



A PHYSICO-CHEMICAL STUDY OF DILUTE

POLYELECTROLYTE SOLUTIONS

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CONTENTS

	Page
Summary	i
Statement	iii
Acknowledgements	iv
CHAPTER I	
INTRODUCTION	1
CHAPTER II	
THEORIES OF POLYELECTROLYTE SOLUTIONS	
1. Electrostatic Potential	8
2. Thermodynamic Properties	17
3. Ion Binding	20
4. Polyion Expansion	
(i) Configuration of uncharged polymers	27
(ii) Configuration of flexible polyions	30
5. Some Criticisms of Polyelectrolyte Theories	35
CHAPTER III	
VISCOSITY OF DILUTE POLYELECTROLYTE SOLUTIONS	
1. Viscosity of Uncharged Polymers	38
2. Viscosity of Charged Particles	
(i) The classical electroviscous effect	45
(ii) The secondary electroviscous effect	46

3. Review of Previous Work	48
4. Solution Properties of Poly-4-vinylpyridinium Chloride	52
5. Viscosity Measurements at High Dilutions on Polyelectrolytes not Subject to Extensive Hydrolysis	66

CHAPTER IV

ELECTROCHEMICAL PROPERTIES OF STRONG POLYELECTROLYTES

1. Counterion Binding	
(i) Methods of measurement	78
(a) Transference methods	78
(b) Tracer diffusion method	84
(c) Thermodynamic methods	85
(d) Hydrodynamic methods	87
(ii) Review of previous work	87
(iii) Experimental results and discussion	
(a) Charge fraction	93
(1) Effect of electrode reactions	94
(2) Effect of field and time of electrolysis	95
(3) Effect of sintered-glass partition	96
(4) Concentration dependence of degree of association	96
(5) An attempted absolute determination of charge fraction	100
(b) Activity coefficients	103
2. Electrophoretic Mobility	104

3. Conductance	108
4. Effect of Change in Temperature and Dielectric Constant on Electrochemical Properties	111
5. General Discussion	113

CHAPTER V

EXPERIMENTAL

1. Materials

(i) Poly-4-vinylpyridine	121
(ii) Poly-N-vinylimidazole	124
(iii) Polymethacrylic acid	124
(iv) Poly-4-vinyl-N-n-butylpyridinium bromide	125
(v) Polyvinylbenzyltrimethylammonium chloride	126
(vi) Polyvinylbenzyltrimethylammonium hydroxide and polyvinylbenzyltrimethylammonium nitrate	127
(vii) Solvents	
(a) Conductivity water	127
(b) Other solvents	128
(viii) Solutions	128

2. Viscosity Measurements

(i) Capillary viscometers	130
(ii) The Couette viscometer	131
(iii) Time dependence of the viscosity	131

3. Spectrophotometry

134

4. Conductance Measurements	136
5. Transference Experiments	
(i) Measurement of mobility	141
(ii) Exchange determinations	143
6. Potentiometric Measurements	
(i) Counterion activity coefficients	146
(ii) Measurement of pH	146
7. Light Scattering	
(i) Light-scattering apparatus	148
(ii) Scattering cell	149
(iii) Calibration and measurements	149
(iv) Clarification	151
(v) Refractometer	152
(vi) Treatment of data	152
REFERENCES	155

Summary.A Physico-Chemical Study of Dilute
Polyelectrolyte Solutions.

The discontinuous concentration dependence of various physico-chemical properties of polyvinylpyridinium chloride in dilute aqueous solutions was studied by means of viscosity, conductance, ultraviolet absorption, and pH measurements. Light-scattering measurements failed to confirm the previous interpretation of the above phenomena in terms of aggregation of the polyions. An alternative interpretation in terms of variations in the degree of hydrolysis of the polyions is proposed.

The viscosity behaviour of a number of other strong polyelectrolytes at very high dilutions was investigated. Provided that suitable precautions were taken to ensure the purity of the water used to prepare solutions, the reduced viscosities were found to increase monotonically with dilution, and an approximate value of the intrinsic viscosity could be obtained by the use of the empirical Fuoss equation. These extrapolated values were found to be higher than those calculated on the basis of a fully stretched configuration of the polyions. This discrepancy

is attributed to the polydispersity of the polyelectrolyte samples used.

Some electrochemical properties of aqueous solutions of polyvinylbenzyltrimethylammonium chloride (PBTA-Cl) and polyvinylbutylpyridinium bromide (PVP-Br) were investigated in the concentration range 5×10^{-5} - 3×10^{-3} gram molar. Electrophoretic mobilities of the polyions, determined by the Hittorf method, were found to increase on dilution. The degree of counterion binding, obtained by combining conductance and mobility data, was found to be essentially constant over most of the concentration range studied. Similar behaviour was observed for the counterion activity coefficients. Several possible sources of error in the determination of the degree of binding were investigated. The product of solvent viscosity and polyion mobility, as well as the degree of counterion binding, was found to be almost independent of temperature in the range 5 - 55°. The degree of counterion binding in ethanol solutions of PVP-Br was found to be markedly greater than in aqueous solutions. The results of measurements of counterion binding were in qualitative accord with the predictions of several current theories based on a rod-like polyion model.

To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, nor any material previously submitted for a degree or diploma in any University, except where due reference is made in the text.

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CHAPTER 1.

INTRODUCTION.

Colloids may be broadly classified, according to the nature of the disperse phase, into three main groups: (1) the classical lyophobic colloids such as the metal sols; (2) the aggregation colloids exemplified by soaps and detergents; and (3) the molecular colloids or macromolecules.

The molecular colloids form at the present time the most active and important aspect of colloid science, from the point of view of both basic research and technical application. Apart from the group of synthetic organic polymers, this field includes materials of widespread natural occurrence, such as polysaccharides, proteins, and nucleic acids.

Macromolecules generally are polymers, that is, they consist of repeating units joined together in the form of a chain. If the chain does not have branch points, it constitutes a linear polymer; branched polymers have not yet been extensively studied, and are not considered in this discussion. A more recently emphasized aspect of polymer structure concerns the configuration of the atoms forming the backbone of the polymer chain.¹ If the

configurations of successive atoms along the chain form a regular sequence, the polymer is tactic, whereas if there is no such correlation of configurations, the polymer is atactic. Naturally occurring macromolecules belong in general to the tactic group. Until relatively recently, most polymers synthesized were of the atactic variety, and all of the polymers used in the present work belong to this class. Over the past few years, however, methods have been developed which enable the synthesis of tactic polymers.¹

An important group of macromolecules consists of the polymeric electrolytes or polyelectrolytes, which may be defined as polymers whose repeating units are electrolytes. One distinguishes strong and weak polyelectrolytes according to whether the repeating units are strong or weak electrolytes. The synthetic linear polyelectrolytes have a comparatively simple structure; examples are the numerous polyelectrolytes prepared from vinyl monomers. Many of the naturally occurring macromolecules are polyelectrolytes; however, their structure is generally more complex than that of the synthetic atactic polyelectrolytes. This complexity gives rise to the special properties of the natural polyelectrolytes, but often makes difficult the preparation of homogeneous, stable samples for study.

Therefore the synthetic substances are more suited to physico-chemical study. Such studies may result in a better understanding of the behaviour of polyelectrolytes of biological origin.

The characterization of macromolecules, both electrolytic and uncharged, is generally carried out in dilute solution. In order to obtain information on the isolated macromolecule, extrapolation to zero concentration is employed to remove the effects of intermolecular interaction. Studies of polyelectrolytes in solution are of particular interest since it is under these conditions that their characteristic behaviour is best displayed.

The configuration of an isolated polymer molecule in solution may be calculated, using the general theory of stochastic processes,² as the path of a random flight with certain restrictions. This simple basic assumption, introduced by Eyring,³ Kuhn,⁴ and others, leads to a theoretical treatment of the solution properties of linear polymers which has met with substantial success. When charges are attached to the polymer chain, the theory must be modified to consider the effects of the interaction of the charges with each other and with the small ions of opposite charge (counterions). A theoretical description of polyelectrolytes requires,

therefore, the simultaneous and superimposed consideration of general electrostatic and linear polymer configurational theories.

The electrostatic part of polyelectrolyte theory may be considered as a modification of the description of ordinary electrolytes in the following respects:

- (1) the charges on the polymeric ion (polyion) are connected by the valency bonds of the chain;
- (2) the polymeric ions are large compared to the dimensions of ordinary molecules, and their shape may change with changes in concentration or charge;
- (3) in general the high charge of the polyion renders the Debye-Hückel approximation inapplicable.

The configurational aspects of the theory of polyelectrolytes are based on configurational theories of uncharged polymers. The influence of charges on the polymer configuration may be calculated in principle, provided their mutual interaction is known. However, this in turn depends on the detailed distribution of charges and hence on the configuration.

The superposition of electrostatic and configurational theories is carried out in general by

calculating the electrostatic contribution to the free energy of the system in terms of a parameter characterizing the extension of the polymer coil. The most probable extension is then obtained as the value for which the electrostatic free energy has a minimum value. From this minimum free energy, the thermodynamic functions of the solution may also be derived. Some of the theories of polyelectrolytes are discussed briefly in Chapter II.

Theories of polyelectrolytes are based on the assumption of the existence of repulsive forces between the like charges attached to different units or segments of the chain. The theory was successful in the qualitative interpretation of early work on polyelectrolyte solutions, particularly of viscosity measurements.⁵ The thread-like, flexible nature of polymers gives rise to a complex hydrodynamic behaviour. When charges are present on the molecule the situation is complicated further by the fact that the intramolecular Coulombic forces, and hence the shape of the molecule, change with the polyelectrolyte concentration. Such changes in shape were assumed in early work to account for the now familiar increase of reduced viscosity on dilution of a salt-free polyelectrolyte solution. Later work, however, showed that at very low concentration, the viscosity generally

goes through a maximum and decreases again.⁶ Additional assumptions were required to reconcile this phenomenon with theory.

