformation is necessary. It has been inferred earlier that PMA has more expanded conformation (corresponding to the conformational form at higher degrees of ionization) in organic solvents. The MHK exponent reported⁸⁶ in methanol at 26°C being 0.51, it may be assumed that PMA in methanol at 26°C has the unperturbed dimensions. However, high osmotic second-virial coefficients (of the order of 10^{-4} mL.g⁻².mole) characteristic of polymers in good solvents have been observed⁸¹ for PMA in methanol at 26°C. Hence use of methanol as the theta solvent was discounted and phase separation behaviour was examined in DMF/1,4-dioxane mixtures to obtain a suitable organic theta solvent.

DMF is a good solvent for unionized PMA. Pure 1,4-dioxane does not dissolve the polymer. However, 1,4-dioxane containing about 5% water dissolves PMA. Use of mixed solvents can result in preferential adsorption of one of the solvents. The theory of light scattering in multi-component systems has been discussed in section I.4. Light scattering results obtained in isorefractive solvents are unaffected by preferential adsorption. The refractive indices (n_D^{25}) of DMF and 1,4-dioxane are 1.4269 and 1.4203 respectively⁷³. DMF/1,4-dioxane mixtures were selected as theta solvent as their refractive indices are very close to each other.



It is believed that the viscosity results are not significantly affected by preferential adsorption due to the use of solvent mixtures.

Phase separation behaviour was examined in differing composition DMF/1,4-dioxane mixtures with a view to select the composition giving the theta temperature in a convenient range. Solvent mixtures of composition 5:7 (v/v) was selected for detailed experimentation. Precipitation temperatures were determined as the average of the temperatures at which the turbidity appeared and disappeared during the cooling/heating cycle, respectively, of known concentration polymer solutions. Fig. 2 shows the plots of precipitation temperatures at varying concentration of the polymer for the six fractions examined. In the concentration range studied, critical miscibility temperatures could not be determined as the T_p vs c plots do not show maxima (Fig. 2).

The procedure followed by Flory-Osterheld⁷⁴ was used to determine the theta temperature. Fig. 3a shows the plots of $1/T_p$ vs $1/x^{1/2} + 1/2x$ where T_p is the precipitation temperature at finite polymer concentration read off from the curves in Fig. 2, and x is the degree of polymerization. The extrapolated precipitation temperatures to zero abscissa value (corresponding to infinite molecular weight) at each concentration of the polymer were further extrapolated to zero polymer concentration as shown in Fig. 3b. The inverse of the intercept of the straight line in Fig. 3b gives the theta temperature as $(27.1 \pm 0.2)^\circ\text{C}$.

Fig. 4 shows the plot of light scattering data as c/R_{90} vs c for six fractions of PMA examined in 5:7 (v/v) DMF/1,4-dioxane mixture at 27.2°C . The figure shows that straight lines with zero slope give

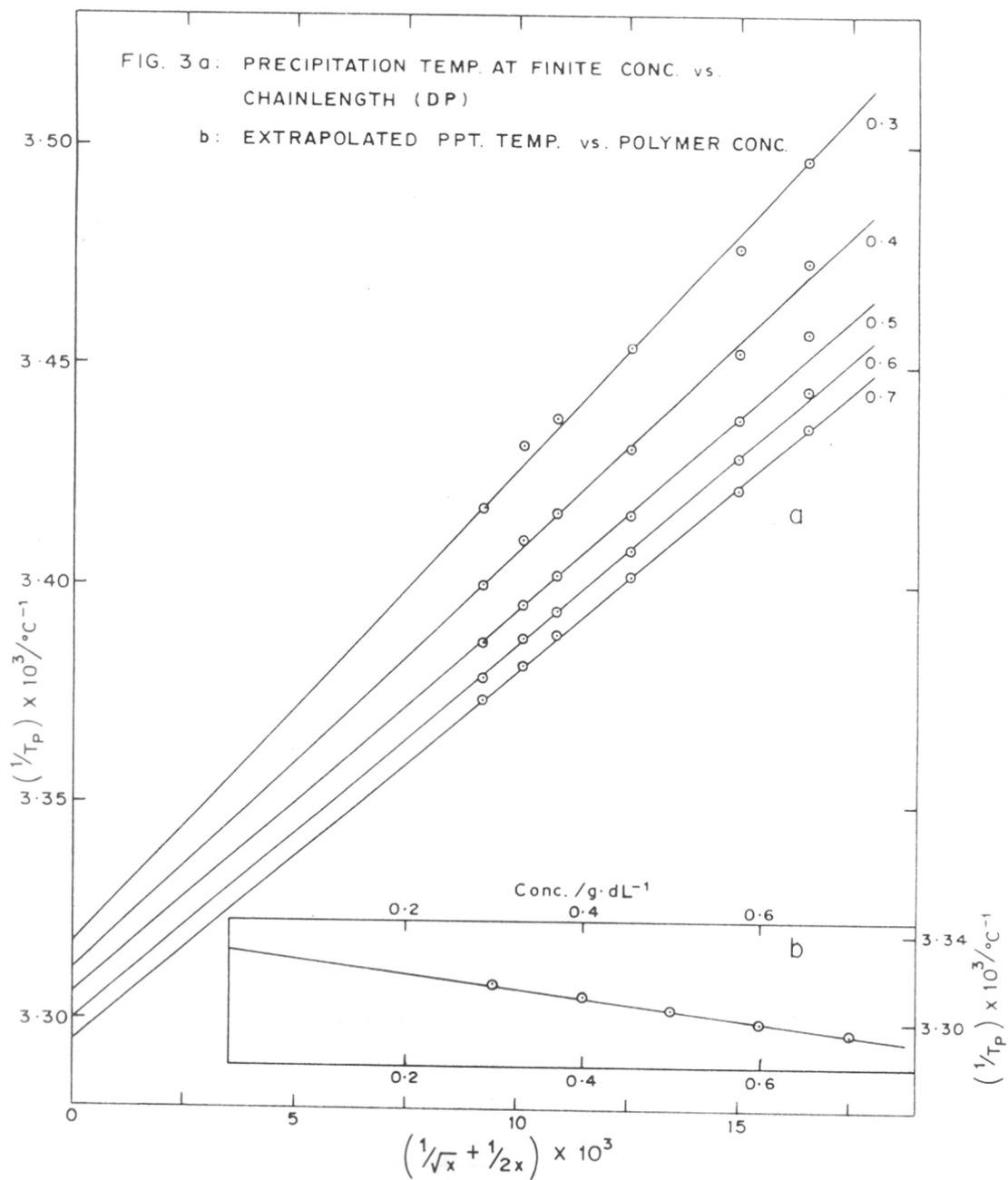
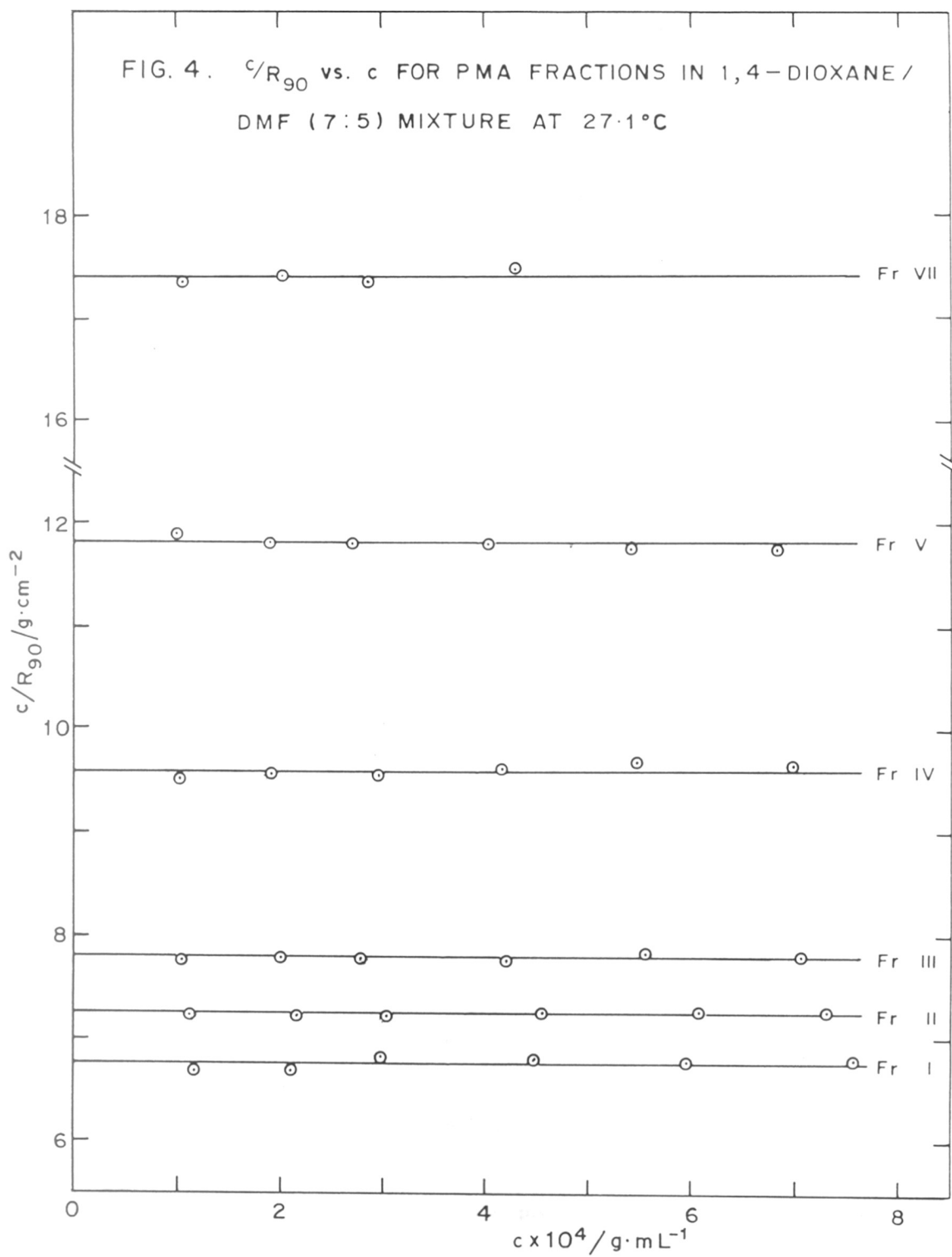


FIG. 4. $\%R_{90}$ vs. c FOR PMA FRACTIONS IN 1,4-DIOXANE /
DMF (7:5) MIXTURE AT 27.1°C



a satisfactory fit of the data indicating zero osmotic second-virial coefficient. The location of the theta temperature is thus satisfactory.

III.3 Molecular Weight

Weight-average molecular weights were determined from light scattering measurements using unpolarized incident light of wavelength 436 nm in cylindrical cells. Measurements were carried out in the scattering angle range 35–135° for solutions in organic solvents. As Zimm plots for aqueous solutions exhibited curvatures at higher scattering angles, seven suitably selected scattering angles below 105° were used. The data were treated by the Zimm method. Values of c/R_Θ at finite scattering angles were linearly extrapolated to zero concentration and the values at fixed concentrations to zero scattering angle. These were linearly extrapolated simultaneously to a common intercept. From the inverse of the intercepts, weight-average molecular weights ($\bar{M}_w$) were calculated.

Measurements were carried out in the theta solvent (DMF:1,4-dioxane :: 5:7 at 27.2°C), methanol and in aqueous solutions containing differing concentrations of the added simple electrolyte (NaCl) and degrees of ionization. Fig. 5 shows the Zimm plot obtained for fraction IV ionized to 0.3 mole fraction in aqueous 0.20M NaCl. Fig. 6 shows the Zimm plot obtained for the first fraction in the theta solvent and Figs. 7-11 the Zimm plots for the aqueous solutions. It is observed that straight line fit for the data is satisfactory. The values of the molecular weights, osmotic second-virial coefficients (A_2) and the dimensions ($\langle s^2 \rangle_z$) were obtained from such linear Zimm plots.

The light scattering method for the determination of $\bar{M}_w$, A_2

FIG. 5. ZIMM PLOT FOR FRACTION IV ($i=0.3$) IN 0.2 M NaCl

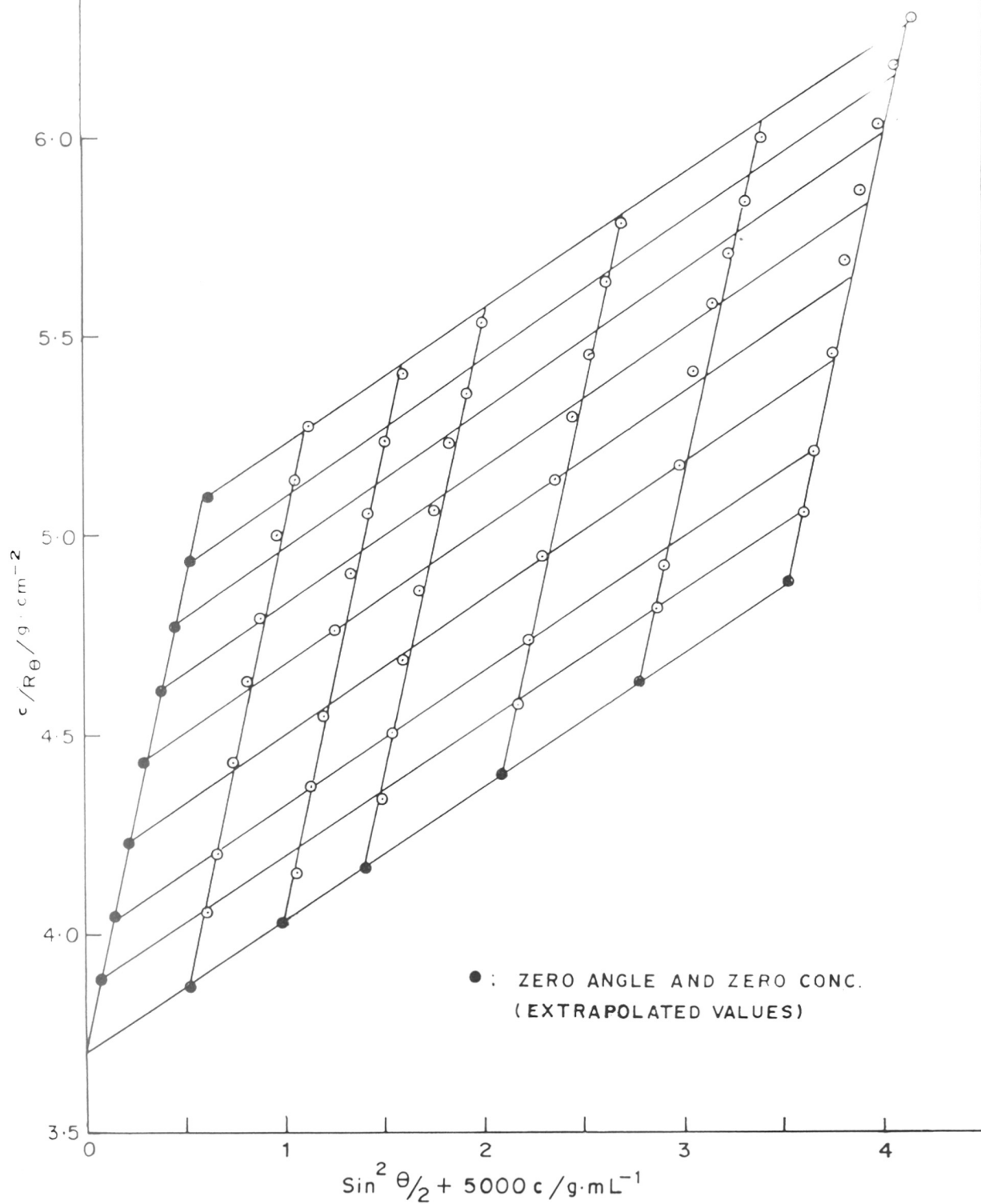
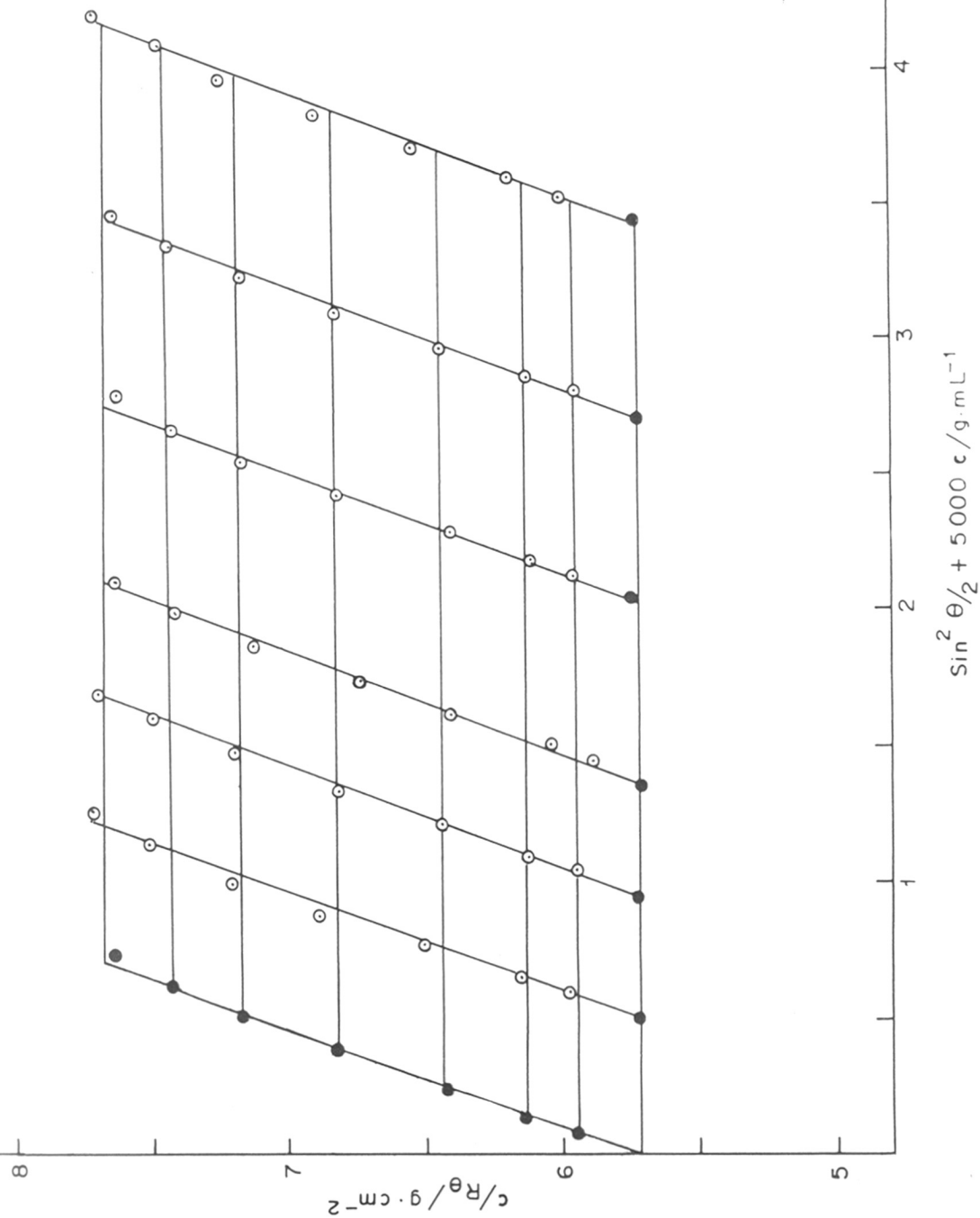
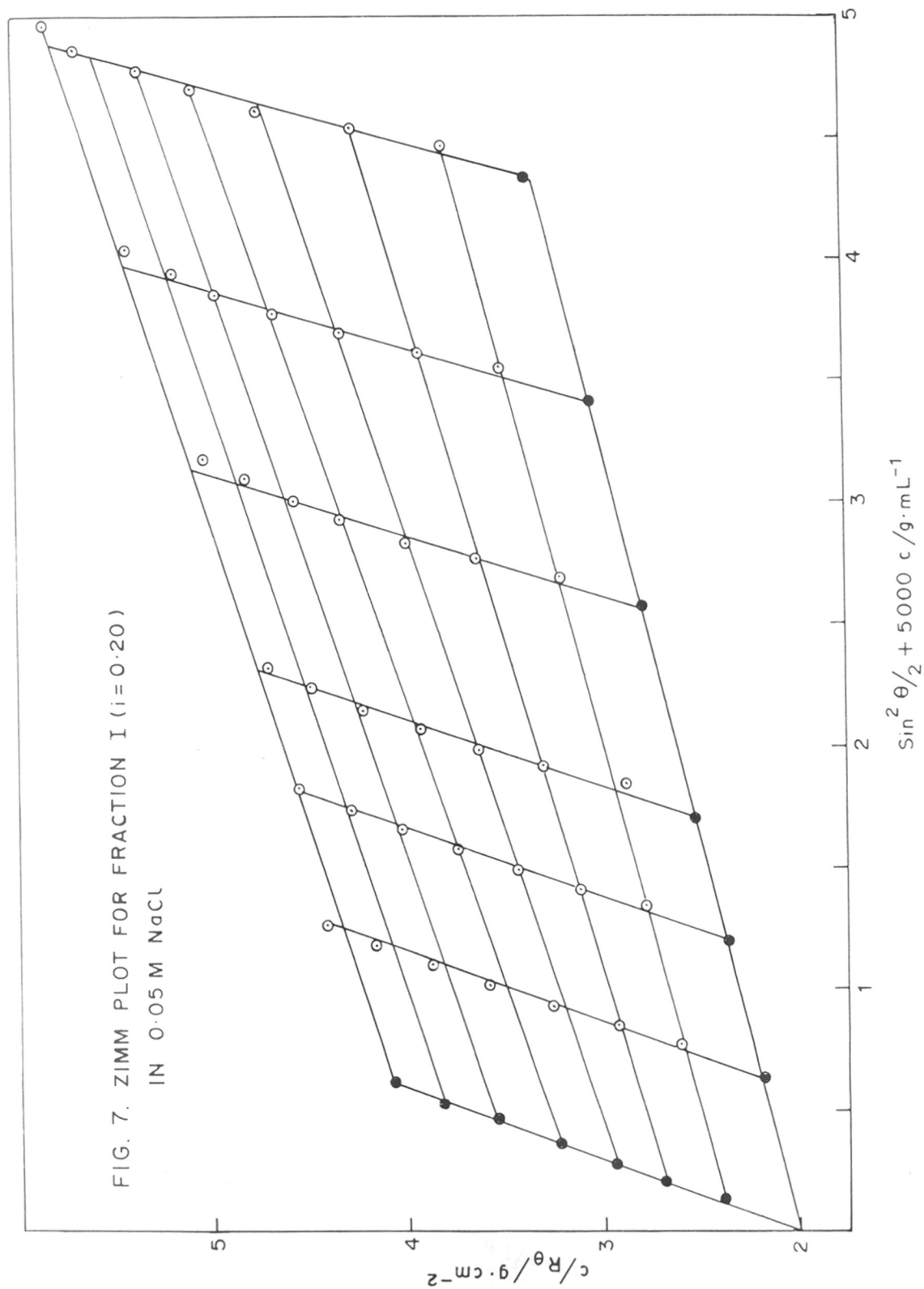
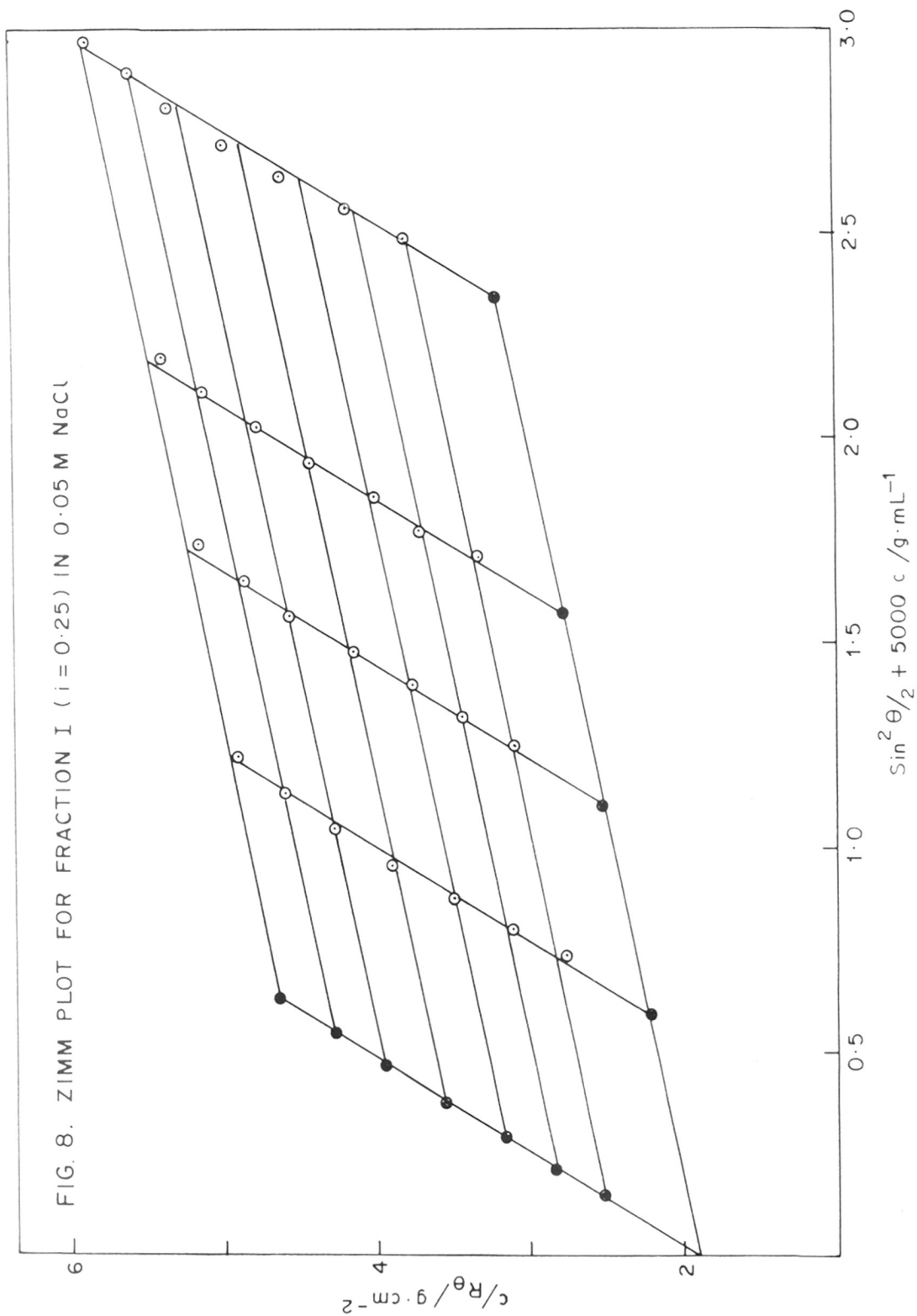
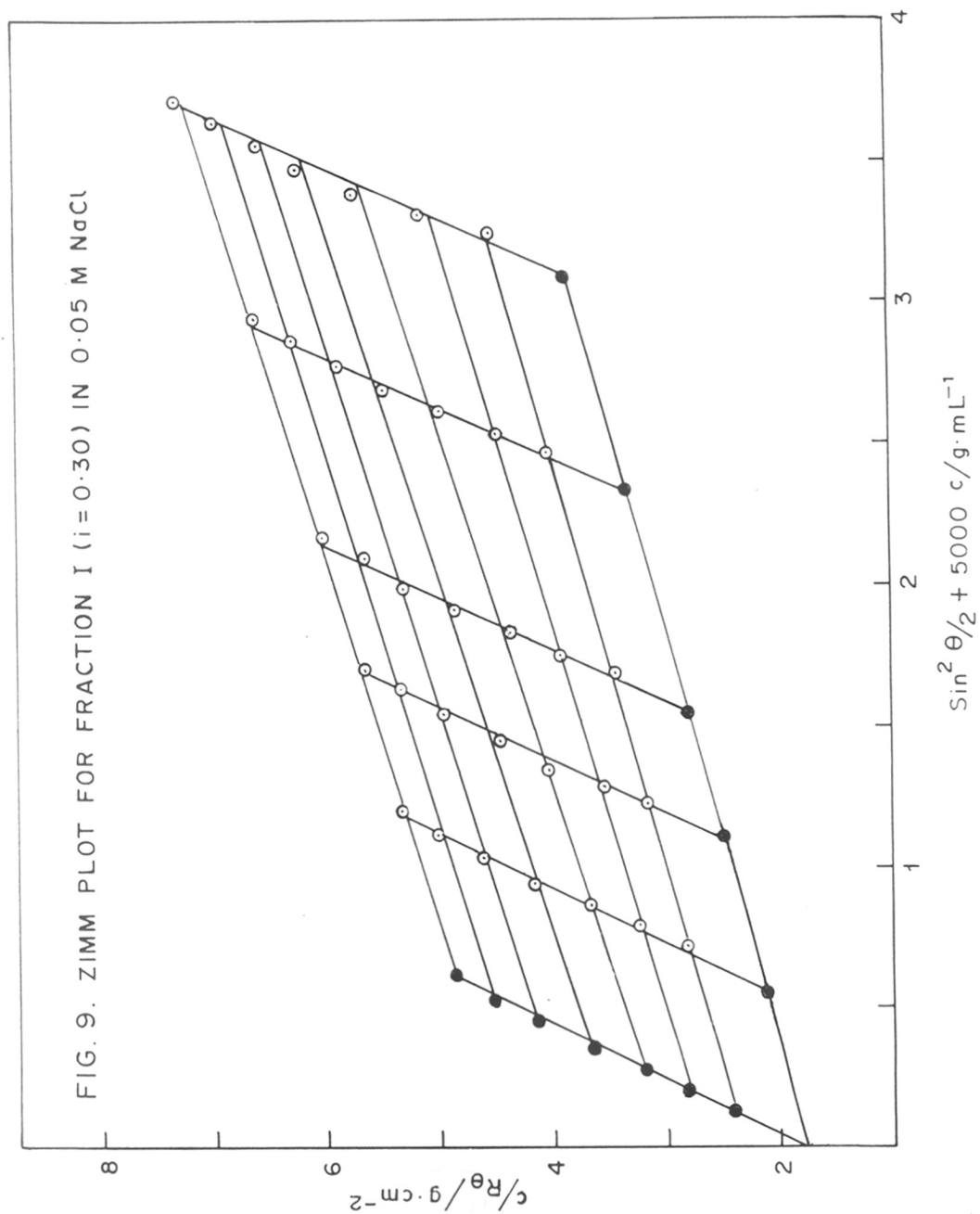