On the basis of extensive experimental investigations of the solution properties of polyvinylpyridinium chloride, Jordan and Kurucsev⁷ suggested a new explanation of polyelectrolyte behaviour based on attractive rather than repulsive forces between polyion segments, which above a certain polyelectrolyte concentration would lead to aggregation of the polyions. This "aggregation hypothesis" is further examined in Chapter III. A direct test of the above theory is the comparison of the molecular weight of a polymer in the charged and uncharged state. Suitable data are lacking in the literature; therefore it was decided to investigate this problem by means of light-scattering. The apparatus available proved to be unsuitable for measurements of sufficient accuracy; therefore while modifications were being made, the problem was approached from several other directions. The results of this work are given in Chapter III.

When it became apparent that the effects observed by Jordan and Kurucsev are not general polyelectrolyte phenomena, but are due largely to extensive hydrolysis of the polyvinylpyridinium ions, other polyelectrolytes, for which the problem of hydrolysis could not arise, were

studied at low concentrations using the technique of viscosity, conductance, Hittorf transference and E.M.F. measurements. None of the anomalies previously reported could be confirmed, and most of the results could be interpreted, at least qualitatively, in terms of the polyelectrolyte theories described in Chapter II. An account of this work is given in Chapters III and IV. Finally, Chapter V contains details of the experimental methods employed in this investigation.

CHAPTER II

THEORIES OF POLYELECTROLYTE SOLUTIONS

1. Electrostatic Potential
2. Thermodynamic Properties
3. Ion Binding
4. Polyion Expansion
 - (i) Configuration of uncharged polymers
 - (ii) Configuration of flexible polyions
5. Some Criticisms of Polyelectrolyte Theories

In this chapter, a brief survey will be made of the theories of polyelectrolytes from the following points of view: the electrostatic potential, the concept of ion binding, and finally the configuration of the isolated molecule in solution.

1. Electrostatic Potential.

In the Debye-Hückel theory of dilute electrolyte solutions, the time-average distribution of i -ions around a k -ion is assumed to be given by the Boltzmann distribution law in the form

$$C_{i,k} = C_i^0 \exp(-z_i e \psi_k / kT) \quad (\text{II-1})$$

where $C_{i,k}$ is the local concentration of i -ions of valency z_i at a point where the potential due to the k -ion and its atmosphere is ψ_k , C_i^0 is the corresponding concentration in a region where $\psi_k = 0$, and k , T and e are respectively Boltzmann's constant, the absolute temperature, and the electronic charge.

Consideration of the distributions given by (II-1) for electrolytes of extremely unsymmetrical valency types shows that⁸ the ionic atmosphere about ions of low valency no longer has the usual physical significance. Although the interaction energy of the multivalent ions

is implicitly considered in a Debye-Hückel type treatment, the use of a continuous, spherically symmetrical charge density due to the macro-ions around a central macro-ion, required in such a treatment, may not be justified because of the relatively small number of these ions.

Most polyelectrolyte theories are constructed, without consideration of polyion interactions, in either of two ways: (1) an isolated polyion in an infinite volume of solvent is considered, i.e., the theory applies only at infinite dilution of the polyelectrolyte; (2) the polyelectrolyte solution is divided into a number of subvolumes, each containing a single polyion and considered to be electrically neutral. It is further assumed that the shape of the subvolume may be approximated by the shape assumed for the polyion. When this latter method is used, the polyelectrolyte concentration enters into the theory since it determines the size of the subvolume. In both the above cases the problem reduces to the determination of the potential and the ionic atmosphere around a single polyion.

The most general expression for the potential of a system of charges at rest is Poisson's equation

$$\text{div } (D \text{ grad } \Psi) = - 4 \pi \rho \quad (\text{II-2})$$

where Ψ is the electrostatic potential at a point where

the charge density is ρ and the dielectric constant is D . The latter is generally assumed to be constant throughout the system, or at least in the region outside the polyion.

In the application of (II-2) to polyelectrolyte solutions, the problem arises of finding a suitable representation for the charge density. The distribution of small ions is generally considered to be given by the Boltzmann equation (II-1). This of course does not apply to the polyion charges since these are not free to move independently. Several modes of representing the polyion (or "fixed") charges have been used; these will be described for each theory in turn. Most authors employ a continuous volume or surface charge. Theories considering the discrete nature of the fixed charges are fundamentally more sound, but the mathematical difficulties involved are correspondingly greater.

The model chosen for the polyion requires a certain degree of symmetry to enable the solution of the Poisson-Boltzmann equation. The boundary conditions are determined by the total charge or the surface charge density of the polyion, and by restrictions on the values of Ψ or its gradient.

Rod-like polyions. Perhaps the simplest model for the polyion is that of a uniformly charged, infinite, impenetrable cylinder. In the absence of added salt,

the Poisson-Boltzmann equation can be solved in closed form,^{9,10} assuming that (1) the cylinders are parallel and hexagonal close packed, (2) the electroneutral subvolume containing a single polyion can be approximated by a cylinder of radius R , (3) the boundary condition $(d\psi/dr)_{r=R} = 0$ applies, where r is the distance from the centre of a selected rod, and (4) end effects may be neglected, i.e., the length of the rods is much greater than $2R$, the distance between them. The result given by Fuoss et al.⁹ for the potential ψ outside the rod is

$$e\psi/kT = \ln \left[2qr^2 \sinh^2(\beta \ln Ar) / \beta^2 (R^2 - a^2) \right] \quad (\text{II-3})$$

where a is the radius of the rod, β and A are concentration-dependent integration constants given by the solution of transcendental equations, and q is the "charge density parameter", given by

$$q = e^2 / DbkT \quad (\text{II-4})$$

where b is the average distance between charged groups along the rod. The solution given by Alfrey et al.¹⁰ is of similar form.

An exact solution of the Poisson-Boltzmann equation for rod-like polyions is not possible in the presence of added low molecular weight electrolyte. Hill¹¹ has used the Debye-Hückel approximation to obtain approximate

solutions for the potential; the results therefore apply only at low charge and potential of the polyions.

A solution of the Poisson-Boltzmann equation under more general conditions than those considered by Hill was obtained by Alexandrowicz¹² by dividing the cylindrical subvolume around the polyion into two coaxial regions. In the outer region, the potential is considered to be low enough to enable the use of the Debye-Hückel linearization, whereas in the inner region, where $|e\psi/kT|$ is high, the small ions with the same sign of charge as the polyion are effectively excluded, and the solution for salt-free conditions may be considered to apply.

Finally, Kotin and Nagasawa¹³ have treated the case of an isolated infinite charged cylinder in a salt solution by numerical integration of the Poisson-Boltzmann equation. Since these authors considered only a few values of the relevant parameters, their results, although accurate, are not of wide applicability.

Validity of a rod-like model. Flexible polyions are not fully stretched, except perhaps at high dilution in salt-free solution (section II-4), and therefore cannot satisfy any of the requirements of the rod-like model discussed above. However, when the degree of coiling

of the polyion is low, the ionic atmosphere close to the chain may be considered to be approximately cylindrical for relatively long distances along the chain. Therefore the potential and radial distribution of counterions may still be given to a useful approximation by consideration of a cylindrical model.

Spherical polyions. The potential in solutions of impenetrable spherical macroions has been investigated extensively; such a model, however, can be used only as a first approximation for chain-like polyions,^{14,15} since, even when these are tightly coiled, solvent and small ions can penetrate into the interior of the coil. Several theories have been constructed representing the polyion as a permeable spherical structure, in which the polyion charges have a continuous distribution. The dielectric constant is generally assumed to be the same inside the polymer domain as in the external solution.

This model was first treated by Hermans and Overbeek¹⁶ by the use of the Debye-Hückel approximation, and with the assumption of a uniform distribution of the fixed charges inside the polyion. According to Kimball, Cutler and Samelson,¹⁷ the net charge density within a polyion immersed in a moderate or high concentration of simple electrolyte is sufficiently low to enable the use

of the Donnan¹⁸ electroneutrality condition, $\rho = 0$, in the solution of the Poisson-Boltzmann equation. The potential is calculated for a polyion in which the fixed charge density decreases with distance from the centre of the sphere according to a modified Gaussian distribution, while a uniform charge density was assumed for a similar model by Nagasawa and Kagawa.¹⁹ A refinement of the Donnan approximation was given by Lifson,²⁰ again using a constant density of fixed charges, by a perturbation method based on the potential calculated from the Donnan condition. The results have been compared, with good agreement, with those of numerical integration^{21,22} of the Poisson-Boltzmann equation for the same model. The low net charge of the polyion has also been utilized by Oosawa, Imai and Kagawa²³ to obtain an approximate analytical solution for the potential of a uniformly charged, spherical polyion.

Validity of a spherical model. The assumption of spherical shape for chain-like polyions is physically reasonable only at low degrees of expansion, that is, at high polyelectrolyte concentrations or at moderate concentrations of added electrolyte. At high degrees of stretching, an ellipsoidal or even rod-like shape is more appropriate. Extension of the theory of

Hermans and Overbeek to ellipsoidal polyions²⁴ shows, however, that the results are not greatly affected by small deviations from spherical form.