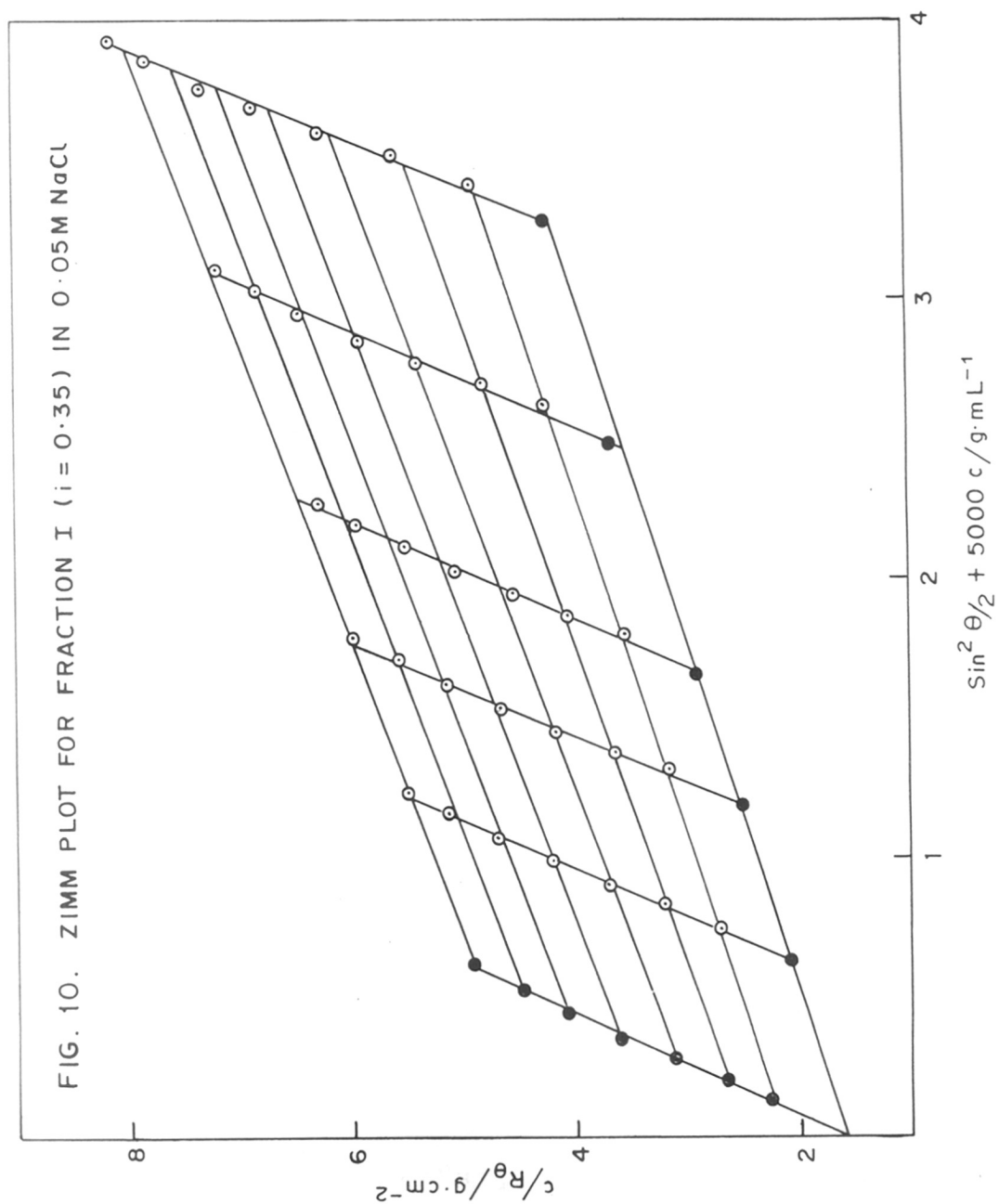
FIG. 6. ZIMM PLOT FOR FRACTION I IN THETA SOLVENT

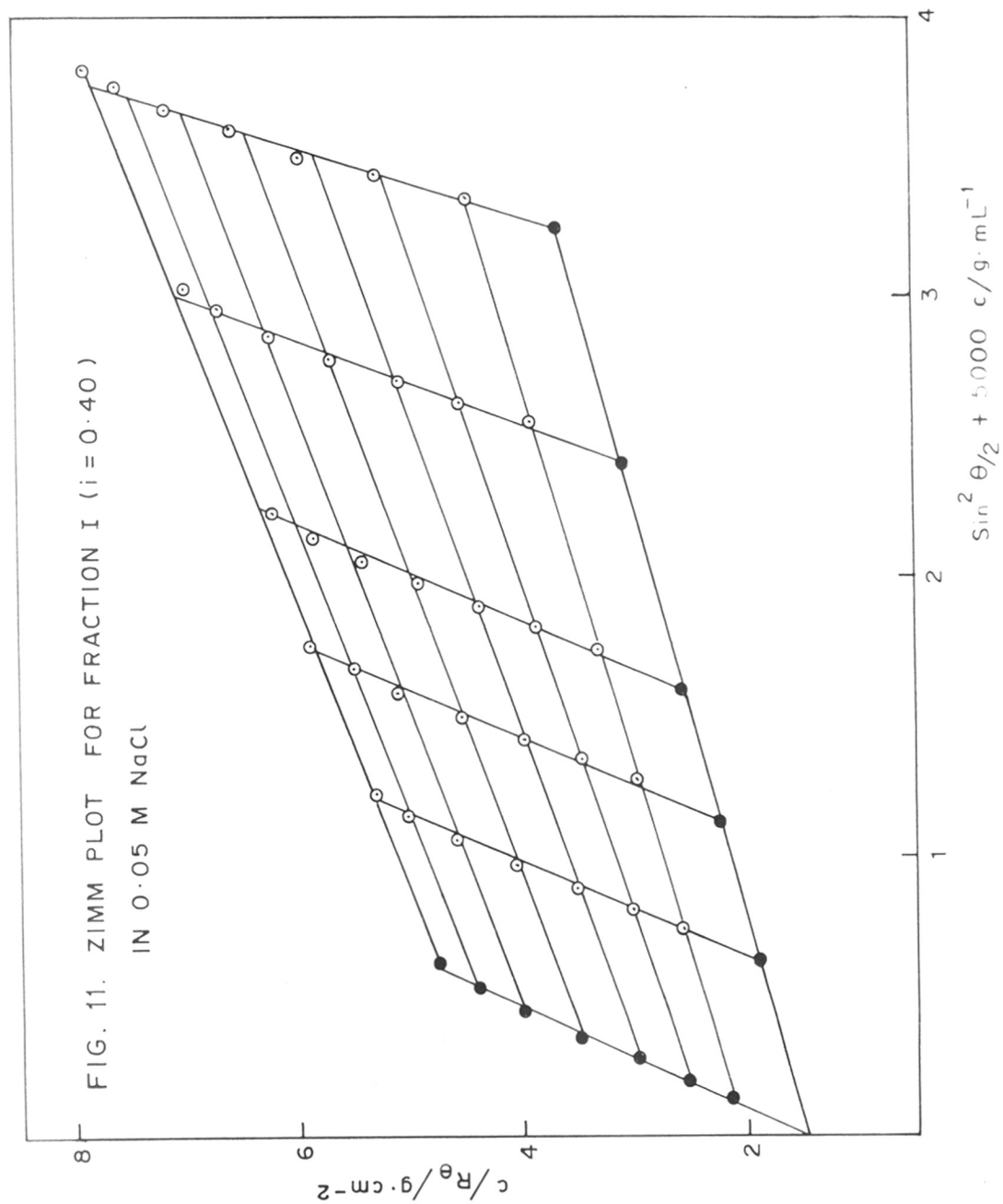












and $\langle s^2 \rangle_z$ in methanol is theoretically exact. However, the use of DMF/1,4-dioxane mixture (as theta solvent) and the aqueous NaCl solutions calls for a closer examination. The polymer preferentially adsorbs the better solvent and this results in the altered composition of the solvent inside and outside the polymer domain. The variation in the solvent composition is to be taken in to account while employing the light scattering technique in mixed solvents⁴. From the theory developed (already discussed in section 1.4), it is seen that the correction term is dependent on the variation of the refractive index of the solution with the composition of the solvent. For solvent mixtures with isorefractive components, the correction term disappears and the light scattering method is applicable⁶ for the exact determination of $\bar{M}_w$, A_2 and $\langle s^2 \rangle_z$ irrespective of preferential adsorption. The refractive indices of DMF and 1,4-dioxane used in the solvent mixture here for the theta solvent are fairly close to each other and the correction term is assumed to be insignificant.

For the aqueous solutions containing the added electrolyte, as discussed in section 1.4, the theory of light scattering has been extended from the theory applicable to mixed solvents⁴. It is shown that the weight-average molecular weights and osmotic second-virial coefficients can be evaluated from light scattering measurements in polyelectrolyte-water-added salt systems provided the refractive index increments at constant chemical potential of the added salt are used. Several investigations have been published confirming^{4,87} the applicability of the technique. The weight-average molecular weights for the aqueous solutions were evaluated by using the values of the refractive index increments obtained for the dialysed solutions.

Table 1 lists the values of dn/dc for unneutralized and partially neutralized (to different extents) PMA containing varying concentrations of the added NaCl. The values of (dn/dc) determined for the undialysed solutions are also included. It is seen that both the values of $(dn/dc)_\mu$ and $(dn/dc)_{c_s}$ are independent of concentration of the added salt, the differences being well within the limits of experimental error. For the ionized solutions, the values of $(dn/dc)_\mu$ are lower than $(dn/dc)_{c_s}$, the decrease being higher at higher degrees of ionization. This shows salt exclusion from within the macromolecular domain to the surrounding. The differences in the values of (dn/dc) for the dialysed and undialysed solutions indicate that the error in the determination of $\bar{M}_w$ by the use of (dn/dc) for the undialysed solutions range from zero (for the unionized solution) to 20% (for the sample with the highest degree of ionization examined). The data in the table also show that (dn/dc) varies linearly with the extent of ionization both for the dialysed and undialysed solutions. For the intermittent extents of ionization, not covered by the data in Table 1, the values wherever required were obtained by linear interpolation.

The values of (dn/dc) for the unneutralized PMA in the theta solvent, methanol and NaCl solutions (0.05 to 0.20M), given in Table 1, are 0.099 ± 0.005 , 0.176 ± 0.002 and 0.153 ± 0.002 , respectively. The values reported for the unneutralized solution in 0.05M NaCl by Kanevskaya et al.⁸⁸ is 0.168. The values obtained here for the aqueous solutions are independent of the NaCl concentration and in agreement with 0.153 and 0.159 reported by Myagchenkov et al.⁸⁹ and Alexander-Stacey⁹⁰ for water solutions. However, these authors do not specify the wavelength of the light employed. The value obtained in this investigation for methanol

Table 1 Specific refractive index increments for polymethacrylic acid at 436 nm (27°C)

Polymethacrylic acid (unneutralized) 0.176 ± 0.002 0.099 ± 0.005
in methanol in DMF/1,4-dioxane mixture

Partially ionized polymethacrylic acid

Added NaCl Conc. (moles)	Degree of ionization (mole fraction)									
	0		$\frac{0.20}{0.30}$		$\frac{0.40}{0.50}$		$\frac{0.40}{0.50}$		$\frac{0.40}{0.50}$	
	$(dn/dc)_C$	$(dn/dc)_\mu$	$(dn/dc)_C$	$(dn/dc)_\mu$	$(dn/dc)_C$	$(dn/dc)_\mu$	$(dn/dc)_C$	$(dn/dc)_\mu$	$(dn/dc)_C$	$(dn/dc)_\mu$
0.05	0.151	0.152	0.177	0.170	0.189	0.177	0.203	0.187	0.215	0.195
0.10	0.154	0.155	0.177	0.168	0.188	0.175	0.202	0.186	0.214	0.196
0.20	0.152	0.153	0.178	0.169	0.188	0.176	0.201	0.189	0.213	0.195

solutions (0.176) is high as compared to the value of 0.134 reported by Trap and Hermans⁹¹ and Kanevskaya et al⁸⁸ at 546 nm. For the ionized solutions, the values obtained appear to be in good agreement with the values obtained by Alexander-Stacey⁹⁰.

The weight-average molecular weights obtained for the PMA fractions in the theta solvent and methanol are listed in Table 2. Some of the values of $\bar{M}_w$ calculated for unneutralized acid from the determined molecular weights for the partially ionized sample (taking in to consideration the extent of ionization and assuming total counterion retention) are included in Table 2. The molecular weights determined in the theta solvent and methanol differ by less than 5%. The molecular weights determined from measurements on ionized solutions closely agree with those determined in the organic solvents. It may be remarked that using the (dn/dc) values of the undialysed solutions, the molecular weights obtained are lower to those listed in Table 2 by 0-20%, depending upon the degree of ionization.

III.4 Intrinsic Viscosities

Polyelectrolytes in aqueous solutions show increase in viscosity with dilution, in the absence of sufficient quantity of added electrolyte. This behaviour has been termed as 'polyelectrolyte effect' and is caused by the progressive diffusion of counterions from inside the macroion domain to the outside with increasing dilution. With increase in quantity of the added simple electrolyte, the departure from the linearity of the viscosity-concentration plots decrease³. With sufficient quantity of the added electrolyte, linear viscosity-concentration plots are obtained.

Table 2 Weight-average molecular weights ($\bar{M}_w \times 10^{-5}$) of polymethacrylic acids in different solvents

Fraction	DMF/ 1,4-Dioxane	Methanol	Aqueous solution						Average*
			i =		0.30				
			$c_s =$		0.05	0.10	0.20	0.50	
			0.10	0.20					
I	10.14	9.99	9.75	9.34	10.03	9.75	9.72	11.24	10.13
II	8.66	8.52	8.75	8.35	8.45	8.20	8.57	9.08	8.47
III	7.45	7.29	--	--	--	--	--	--	7.37
IV	5.62	5.31	5.23	5.32	5.59	5.16	5.02	6.12	5.52
V	4.06	3.86	4.05	3.85	--	3.79	3.51	--	3.87
VI	--	3.23	--	--	--	--	--	--	3.23
VII	2.75	2.65	2.85	2.71	--	2.66	2.52	--	2.69

* Values not included in the table are also used for calculating average.

The η_{sp}/c vs c plots in the presence of sufficient concentration of added simple electrolyte is similar to the familiar Huggins' plot for the nonionic polymers and the intercept gives the intrinsic viscosity.

The viscosity-concentration behaviour of the ionized solutions of PMA examined at varying concentration of NaCl showed that linear η_{sp}/c vs c plots were obtained with $c_s \geq 0.05M$ NaCl. Hence the intrinsic viscosities were obtained with added salt concentration in the range $0.05 \leq c \leq 0.20M$.

The intrinsic viscosities for the methanol solutions and in the theta solvent were obtained from the linear plots of η_{sp}/c vs c . Table 3 lists the values for all the fractions. The values in the theta solvent range from 0.54 to 1.02 $dL \cdot g^{-1}$. Intrinsic viscosities in methanol are higher than those obtained in the theta solvent and range from 0.9 to 2.1 $dL \cdot g^{-1}$. As concluded in the section III.2, methanol is a good solvent for PMA.

Table 3 also lists the values of $[\eta]$ for the samples ionized to 0.3 mole fraction in the presence of varying concentrations of the added NaCl for five of the fractions examined. It is seen that the values at finite concentration of the added salt decrease with decreasing molecular weight. For the same molecular weight sample, the values decrease with increasing concentration of the added salt. In Table 4 are listed the values of $[\eta]$ at various degrees of ionization with finite concentration of added NaCl (0.20M). The values increase with increasing ionization, but beyond $i \geq 0.50$, the increase in $[\eta]$ is marginal.

The values of the Huggins' slope constant (k') ranged from 0.37 to 0.42 in methanol and 0.38 to 0.50 in the theta solvent. For the aqueous

Table 3 Intrinsic viscosities ($\text{dL}\cdot\text{g}^{-1}$) of unionized PMA in theta solvent, methanol and ionized (0.30M) PMA solutions at varying NaCl concentrations

Fraction	DMF/Dioxane (5:7; v/v) at 27.1°C	Methanol at 26°C	Aqueous solution at 30°C			
			0.05	0.07	0.10	0.14
I	1.02	2.10	6.30	5.18	4.00	3.12
II	0.92	1.80	5.53	4.39	3.40	2.59
III	0.88	1.68	--	--	--	--
IV	0.78	1.37	4.23	3.45	2.72	2.14
V	0.67	1.12	3.37	2.70	2.13	1.64
VI	0.59	0.95	--	--	--	--
VII	0.54	0.90	2.51	2.05	1.64	1.27
						1.01

Table 4 Intrinsic viscosities ($\text{dL}\cdot\text{g}^{-1}$) of partially ionized PMA containing 0.2M NaCl at 30°C

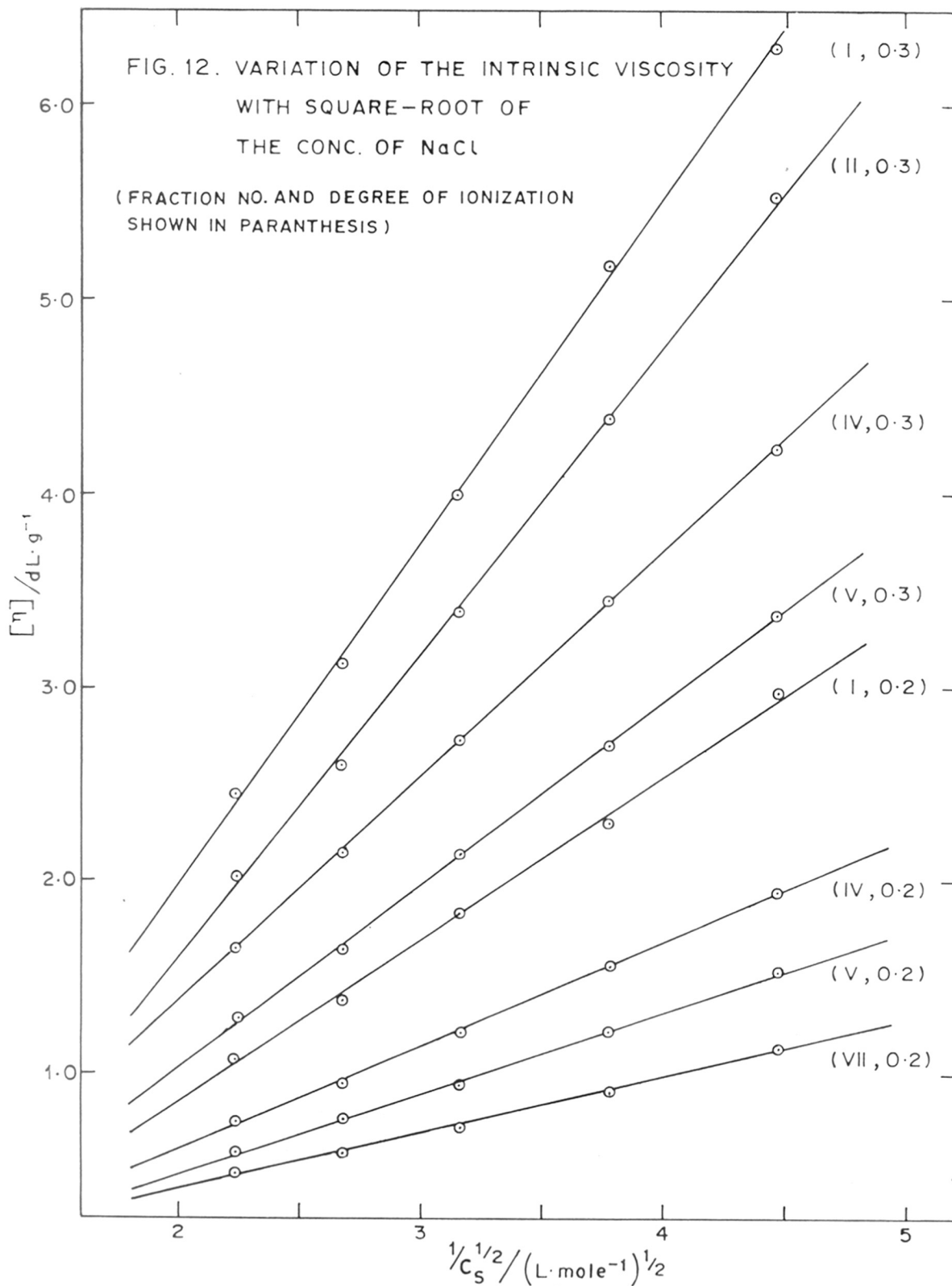
Fraction	Extent of ionization (i)							
	0.20	0.25	0.30	0.35	0.40	0.50	0.60	0.70
I	1.07	1.65	2.44	3.25	4.00	4.90	5.20	5.30
II	0.95	1.48	2.01	2.76	3.53	4.35	4.55	4.65
IV	0.75	1.12	1.65	--	--	3.20	3.44	3.56
V	0.59	0.87	1.29	1.75	2.24	2.63	2.75	2.90
VII	0.47	0.70	1.01	1.36	1.67	1.99	2.10	2.13

solutions, the values of k' ranged from 0.20 to 0.42. At finite concentration of the added salt, the values generally decreased with increasing extent of ionization and at the same extent of ionization, increased with increasing salt concentration.

There have been numerous investigations reported in literature on the effect of the added salt concentration on the intrinsic viscosity of polyelectrolytes. Pals and Hermans⁹² demonstrated the variation of the intrinsic viscosity with the inverse half-power of the concentration of the added salt. Experimental investigations⁹³⁻⁹⁶ have confirmed the conclusion that the $[\eta]$ of polyelectrolytes varies as inverse half-power of the concentration of the added salt. Fig. 12 shows the plots of $[\eta]$ vs $1/c_s^{1/2}$ for some of the fractions at degrees of ionization 0.2 and 0.3, as typical plots. The data demonstrate the linear decrease of $[\eta]$ with the square-root of the concentration of the added salt.

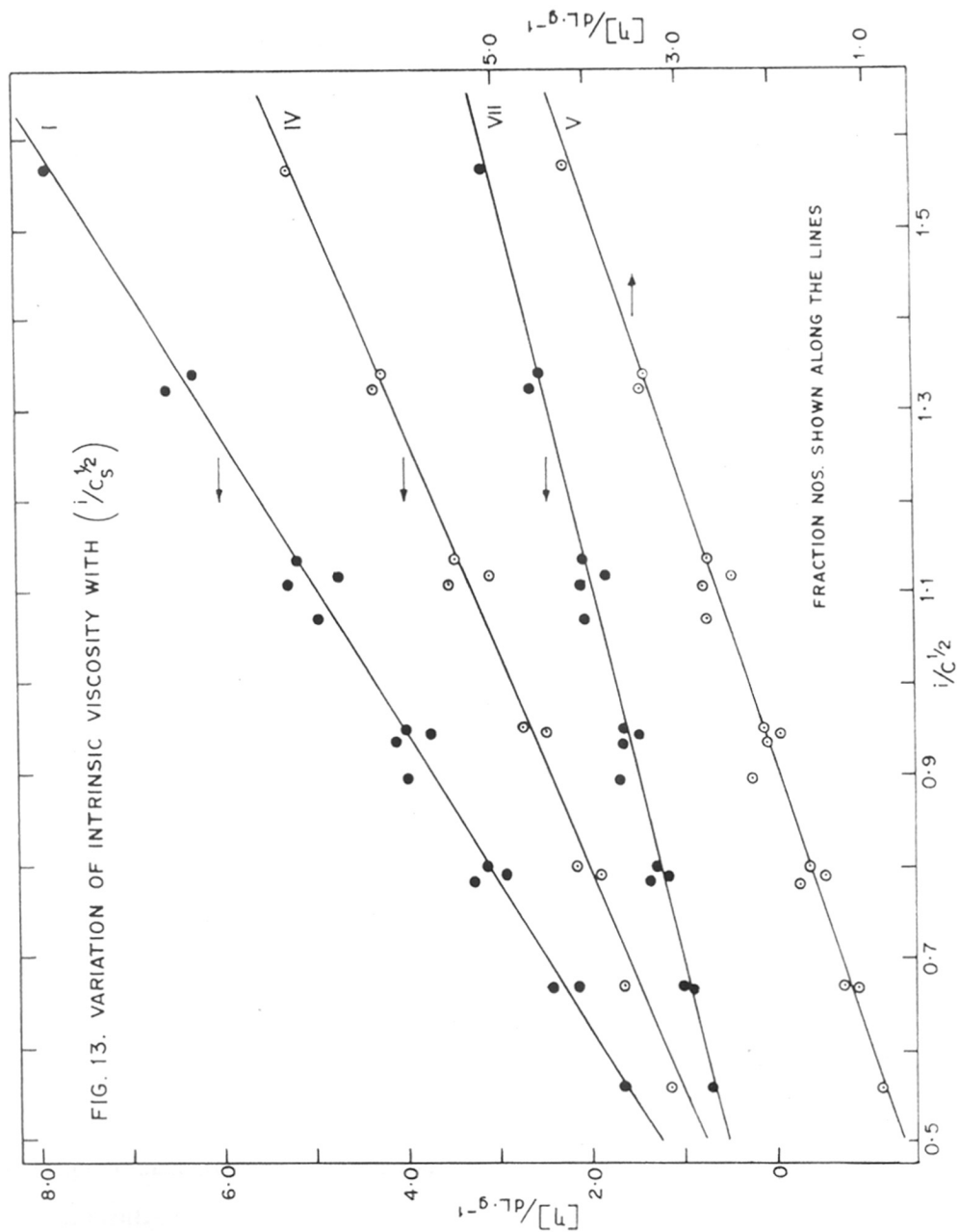
Data in Table 4 show that the intrinsic viscosity increases with ionization upto about $i = 0.5$ and further increase in ionization does not bring about meaningful increase in intrinsic viscosity. This limiting behaviour of $[\eta]$ at higher degrees of ionization is understood in the light of Manning's theory²⁵ of counterion condensation. At higher degrees of ionization, counterion condensation becomes significant and the expected increase in viscosity is not observed. Hence for the purpose of macroion expansion theories, data in the range of ionizations $0.25 \leq i \leq 0.5$ were used.

It is well recognised that with increasing ionization, the $[\eta]$ of the polyelectrolyte increases. With reference to the added salt concentration, the variation of the intrinsic viscosity has been demonstrated in



several cases to follow a linear inverse square-root relationship. These facts are easily understood qualitatively. With increase in ionization, the electrostatic interaction of the like charges along the polymeric backbone results in increased hydrodynamic radius and thus in increasing intrinsic viscosity. The incorporation of a low molecular weight electrolyte brings about screening of the macroion charges by the counterions from the added electrolyte. Though the degree of ionization directly influences the analytical charge density, the effective charge density is influenced by the concentration of the added electrolyte also. Hence $[\eta]$ should be influenced by a composite variable consisting of the degree of ionization and the concentration of the added salt. In view of the almost linear increase of the $[\eta]$ with degree of ionization as indicated by the data in Table 4 and the well known $[\eta] - c_s^{-1/2}$ dependence, it is assumed that the composite variable is $(i/c_s^{1/2})$. Fig. 13 shows the plots of $[\eta]$ vs $(i/c_s^{1/2})$ for fractions of polymethacrylic acid. The data show considerable scatter as compared to the data in Fig. 12.

Intrinsic viscosities are highly sensitive to minor errors in the degree of ionization and concentration of the added salt (especially at low concentrations of the added salt). This was recognized at the beginning of the investigation and care was exercised to minimise the stray variations affecting the results. Stock solutions of NaCl and NaOH were prepared and periodically standardized. Required quantity of alkali was added as alkaline NaCl solution prepared from the stock solutions for achieving the desired degree of ionization. In spite of these precautions, the uncertainty in the determination of the $[\eta]$ is higher ($\pm 5\%$) especially in low salt concentration solutions. The scatter in the value of $[\eta]$ from the



straight lines drawn in Fig. 13 is 3 to 7%, the higher being for the data at the lowest salt concentration employed (0.05M). In view of the high sensitivity of the values of $[\eta]$ to 'i' and 'c_s', the linear representation in Fig. 13 may be considered satisfactory.

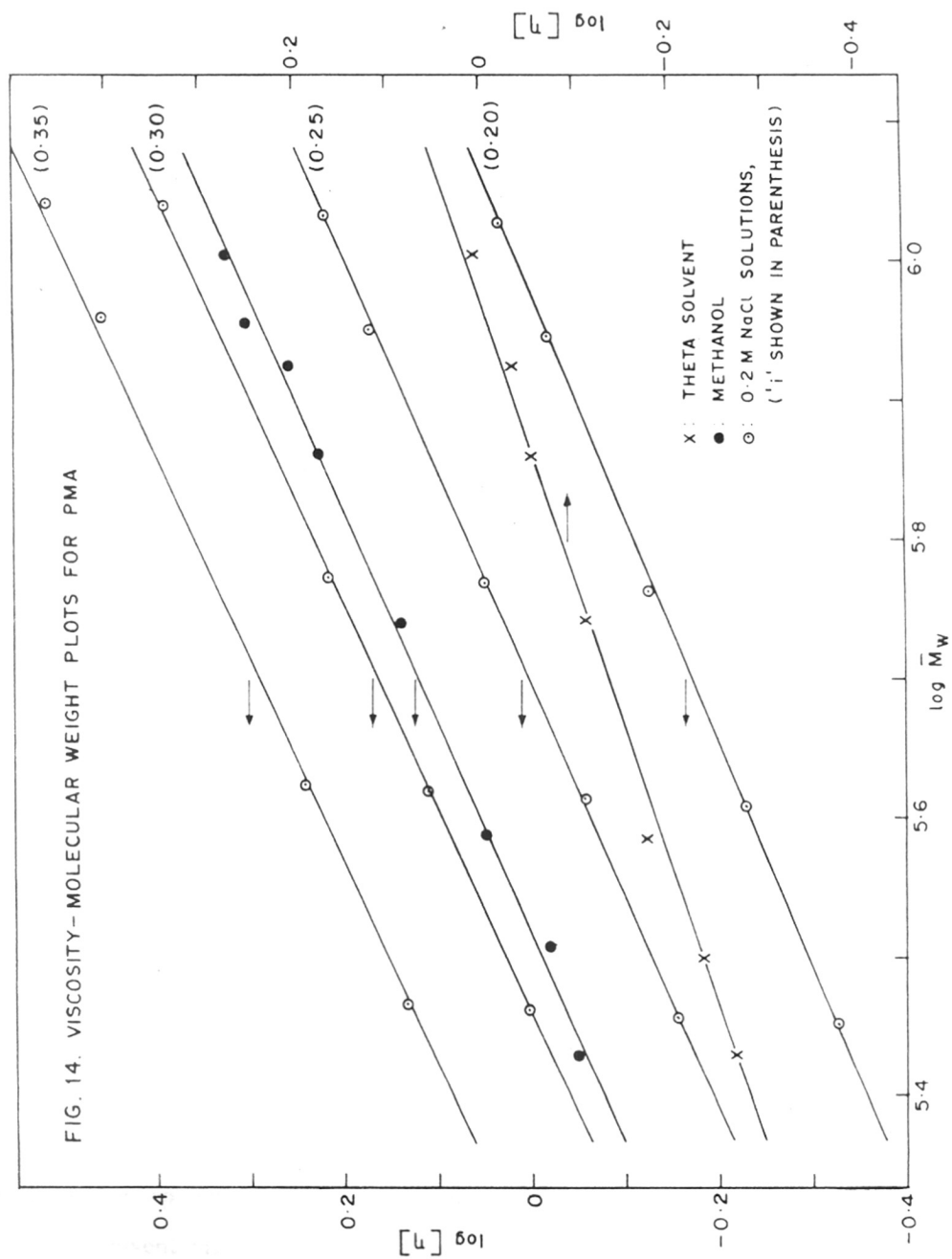
III.5 Viscosity - Molecular Weight Relationships

Viscosity-molecular weight relationships for the unionized PMA in the theta solvent and in methanol are shown in Fig. 14. The relationships obtained with $[\eta]$ in dL.g^{-1} are :

$$[\eta] = 1.03 \times 10^{-3} \bar{M}_w^{0.5}, \text{ DMF/1,4-dioxane (5:7, v/v) at } 27.1^\circ\text{C.}$$

$$[\eta] = 2.94 \times 10^{-4} \bar{M}_w^{0.64}, \text{ Methanol at } 26^\circ\text{C.}$$

Heterogeneity corrections have not been applied to these relationships. The fractionated samples were used up in many of the light scattering and viscosity measurements carried out with varying concentrations of the added salt and degrees of ionization. Sufficient quantity of the samples were not available for osmotic pressure measurements. Gel permeation chromatography was attempted using styragel columns with DMF (containing 0.05M NaNO_3) as the mobile phase. Partial polymer insolubility and high back up pressures (indicating adsorption of the polymer on to the stationary phase) were encountered. Hence GPC measurements had to be abandoned. As the fractions were obtained by employing a two stage fractionation method (discussed in section II.2), it was assumed to be efficient.



Two of the most commonly used viscosity-molecular weight relationships for unionized PMA are the Katchalsky - Eisenberg equation⁷¹ in 0.002N HCl at 30°C, $[\eta] = 6.6 \times 10^{-4} \text{ M}^{0.5}$ and the relationship in methanol at 26°C due to Wiederhorn and Brown⁸⁶, $[\eta] = 2.42 \times 10^{-3} \text{ M}^{0.51}$. It is seen that the MHK constants obtained in this investigation for the unionized PMA differ from the values reported in literature.

We discount heterogeneity corrections as the probable reason for the differences in the values of MHK constants reported in the literature and obtained in this investigation. MHK exponent 'a' obtained in methanol (0.64) is higher than the value (0.51) reported by Wiederhorn and Brown. These authors have used molecular weights determined by osmometry for some of the samples and estimated $\bar{M}_v$ (from viscosity-molecular weight relationship in 0.002N HCl) for other samples in establishing the relationship in methanol. The intrinsic viscosities for all the fractions examined here are higher by about 75-100% in methanol than the values in the theta solvent. The osmotic second-virial coefficients obtained in this investigation as well as those reported in literature^{81,88} are of the order of $10^{-4} \text{ mL.g}^{-2} \cdot \text{mole}$ showing that methanol is a good solvent for unneutralized PMA. Hence, we are led to believe that the MHK relationship reported by Wiederhorn and Brown, though widely employed, is grossly in error.

The MHK constant K in the theta solvent (1.03×10^{-3}) obtained here is higher to the value of 6.6×10^{-4} reported in 0.002N HCl. The results, in our opinion, are due to the higher unperturbed dimension in the organic solvent than in aqueous solutions because of different conformational states in organic and aqueous solutions. It may be recalled here

that Tan and co-workers^{14,15} have also reported a 30% higher unperturbed dimensions in organic solvents as compared to the values in aqueous solutions for poly(2-acrylamido-2-methylpropane sulphonate) and a copolymer of acrylic acid/ethyl acrylate. These polymers also exhibit conformational transition during the course of their ionization.

The intrinsic viscosities at various degrees of ionization and differing added salt concentrations were used to determine the viscosity-molecular weight relationships valid for the partially ionized PMA containing varying amounts of added NaCl. The plots for the samples containing 0.20M NaCl at differing degrees of ionization are included in Fig. 14. The values of MHK constants 'K' and 'a' at different values of 'i' and 'c_s' are listed in the Table 5. The values of 'a' decrease with increasing concentration of the added salt, ionization being constant. At finite concentration of the added salt, the values of 'a' generally increase with increasing degree of ionization. However, the increase in the value of 'a' with extent of ionization is significantly higher for the highest concentration salt-containing solution. At the lowest concentration of the added salt (0.05M) examined the variation in the value of 'a' is insignificant and within the experimental uncertainty. More importantly, the value of 'a' ($0.62 < a < 0.75$) obtained for the total range of ionization and concentration of the added salt is in the range normally observed for random-coil polymers in good solvents.