Chain polyion models. The calculation of the potential of a kinked chain polyion is very difficult because of the unsymmetrical nature of the model. The potential in an electroneutral volume containing a single polyion was calculated by Künzle²⁵ by solving the Poisson-Boltzmann equation, with the Debye-Hückel linearization, for each fixed polyion charge separately, and superposition of the solutions for all the polyion charges. The fixed charges are treated as point charges, whereas the mobile charges are considered as usual as a diffuse atmosphere. Under conditions where the atmospheres of each polyion charge can be considered to be independent, the potential calculated by Künzle reduces to the screened Coulomb potential of the Debye-Hückel theory of simple electrolytes, and this potential has been used by a number of authors in their treatment of the chain model.^{26,27}

An expression for the screened Coulomb potential was also obtained by Harris and Rice²⁸ using the Debye-Hückel approximations of linearizing the Poisson-Boltzmann equation, and of considering a spherically

symmetrical distribution of polyion and simple ion charges about a central polyion. The elements of the polymer chain are considered to be contained in a spherical volume; the model used is therefore intermediate between the uniform sphere and the chain models previously discussed.

2. Thermodynamic Properties.

The electrostatic contribution F_e to the free energy of a polyelectrolyte solution may be obtained from the potential and charge distribution in the system by the use of a suitable charging process. If then all deviations from ideal solution behaviour are ascribed to electrostatic forces, the activity coefficients of the mobile ions and of the solvent may be calculated using standard methods. The standard state is generally taken to be a hypothetical solution in which all ions are discharged.

Calculations by the above method for the porous sphere model have been made by Gosawa, Imai, and Kagawa,²³ and by Gosawa.²⁹ The electrostatic free energy was also considered by Harris and Rice.²⁸ An expression for the osmotic coefficient, g , of the solvent was obtained by Lifson and Katchalsky³⁰ for the case of a salt-free solution of rod-like polyions. The activity coefficient of the counterions, f_c , was calculated for the chain model by Katchalsky and Lifson.²⁶

The thermodynamic properties can be obtained, with certain assumptions, directly from the potential and mobile ion distribution, thus avoiding the lengthy

calculations involving the electrostatic free energy.^{12,31} This method utilizes the fact that the boundary of an electroneutral subvolume containing the polyion is an equipotential surface where $\text{grad } \Psi = 0$. The solution in this boundary layer may therefore be considered to be ideal in the sense that no forces are exerted on it by the polyions. By considering the equilibrium of solvent or mobile ions between this surface solution and the interior of the subvolume, the osmotic coefficient of the solvent and the activity coefficients of the mobile ions may be evaluated. A general result of this treatment¹² is that $g \sim f_c$ in dilute salt-free polyelectrolyte solutions. Thermodynamic properties were calculated by Alexandrowicz¹² for the rod-like polyion model, both in the presence and absence of salt. In the latter case, the equation

$$f_c = g = (1 - \beta^2) / 2q \quad (\text{II-5})$$

is obtained, where β and q have been previously defined; the results can be shown to be identical to those obtained by the conventional method from the free energy.³¹ In both methods it is assumed implicitly that $\text{div grad } \Psi$, as well as $\text{grad } \Psi$, is zero at the surface of the subvolume, a condition which can never be fulfilled at finite polyelectrolyte concentrations.¹²

In order to calculate the thermodynamic functions of the polyions, their interactions must be included in the theory. Interactions among macrolons have been treated by Verwey and Overbeek³² and other authors; these theories are not considered here.

3. Ion Binding.

When the potential and the counterion distribution about a rod-like polyion are evaluated using numerical values of the parameters in equation (II-3) appropriate to those normally encountered in solutions of strong polyelectrolytes, it is found that a large fraction of the counterions exists in a region where $|e\psi| > kT$. It has been proposed³³ that such a distribution could result in some kind of binding of the counterions to the polyion.

Several types of association between counterions and polyions may be visualized:²⁰

- (a) Specific short-range interactions, e.g., chelation of metallic counterions, or reactions at weakly acidic or basic groups. Such interactions are in general not observed for alkali metal ions or univalent anions as counterions, and they will not be considered here.
- (b) Ion-pair formation, where an ion pair may be defined as a counterion in such proximity to a polyion fixed charge that the pair acts on

other charges as an uncharged entity. This mechanism has been termed "site-binding"^{34,35} or "p-binding".²³ On the basis of the calculated potential and counterion distribution one would expect the effect to be more pronounced than in simple electrolytes under similar conditions. On the other hand, Lifson,²⁰ and Oosawa, Imai and Kagawa²³ concluded that the amount of ion pairing is independent of the polymeric nature of the electrolyte.

- (c) Physical occlusion of counterions within the domain of a permeable macroion with the formation of a compound kinetic unit.
- (d) The counterions for which $|e\Psi| > kT$ can be considered to be trapped in the potential well created by the charges on the polyion. In order to diffuse away from the polyion, these counterions require kinetic energies in excess of the average thermal energy. Therefore, on movement of the polyion as in electrophoresis, the trapped counterions may be dragged along with the polyion for a short distance before

they escape; since their place is then taken by other counterions, there will always be a certain fraction of counterions moving, on the average, with the polyion. This phenomenon will be referred to as Ψ -binding.²³ Since the translational energy of an ion in the usual fields encountered in electrical measurements is very much less than kT , the average fraction of counterions moving with the polyion is expected to be independent of the applied field except when the latter is very high (kilovolts/cm.). Nevertheless, suggestions to the contrary have been made.^{26,27}

In systems where a significant amount of site-binding occurs, calculations of the potential and related quantities should be modified by the cancellation of the charges of the paired ions. Binding of types (c) and (d) has no effect on the calculated potential since it is implicitly included in the Poisson-Boltzmann equation.

Theories of binding. The theoretical calculation of the degree of binding is very difficult; the main source of difficulty appears to be the lack of a suitable criterion of binding.

The criterion for association of two simple ions proposed by Bjerrum has recently been extended to the rod-like polyelectrolyte model.^{13,38} The degree of binding, $1-\alpha$, is thus assumed to be given by the fraction of counterions contained within the cylindrical envelope defined by the minimum in the counterion distribution function. This procedure leads, in the case of salt-free polyelectrolytes,³⁸ to the relation

$$\alpha = q/2 = DkTb/2e^2 \quad (\text{II-6})$$

where q is the charge density parameter defined in equation (II-4). According to this treatment, therefore, the degree of binding is independent of polyelectrolyte concentration. The same equation (II-6) was found to apply in a salt-containing solution at zero polyelectrolyte concentration.¹³ Evidently the calculations apply only to polyelectrolytes of relatively high charge density, since at high values of the charge separation b , the value of α obtained from equation (II-6) may exceed unity.

Several authors classify the counterions within the polyion as bound. Since in general there is a large potential gradient at the surface of the polyion, this definition of binding may coincide approximately with that of Ψ -binding. Spherical models have been considered by Oosawa, Imai and Kagawa,²³ Oosawa,²⁹ and

Wall et al.^{21,22,39} For the case of an infinitely long cylindrical polyion, the following equation was obtained by Oosawa:²⁹

$$\ln[(1-\alpha)/\alpha] = \ln[\varphi/(1-\varphi)] - \alpha q \ln q \quad (\text{II-7})$$

Here φ is the volume fraction occupied by the cylinders in the solution. The application of the above equation to rigid rod-like polyions may be ambiguous since these are not permeable to counterions; however, in dilute solutions ($C < 10^{-2}$ eq./l.) the result obtained is very insensitive to the value of φ and hence to the location of the boundary within which the counterions are considered to be bound. The above equation predicts, for polyelectrolytes with $q > 1$, a slight increase of α with polyelectrolyte concentration; at low concentrations eq.(II-7) reduces to

$$\alpha = 1/q = DkTb/e^2 \quad (\text{II-8})$$

For polyelectrolytes of low charge density, more specifically with $q < 1$, α approaches unity at low concentrations.

An approximate estimate of the degree of Ψ -binding can be obtained⁴⁰ as the fraction of counterions for which $(e\Psi) \geq kT$. From the curves of counterion distribution about a rod-like polyion given by Alfrey

et al.¹⁰ it can be seen that this fraction decreases slightly with concentration.

In the theory of Harris and Rice,^{34,35} binding is treated as occurring at specific sites, namely charged groups, along the polymer chain. From the entropy of mixing of charged and ion-paired groups, together with an assumed value of the ion-pair dissociation constant, the degree of binding as a function of charge density was calculated. The numerical evaluation of the equations given by these authors appears to be rather laborious.

Theories based on the rod-like polyion of high charge density lead to values of α which are either constant or decrease as the polyelectrolyte concentration is reduced. At infinite dilution in salt-free solvents the isolated polyion has a finite potential, given by electrostatic theory, whereas the counterions have an infinite volume in which to distribute themselves. Under these conditions there should therefore be no binding. The prediction of a finite degree of binding at infinite dilution by several of the theories discussed may be due to a breakdown of the parallel rod model as the concentration is reduced. Thus an increasing distance between the rods results in

increased end effects,²⁹ especially for short rods, until the isolated rod is obtained. The concentration range where α begins to approach unity may not be accessible to experiment,⁴¹ since residual ions in the solvent, due to impurities or self-ionization, may suppress this increase of α .

All of the above theories treat ion binding as a purely electrostatic phenomenon. Therefore, the degree of binding should, for chains which are long, depend on the product DkT , the valency of the counterions, and the spacing of the charges along the chain, but not on the nature of the polymer or counterion except for small size effects. Further, the rate of exchange of the bound and free counterions should be extremely high.

Relation of binding to thermodynamic properties. A number of authors⁴² identify the osmotic coefficient of the solvent or the counterion activity coefficient in a polyelectrolyte solution with the "apparent degree of dissociation", α . This is equivalent to the assumptions that the bound counterions are osmotically inactive, while the activity coefficient of the free counterions is close to unity. Both these assumptions appear somewhat artificial,⁴³ and further theoretical work on this subject is required.

4. Polvion Expansion.

(i) Configuration of uncharged polymers.^{44,45}

Owing to the possibility of rotation about bonds of the chain "backbone", the number of stable configurations available to a linear long-chain polymer molecule in solution is extremely large, making it necessary to apply statistical methods to the theoretical treatment of chain configuration. Since it is not practicable to specify the location of each atom in the chain, a given configuration is characterized by a dimension of the chain such as its radius of gyration R_G , or the distance h between its ends. Theories of chain configuration aim at evaluating the probability $W_0(h)$ of a given end-to-end distance in terms of the properties of the repeating units. Such theories are incomplete in that to each value of h , there correspond generally a large number of different configurations.

The rigorous calculation of $W_0(h)$, and hence of the various averages of h , although possible in principle, has not yet been achieved, and it is necessary to use simplifying assumptions. The simplest model, that of the "freely jointed" chain,

treats the polymer chain as a series of links of zero volume, joined such that all values of the angles between successive links are equally probable. For this model the probability distribution function $W_0(h)$ is given by the random-flight statistics, and for a chain with a large number of links can be approximated by a Gaussian function. The mean square end-to-end distance of the chain is then given by

$$\langle h_0^2 \rangle = nb^2 \quad (\text{II-9})$$

where n is the number of links of length b . When the angle between successive links has the constant value θ , this equation is modified to read

$$\langle h_0^2 \rangle = nb^2(1-\cos \theta)/(1+\cos \theta) \quad (\text{II-10})$$

The effect of restricted rotation about the links of the chain, and of steric interferences between substituent groups attached to neighboring monomer units, is to reduce greatly the number of configurations available to the chain. Owing to the complex nature of this effect, recourse is often made to the concept of the equivalent Kuhn chain, which represents the polymer as a series of N links or "statistical elements", each of length A , which are freely jointed in the sense indicated above. The values of N and A

are determined empirically from the conditions that the real and the equivalent chain have the same maximum extension h_{\max} and the same value of h_0^2 , i.e.

$$h_{\max} = NA,$$

$$\langle h_0^2 \rangle = NA^2$$

By means of this device, the validity of the random-flight statistics is restored on replacing n and b with N and A .

An important effect which cannot be incorporated in the random-flight treatment is the exclusion of a segment of the chain from the volume occupied by another segment. The proportion of configurations excluded in this way is highest for a tightly coiled structure, so that this "excluded volume effect" results in a most probable end-to-end distance greater than that calculated on the basis of random-flight statistics.

The nature of the solvent may also be important in determining the configuration of a dissolved polymer molecule. If the heat of solution of the polymer in a given solvent is negative, configurations involving contacts between polymer segments are of higher energy than those involving only polymer-solvent contacts.

Therefore more expanded configurations are favoured, and the excluded volume effect is enhanced. The reverse is true for polymer-solvent systems in which the heat of solution is negative.

In the treatment of Flory,⁴⁵ the combined effect of excluded volume and of polymer-solvent interaction is assumed to be described by the equation

$$\langle h^2 \rangle = \alpha_E^2 NA^2 \quad (\text{II-11})$$

where the "expansion factor" α_E is a function of the degree of polymerization. Although the proportionality $\langle h^2 \rangle \propto n$ is thus no longer valid, the probability distribution function is generally assumed to retain a Gaussian form, provided n is not too low.

(ii) Configuration of flexible polyions.^{43,44}

When charged groups are attached to the polymer chain, the repulsive forces among chain elements become very high and act over relatively long distances, resulting in an increase in the magnitude of the excluded volume effect, that is, the displacement length of the chain is increased above that of the uncharged configuration. In most theories, the probability distribution $W(h)$ is assumed to be given by the distribution function of the uncharged polymer

modified by a Boltzmann factor involving the electrostatic free energy of a given configuration:

$$W(h) = W_0(h) \exp(-F_e/kT) \quad (\text{II-12})$$

Accordingly, the problem of the configuration of linear polyions reduces to that of obtaining an explicit expression for F_e in terms of the parameter h . The excluded volume effect on $W_0(h)$ is generally neglected, i.e., the Gaussian approximation to $W_0(h)$ is used except at high chain extensions or for low values of n , where a more complicated function is required.

For the purpose of calculating F_e , Hermans and Overbeek,¹⁶ Oosawa, Imai and Kagawa,²³ and Nagasawa and Kagawa¹⁹ represent the polyion as a permeable sphere, as mentioned in a previous section. In calculating the expansion of the polyion, however, the chain structure is recognised by the use of the distribution function $W(h)$ in calculating the average extension of the polyion.

In the theory of Kuhn, Künzle, and Katchalsky,⁴⁶ the chain structure of the polyion is retained throughout; however, since a simple Coulomb interaction is assumed among the polymer charges, this theory applies only in the absence of mobile ions, i.e., at infinite

dilution of the polyelectrolyte in a salt-free solution. These authors found⁴⁷ that a typical vinyl polyion would be stretched essentially to its maximum extension if the charges are spaced at intervals of 4 A.U. or less along the chain. Such charge densities are encountered for many polyelectrolytes.

Calculations including the effect of mobile ions were made by Künzle,²⁵ Katchalsky and Lifson,²⁶ and Harris and Rice,²⁸ with the use of the Debye-Hückel linearization. These theories are therefore limited to solutions of moderate ionic strength.

In calculating F_e , the chain models discussed above employ the distribution $W_0(h)$, neglecting the effect of charge interactions on the configuration at any given value of h . A further objection is that these theories assume that all of the electrostatic free energy is effective in the expansion of the polyion, whereas in fact the interaction energy of neighbouring monomer units, which is a large fraction of the total electrostatic energy, can have little effect on the chain extension. Both of the above approximations result in an overestimate of the chain extension.

An attempt to avoid these difficulties was made by Harris and Rice,^{34,35} who consider an equivalent

chain with the charges concentrated at the centroids of the statistical elements. The interactions between neighboring elements impose restrictions on the orientation of successive statistical elements, causing an increase in the average end-to-end distance. According to the theory of random flight processes with partial correlations,⁴⁸ the mean square displacement length is given by

$$\langle h^2 \rangle / \langle h_0^2 \rangle = (1 - \langle \cos x \rangle) / (1 + \langle \cos x \rangle) \quad (\text{II-13})$$

where $\langle \cos x \rangle$ is the average cosine of the angle x between adjoining elements. The value of $\langle \cos x \rangle$ is calculated in first approximation from the interactions between nearest neighboring elements only, assuming an effective dielectric constant much lower than that of the pure solvent. The theory includes the effect of site-binding. Owing to the complexity of this theory, it has not been used extensively in the interpretation of experimental data.

In the theory of Kimball, Cutler, and Samelson,¹⁷ in which the free energy is calculated for a spherical polyion in the Donnan approximation, the contractile chain forces are replaced by a central force of attraction. The predicted expansion is much too small owing to the use of a contractile force which

is too large.^{49,50.}

The Donnan approximation was also used by Flory⁴⁹ to calculate the polyion expansion without derivation of the potential. The difference in free energy of the solvent inside and outside the polyion domain is calculated from the distribution of the mobile ions between the interior of the sphere and the external solution. On equating the expanding force, considered as the osmotic pressure of the solution inside the polyion, to the entropic contractile force of the chain, the equilibrium extension of the polyion is obtained. The excluded volume and solvent effects are included in Flory's treatment. However, the markedly non-ideal behaviour of the mobile ions in the solution is not considered, since the "ideal" Donnan distribution is employed.

5. Some Criticisms of Polyelectrolyte Theories.

The validity of the appearance of the product $z_1 e^{\psi/k}$ in the exponential of the Boltzmann distribution (II-1) has been extensively investigated,⁴³ with the result that, at finite concentrations, errors may be expected at high charges or potentials such as are encountered in solutions of strong polyelectrolytes. The extent of the deviations from equation (II-1) is not known. Since no rigorous distribution amenable to analysis is available at present, the Boltzmann equation in the above approximate form is basic to most polyelectrolyte theories. A further criticism of equation (II-1) is that short-range forces, which determine the finite sizes of the ions, are not considered, so that the equation can apply only in dilute solutions.⁵¹ The modified Boltzmann distribution proposed by Eigen and Wicke⁵¹ has been applied to polyelectrolyte solutions by Ise and Hosono;¹⁴ however, at concentrations high enough to warrant this refinement, the Poisson-Boltzmann equation is probably also in error due to the approximation mentioned above.

The Debye-Hückel linearization of the Poisson-Boltzmann equation is often a serious approximation in polyelectrolyte solutions since the average value of $e^{\psi/kT}$

in the solution may be comparable to unity. The breakdown of the ionic strength principle in colloidal solutions is connected with the failure of this approximation.⁸ Thus the effects of the addition of extraneous electrolytes on the thermodynamic and configurational properties of a polyelectrolyte are determined mainly by the concentration and valency of the added counterions, and only to a secondary extent by the total ionic strength due to the added electrolyte.

Apart from the above questions of validity, the electrostatic and statistical theory of polyelectrolyte solutions is generally of a somewhat crude nature. In the extremely high fields near the polyion charges, a significant amount of dielectric saturation of the solvent must occur; this effect is considered only in the work of Harris and Rice,^{27,28,34,35} who assume an arbitrary value of $D = 5.5$ for the local dielectric constant of water. The "smearing out" of the ionic charges on the polyion into a continuous surface or volume charge obscures the strong interactions of neighboring charged groups. Thus, although the average charge density of the porous sphere model may be relatively low, and decreases on expansion of the sphere, the local charge density along the chain remains very high.