III.5.a Stockmayer-Fixman plots

It has been the common practice to resort to Stockmayer-Fixman (S-F) extrapolation method to evaluate the characteristic unperturbed

Table 5 MHK constants for polymethacrylic acid

Unionized PMA; Theta solvent - $K_o = 1.03 \times 10^{-3}$; $a = 0.50$; Methanol - $K = 2.94 \times 10^{-4}$; $a = 0.64$
 Partially ionized PMA

	i	Added NaCl concentration (c_s)				
		0.05	0.07	0.10	0.14	0.20
a	0.20	0.74	0.71	0.69	0.66	0.62
	0.25	0.74	0.73	0.72	0.69	0.65
	0.30	0.75	0.74	0.73	0.71	0.67
	0.35	0.75	0.75	0.74	0.72	0.68
	0.40	--	--	--	0.72	0.69
	0.50	--	--	--	0.72	0.70
$K \times 10^4$	0.20	1.38	1.24	1.25	1.50	2.01
	0.25	1.65	1.50	1.33	1.57	2.12
	0.30	2.21	1.82	1.65	1.64	2.19
	0.35	2.46	2.02	1.86	1.86	2.59
	0.40	--	--	--	2.28	2.67
	0.50	--	--	--	2.62	2.86

dimensions of macromolecules when a suitable solvent with theta temperature in convenient ranges cannot be realized. For polyelectrolyte solutions as well, S-F extrapolation method has been extensively used^{3,5}. S-F plots at different degrees of ionization were constructed from the measured intrinsic viscosities and molecular weights. Fig. 15 shows the plots for PMA with $i = 0.25$. It is seen that at higher concentrations of the added NaCl, good straight lines which can be extrapolated to a common intercept are obtained. However, at lower concentration of the added salt, the straight lines intersect the ordinate axis at different points. The same behaviour was also observed for the data at other extents of ionization.

The S-F plots for polyelectrolytes may depart from linearity at high molecular expansions but are generally extrapolated to a common intercept. The data at varying solvent power (corresponding to varying salt concentration) resulting in greatly varying ordinate values are not generally encountered. Small differences in the values of intercept with varying solvent power may be ascribed⁹⁷ to 'specific solvent effect' on the unperturbed dimension. The values of K_0 obtained here at the lowest and the highest salt concentrations differed by 100% and more. The reason is not understood. We note, however, that similar behaviour has been reported for PMA by Nekrasova et al⁹⁸. Values of K_0 were obtained from the common intercept for the data in higher salt concentrations (0.14 and 0.20M).

The values of K_0 obtained for PMA in the ionization range 0.20 to 0.40 (listed in Table 6) range from 0.8×10^{-3} to 2.3×10^{-3} , and increase with increasing ionization. The increase in the value of K_0 with increasing

FIG. 15. STOCKMAYER-FIXMAN PLOT FOR PMA ($i = 0.25$)
(C_S VALUES SHOWN ALONG THE LINES)

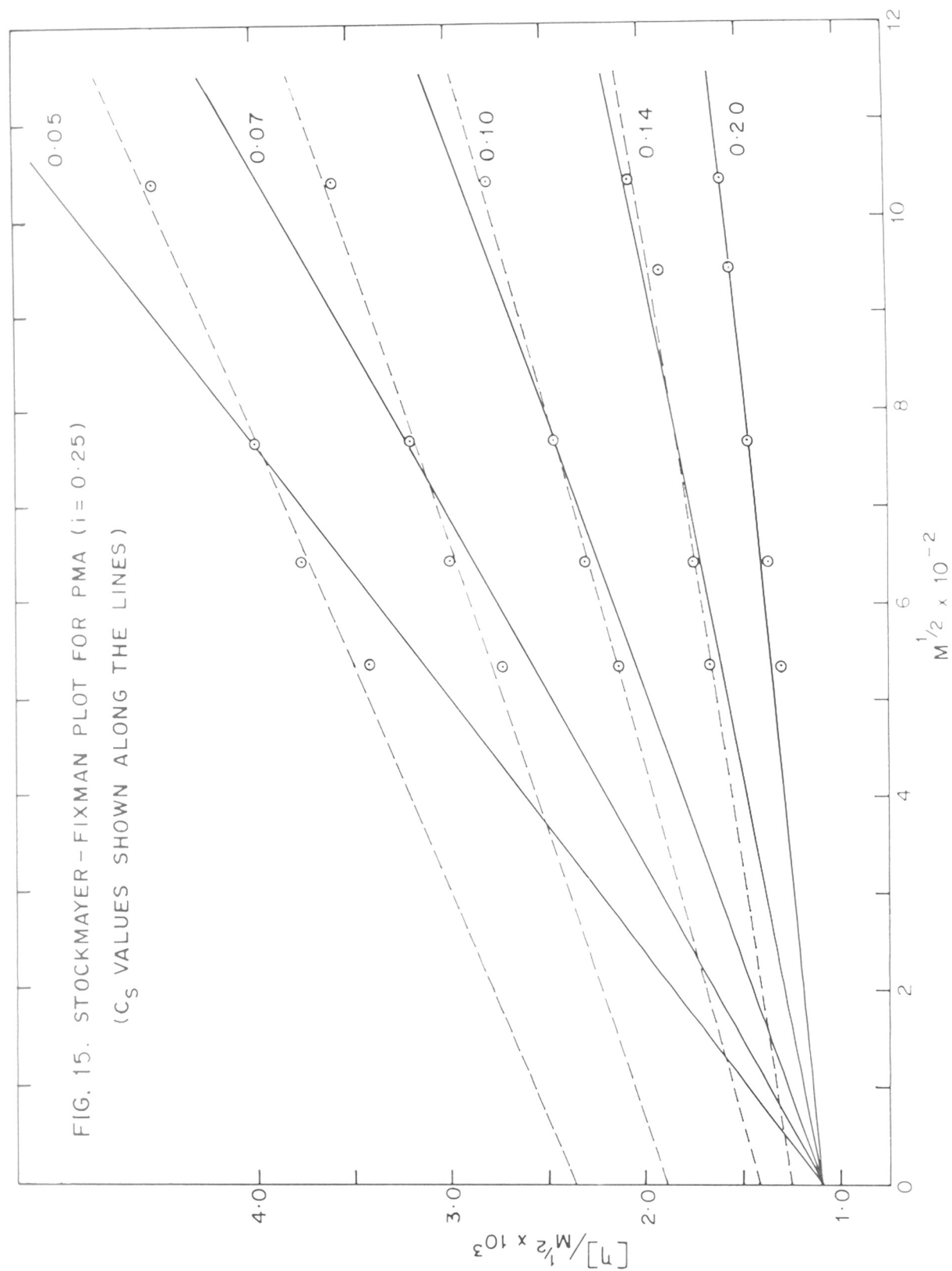


Table 6 Steric factor, Kuhn statistical segment length for the partially ionized PMA

i	$K_o \times 10^3$ from S-F plots	σ	λ^{-1} (Å)
0	1.03 [*]	2.13	17.0
0.20	0.80	1.98	14.8
0.25	1.10	2.26	19.5
0.30	1.30	2.42	22.1
0.35	1.80	2.71	27.7
0.40	2.30	3.32	41.6

* From theta solvent

ionization has been reported by other investigators^{9,11,98}. The value of 0.8×10^{-3} at $i = 0.2$ obtained is lower than the value 1.03×10^{-3} for the unneutralized acid in theta solvent. As PMA undergoes a conformational transition in the ionization range $0.1 < i < 0.3$, the lower value at $i = 0.2$ may be ascribed to the polyacid existing partly in a tightly coiled conformation at this extent of ionization.

As discussed in section 1.2, the extension of the macromolecule is influenced, apart from bond lengths and bond angles, by steric hindrances to free rotation around the skeletal bonds. This can be expressed by the steric factor

$$\sigma^2 = \langle r^2 \rangle_o / \langle r^2 \rangle_{of}$$

where $\langle r^2 \rangle_o$ and $\langle r^2 \rangle_{of}$ are the mean-square end-to-end distances for the unperturbed chain and the chain with no hindrance to free rotation, respectively. The values of steric factor, σ , calculated from K_o values at different degrees of ionization are included in Table 6. In the same table, the value for the steric factor for the unneutralized PMA obtained from K_Θ in DMF/1,4-dioxane mixture is also given. The value (2.13) is very close to that reported⁹⁹ for polymethyl methacrylate (2.08 ± 0.2). This indicates that a change of the substituents far removed from the skeletal bonds does not greatly affect the steric hindrances to rotation around the skeletal bonds.

Also listed in the Table 6 are the segment lengths for the Kuhn's equivalent chains (λ^{-1}) at different extents of ionization. These values were calculated using the values of $\langle r^2 \rangle_o$ and by solving the simultaneous equations $\langle r^2 \rangle_o = n'l'^2$ and $\langle r \rangle_{\max} = n'l'$. The values of $\langle r \rangle_{\max}$

were evaluated using $1.54 \text{ \AA}$ for the skeletal C - C bond and $109^\circ 30'$ for the bond angles. The values range from $17 \text{ \AA}$ for the unionized acid to $42 \text{ \AA}$ for the highest degree of ionization examined. It is seen that the Kuhn segment lengths are in the range normally encountered for random-coil polymers¹⁰⁰.

III.6 Osmotic Second - Virial Coefficients

The values of the osmotic second-virial coefficients (A_2) were determined from the zero angle extrapolated lines in the Zimm plots. As expected, the c/R_θ vs c plots for the DMF/1,4-dioxane mixture at 27.1°C exhibited zero slope. For methanol solutions, the values of A_2 ranged from $(2.15 - 4.38) \times 10^{-4} \text{ mL}\cdot\text{g}^{-2}\cdot\text{mole}$ increasing with decreasing molecular weights. The obtained values of A_2 in methanol is in the range reported by other investigators^{81,88}.

As already discussed in sections I.4 and II.3, the determination of the values of A_2 from light scattering measurements for the polyelectrolyte solutions in water containing added salt is valid, provided the values of dn/dc for the dialysed solutions are used. The values thus determined are shown in Table 7 and range from $(1.63 - 14.2) \times 10^{-4} \text{ mL}\cdot\text{g}^{-2} \text{ mole}$. At constant concentration of the added salt and ionization, the values increase with decreasing molecular weight. For the same molecular weight sample, the values increase with increasing extent of ionization at constant salt concentration. The increase in the value of A_2 with varying molecular weight at constant concentration of the added salt and degree of ionization is rather low. For instance, at $c_s = 0.20\text{M}$, $i = 0.2$,

Table 7 Osmotic second-virial coefficients ($A_2 \times 10^4$ in mL.g⁻² mole) for the partially ionized PMA

i	c _s	Fr I	Fr II	Fr IV	Fr V	Fr VII
0.20	0.20	1.63	1.75	1.83	1.86	2.09
	0.10	2.81	3.08	3.66	3.85	3.93
	0.05	4.95	5.18	5.39	--	--
0.25	0.10	--	4.11	--	--	--
	0.05	7.31	7.36	7.43	--	--
0.30	0.20	3.91	4.04	4.24	4.46	4.50
	0.10	6.94	6.99	7.08	7.28	7.33
	0.05	8.67	10.87	10.90	--	--
0.35	0.10	--	8.62	--	--	--
	0.05	9.76	--	--	--	--
0.40	0.10	--	11.32	--	--	--
	0.05	9.90	--	--	--	--
0.50	0.10	--	12.80	--	--	--
	0.05	10.81	14.20	12.72	--	--

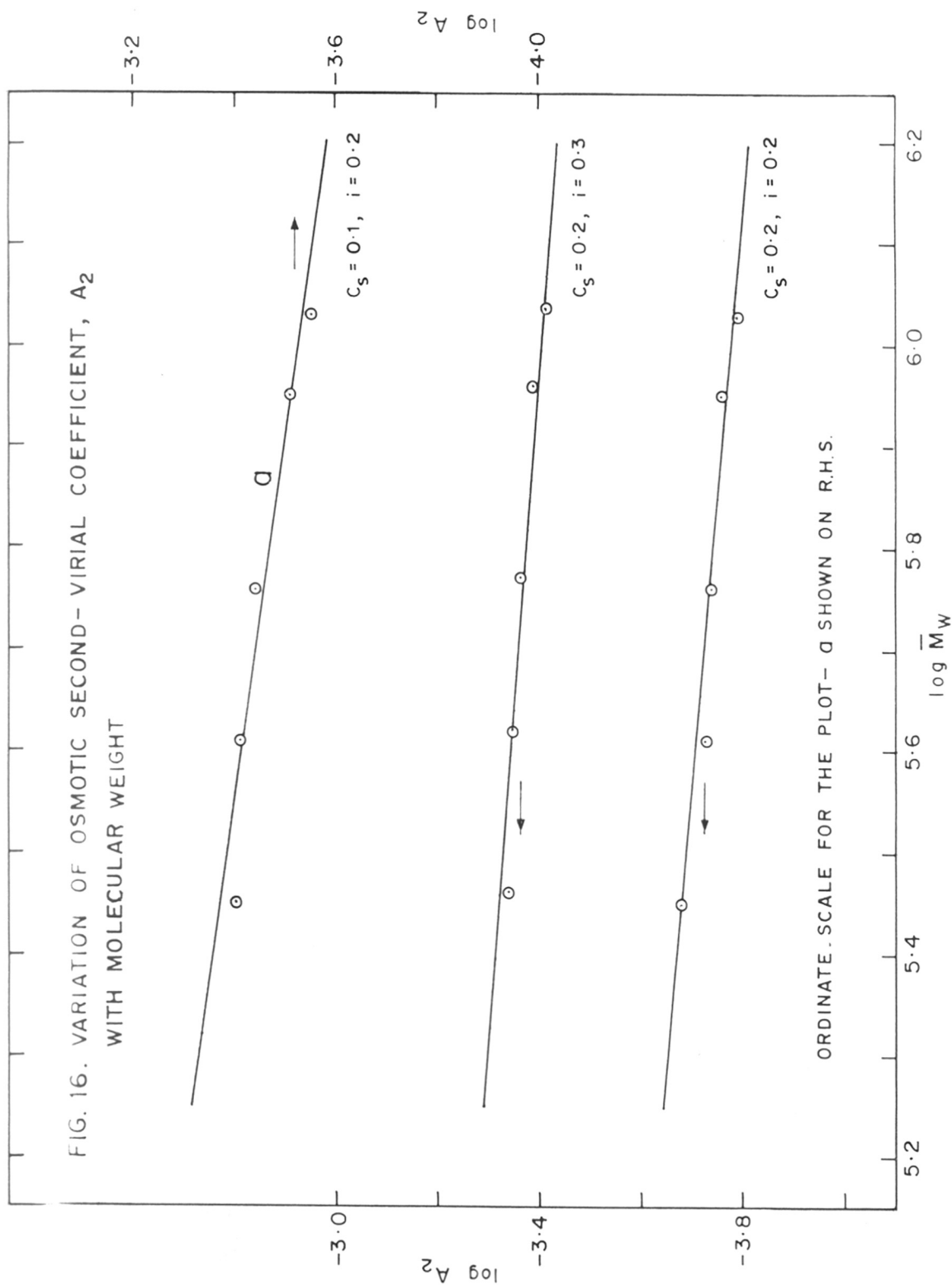
the values ranged from $(1.63 - 2.09) \times 10^{-4} \text{ mL}\cdot\text{g}^{-2}\cdot\text{mole}$. In contrast, for the same molecular weight sample, increasing ionization brings about a large increase in the value of A_2 . For example, for fraction II at $c_s = 0.05\text{M}$, the values increase from 5.18×10^{-4} to $14.2 \times 10^{-4} \text{ mL}\cdot\text{g}^{-2}$ mole with the increase of ionization from 0.2 to 0.5. The increase in the value of A_2 with decrease in the concentration of the added salt for the same molecular weight sample is also relatively large. For fraction IV, for example, at $i = 0.3$, the values decrease from $10.9 \times 10^{-4} \text{ mL}\cdot\text{g}^{-2}$ mole at $c_s = 0.05\text{M}$ to $4.24 \times 10^{-4} \text{ mL}\cdot\text{g}^{-2}\cdot\text{mole}$ at $c_s = 0.20\text{M}$.

The molecular weight dependence of A_2 at finite salt concentration and extent of ionization is shown in Fig. 16 for some of the solutions varying in degree of ionization and added salt concentration. The slopes of such plots were in the range (-0.15) to (-0.20) , similar to those observed for nonionic polymers in good solvent.

There have been several theoretical considerations of the osmotic second-virial coefficients of polyelectrolytes in the presence of added salt. The various attempts have been detailed by Nagasawa and Takahashi⁴. The osmotic second-virial coefficient of a colloidal particle bearing point charge has been calculated by Donnan and Guggenheim¹⁰¹. The expression (familiarily known as Donnan term) shows that the osmotic second-virial coefficient varies as the square-root of the charge on the polyelectrolyte and inversely as the first power of the added salt concentration. A term representing macromolecular character of the polyelectrolyte is incorporated to the ideal Donnan term. Perhaps, an equation of the form

$$A_2 = A_2^0 \Gamma_1 \Gamma_2 (\alpha)$$

FIG. 16. VARIATION OF OSMOTIC SECOND-VIRIAL COEFFICIENT, A_2
WITH MOLECULAR WEIGHT



where A_2 is the second-virial coefficient of the polyelectrolyte in presence of the added salt, A_2^0 the ideal Donnan term, T_1 represents the variation of the A_2 with the charge of the polyelectrolyte and $T_2(\alpha)$ incorporates the variation of A_2 with expansion coefficient of the polyelectrolyte, represents a closer approximation⁴.

Fig. 17 shows the plots of A_2 vs (i^2/c_s) , the corresponding variable according to the ideal Donnan term. It is seen that at lower values of abscissa, the data can be represented by a straight line but systematically depart from linearity at higher abscissa values. It is also observed that at identical values of (i^2/c_s) , the values of A_2 depend on the molecular weight and this behaviour is more clearly seen at higher values of abscissa.

From the two parameter theory of polymer solutions discussed earlier in section I.4, the A_2 for nonionic polymers is given by⁶

$$A_2 = (N_A \beta n^2 / 2M^2) h(z)$$

$h(z)$ is a function of the form

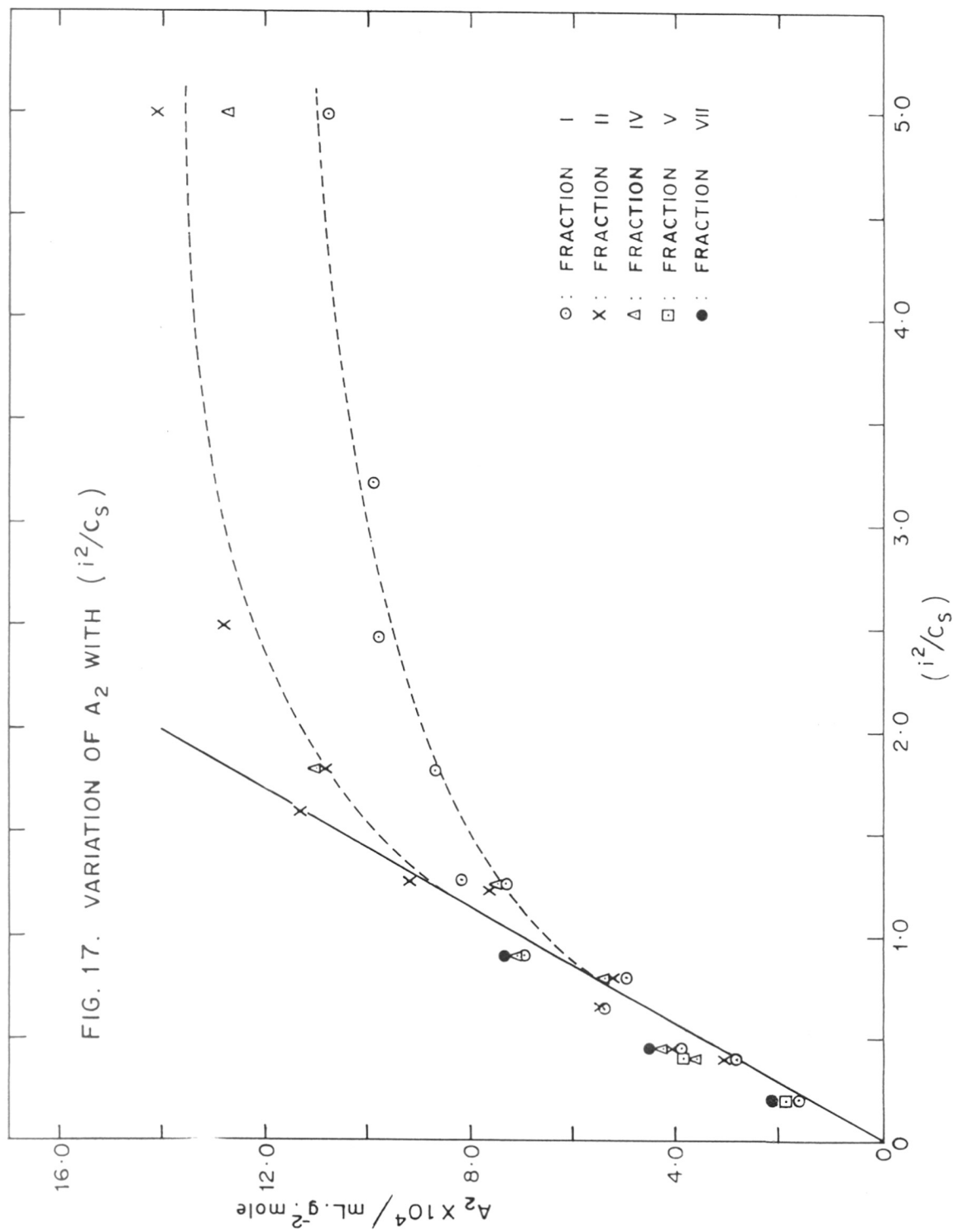
$$h(z) = 1 - C_1 z + C_2 z^2$$

with z the excluded volume parameter. The above expression correctly predicts the decrease of the value of A_2 with increasing molecular weight.