In most polyelectrolyte theories, interactions among polyions, as well as interactions among the small ions as

normally treated in the theory of simple electrolytes, are neglected. These approximations are expected to become more serious the higher the polyelectrolyte concentration.

Despite the numerous simplifications made in the theory, some of the properties of polyelectrolytes can be derived with reasonable accuracy. The most successful aspect of the theory, not considered here, appears to be the titration behaviour of weak polyelectrolytes. In general, however, no more than qualitative agreement with experiment may be expected.

CHAPTER III

VISCOSITY OF DILUTE POLYELECTROLYTE SOLUTIONS

1. Viscosity of Uncharged Polymers
2. Viscosity of Charged Particles
 - (i) The classical electroviscous effect
 - (ii) The secondary electroviscous effect
3. Review of Previous Work
4. Solution Properties of Poly-4-vinylpyridinium Chloride
5. Viscosity Measurements at High Dilutions on
Polyelectrolytes not Subject to Extensive Hydrolysis

(1) Viscosity of Uncharged Polymers. 52,53

The viscosity of macromolecular solutions is described in terms of the reduced viscosity η_{sp}/c , defined by

$$\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c$$

where η_0 and η are the viscosity coefficients of the solvent and the solution respectively, and c is the polymer concentration expressed as weight per unit volume of solution.

The reduced viscosity can in principle be related to molecular parameters by the application of the hydrodynamics of continuous media to some suitable model of the dissolved macromolecules. Reliable equations are available for the viscosity of solutions of rigid, impenetrable, non-interacting particles of spherical, ellipsoidal and cylindrical shape; such models, however, cannot generally be applied to chain molecules without modification. The treatment of intermolecular interactions is at present not well developed. For comparison with theory, experimental results are therefore generally extrapolated to infinite dilution to give the intrinsic viscosity $[\eta]$, defined by

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/c)$$

Some of the models used for chain molecules in theories of

viscosity are outlined below.

In the equivalent particle concept the assumption is made that the hydrodynamic effect of the molecule can be replaced by that of a rigid impenetrable body having a shape approximating the average form of the polymer coil. A difficulty in this approach is to relate the dimensions of the equivalent particle to the average dimensions of the chain; however it has proved to be very useful for treating experimental results on uncharged polymers.⁴⁵ When the degree of coiling of the polymer chain is very low, as may be the case for very short chains or for highly extended charged chains, the equivalent particle may be taken to be a cylindrical rod. Simha's equation for the viscosity of randomly oriented cylinders is, in the limit of large values of the axial ratio,⁵⁴

$$\frac{\eta - \eta_0}{\eta_0 \varphi} = \frac{14}{15} + \frac{p^2}{15(\ln 2p - 1.80)} + \frac{p^2}{5(\ln 2p - 0.80)} \quad (\text{III-1})$$

where φ is the volume fraction of the cylinders in the solution, and p is their axial ratio (equal to the ratio length/diameter). For tightly coiled macromolecules, on the other hand, the equivalent particle is a sphere, and the viscosity is given by the Einstein equation

$$(\eta - \eta_0)/(\eta_0 \varphi) = 2.5 \quad (\text{III-2})$$

The pearl-necklace or porous sphere model replaces the polymer chain by an assemblage of unconnected spherical beads corresponding to the statistical chain elements, contained in a spherical region. The viscosity is calculated as the sum of contributions from the individual beads, together with the contribution of the hydrodynamic interactions among them. Since neither the number of statistical elements in the molecule, nor the frictional coefficients of the beads representing them, can at present be calculated rigorously from molecular dimensions, the theories based on this model contain two adjustable parameters, which must be determined by experiment.

An essentially different theoretical approach to the problem of the solution viscosity of flexible chain molecules is the recent application of normal-coordinate analysis to the model of a chain of point masses connected by springs.⁵⁵ Relaxation phenomena as well as the steady state viscosity are considered by the above theory.

A semi-empirical treatment of the viscosity of macromolecular solutions was given by Kuhn and co-workers,⁵⁶⁻⁵⁸ who used scale models to represent the hydrodynamic behaviour of various types of macromolecules, including chain molecules. The form of previously derived equations for viscosity, diffusion and other hydrodynamic properties was retained; the observed frictional coefficients of the

scale models were used to obtain the values of the coefficients appearing in these equations.

In general, the intrinsic viscosity is related to the frictional properties of the chain units, the permeability of the molecule, and its radius of gyration or some other average dimension. From the dependence of the average dimension on degree of polymerization, the viscosity-molecular weight relation for a given polymer homologous series can be obtained. In the range of high molecular weights, this relation can generally be well approximated by the equation

$$[\eta] = K \langle M_v \rangle^a \quad (\text{III-3})$$

where K and a are constants, usually empirically determined, and the viscosity-average molecular weight $\langle M_v \rangle$ is defined by

$$\langle M_v \rangle^a = \frac{\sum \nu_i M_i^{1+a}}{\sum \nu_i M_i} \quad (\text{III-4})$$

where ν_i is the number of molecules of molecular weight M_i .

The viscosity of solutions of rigid anisometric colloids is strongly dependent on the orientation of the particles in the field of flow. Large solute particles with a high axial ratio are readily oriented with their major axes parallel to the direction of flow, resulting in a decrease of the solution viscosity with increasing velocity gradient. Orientation is opposed by the Brownian

motion; thus the effect of shear rate on the viscosity contribution of small particles of relatively low axial ratio does not become noticeable until high velocity gradients are reached. A number of authors have treated the shear dependence of the viscosity for various models;⁵⁹ at sufficiently low values of the velocity gradient G , their equations generally reduce to

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c} \right)_{G=0} \left[1 - b \left(\frac{G}{\theta} \right)^2 \right] \quad (\text{III-5})$$

where θ is the rotational diffusion coefficient of the solute, and b is a constant. This limiting law has recently been confirmed by experiment,⁶⁰ and it was shown that previous methods of extrapolation of the viscosity of polyelectrolytes to zero rate of shear from high shear rates, based on other functions of G , may lead to serious errors.

In addition to orientation effects, the viscosity of uncharged particles may show shear dependence due to deformation in the field of flow. Further, the viscosity contribution due to particle interaction is generally a function of G , especially in the case of charged solutes. Thus even solutions of spherical particles may have shear-dependent viscosities.

The above theories apply to solutions of non-interacting particles. In the experimentally accessible range

of concentration there is always some interaction, which increases the viscosity above its limiting value at infinite dilution. Various types of interaction are recognized.⁵³ Hydrodynamic interaction arises from the overlap of flow patterns due to two or more particles. Actual contacts between particles result in the temporary formation of doublets or higher aggregates which contribute more to the viscosity than the separate molecules. Electrostatic interactions are considered in the next section. The dependence of the viscosity of a dilute suspension on concentration can generally be represented as a power series

$$\eta_{sp}/\varphi = [\eta]_v + k_1 [\eta]_v^2 \varphi + k_2 [\eta]_v^3 \varphi^2 + \dots \quad (\text{III-6})$$

where $[\eta]_v$ is the intrinsic viscosity based on volume fractions, and k_1 , k_2 , etc., are dimensionless interaction coefficients, independent of φ . Their value depends on the shape and flexibility of the interacting particles, and is made up of contributions from the various types of interactions which may be present in the system. Theoretical calculation of the interaction coefficients is a difficult problem; some of the results for the purely hydrodynamic part of k_1 are:⁵³ spheres 2.26, rods 0.77, random coils 0.60. The viscosity of dilute solutions of uncharged polymers is generally well represented by the equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad (\text{III-7})$$

where k' , referred to as the Huggins coefficient, has been found to vary with polymer and solvent in the range $0.3 < k' < 0.7$. The interaction coefficients k_1 and k' are generally insensitive to molecular weight for a given model.

Although a rigorous treatment of the concentration dependence of the viscosity of polymer solutions is not available, the experimental values of k' may be used qualitatively to infer the nature of the interactions occurring in the solution.

2. Viscosity of Charged Particles.

(i) The Classical Electroviscous effect.

The presence of an electrical double layer around a charged particle increases its contribution to the solution viscosity, since the deformation of the double layer during shear results in an increased dissipation of energy. Theoretical treatments of this effect are restricted to spherical particles. The most satisfactory theory appears to be that of Booth.⁶² According to this theory, the electroviscous viscosity increment is negligible except for highly charged spheres at low ionic strength, under which conditions it may exceed the "normal" viscosity contribution of the uncharged spheres. An effect of this magnitude has been observed recently for detergent micelles;⁶³ other data have been reviewed by Conway and Dobry-Duclaux.⁶¹

The surface charge densities of strong polyelectrolytes are comparable to those of the micelles referred to above. It is generally assumed, however, that in comparison with the very high viscosity of dilute salt-free polyelectrolyte solutions, the electroviscous contribution is negligible. In the absence

of relevant theoretical or experimental information on chain-like or rod-like molecules, it is difficult to assess the validity of this assumption.

(ii) The secondary electroviscous effect.

At finite concentrations, the presence of long-range repulsive forces between the double layers around the solute particles may cause an increase in solution viscosity by the following mechanism:⁶⁴ as the particles pass each other in laminar flow, they are displaced perpendicularly to the streamlines by the intermolecular repulsions. This displacement is a source of energy dissipation and therefore manifests itself as an additional viscosity contribution, which is proportional to the number of particle encounters, and hence to the second and higher powers of the concentration. Thus whereas the classical electroviscous effect causes an increase in the intrinsic viscosity, the secondary effect increases the interaction coefficients only. The magnitude of the effect is expected to be highest for small particles at low ionic strengths,⁶⁴⁻⁶⁶ such as the silver iodide sols studied by Harmsen et al.,⁶⁴ who found a variation of k_1 in the range 2.3-28 when the concentration of added electrolyte was varied between 3.9×10^{-1} and 3.5×10^{-5} eq./l.

There is at present no quantitative theory for the concentration dependence of the viscosity of charged macromolecular solutes. Owing to the presence of charges on the polyions, the frequency of collisions will be much lower than in a similar non-electrolytic solution. Ordinary hydrodynamic interactions may also be reduced by the lower average distance of approach of the colloidal ions. From the results of Harmsen et al.⁶⁴ and of Dobry⁶⁵ it would appear, however, that the expected reduction of k_1 for small charged spheres has been swamped by the increase produced by the secondary electroviscous effect.

3. Review of Previous Work.⁶¹

On ionization of a flexible polymer, the viscosity of its salt-free solution increases markedly, often by several orders of magnitude. This phenomenon is explained by the "folding-chain" theory in terms of the unfolding of the polymer coil due to the mutual repulsion of the like charges attached to it. Observations of other solution properties, in particular of streaming birefringence⁶⁷ have substantiated this interpretation. The theoretical basis of the change in coil dimensions is summarized in Chapter II.

On dilution of a salt-free polyelectrolyte solution, the reduced viscosity curve increases steeply, due presumably to the decreased screening of the fixed charges by the counterions and consequent coil expansion. Fuoss and Strauss⁶⁸ proposed the empirical equation

$$\eta_{sp}/c = A/(1+Bc^{\frac{1}{2}}) + E \quad (\text{III-8})$$

where A, B and E are constants, to fit the curve; the function $c^{\frac{1}{2}}$ is replaced by c in some cases.⁶⁹ Equation (III-8) is often employed to evaluate the intrinsic viscosity by extrapolating a graph of $(\eta_{sp}/c)^{-1}$ vs. $c^{\frac{1}{2}}$ to $c = 0$. The limitations of this procedure are discussed in a later section.

The addition of simple electrolytes to polyelectrolyte solutions results in general in a considerable reduction of η_{sp}/c , as expected from the screening action of the simple ions on the intramolecular Coulombic repulsions. At moderate or high electrolyte concentrations, the concentration dependence of the viscosity is the same as for uncharged polymers, and the intrinsic viscosity can be obtained by linear extrapolation. At low electrolyte concentrations, m , the reduced viscosity curves possess maxima, which become sharper and occur at lower polyelectrolyte concentrations as m is reduced. The current explanation of these maxima is as follows: on dilution, the polyion expands until the counterion concentration is determined essentially by m alone. On further dilution the dimensions of the polyion remain constant, and the viscosity begins to decrease because of the decreasing effects of intermolecular interaction. Both the limiting coil extension and the interactions are increased on decreasing m .

Eirich⁷⁰ first pointed out that a maximum in the viscosity curve should also occur in salt-free solution, since after the polyions reach their maximum extension, the concentration dependence is determined solely by intermolecular interactions. If this limiting extension is reached at concentrations which are not vanishingly low,

the evaluation of $[\eta]$ by means of equation (III-8) may result in a value which is much too high. Subsequent experimental work⁷¹⁻⁸² confirmed the presence of maxima in aqueous solutions of almost all polyelectrolytes which have been studied at sufficiently low concentrations. The concentration corresponding to the maximum is generally found to be in the vicinity of 5×10^{-5} g./ml. Measurements on such dilute solutions are complicated by poor reproducibility of the results,⁷³ and Flory and Osterheld⁴¹ have suggested that the viscosity maxima are artifacts caused by the presence of ionic impurities in the solvent. Some evidence for this suggestion is presented in section III-5.

For polyelectrolyte solutions with maxima in the reduced viscosity-concentration curves, it is often impossible to obtain a value for $[\eta]$. It has been proposed⁸³ that the complicated dependence on c could be eliminated by performing dilutions with the total concentration, $(m + c)$, of counterions held constant, in order to keep their screening effect, and hence the polyion configuration, independent of c . A modified "isoionic" dilution technique^{84,85} consists in keeping $(m + rc)$ constant, with r empirically determined to give a linear graph of η_{sp}/c vs. c . The parameter r was supposed to represent the fraction of counterions not bound to the

polyion;⁸⁵ this assumption may be criticized⁸⁶ since r in some cases exceeds unity, invalidating the above interpretation. These isoionic dilution methods assume the screening action of the counterions to be determined by their stoichiometric concentration, although it is known that their distribution in the solution is very non-uniform, and may be influenced by the presence of co-ions (small ions of like charge to the polyion). A further criticism is that a linear concentration dependence of viscosity is no proof of a constant configuration, since the presence of the pronounced interactions postulated by the current qualitative theory would result in large contributions from terms of higher order. Finally, application of the Huggins equation (III-7) to the linear graphs obtained by the isoionic dilution method generally leads to an increase in the value of k' with decreasing m , the highest value reported so far being $k' = 400$ at $m = 2 \times 10^{-5}$ eq./l. for solutions of sodium lignin sulphonate.⁸⁷ The theoretical interpretation^{72,87} of such very large interaction coefficients is based on a series of assumptions of doubtful validity, such as the inclusion of the volume of the electrical double layer in the effective hydrodynamic volume of the polyion.⁸⁷ If these high values of k' are real, then the viscosity of salt-free polyelectrolytes at finite concentrations is due largely to the effects of interaction.

4. Solution Properties of Poly-4-vinylpyridinium Chloride (PVP-HCl).

As pointed out in the previous section, the reduced viscosity-concentration curves reported in the literature for most polyelectrolytes possess maxima at low polymer concentrations in solutions of low ionic strength. Aqueous solutions of PVP-HCl have been studied^{76,88,89} at concentrations well below those corresponding to the viscosity maxima, and it was found that the relative viscosity (η/η_0) -concentration curve cut the c-axis at a finite value of c, designated c_0 . Below this concentration c_0 , the viscosity of the solution was indistinguishable from that of the solvent. A similar effect was observed for the magnitude of the birefringence of the solutions. Further, the curve of specific conductance against concentration exhibited a sudden change in slope at a certain concentration c_0 , identical with the concentration at which the anomalies in the viscosity and streaming birefringence curves occurred. On increasing the charge density of the polymer chain by increasing the degree of neutralization of the PVP with HCl, the "critical concentration" c_0 was found to decrease; a similar effect was generally produced by the addition of small amounts of simple electrolytes. The value of c_0

appeared to be independent of molecular weight.

By analogy with the behaviour of micelle-forming soaps and detergents, these observations were interpreted in terms of reversible aggregation of the polyions above the critical concentration c_c . The forces leading to aggregation were considered to be mainly of electrostatic origin, and a mechanism involving triple ion formation between segments of neighboring polyions, with the counterions occupying the central or bridging positions, was suggested.

Interpretation of the above anomalies in terms of hydrolysis of the polyions to the very weakly basic polyvinylpyridine was not considered since the observed effects were believed to be a general property of all polyelectrolytes, including those where no significant hydrolysis could occur. Although actual discontinuities have not been observed in systems other than PVP-HCl, their presence is suggested by the trend of many published reduced viscosity curves below the maximum.

Since the presence of attractive forces between polyion segments, as postulated by the above "aggregation hypothesis", would invalidate previous polyelectrolyte theories and interpretation of experimental observations, it was necessary to study this hypothesis in greater detail.

The reversibility of the viscosity curves was first investigated, using materials of high molecular weight (the

characterization of the samples used is described in Chapter V), in order to obtain measurable viscosity increments at the low concentrations at which the anomalies occur. Solid PVP-HCl was recovered from a solution having a concentration well below c_0 by freeze-drying; the viscosities of solutions of this material are shown in fig. III-1, together with those of the untreated sample (polymer concentrations in this section are expressed in terms of the weight of the free polybase per ml. of solution). The value of c_0 is unchanged by the above procedure. The difference between the two curves above c_0 may be explained in terms of the time effect described in section V-2-(iii). Below c_0 , viscosities of all solutions studied were indistinguishable from that of the solvent in both the Couette and capillary viscometers, that is, $\eta_{sp}/c \leq 40$ ml/g., compared with a value of 3000 ml/g. expected for the parent uncharged polymer (sample RD) in ethanol under similar conditions. On the basis of the aggregation hypothesis,⁸⁹ this contraction on ionization can be explained as being due to intramolecular segment association below c_0 .