The observed molecular weight dependence of the values of A_2 , shown in Fig. 16, are of the form $A_2 \propto M^{-\gamma}$, with γ in the range usually observed for nonionic polymers in good solvent. A correction factor of the form $M^{-0.25}$ can be incorporated to the predicted dependence on ' i ' and ' c_s ', according to the Donnan term. The expression obtained is of the form

$$A_2 \propto (i^2/c_s) M^{-0.25}$$

FIG. 17. VARIATION OF A_2 WITH (i^2/c_s)



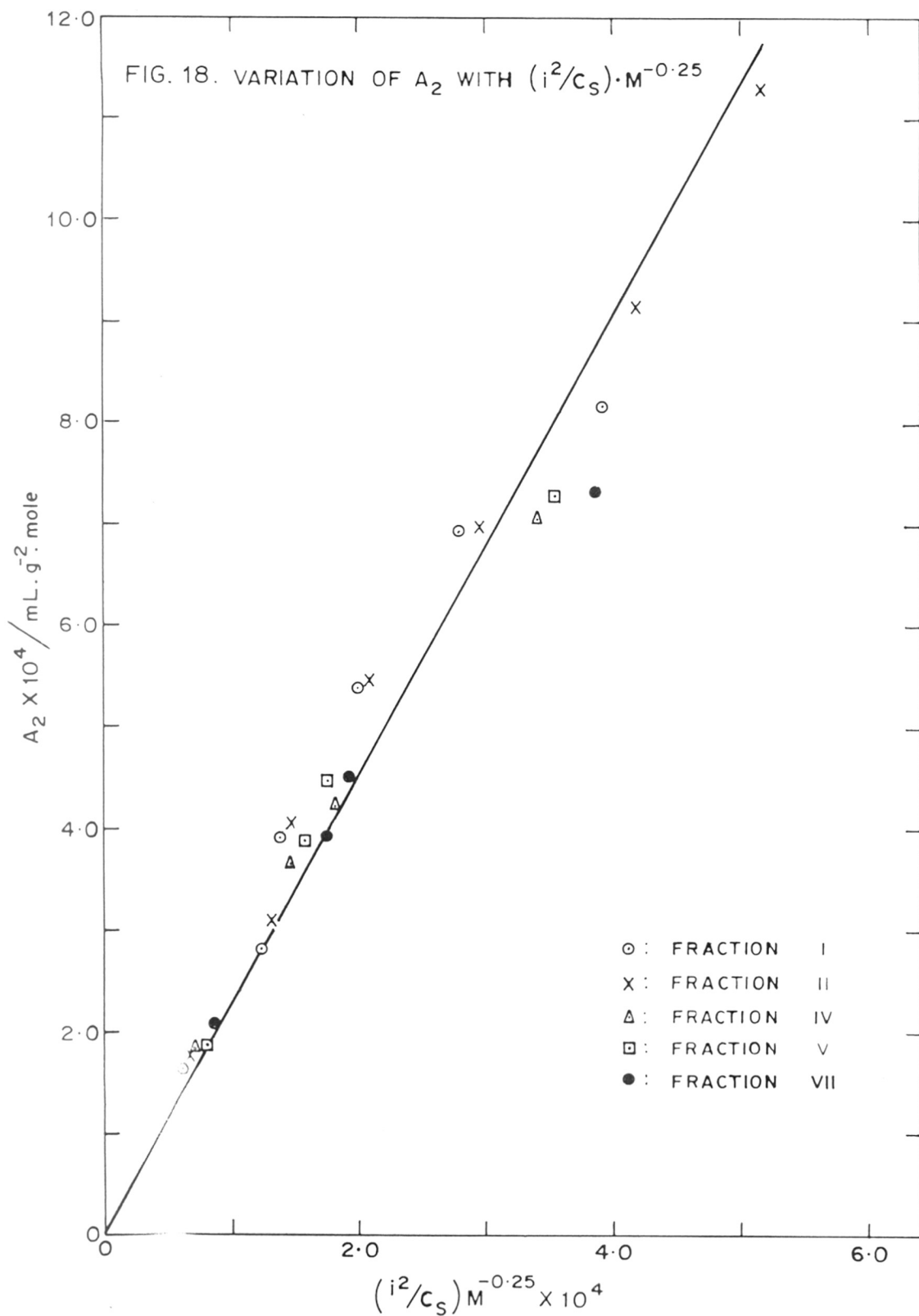


Fig. 18 shows such plots. The data at $c_s = 0.05M$ were omitted as these systematically depart from linearity (at higher values of i^2/c_s) in Fig. 17. The straight line passing through origin is a good fit of the data showing that this empirical method of representation may be valid for polyelectrolyte solutions.

III.7 Dimensions

Light scattering measurements have been carried out, in this investigation, in DMF/1,4-dioxane mixture (theta solvent) and in aqueous solution containing varying concentrations of added salt. The uncertainty in the determination of the dimensions by light scattering due to the nonapplicability of the fluctuation theory for these multicomponent systems have been considered. In the theta solvent, the components used in the mixture have very near refractive indices. It is shown by Yamakawa⁶ that preferential adsorption will not affect the dimension obtained in the mixed solvent system if isorefractive solvent mixtures are selected. The situation regarding the determination of dimensions of polyelectrolytes from light scattering measurements using polyelectrolyte-water-added salt system is rather uncertain. It is recognized that the fluctuation theory may not be applicable⁴. However, it is generally assumed that the errors are not serious. In the case of hydrolysed polyacrylamides assuming that the value of the Flory's viscosity constant, Φ , for nonionic polymers is also applicable for the polyelectrolytes, it has been concluded that the dimensions determined by light scattering are grossly in error. It is known¹⁰² that for random copolymers the dimensions determined are in error and the Φ values are lower¹⁰³⁻¹⁰⁵ than those obtained for homopolymers.

The values of Φ calculated from the measured intrinsic viscosities and dimensions for the theta solvent, methanol and for the salt containing ionized PMA are listed in Table 8. It is seen that the values (with $[\eta]$ in dL.g^{-1} and dimensions in cm) in the theta solvent, ranged from 2.83×10^{21} to 3.00×10^{21} with an average of $(2.93 \pm 0.07) \times 10^{21}$ close to the predicted^{58,61,62} theoretical value of 2.87×10^{21} . The values of Φ in methanol ranged from 2.25×10^{21} to 2.92×10^{21} with an average of $(2.46 \pm 0.17) \times 10^{21}$. The result is in agreement with the predicted decrease^{60,63,64} of Φ with increasing solvent power.

The values of Φ in the aqueous solutions, however, are relatively lower than expected. The predicted maximum decrease⁶ in the value of Φ with increasing solvent power is about 20%, whereas the observed values are lower by about 50% of the theoretical value. It is well known¹⁰⁶ that molecular weight heterogeneity lowers the value of Φ . However, the observed values (ranging from 1.08×10^{21} to 1.59×10^{21}) cannot be reconciled to be due to heterogeneity correction as the values obtained for the same fractions in the theta solvent are in the neighbourhood of the theoretically predicted value. We are inclined to believe that the lower values in the salt containing aqueous solutions are primarily due to the uncertainty in the determined dimensions. Fortunately the values of Φ , unlike in the case of hydrolysed polyacrylamides (which has a copolymer character as well) do not greatly vary with either the extent of ionization or the concentration of the added salt. The observed differences in the values for the aqueous solutions are well within the large uncertainty in the estimate of Φ due to combined uncertainties in the values of $[\eta]$ and $\langle s^2 \rangle$. The averaged value in the aqueous salt

Table 8 Flory's viscosity constant ($\bar{\Phi} \times 10^{-21}$) for unionized and partially ionized PMA

Solvent	Fr I	Fr II	Fr III	Fr IV	Fr V	Fr VII	Average
Theta solvent (DMF/1,4-Dioxane)	2.88	2.83	2.97	2.95	3.03	2.93	2.93 ± 0.07
Methanol	2.26	2.30	2.54	2.61	2.59	--	2.46 ± 0.17
<u>Aqueous solutions</u>							
i							
c_s							
0.20	1.41	1.59	--	1.59	1.26	1.32	
0.10	1.28	1.18	--	1.53	1.32	1.30	
0.05	1.13	1.43	--	1.44	--	--	
0.25	1.10	--	--	1.40	--	--	
0.30	1.41	1.41	--	1.56	1.58	1.54	
0.10	1.19	1.24	--	1.60	1.35	1.40	
0.05	1.08	1.16	--	1.29	--	--	
0.35	1.04	--	--	--	--	--	
0.40	--	1.29	--	--	--	--	
0.50	--	1.32	--	--	--	--	
0.05	--	1.0	--	--	--	--	1.33 ± 0.16

solutions is $(1.35 \pm 0.16) \times 10^{21}$. This amounts to the measured dimensions being about 20% higher due to the inapplicability of the fluctuation theory of light scattering for the determination of dimensions of the polyelectrolyte in water-added salt system.

An attempt was also made to estimate the uncertainty in the determined dimensions (in aqueous salt solutions) using the theoretically predicted asymptotic limit for the 'penetration factor' or 'penetration function' for the nonionic polymers. Ψ , a dimensionless quantity, relevant to the discussion of the osmotic second-virial coefficient in excluded volume theories, is defined as

$$\Psi(z) = \frac{1}{4 \eta^{3/2}} \frac{A_2 M^2}{N_A \langle s^2 \rangle^{3/2}}$$

The limiting values predicted⁵⁰ for $\Psi(z)$ range from 0.219 to 0.240 for neutral polymers. As the measurements of A_2 and $\bar{M}_w$ for polyelectrolyte-water-added salt systems from light scattering are theoretically valid, it was thought that the asymptotic value of Ψ may be used to determine the nature of uncertainty in determining the values of dimensions. The attempt had to be abandoned as the Donnan term contributes sizably to the measured A_2 . It is readily seen, from the data in Tables 2, 3, 4 and 7, that the values of $A_2 M / [\eta]$, another parameter with an asymptotic value⁵⁰ of 1.2 for neutral polymers, gave an asymptotic value of 1.8 for ionized PMA. The higher value in this case is due to the larger value of A_2 for which the additional Donnan term contributes substantially.

With the assumption of a constant error (independent of the added

Table 9 Radius of gyration ($\langle s^2 \rangle^{1/2} \times 10^8$ cm) for unionized and partially ionized PMA

Solvent	Fr I	Fr II	Fr III	Fr IV	Fr V	Fr VII
Theta solvent (DMF/1,4-Dioxane)	290	265	245	215	180	150
Methanol	400	355	320	270	225	--
<u>Aqueous solutions</u>						
$\frac{i}{C_s}$						
0.20	380	330	--	265	235	190
0.10	470	425	--	315	270	220
0.05	575	480	--	375	--	--
0.25	--	480	--	--	--	--
0.05	680	585	--	445	--	--
0.30	505	445	--	350	285	235
0.10	630	550	--	410	355	285
0.05	755	665	--	510	--	--
0.35	--	590	--	--	--	--
0.05	830	--	--	--	--	--
0.40	--	630	--	--	--	--
0.05	855	--	--	--	--	--
0.50	--	660	--	--	--	--
0.05	890	820	--	630	--	--

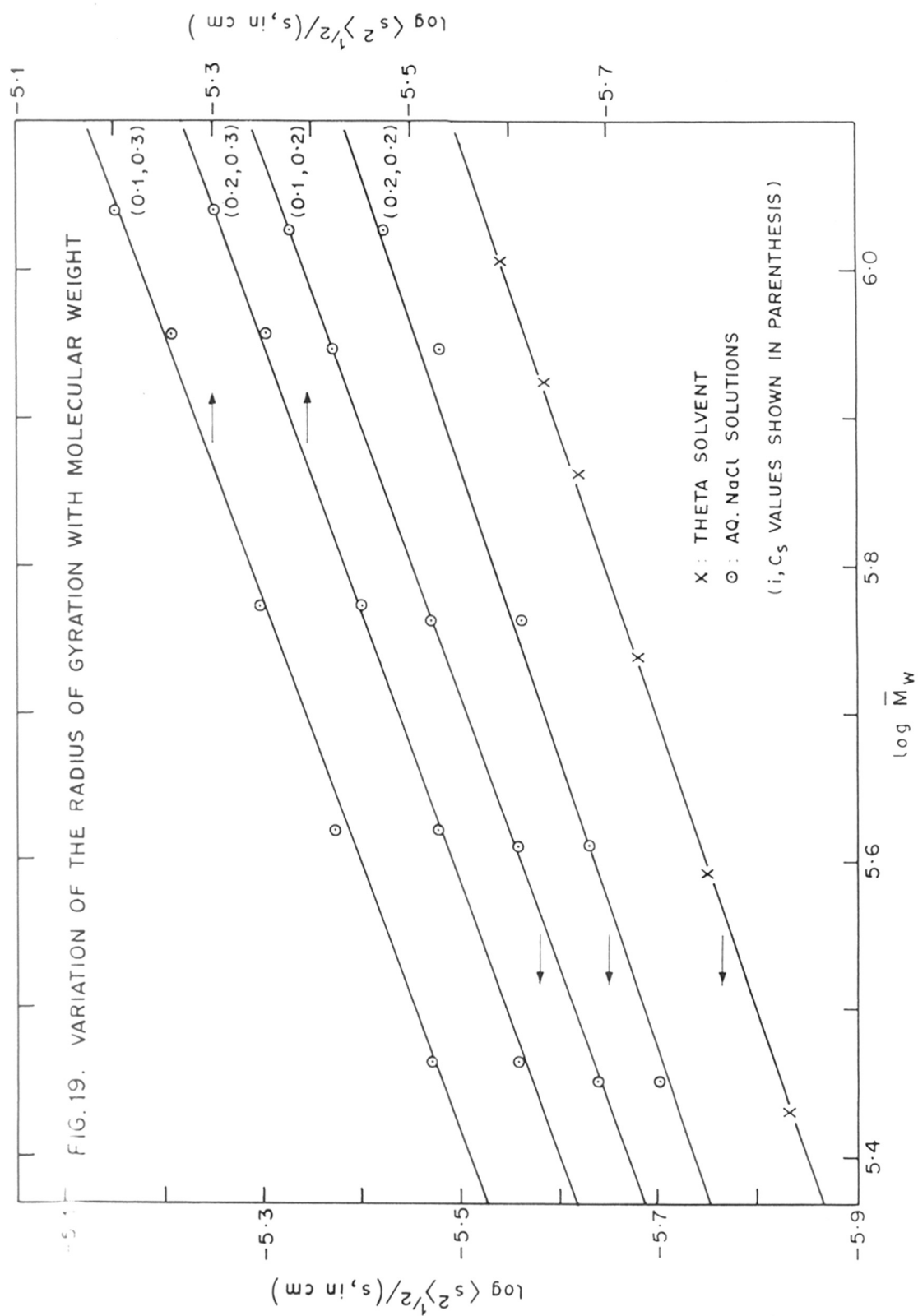
salt concentration and degree of ionization) in the determination of $\langle s^2 \rangle$, the determined apparent dimensions in aqueous solutions also can be used for obtaining qualitative $\langle s^2 \rangle - \bar{M}_w$, $\langle s^2 \rangle - i$ and $\langle s^2 \rangle - c_s$ relationships. The dimensions determined in the theta solvent and in aqueous solutions containing different added salt concentrations and the polymer ionized to various extents are listed in Table 9. The unperturbed dimensions range from 150 to 290 Å. For the aqueous solutions, the dimensions increase with ionization at finite concentration of the added salt, e.g. 575 Å at $i = 0.2$ to 890 Å at $i = 0.5$ when $c_s = 0.05M$, for the highest molecular weight fraction. At finite extent of ionization, the dimensions decrease with increasing concentration of the added salt, e.g. 665 Å at $c_s = 0.05M$ to 445 Å at $c_s = 0.20M$ when $i = 0.3$, for the second fraction.

Fig. 19 shows the variation of the root-mean square radius of gyration with molecular weight for the theta solvent and for four of the partially ionized acid containing differing concentration of the added salt. The relationship obtained for the theta solvent is

$$\langle s^2 \rangle^{1/2} = 2.84 \times 10^{-9} \bar{M}_w^{0.5} \quad (\langle s^2 \rangle^{1/2} \text{ in cm})$$

As earlier discussed, the uncertainty in the dimensions for the aqueous solutions being independent of the degree of ionization and concentration of the added salt, the $\langle s^2 \rangle^{1/2} - \bar{M}_w$ relationship deduced will be valid regarding the power law, the uncertainty being absorbed in the constant term. The relationships obtained for the aqueous solutions are

$$\langle s^2 \rangle^{1/2} \propto \bar{M}_w^{0.51} \quad (c_s = 0.20M; i = 0.2)$$



$$\begin{array}{ll}
\langle s^2 \rangle^{1/2} \propto \bar{M}_w^{0.52} & (c_s = 0.20M; i = 0.3) \\
\langle s^2 \rangle^{1/2} \propto \bar{M}_w^{0.54} & (c_s = 0.10M; i = 0.2) \\
\langle s^2 \rangle^{1/2} \propto \bar{M}_w^{0.55} & (c_s = 0.10M; i = 0.3)
\end{array}$$

The exact relationships at other extents of ionization and added salt concentrations were not deduced due to the limited data available. However, the exponent was in the range 0.51 to 0.60 for the total range of ionization and added salt concentration examined. The values of exponent increased with increasing extent of ionization, at finite concentration of the added salt. When the ionization was kept constant, the values decreased with increasing concentration of the salt. The range of the values of exponents obtained also supports the conclusion^{6,107} that random-coil representation is valid for PMA in the range of salt concentration and degrees of ionization examined.

III.8 Hydrodynamic Theories

Irrespective of the causes (electrostatic or otherwise) for the expansion of the macromolecules over its unperturbed dimension, the resultant expansion affects both the hydrodynamic radius as well as the radius of gyration. In principle, therefore, the data obtained in this investigation can be used for checking the applicability of different hydrodynamic theories of polymer solutions (section I.5). Perturbation theories are exact (section I.2) for low expansions, corresponding to small values of z in the neighbourhood of theta temperature. Experimental uncertainties predominate in these regions of expansions. Asymptotic expressions relating the expansion coefficient, α , to the excluded volume parameter, z ,

have been derived. Experimental investigations which can throw light on the relationships between the hydrodynamic radii and radii of gyration are of practical importance.

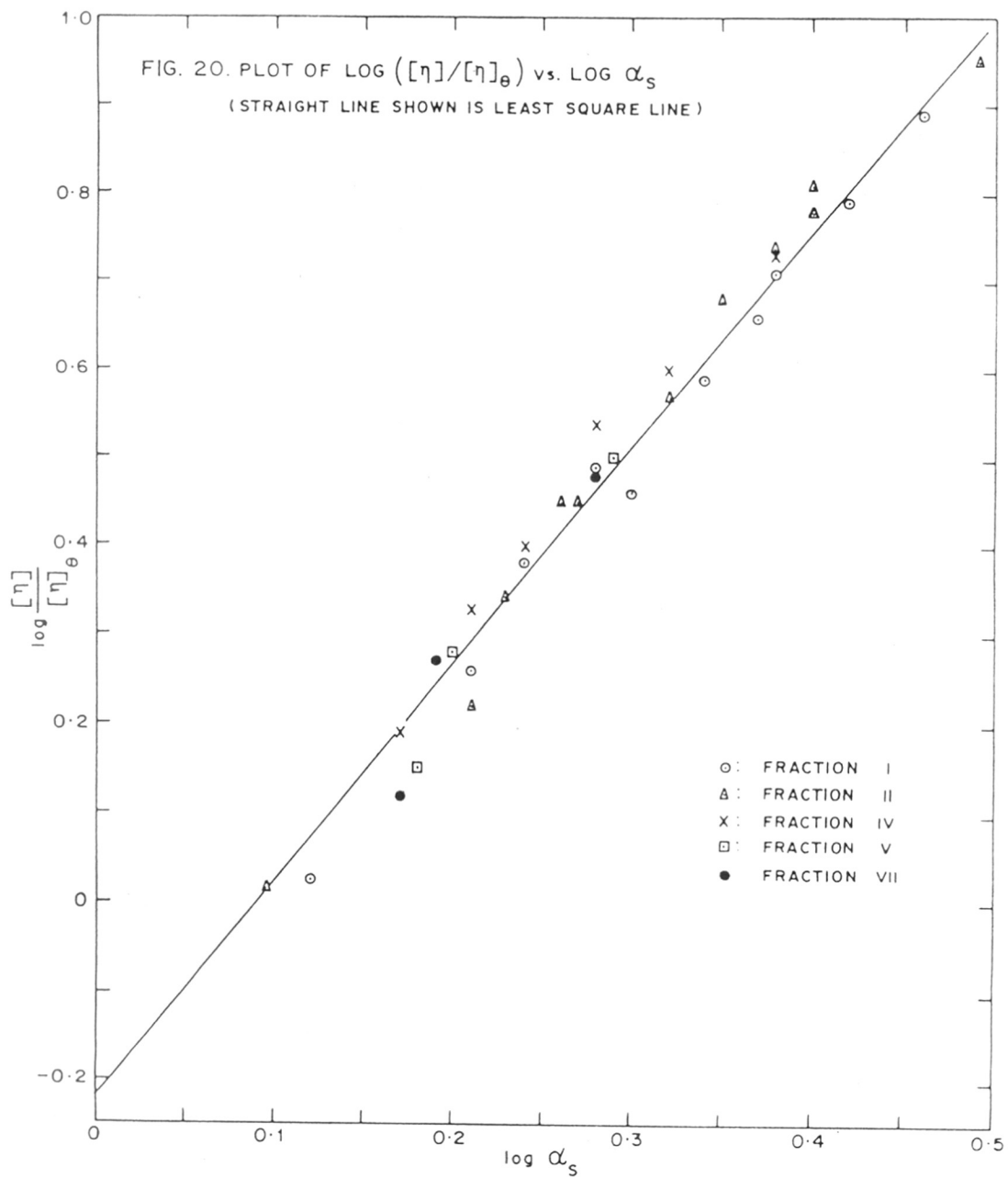
Amongst the various perturbation theories, the more exact theories valid in the neighbourhood of theta temperature yield the two relationships^{19,21,22}.

$$\alpha_r = 1 + 1.333 z - 2.075 z^2 + \dots$$

$$\alpha_s = 1 + 1.276 z - 2.082 z^2 + \dots$$

Flory's theory⁷, generally treated valid²⁴ as an asymptotic α - z relationship in the practical ranges of expansions encountered, assumes isotropic swelling of the polymer coil in the surrounding solvent medium. The hydrodynamic expansion coefficient is obtained as $[\eta]/[\eta]_0 = \alpha_\eta^3$ and the α - z relationship valid is $\alpha^5 - \alpha^3 = 2.60 z$. Kurata-Yamakawa proposed⁶⁰ $\alpha_\eta^3 = \alpha_s^{2.43}$ based on Fixman's third power law¹⁹ $\alpha^3 - 1 = 2z$. The available experimental data appear to confirm¹⁰⁸ Flory's relationship. However, amongst the extrapolation methods used to estimate the unperturbed dimensions from intrinsic viscosities in good solvents, Stockmayer-Fixman relationship based on Fixman's third power α - z relationship is very widely used. S-F plots have been found valid for a large number of polymer-solvent systems including many polyelectrolyte-water-salt systems⁹. This apparent contradiction has not been satisfactorily resolved.