The discontinuity in the specific conductance of PVP-HCl solutions⁸⁹ was also observed in the present work. An example is shown in fig. III-2, where the specific conductance K of sample E6, 80% neutralized with HCl, is

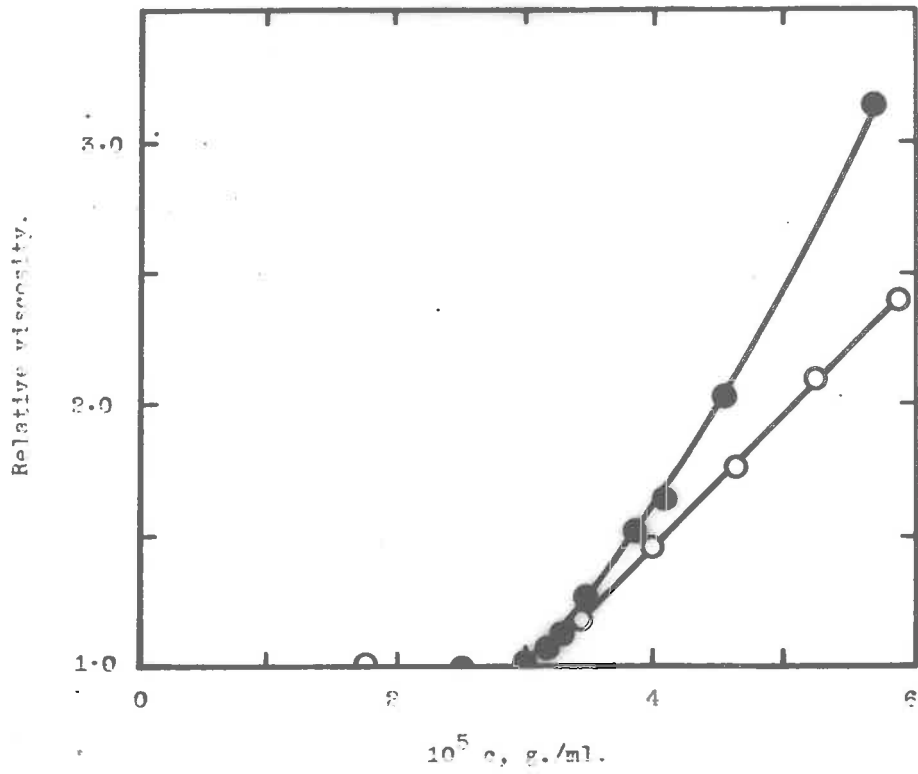


Fig. III-1. Relative viscosity of PVP-60% HCl (sample RD).
(Couette viscometer.)

● Untreated sample. ○ Sample diluted below c_0

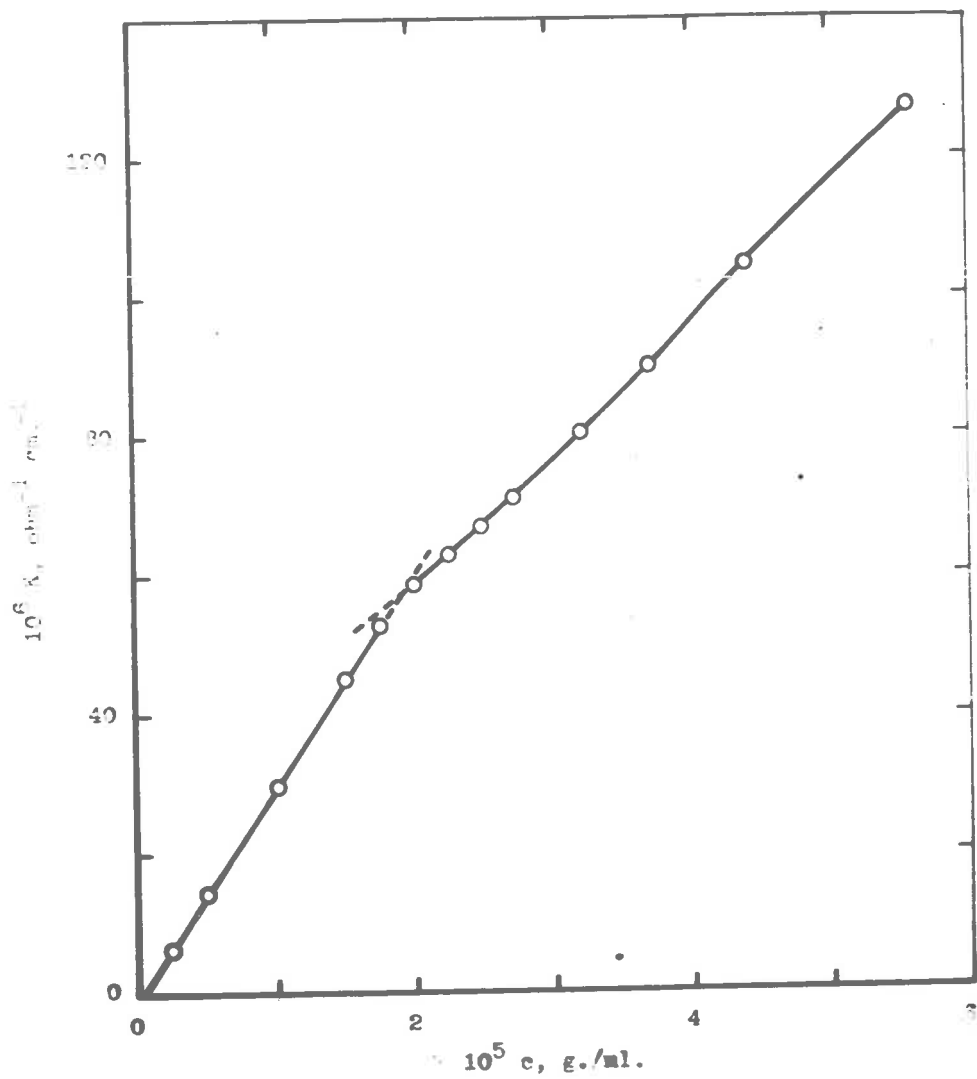


Fig. III-2. Specific conductance of PVP-60% PCl (sample ES).

plotted against the concentration. At concentrations below c_0 the graph is linear; at c_0 a sudden decrease in slope is observed. This decrease is not due to the increase in viscosity of the solution above this point, since the same effect is obtained on plotting the product of conductance and solution viscosity against concentration. Such behaviour is similar to that encountered in solutions of soaps and ionic detergents.

The equivalent conductance Λ of the polyelectrolyte, calculated on the basis of the equivalent concentration of chloride ions, is in the vicinity of $300 \text{ cm.}^2 \text{ ohm}^{-1} \text{ eq.}^{-1}$, which is much higher than that expected (cf. Chapter IV). It may therefore be suggested that the main contribution to the conductance in this concentration range is that of the hydrogen ions produced by the hydrolysis of PVP-HCl. The degree of hydrolysis may be calculated approximately from the conductance data by neglecting the polyion conductance and the effect of binding of chloride ions. The errors introduced by these two assumptions are to some extent mutually compensating. Thus the degree of hydrolysis, h , is given by $h = (\Lambda - 76.3)/350$ to the above approximation, and is shown as a function of concentration in fig.III-3(a) for sample E6 (80% neutralized with HCl). Values of Λ used in the calculation have been corrected for adsorption of the polyelectrolyte as described in

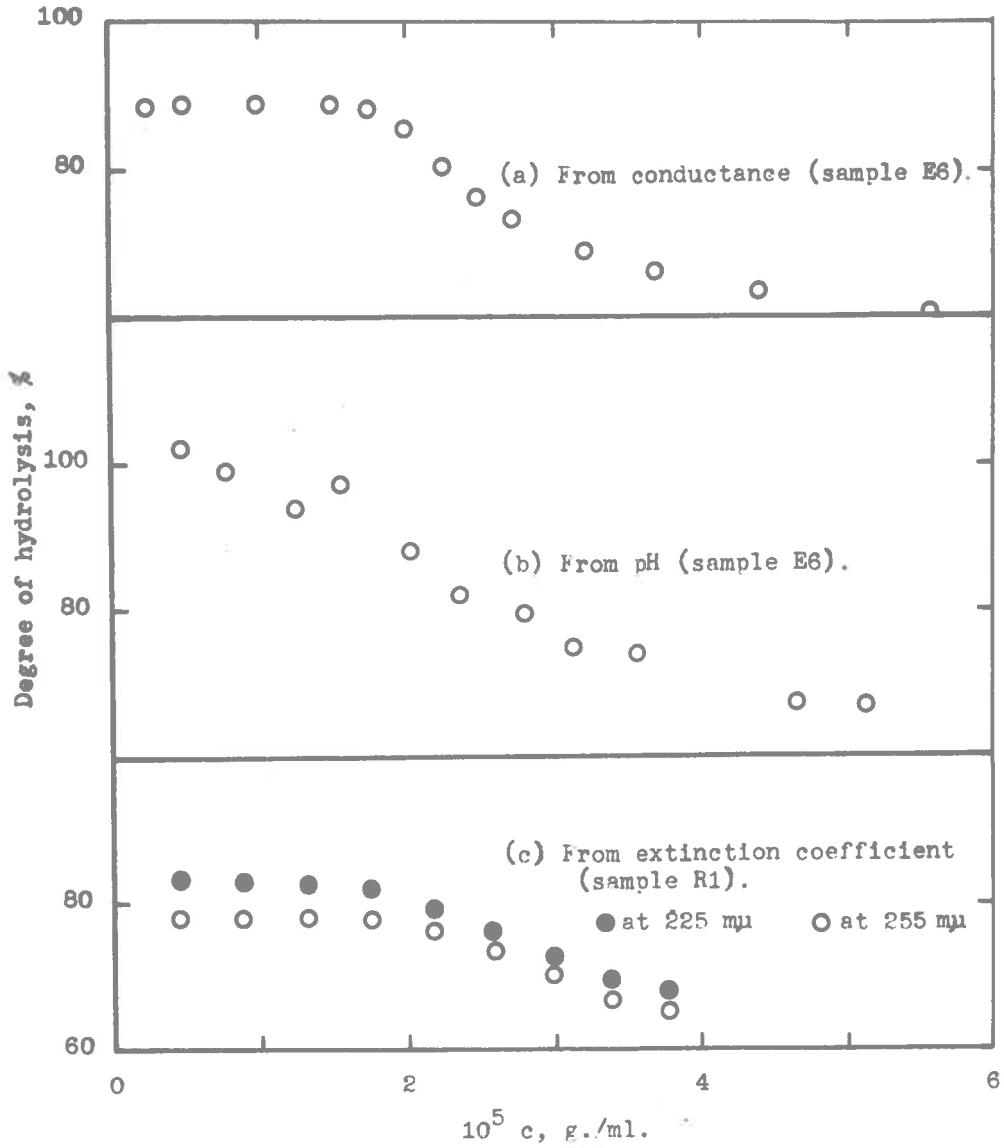


Fig. III-3. Degree of hydrolysis of PVP-80% HCl, determined by various methods.

section V-4.