We used the measured dimensions and intrinsic viscosities to test the possible α_η - α_s relationship. As already mentioned, the Flory's viscosity constant (Φ) values remaining invariant with the salt concentration



and ionization, a constant error (independent of ionization and salt concentration) occurs in the measured values of $\langle s^2 \rangle^{1/2}$ which will not affect the power law relating the $[\eta]$ with expansion coefficient. The constructed $[\eta]/[\eta]_0$ vs α_s plot is shown in Fig. 20. The least-square line drawn has a slope of 2.42 in very good agreement with the predicted value of 2.43 based on Fixman's third-power law. Thus the data obtained in this investigation is in accord with the Fixman's third power law. It may be remarked that the high expansion coefficients of PMA as compared to those normally observed in nonionic polymers lead to a higher experimental accuracy in the measured values of apparent dimensions and $[\eta]$. This may be partly responsible for obtaining an unequivocal α_η - α_s relationship.

More important, from the point of view of the accuracy of the determination of the dimensions of these polyelectrolytes, is the negative intercept obtained (- 0.21) in Fig. 20. This indicates that the estimated values of α_s are higher than their true values. As earlier remarked, Φ being independent of the ionization and salt concentration, the slope of the line is unaffected by uncertainty in the values of α_s . Assuming the error in the value of α_s as a vertical shift in the experimentally obtained straight line, the negative intercept in Fig. 20 can be used to estimate the error in the values of α_s . This error can be totally assigned to the error in the determined values of the dimensions in the aqueous solutions as the determined dimensions in the theta solvent are considered to be reliable. The abscissa value at zero ordinate is + 0.092, corresponding to a 23% higher value for the determined dimensions in aqueous salt solutions. The obtained estimate of the uncertainty compares very

well with the value of 20% estimated from the Flory's viscosity-constant Φ . Hence, in our opinion, the measured dimensions in the aqueous salt solutions are about 20% higher to the actual values due to the inapplicability of the fluctuation theory of light scattering for the determination of dimensions of these charge bearing macromolecules.

III.9 Macroion Expansion Coefficients

The most interesting and easily observable property of linear synthetic polyelectrolytes is the large variation in their dimensions brought about by changes in experimental conditions such as p^H and concentration of the added simple electrolyte. It has been recognised^{1,2,3} that with increasing neutralization of the polyelectrolyte in solution progressive ionization takes place and the strong electrostatic repulsions of the like charges along the backbone bring about large increases in dimension. One of the major purposes of theoretical and experimental studies in polyelectrolytes is to quantify the expansions that can be brought about by changes in the charge density of the polyion.

There have been several models used for the theoretical calculations of macroion expansions. These have been detailed in section I.3. One of them is that of an equivalent chain with the electrostatic charges localized at the end points or at the centre of the statistical elements. Another model used is that of an equivalent sphere with charges distributed in concentric shells and for each concentric shell Donnan electroneutrality condition has been assumed to apply. Excluded volume approach has also been applied to the theoretical treatments of macroion expansions. In several of these models, the equilibrium configuration of the poly-

electrolyte molecule is calculated as a balance of the expansion due to electrostatic repulsions and the elastic retractive force opposing expansions.

Experimental investigations of polyelectrolyte expansions and specifically those aimed at the verification of the macroion expansion theories, are severely limited. However, it has been recognised^{1,2,3} that the experimentally observed expansions are low as compared to the theoretically predicted values. This has been qualitatively explained to be due to counterions condensing on to the macroion and thus lowering its effective charge density. The very high charge density of the macroion, it has been proposed, attracts a large fraction of the counterions to the vicinity of the macroion charges resulting in lower effective charge density. The phenomenon of counterion condensation is better understood in the light of Manning's theory²⁵. Manning proposed that a critical charge density parameter equal to the inverse Bjerrum length exists, above which counterion condensation occurs.

Apart from experimentally determined expansions being lower than those theoretically predicted (due to counterion condensation), experimental studies have not established any definite conclusion regarding the variation of the expansion with charge density. The major problem is that the theories predict expansions with reference to a hypothetical discharged state of the macroion i.e. an equivalent polymer identical to the macroion under investigation except for the absence of charges. This reference state cannot be experimentally realized. Nagasawa and coworkers^{4,9,109} have carried out the most significant investigation in this direction. They used the model of the ionized polyelectrolyte

containing infinite concentration of the added simple electrolyte as the reference state. The justification for such a step is that the macroion charges are shielded by the counterions of the added electrolyte. Presumably, complete charge shielding occurs at infinite concentration of the added electrolyte. The ionized polyelectrolyte with infinite concentration of the added salt behaves as the macromolecule identical to the polyelectrolyte investigated except that the charges are completely shielded. This approach is difficult to reconcile on the basis of the available experimental evidence that theta conditions for several polyelectrolytes are obtained at finite concentrations of the added salt^{4,5}. Further increase in the concentration of the added salt should lead to an immiscible two phase system (with the polymer insoluble in the medium). It is thus difficult to visualize that the configuration of the polyelectrolyte precipitated out of solution corresponds to that of the reference macromolecule in solution.

The only other approach to electrostatic expansions is the investigation carried out on hydrolysed polyacrylamides¹¹. Electrostatic expansion coefficients were evaluated with reference to the parent polyacrylamides. These could not be reconciled with any of the macroion theories. The investigators proposed that the total expansion with reference to the unperturbed state of the parent polyacrylamides can be ascribed to the electrostatic interactions alone. This approach has parallel in the theories¹ of simple electrolytes wherein electrostatic interactions are treated as predominant to the total exclusion of the nonelectrostatic interactions. They concluded that the results are qualitatively in agreement with Chien-Ishihara¹¹⁰ theory on the basis of intrinsic viscosity data. It may be

noted that the Chien-Ishihara derivation is for the polyelectrolyte ionized to the maximum extent and thus ignores one of the important variables viz. the degree of ionization of the polyelectrolyte. They also used an ad hoc assumption that (i^2/c_s) is proportional to the number of ionizable groups present, to obtain equivalent expressions relating expansions to the charge density.

In the light of the above discussion, it is apparent that more experimental investigations of the polyelectrolyte expansions are desirable. We chose PMA, a widely investigated polyelectrolyte as the typical polyelectrolyte. Fractionated samples were used to eliminate molecular weight heterogeneities affecting the results. Viscosity and light scattering measurements were carried out in the ionization range $0.20 \leq i \leq 0.50$ with added salt concentration ranging from 0.05M to 0.20M. However, as PMA undergoes a conformational transition during its ionization, the data only in the ionization range 0.25 to 0.50 were used. It is reported^{10,87} that the determination of dimensions of hydrolysed polyacrylamide in solution by light scattering measurements involves a large uncertainty. This conclusion was based on the very low values of Flory's viscosity constant $\bar{\Phi}$ obtained for the hydrolysed samples. Whether the uncertainty in the determined dimensions is due to the copolymer character of the polymer employed or due to its polyelectrolyte nature is not explained. As already discussed in section III.7, the values of the Flory's viscosity constant $\bar{\Phi}$ for the ionized PMA solutions were independent of the degree of ionization and added salt concentration. It has been estimated that the values of measured dimensions for the ionized solutions in the presence of the added salt are about 20% higher. The error is independent

of i and c_s , the factors influencing the effective charge density. Hence both intrinsic viscosity and dimensions determined by light scattering were used for evaluating the relative applicability of macroion expansion theories, especially with respect to the functional form of the dependence of the expansion coefficient with i and c_s .

As emphasized earlier, the macroion expansion theories deal with the extra expansion that can be brought about by the presence of electrostatic charges on the macromolecule. The reference state used by Nagasawa and coworkers⁹ is the configuration of the polyelectrolyte with infinite concentration of the added salt. Apart from the reasons discussed earlier, it was observed that the extrapolation of $([\eta]/[\eta]_0 - 1)$ vs $c_s^{-1/2}$ to infinite salt concentration (the suggested method by Nagasawa et al⁹) resulted in a negative value for $[\eta]/[\eta]_0$ at $c_s \rightarrow \infty$ for the total range of the data obtained in this investigation. Significance of negative intrinsic viscosity and negative dimension are not understood. From this point of view we employed total expansion coefficients for evaluating the macroion expansion theories.

Different theoretical approaches have been used to the macroion expansions, as discussed in section 1.3. However, the final expressions obtained by the different theories can be expressed^{5,9} in terms of 'electrostatic excluded volume parameter', z_{el} , similar to the excluded volume parameter z encountered in the theories of neutral macromolecules in solution. The expressions obtained are:

$$\begin{array}{ll} \text{Katchalsky-Lifson}^{27} & (\alpha_e - 1/\alpha_e) \propto z_{el} \\ \text{Kurata}^{33} & \alpha_e^3 \propto z_{el} \end{array}$$

Ptitsyn ³⁷	$\alpha_e^3 \propto z_{el}$
Alexandrowicz ³⁴	$\alpha_e^2 \propto z_{el}^{1/2}$
Hermans-Overbeek ³⁰	$\alpha_e^5 - \alpha_e^3 \propto z_{el}$
Fixman ³⁸	$\alpha_e^3 \propto z'_{el}$
Flory ³²	$\alpha_e^5 - \alpha_e^3 \propto z_{el}$

z_{el} in the above expressions is defined as,

$$z_{el} = \left(\frac{3}{2}\right)^{3/2} m_s^{-2} (M/\bar{r}_o^2)^{3/2} \left(\frac{10^3 i^2}{2 N_A c_s}\right) M^{1/2}$$

The terms occurring in z_{el} have already been defined in section I.3. As discussed above, we used the total expansion coefficients with respect to the unperturbed dimension of the unneutralized PMA (in an organic solvent and hence corresponding to the conformational state of PMA at the degrees of ionization experimentally examined) for the electrostatic expansion coefficients. The expansion coefficients from viscosities were calculated using $[\eta]/[\eta]_0 = \alpha_\eta^3$, where $[\eta]$ is the measured intrinsic viscosity at the degree of ionization 'i' and added salt concentration c_s , $[\eta]_0$ is the intrinsic viscosity of the unionized sample in DMF/1,4-dioxane (5:7) mixture at 27.1°C. Similarly, expansion coefficients from light scattering were deduced as $\alpha_s^2 = \langle s^2 \rangle / \langle s^2 \rangle_0$ where $\langle s^2 \rangle$ and $\langle s^2 \rangle_0$ are the root-mean square radii of gyration of the partly ionized PMA with the added salt and in the organic theta solvent, respectively. The molecular weights used for the expansion coefficient-charge density

relationships were calculated using the averaged molecular weights listed in the last column of the Table 2, and applying necessary correction for the extent of ionization. From the calculated expansion coefficient, α^3 , α^5 , etc. (required for correlations) were calculated. The relative applicability of the various macroion theories were evaluated qualitatively based on the linearity of the relationships between α^3 and $[(i^2/c_s) M^{1/2}]$, z_{el} being proportional to $[(i^2/c_s) M^{1/2}]$.

The calculated values of α_η and α_s at different degrees of ionization and concentration of the added salt are listed in Tables 10-14 for the differing molecular weight fractions. For the total range of data, α_η ranged from 1.09 (fraction VII, $i = 0.25$, $c_s = 0.20M$) to 2.0 (fraction II, $i = 0.40$, $c_s = 0.05M$). Similarly, the values of α_s ranged from 1.57 (fraction VII, $i = 0.3$, $c_s = 0.20M$) to 2.95 (fraction I, $i = 0.40$, $c_s = 0.05M$). It is seen that the expansion coefficients obtained from light scattering are significantly higher to those obtained from viscosities. This is in qualitative accord with the conclusion reached earlier that the determined dimensions from light scattering are higher (about 20%) than the true dimensions. However, this error only affects the proportionality constant and not the functional relationship of α^3 with i , c_s and $\bar{M}_w$.

The variation of the expansion coefficients with the charge density, according to various theories discussed above, are shown in Figs. 21-25. The data obtained from both the light scattering and viscosity measurements are included in each figure. The expansion coefficients obtained from light scattering being higher, the curve at the top shows the light scattering data.

Table 10 Expansion coefficients for partially ionized PMA (Fraction I)

i	c_s	α_η^*	α_s^{**}	$\alpha_{1,\eta}^{*+}$
0.25	0.05	1.66	2.34	1.60
	0.07	1.54	--	1.48
	0.10	1.42	--	1.37
	0.14	1.28	--	1.23
	0.20	1.17	--	1.13
0.30	0.05	1.84	2.60	1.62
	0.07	1.72	2.38	1.52
	0.10	1.58	2.17	1.39
	0.14	1.45	1.90	1.28
	0.20	1.34	1.74	1.18
0.35	0.05	1.98	2.86	1.62
	0.07	1.86	--	1.52
	0.10	1.73	--	1.41
	0.14	1.59	--	1.29
	0.20	1.47	--	1.20
0.40	0.05	--	2.95	--
	0.14	1.69	--	1.29
	0.20	1.58	--	1.20

$$* \alpha^3 = [\eta]/[\eta]_0$$

$$** \alpha_s^2 = \langle s^2 \rangle / \langle s^2 \rangle_0$$

$$+ \alpha_{1,n} = [\eta]/[\eta]_{\theta,i}$$

Table 11 Expansion coefficients for partially ionized PMA (Frinction II)

i	c_s	α_η	α_s	$\alpha_{l,\eta}$
0.25	0.05	--	2.21	--
	0.10	--	1.81	--
	0.14	1.25	--	1.20
	0.20	1.17	--	1.12
0.30	0.05	1.82	2.51	1.60
	0.07	1.68	2.25	1.48
	0.10	1.55	2.08	1.37
	0.14	1.41	1.87	1.24
	0.20	1.30	1.68	1.14
0.35	0.10	--	--	--
	0.14	1.56	--	1.27
	0.20	1.44	--	1.17
0.40	0.05	2.0	--	--
	0.07	1.88	--	--
	0.10	1.77	2.38	--
	0.14	1.67	--	1.25
	0.20	1.56	--	1.17

Table 12 Expansion coefficients for partially ionized PMA (Fraction IV)

i	c_s	α_η	α_s	$\alpha_{l,\eta}$
0.25	0.05	1.58	2.07	1.54
	0.07	1.46	--	1.43
	0.10	1.34	--	1.32
	0.20	1.13	--	1.10
0.30	0.05	1.75	2.37	1.57
	0.07	1.64	--	1.47
	0.10	1.52	1.91	1.36
	0.14	1.40	--	1.25
	0.20	1.28	1.63	1.15
0.35	0.05	1.89	--	1.55
	0.07	1.77	--	1.46
	0.10	1.66	--	1.36

Table 13 Expansion coefficients for partially ionized PMA (Fraction V)

i	c_s	α_η	α_s	$\alpha_{1,\eta}$
0.25	0.05	1.53	--	1.50
	0.07	1.42	--	1.39
	0.10	1.30	--	1.28
	0.14	1.18	--	1.16
	0.20	1.09	--	1.07
0.30	0.05	1.71	--	1.54
	0.07	1.59	--	1.43
	0.10	1.47	1.97	1.32
	0.14	1.35	--	1.21
	0.20	1.24	1.58	1.12
0.35	0.05	1.85	--	1.54
	0.07	1.72	--	1.43
	0.10	1.61	--	1.33
	0.14	1.46	--	1.21
	0.20	1.38	--	1.14
0.40	0.14	1.59	--	1.22
	0.20	1.50	--	1.13

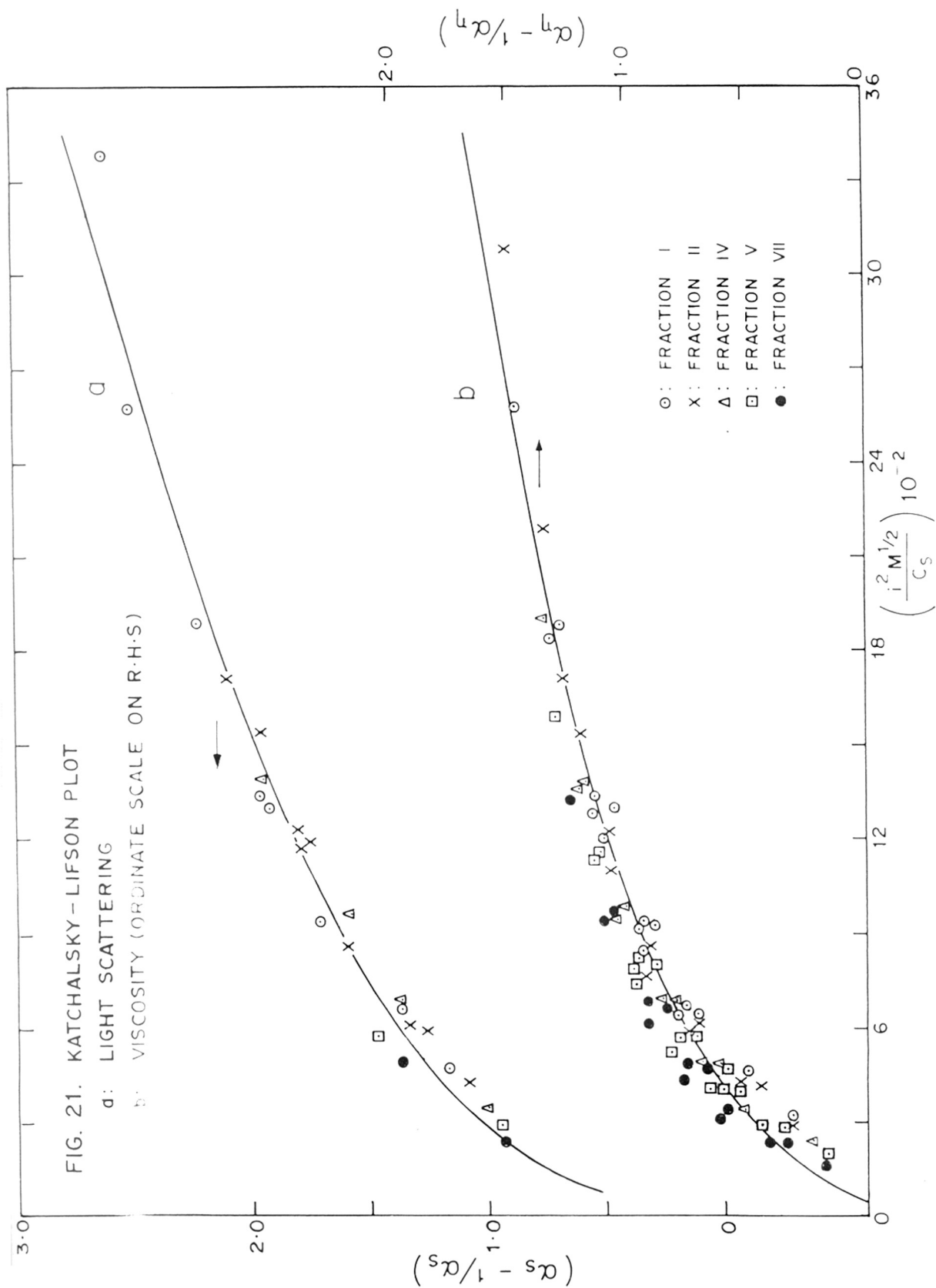
Table 14 Expansion coefficients for partially ionized PMA (Fraction VII)

i	c_s	α_η	α_s	$\alpha_{1,\eta}$
0.25	0.05	1.50	--	1.46
	0.07	1.39	--	1.35
	0.10	1.28	--	1.25
	0.14	1.18	--	1.15
	0.20	1.09	--	1.06
0.30	0.05	1.67	--	1.48
	0.07	1.56	--	1.39
	0.10	1.45	1.90	1.29
	0.14	1.33	--	1.18
	0.20	1.23	1.57	1.09
0.35	0.05	1.80	--	1.48
	0.07	1.69	--	1.39
	0.10	1.57	--	1.29
	0.14	1.45	--	1.19
	0.20	1.36	--	1.12
0.40	0.14	1.56	--	1.18
	0.20	1.46	--	1.10

Fig. 21 shows the Katchalsky-Lifson plot. Linear representation of the data is not possible. Fig. 22 shows the variation of the expansion coefficient with charge density as per Ptitsyn theory. The same may be treated as representing the data fit according to Kurata equation. These plots also do not result in straight lines. Figs. 23-25 represent Alexandrowicz, Flory and Fixman theories, respectively. It is observed that the plots according to these theories result in linear variation of the expansion coefficients with charge density. However, Fixman plots exhibit considerable scatter. In all the above figures, the variation of the expansion coefficients with charge density is identical both for viscosity and light scattering data.

The results obtained thus do not clearly discriminate between the relative merits of the Alexandrowicz, Flory and Fixman theories. The data only show that Katchalsky-Lifson, Kurata and Ptitsyn expressions do not hold good even qualitatively.

On comparing the results obtained here for PMA with those reported for hydrolysed polyacrylamide (HPAA), the conclusion that can be drawn is rather confusing. In both the cases, Katchalsky-Lifson, Kurata and Ptitsyn representations do not hold good and Fixman theory is qualitatively valid but the data show a large scatter. It may be remarked that Nagasawa and coworkers have reported⁹ that Fixman representation gave a very good fit of the data for the electrostatic expansion coefficients computed with reference to the infinite concentration of the added salt. Regarding the applicability of the other theories, the conclusions drawn are contradictory. Plots according to Alexandrowicz theory result in straight lines for PMA whereas slight curvatures at higher charge densities were reported



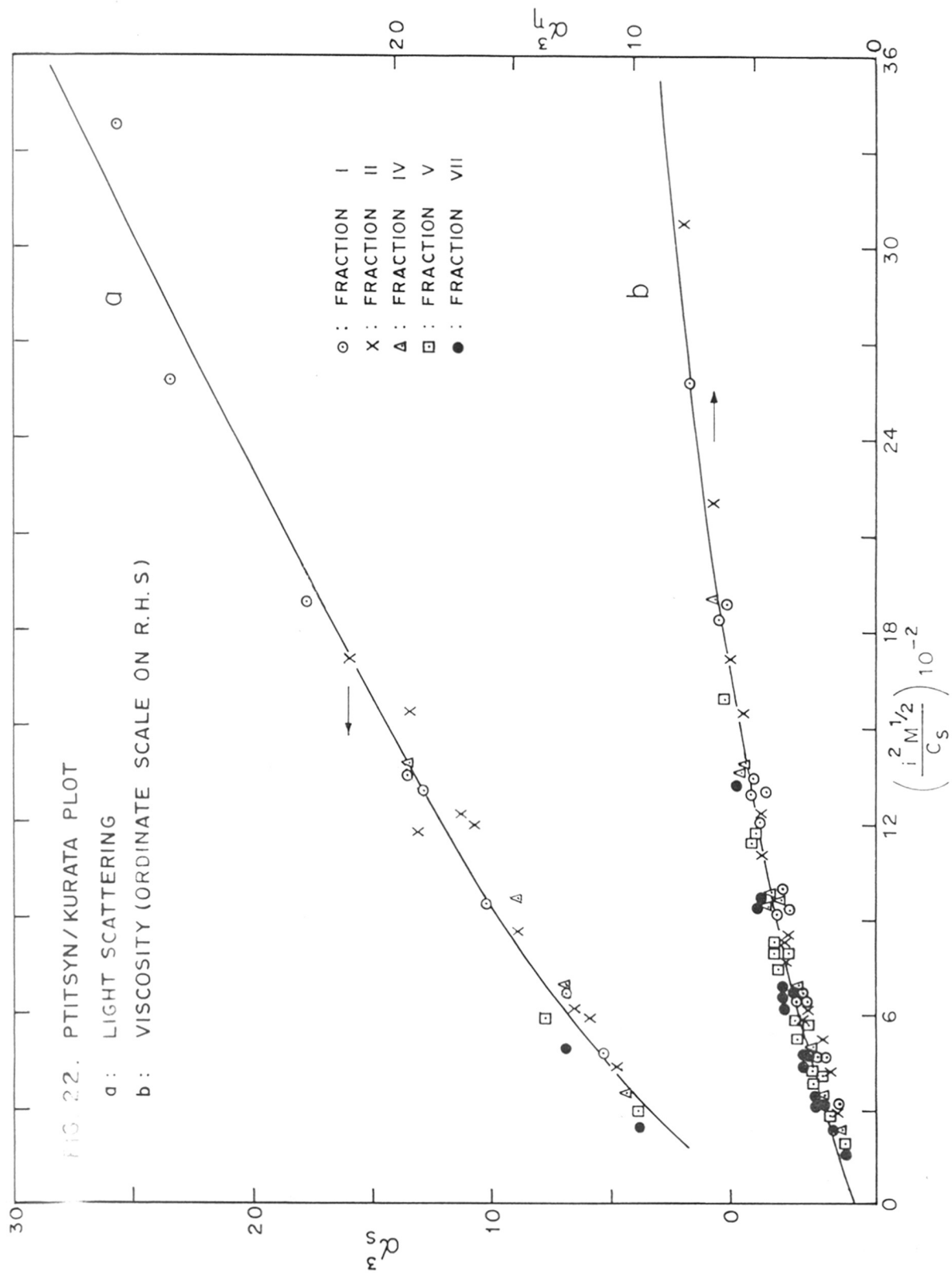
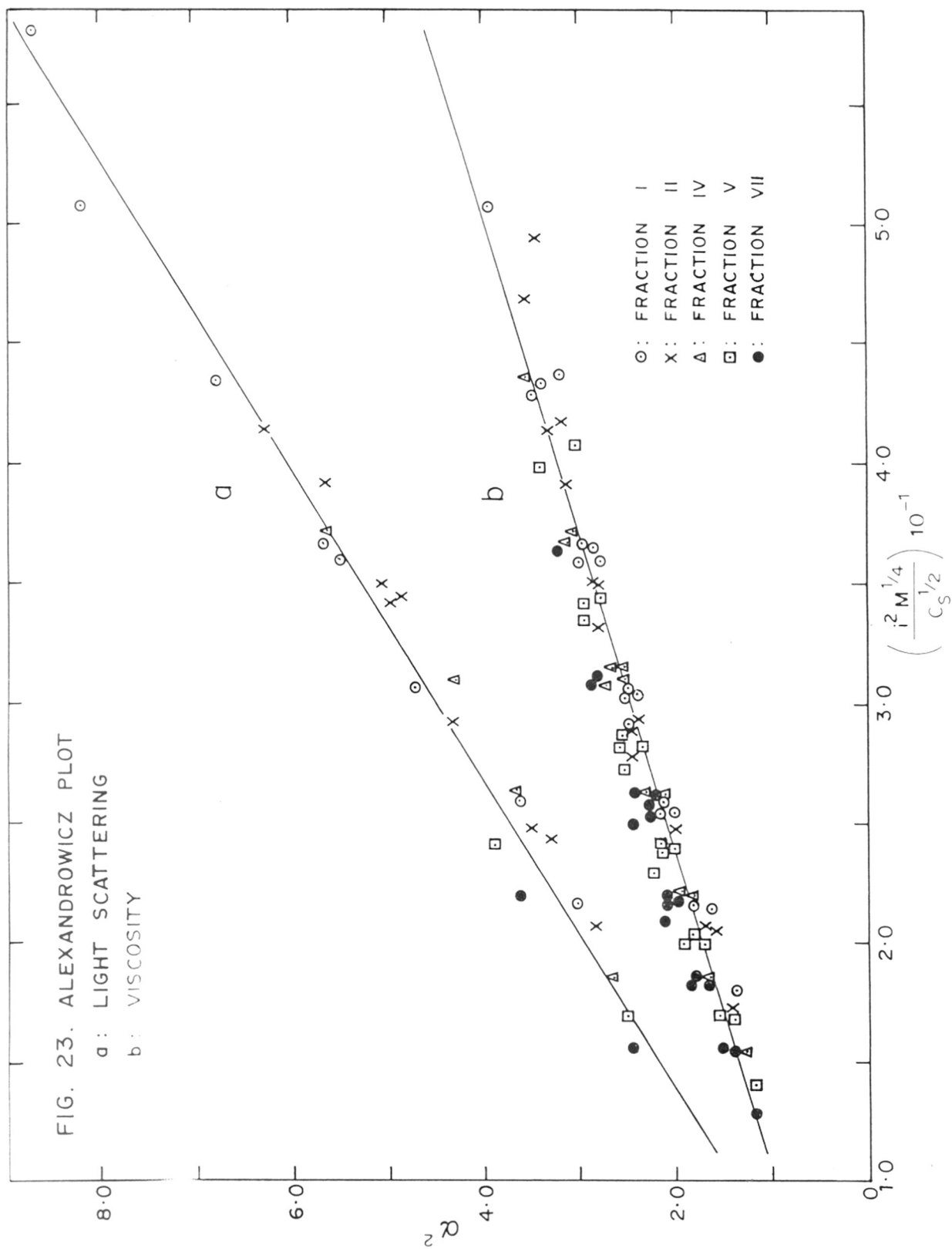
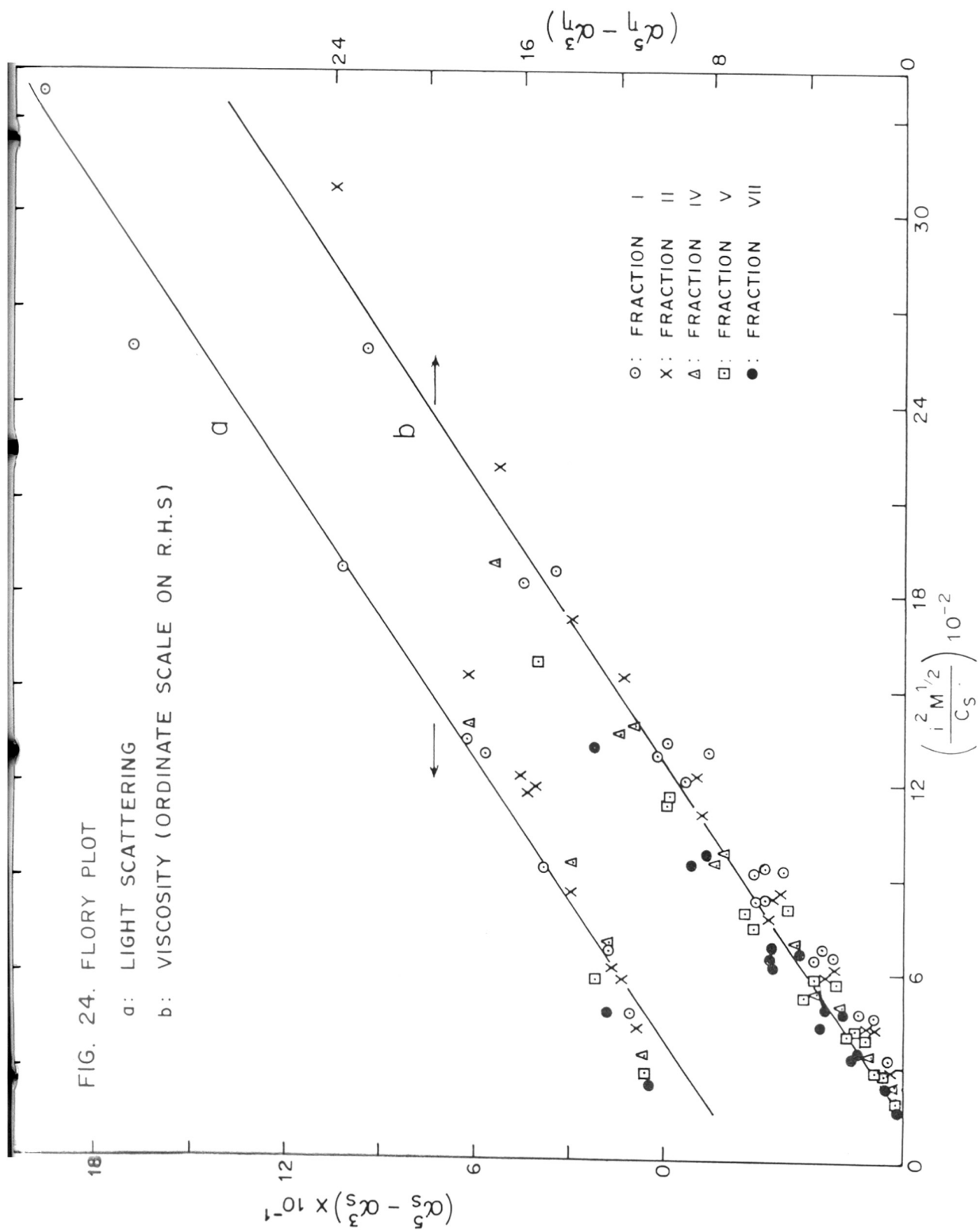


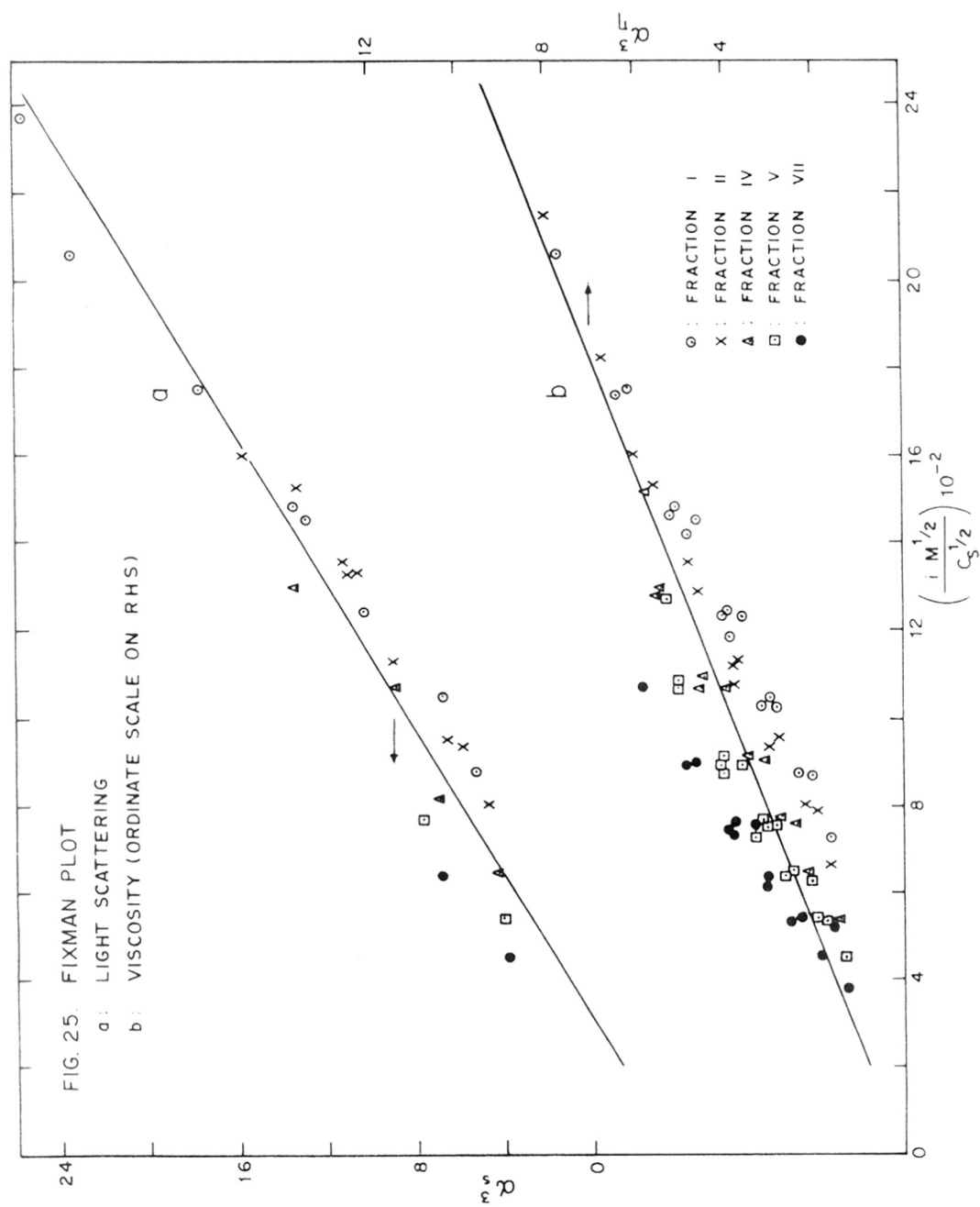
FIG. 23. ALEXANDROWICZ PLOT

a: LIGHT SCATTERING

b: VISCOSITY







for HPAA. Moreover, three curves were needed for HPAA for the total range of the data. Both for PMA and HPAA, linear dependence of the expansion coefficients with charge density are observed according to Flory representation. However, three straight lines were required for the total range of the data for HPAA whereas a single straight line suffice for PMA.

It may be pointed out that fractionated samples of PMA were used in this investigation whereas samples of HPAA employed were unfractionated. The molecular weights of HPAA covered relatively a wider range as compared to PMA samples used here. However, in our opinion, these differences are minor. Other reasons are to be ascribed to explain the differences in the observed behaviour of the functional dependence of the expansion coefficients on charge density for PMA and HPAA.

In examining the functional dependence of expansion coefficient on charge density, we have not considered Chien-Ishihara¹¹⁰ and Odijk-Houwaart³⁹ expressions. Chien-Ishihara relationship has been derived for polyelectrolytes ionized to maximum extent and was reported¹¹ to best represent the expansion coefficients obtained from viscosity for HPAA. It is valid for HPAA examined at varying degrees of hydrolysis as ionization was not varied. However, as the final expression derived is devoid of the degree of ionization (an important variable for polyelectrolytes), we did not consider the Chien-Ishihara relationship. Odijk-Houwaart derivation is based on the worm-like chain model with an electrostatic persistence length for the Kuhn's segment. It may be noted that amongst the theoretical derivations available, only Odijk-Houwaart treatment can account for the variation of the value of K_0 (representing the

short-range interaction) with ionization as charge density dependent electrostatic persistence length. As discussed in earlier sections, random-coil representation is satisfactory for PMA for the ranges of ionization and concentration of the added salt examined here. Hence we did not apply the Odijk-Houwaart derivation to the treatment of the data obtained.

III.9.a Long-range effect on the macroion expansion

The backbone charges on a polyelectrolyte severely affect the potential energy barriers hindering free rotation around the skeletal bonds. Hence short-range interactions for polyelectrolytes depend upon the degree of ionization. Increasing values of K_0 in the SF plots with increasing degree of ionization have been reported for polyacrylic acid⁹, polymethacrylic acid^{9,98} and hydrolysed polyacrylamides¹¹. This is also demonstrated by the data obtained here (Table 6).

Even the ionized polyelectrolyte finds itself in a favourable environment in the dissolved state. Hence it would be interesting to compute the expansions of the polyelectrolyte which could be ascribed to the long-range effects. For the PMA examined here, corresponding intrinsic viscosities in theta condition were calculated as $[\eta]_{\theta} = K_0 \times M^{1/2}$. The values of α_1 , the expansion coefficient attributable to the long-range effect was calculated as $\alpha_1^3 = [\eta]_{i,c_s} / [\eta]_{\theta,i}$. $[\eta]_{i,c_s}$ is the measured intrinsic viscosity at degree of ionization i and added salt concentration c_s and $[\eta]_{\theta,i}$ is the calculated intrinsic viscosity at theta temperature at degree of ionization i .

These values (also included in Tables 10-14) vary from 1.1 to 1.6. It is seen that the values of α_1 at finite degree of ionization decrease

with increase in salt concentration. For example, at $i = 0.25$, the value of 1.6 at $c_s = 0.05M$ decreases to 1.1 at $c_s = 0.20M$ for the fraction I. Comparing the values at the same degree of ionization and concentration of the added salt, it is seen that the values decrease with decrease in molecular weight. More surprisingly, the values of α_1 are independent of degree of ionization. For example, for the first fraction at $c_s = 0.05M$ the values obtained for the differing degrees of ionization are 1.60, 1.62 and 1.62, and 1.07, 1.12, 1.14 and 1.13 for fraction V at $c_s = 0.20M$. At each salt concentration examined, it is seen that α_1 is independent of degree of ionization. On the contrary, both the measured intrinsic viscosities and calculated values of $[\eta]_0$ are highly sensitive to the degree of ionization.

Since a common intercept was not obtained in SF plots for the data at varying concentration of the added salt there is an uncertainty in the values of α_1 listed in Tables 10-14. At each degree of ionization, the intercepts in the SF plots were determined at varying concentrations of the added salt and the values of α_1 were calculated taking the dependence of K_0 on c_s into consideration. In this case also, it was observed that the values of the α_1 obtained were independent of the degree of ionization.

It has been reported¹¹ that the values of α_1 , similarly calculated, for HPAA also were independent of the degree of hydrolysis. For PMA and HPAA therefore, the values of α_1 show similar behaviour. They are independent of the number of charged groups on the polyelectrolyte but increase with increasing molecular weights. These expansion coefficients thus show typical characteristics of the expansion coefficients

obtained for nonionic polymers-variations with solvent power (as evidenced by the decreased value with increasing salt concentration for PMA) and increase with increasing molecular weight. In fact, the data listed in Tables 10-14 show a linear dependence of $(\alpha^5 - \alpha^3)$ on $M^{1/2}$, according to Flory's theory⁷. This leads us to believe that α_1 represents the expansion due to the macromolecular character of the polyelectrolyte. Assuming additivity of the expansions due to ionic and nonionic interaction (as is generally assumed for polyelectrolytes¹), the electrostatic contribution to the expansion coefficient mainly rests with the changes in the short-range interactions alone. This is true at least for the data obtained for PMA in this study and HPAA reported in literature¹¹ in the ranges of charge densities not too low or too high. Charge density is reported¹¹ to affect both short-range and long-range interactions for HPAA at very low degrees of hydrolysis. At very high charge densities (when counterion condensation is considerable) no conclusion can be arrived at in the absence of data.

The results obtained are contrary to expectations. From the variation of K_o with the degree of ionization, it is seen that only the short-range interactions are affected by charge density and short-range interactions are also molecular weight independent. The molecular weight dependent expansion coefficient is α_1 , the expansion coefficient attributable to long-range effects which is independent of charge density. The variation of the short-range interaction with charge density can be explained in terms of a charge density dependent electrostatic persistence length in the realm of worm-like chain representation, according to Odijk-Houwaart theory³⁹. However, for the ranges of ionization and concentration

of the added salt used for PMA a random coil representation is more appropriate. In our view, in the ranges of ionization and concentration of the added salt usually encountered in polyelectrolyte investigations random-coil representation is preferred.

The theories of polyelectrolyte expansions have been recognized to be inadequate by several investigators^{4,111}. Nagasawa and Takahashi note that the failure of the Debye-Hückel interactions in the excluded volume theory of polyelectrolytes is very gross and 'something has gone wrong in its application'. Fixman and Skolnick have pointed out that the simplest use of the Debye-Hückel interaction in the excluded volume theories of polyelectrolytes leads to the excluded volume parameter proportional to $M^{1/2}/c_s$, whereas the experiments clearly indicate that $z \propto (M/c_s)^{1/2}$. The results obtained on PMA and HPAA appear to indicate that electrostatic effects are to be included in the short-range interactions alone. This can explain, amongst others, the fact that most of the polyelectrolyte expansion theories predict a c_s^{-1} dependence for the expansion coefficient whereas experimentally observed dependence is $c_s^{-1/2}$. This would lead to the conclusion that the electrostatic expansions are to be approached by other theoretical models than those used so far. Rotational isomeric state theory appears to be more appropriate. This approach has been applied in a few cases¹¹². It may be noted that the rotational isomeric state theory yields correct temperature coefficient of the unperturbed dimensions for polyelectrolytes also. However, the value used for the local dielectric constant introduces too much uncertainty in the relative conformational probabilities and the application of the rotational isomeric state theory to the polyelectrolyte expansions is complex.

III.9.b An empirical approach to polyelectrolyte expansions in solution

We have seen so far that using the total expansion as electrostatic expansion, the experimental fits of the data according to various macroion theories are not satisfactory. One of the major problems encountered in the experimental studies of macroion expansion is the reference state, i.e. the dimension of the polyelectrolyte molecule in the absence of the electrostatic charges. Nagasawa and coworkers⁹ used the dimension of the polyelectrolyte with infinite concentration of the added simple salt as the reference state. We have seen this approach is open to objections. The other experimental approach to macroion expansion is to treat the total expansion as electrostatic expansion. By this method, the data obtained for PMA do not clearly differentiate between the relative merits of Alexandrowicz³⁴, Flory³² and Fixman³⁸ theories. As far as the dependence of the z_{el} on added salt concentration is concerned, Alexandrowicz and Flory theories cannot be accepted as correct^{110,111}. The predicted dependence is c_s^{-1} , but experimentally observed dependence is usually $c_s^{-1/2}$. The Fixman representation, though not subject to the same shortcoming, exhibits a very large data scatter for PMA and HPAA, not easily ascribable to the experimental errors. We have not considered the Chien-Ishihara approach as it restricts itself to the polyelectrolytes at the maximum degree of ionization.

The available data, therefore, leave much to be desired regarding the experimental validity of the macroion expansion theories. Even the applicability of the Debye-Hückel potential (in the excluded volume theories of polyelectrolytes) has been debated⁴ though Fixman and Skolnick¹¹¹

are of the opinion that Debye-Hückel potential is valid and the difficulties lie elsewhere.

The experimental data obtained in the two systems viz. PMA in this investigation and HPAA reported in literature¹¹, show that the long-range expansion coefficients calculated with reference to the unperturbed dimensions of the ionized polyelectrolyte exhibit typical characteristics of the expansion coefficients of the macromolecules. They are independent of charge concentration, vary with solvent power and increase with increasing molecular weight. This leads us to believe that the expansions due to the chain-like character of polyelectrolyte is reflected only in α_1 , the long-range expansion coefficient. As the charge density dependent term is only K_0 , the expansion deduced from K_0 with reference to the unperturbed state of the unionized polyelectrolyte can be treated as the electrostatic expansion. This electrostatic expansion (if it can be obtained by the method discussed above), shows the irreconcilable characteristics of being molecular weight independent whereas in macroion theories, the predicted electrostatic expansion coefficient is molecular weight dependent and increases with molecular weight.

As the theoretical approaches are not satisfactory, we suggest here an empirical approach to the expansions of linear polyelectrolytes. In common with the usual assumption in polyelectrolyte expansions, we assume additivity of expansions due to electrostatic and nonelectrostatic interactions. Since the experimentally observed electrostatic expansions affect only the short-range interactions, it is proposed that the electrostatic expansion is a function of $(i/c_s)^{1/2}$. The basis for this assumption is the experimental fact that the intrinsic viscosities are proportional

to $(i/c_s)^{1/2}$. We use α_1 as representing the nonelectrostatic expansion. It is well known^{6,7,107} that for nonionic random-coil polymers $\langle s^2 \rangle \propto M^{1+\delta}$ with δ in the range $0 \leq \delta \leq 0.2$. The expansion coefficient α for random-coil polymers depend on molecular weight as $\alpha^2 \propto M^\delta$. Aqueous solutions used for polyelectrolytes are generally good solvents and the maximum value of 0.2 for δ is perhaps applicable, though the exact value is uncertain.

Assuming the additivity of the expansion coefficients due to electrostatic and nonelectrostatic interactions the total expansion of polyelectrolyte in solution is given by

$$\alpha_\eta^3 \propto (i/c_s)^{1/2} M^{0.30}$$

The electrostatic expansion coefficient is represented as a molecular weight independent term $(i/c_s)^{1/2}$ and the molecular weight dependence is incorporated in the nonelectrostatic expansions.

The expansion coefficient from light scattering is similarly obtained as

$$\alpha_s^{2.43} \propto (i/c_s)^{1/2} M^{0.30}$$

We have used the relationship $\alpha_\eta^3 = \alpha_s^{2.43}$ based on Fixman theory and found valid for the experimental data obtained in this investigation.

Fig. 26 shows the data fit according to the empirical equations discussed above. Here we have used a lower value (0.25) for the exponent for the molecular weight dependence of expansion coefficient as the $\langle s^2 \rangle - \bar{M}_w$ relationship for the ionized solutions of PMA (section III.7) showed exponents lower than 0.6, the maximum predicted for random-coil

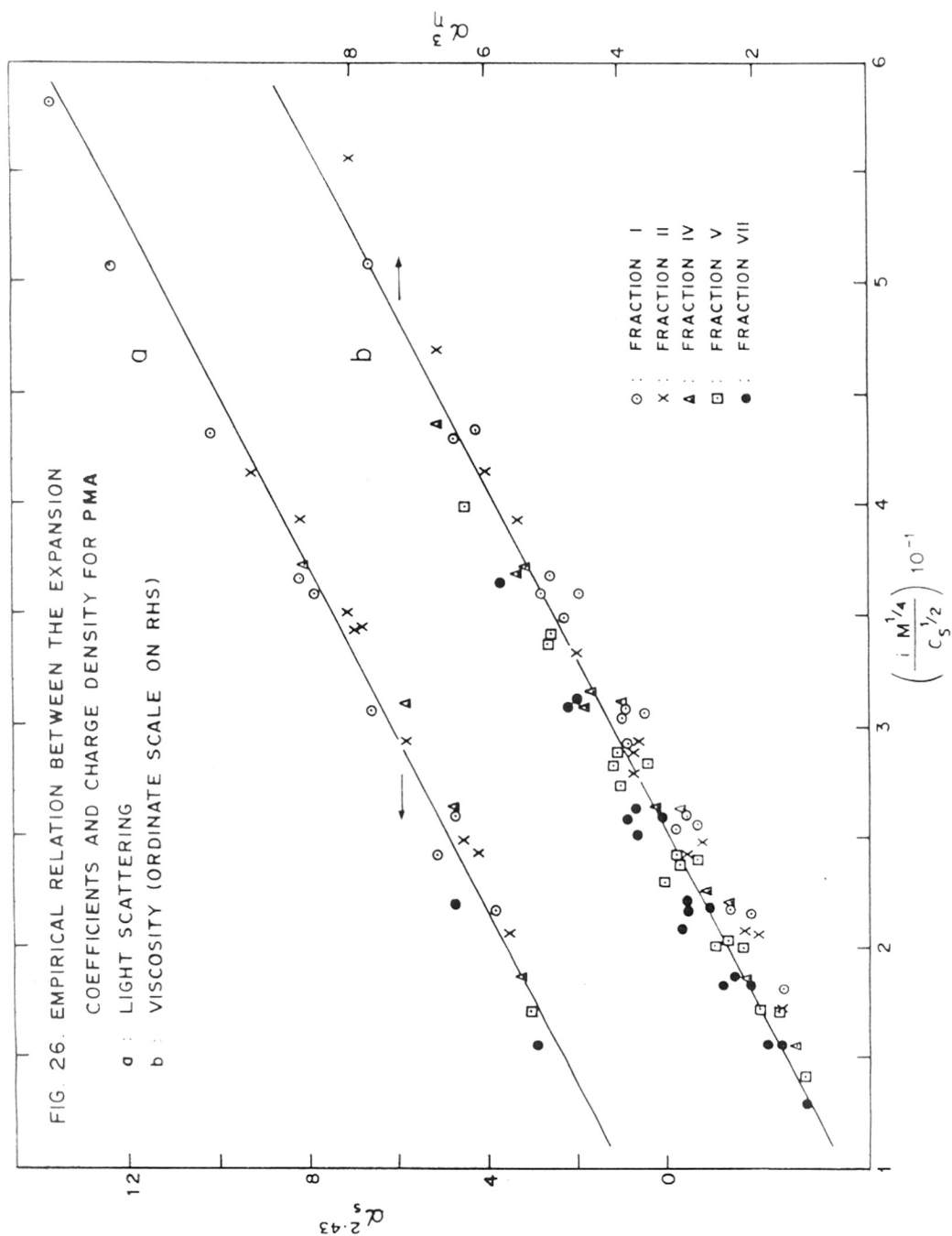
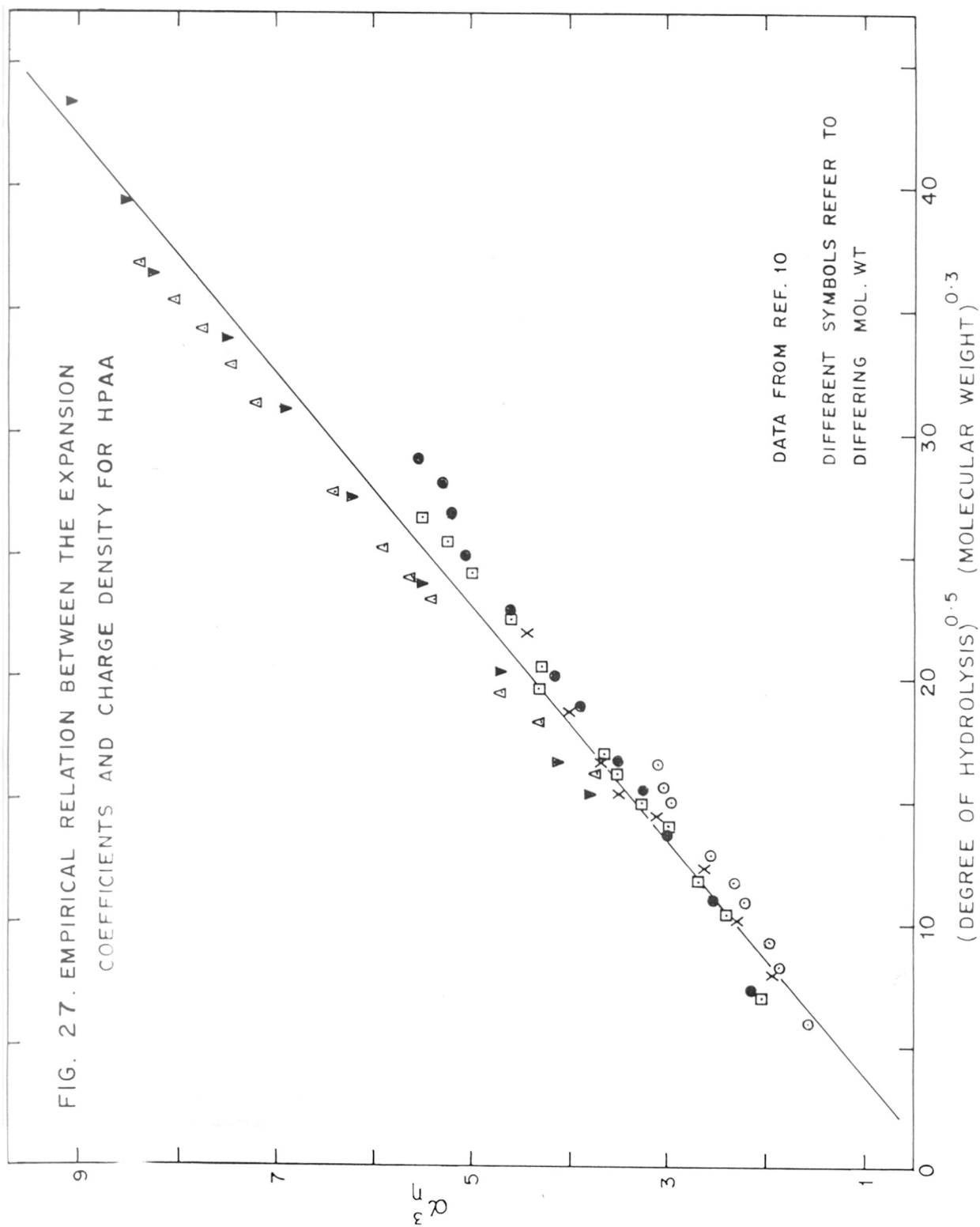


FIG. 27. EMPIRICAL RELATION BETWEEN THE EXPANSION
COEFFICIENTS AND CHARGE DENSITY FOR HPAA



polymers^{6,107}. Satisfactory straight lines were obtained for both light scattering and viscosity data. As discussed in earlier sections, a relative 20% higher value for the dimensions obtained from light scattering does not affect the intended linear relation. Fig. 27 shows the viscosity data for hydrolysed polyacrylamide, represented as per the empirical equation. For verifying the macroion theories, the investigators assumed (i^2/c_s) is proportional to the number of hydrolysed groups on the HPAA. Similarly i^2/c_s in the above relationships have been substituted by 'n' the degree of hydrolysis. The abscissa in Fig. 27 is $(n^{0.5} M^{0.3})$. The higher value of the exponent for the molecular weight term used for HPAA may be justified as polyacrylamides have an exponent of the order of (0.57 to 0.60) in the $\langle s^2 \rangle - \bar{M}_w$ relationship¹¹³⁻¹¹⁵. It may be remarked that the Fixman plot constructed for the same data showed large scatter as in Fig. 25.

The data for polymethacrylic acid and hydrolysed polyacrylamide presented in Fig. 26 and 27 demonstrate the applicability of the empirical method. A molecular weight independent electrostatic expansion coefficient, the molecular weight dependence of the total expansion coefficient arising from the nonelectrostatic interactions alone and the additivity of the electrostatic and nonelectrostatic expansions are assumed in this method.

III.10 Conclusions

Solution polymerized polymethacrylic acid was fractionated. Five of the fractions were studied by light scattering and viscosity methods in organic solvents and in aqueous solutions in the presence of added salt for the polymer ionized to various degrees of ionization.

- (i) 1,4-Dioxane/DMF mixture (7:5; v/v) at 27.1°C was found to be a theta solvent for the unionized polymer. The unperturbed dimensions were higher than their estimated dimensions in 0.002N HCl at 30°C, a reported theta solvent. This has been ascribed to higher unperturbed dimensions in the organic solvent as compared to the aqueous solutions for PMA which undergoes a conformational transition during its ionization.
- (ii) The apparent dimensions determined by light scattering for the aqueous solutions were estimated to be uniformly higher by about 20% to their true dimensions because of the inapplicability of the fluctuation theory of light scattering to the polyelectrolyte-added salt-water multi-component system.
- (iii) The variation of the intrinsic viscosity and dimensions with the molecular weight, and the values of Kuhn equivalent segment length calculated indicated that a random-coil representation is valid for the partially ionized polymethacrylic acid in the ranges of ionization and concentration of the added salt examined.
- (iv) Total expansion coefficients for the partially ionized polymer were deduced with reference to the dimensions in the organic theta solvent and used as electrostatic expansion coefficients for evaluating the applicabilities of macroion expansion theories. The data did not discriminate between the relative merits of Alexandrowicz, Flory and Fixman expressions

and showed that Katchalsky-Lifson, Ptitsyn and Kurata expressions do not hold good even qualitatively. The macroion expansion theories were found to be still grossly inadequate.

(v) The expansions attributable to long-range interference effects for the partially ionized samples were found to be independent of degree of ionization, increase with increasing molecular weight and to vary with the concentration of the added simple electrolyte (corresponding to varying solvent power)- typical characteristics of expansion coefficients of nonionic polymers in solutions. It was thus deduced that expansion due to macromolecular character of polyelectrolyte is accounted by the long-range interference effects only. It appears that electrostatic charges affect almost totally the short-range interactions alone.

(vi) An empirical approach to the total expansion of the polyelectrolyte in solution is suggested. This is based on a charge dependent expansion of the short-range interaction and a charge independent long-range interference effect incorporating macromolecular character of the polyelectrolyte. The expression was found valid for the data obtained. A similar empirical equation was found valid for the osmotic second-virial coefficients also.

(vii) The expansions obtained from the viscosity and light scattering data unequivocally showed a 2.43 power dependence of the linear expansion coefficients on hydrodynamic volume, in accordance with the asymptotic Fixman α -z relationship.

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of solution, which large changes in dimensions is expected to occur at high-salt conditions. There have been several studies

ABSTRACT

with an effective charge density. The excluded volume effect of the monomeric charges are calculated assuming a uniform charge density. The charges are assumed to interact via a screened Coulomb potential or Debye-Hückel potential. Alternatively the excluded volume approach has been employed in polyelectrolyte systems as well. There is a wide divergence of the predicted behavior according to various theoretical models. For a more quantitative understanding of the configurational properties of these charge bearing macromolecules, it is necessary that more investigations are this method.

Polyacrylic acid (PAA) was studied by solution viscometry under various experimental conditions. The theoretical predictions of the excluded volume effect were tested in solution and in the solid state. Several fractions of the molecular weight range 3×10^4 to 1.5×10^5 were analyzed. The solution behavior of the fractions was investigated by viscosity and light scattering methods. These studies have shown that the theoretical predictions of the excluded volume effect are in good agreement with the experimental results. The results of the present study are in good agreement with the theoretical predictions. In addition, the results

Polyelectrolytes, macromolecules possessing pendant groups capable of ionization, exhibit large changes in dimension in solution depending on experimental conditions. There have been several theoretical attempts to correlate the changes in dimension of the dissolved polyelectrolyte with its effective charge density. The expansions brought about by the electrostatic charges are calculated assuming a suitable molecular model. The charges are assumed to interact via a screened coulomb potential or limiting Debye-Huckel potential. Alternatively the excluded volume approach has been employed to polyelectrolyte expansions as well. There is a wide divergence of the predicted behaviour according to various theoretical models. For a more quantitative understanding of the configurational properties of these charge bearing macromolecules in solution, extensive investigations are thus needed.

Polymethacrylic acid (PMA) synthesized by solution polymerization method was separated to fractions by the fractional precipitation technique using methanol as solvent and diethyl ether as non-solvent. Seven fractions in the molecular weight range 3×10^5 to 1.1×10^6 were obtained. The solution behaviour of the fractions were investigated by viscosity and light scattering techniques. Phase separation studies showed that dimethyl formamide/1,4-dioxane (5:7, v/v) mixture at $(27.1 \pm 0.2)^\circ\text{C}$ behaves as a theta solvent for the unneutralized PMA. Light scattering and viscosity measurements were carried out in the theta solvent and in aqueous solutions. Varying degrees of ionization and concentrations of the added salt were employed for the aqueous solutions. In common with the usual

practice with polyelectrolyte solutions the values of the specific refractive index increments determined for the dialysed solutions were employed for evaluating the light scattering data in aqueous solutions.

From the viscosity-molecular weight relationship deduced for the unionized acid, it was observed that the widely used MHK relationship in methanol, due to Wiederhorn and Brown, is grossly in error. The higher value obtained for K_{θ} (1.03×10^{-3}) in the organic theta solvent employed as compared to the literature reported value (6.6×10^{-4}) for aqueous HCl solutions is ascribed to the higher unperturbed dimensions in the organic solvent for this hydrophobic group containing polyelectrolyte which undergoes conformational transition during its ionization. The exponents obtained in the dimension - molecular weight and viscosity - molecular weight relationships for the ionized acids (< 0.60 and < 0.80 respectively) indicate that the polymer exists in a random coil conformation in the ranges of ionization and concentration of the added salt studied. The osmotic second-virial coefficients for the ionized acids decreased with increasing molecular weight and the molecular weight dependence obtained was similar to those observed for nonionic polymers in solution.

The determination of the dimensions of polyelectrolytes in solution by light scattering technique is uncertain due to the applicability or otherwise of the fluctuation theory of light scattering to these multicomponent systems. The expansion coefficient obtained by light scattering were uniformly higher to those evaluated from intrinsic viscosities. From the values of Flory's universal viscosity constant $\bar{\Phi}$ obtained for the ionized solutions, it is estimated that the determined dimensions are higher by about 20% of their true value. However, the values of $\bar{\Phi}$ were

independent of the degree of ionization and concentration of the added salt demonstrating almost a constant error in the determined values of dimensions. Hence dimensions determined by light scattering were also employed for evaluating the macroion expansion theories.

The expansion coefficients obtained by light scattering and viscosity showed that the Fixman asymptotic third power α -z relation is valid.

The data obtained for the ionized polymer in aqueous solutions were utilized to evaluate the relative applicability of the various macroion expansion theories. The macroion expansion theories predict the variation of the expansion attributable to the presence of electrostatic charges with varying charge density of the polyelectrolyte. The configuration of the ionized macroion containing infinite concentration of the added salt has been used as the reference state by earlier investigators. This approach resulted in negative values for the extrapolated intrinsic viscosities and dimensions at infinite concentration of the added salt for most of the data obtained here and hence was not used. Instead, total expansion coefficients computed with respect to the unperturbed dimension of the unneutralized acid were used as the electrostatic expansions attributing the total expansions to the presence of electrostatic charges alone. To overcome the conformational transition affecting the computed expansion coefficients, the expansions with respect to the unperturbed dimension in the organic theta solvent was employed.

The data obtained demonstrated that Katchalsky-Lifson, Ptitsyn and Kurata expressions are not even qualitatively valid. Relative merits of the Flory and Alexandrowicz theories could not be evaluated on the basis of the data obtained. On comparing the results obtained with those

reported in the literature for the hydrolysed polyacrylamides, it is concluded that the macroion expansion theories are grossly inadequate.

The expansion coefficients attributable to the long-range interference effects for the ionized polymer were computed. It was observed that the values were independent of the degree of ionization, vary with salt concentration and molecular weight of the polyelectrolyte. It is proposed that the chain-like character of the polyelectrolyte affects only the long-range interference effects and electrostatic interactions greatly influence the short-range interactions. An empirical equation based on the above and assuming the additivity of the electrostatic and nonelectrostatic interactions was found to represent the data satisfactorily. A similar approach to osmotic second-virial coefficients of polyelectrolytes was found valid for the data obtained.

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