Further evidence for the extensive hydrolysis of the polyions at low concentrations was obtained from pH measurements. The degree of hydrolysis was obtained by comparing the pH values with those of a series of standard HCl solutions, measured under conditions identical to those used for the PVP-HCl solutions. This procedure assumes that the liquid junction potentials in the two solutions to be compared are either equal or negligibly small. Some results are shown in fig. III-3-(b). No discontinuity was found in the pH of the polyelectrolyte solutions, but in view of the experimental difficulties involved in carrying out pH measurements at such low concentrations, the present results do not exclude the possibility of such a discontinuity.

The existence of a relationship between the critical concentration effects and the hydrolysis of the polyions is shown by the results in fig. III-4, where the effects of the addition of .001 N HCl and KCl to the polyelectrolyte solution are compared. The decrease in c_0 due to the addition of HCl, which is expected to result in a considerable decrease in the degree of hydrolysis, is much more marked than that produced by the addition of KCl.

A study of the spectral properties of PVP-HCl

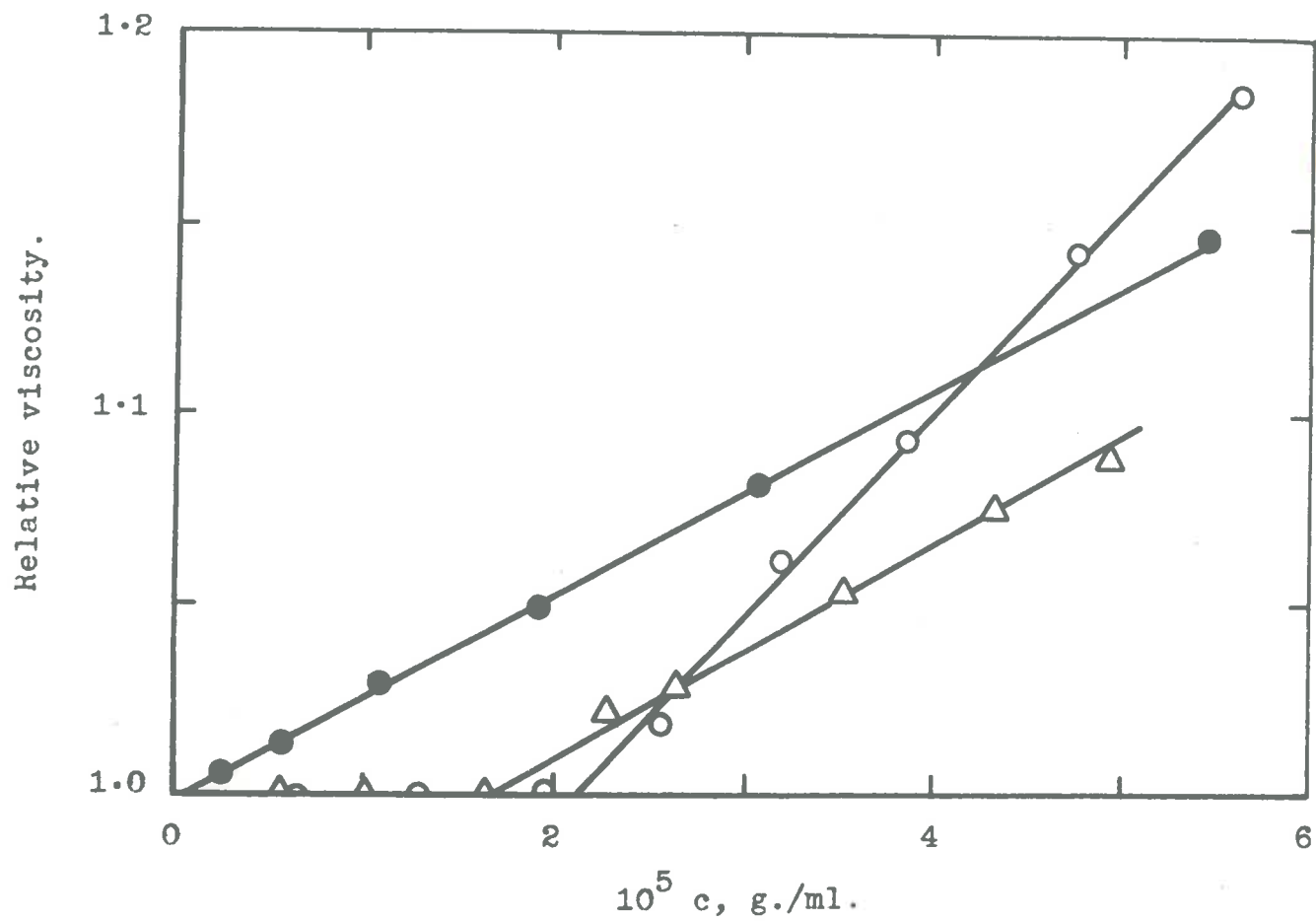


Fig. III-4. Relative viscosities of PVP-80% HCl (sample E6, Ubbelohde viscometer).

○ Aqueous, △ 10^{-3} M KCl, ● 10^{-3} M HCl.

solutions may lead to further insight into the role of hydrolysis of the polyions in the critical concentration effects observed. Deviations from Beer's Law of aqueous PVP-HCl at the long wavelength absorption maximum near 255 m μ , and also at the minimum near 225 m μ , are shown in fig. III-5. The position of the change in slope of the concentration dependence of the extinction coefficient at both wavelengths corresponded approximately to the point of discontinuity, c_c , of the viscosity and conductance curves.

The molecular extinction coefficients ϵ , expressed in terms of the number of gram atoms of nitrogen per litre of the polymer solutions, were found to be independent of the molecular weight of the samples. The ultraviolet absorption spectra of solutions of PVP in ethanol and in 0.1 N HCl are shown in fig. III-6. These spectra are considered to represent the extremes of uncharged and fully ionized PVP respectively; in both cases, the molecular extinction coefficients proved to be independent of concentration.

These spectra may be compared with those of the corresponding monomer analogue, 4-ethylpyridine.^{90,91} The near ultraviolet spectral activity of pyridine in neutral polar solvents or in alkaline solutions has been attributed⁹² to two $\pi - \pi^*$ transitions: the ${}^1A - {}^1L_b$

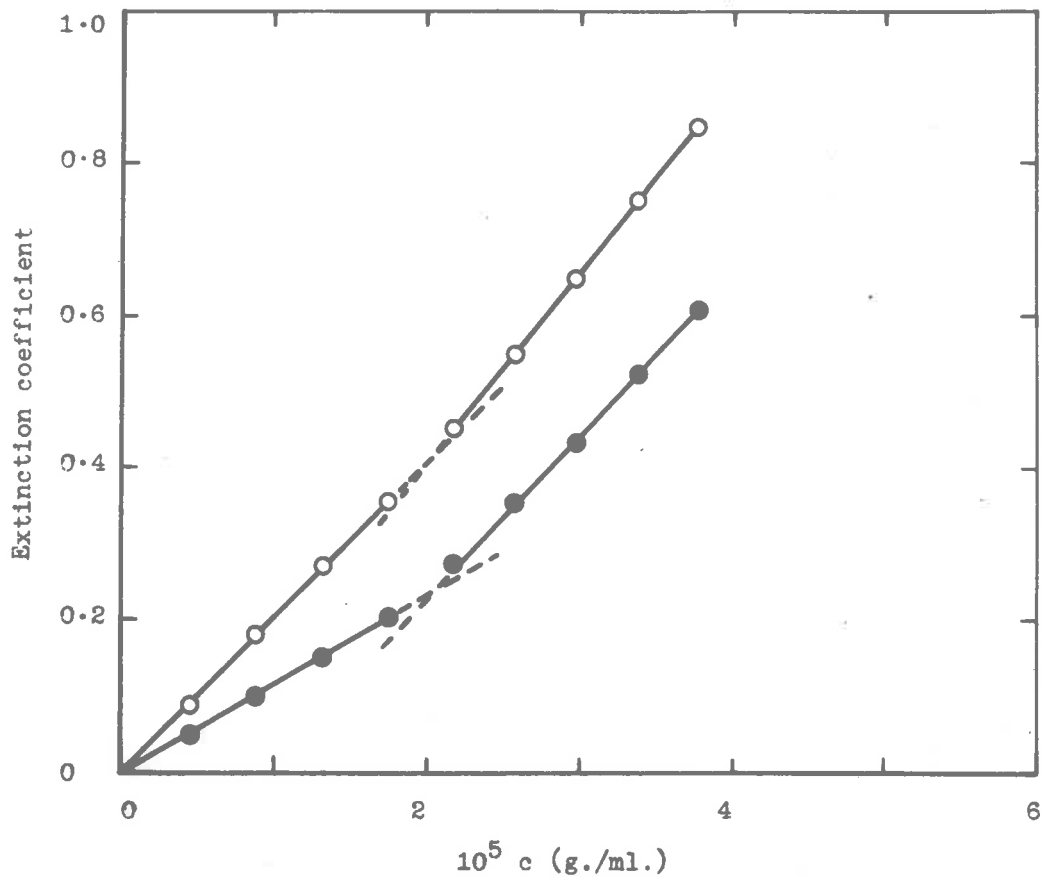


Fig. III-5. Extinction coefficients of PVP-80% HCl (sample R1)

○ at 255 mμ
● at 225 mμ

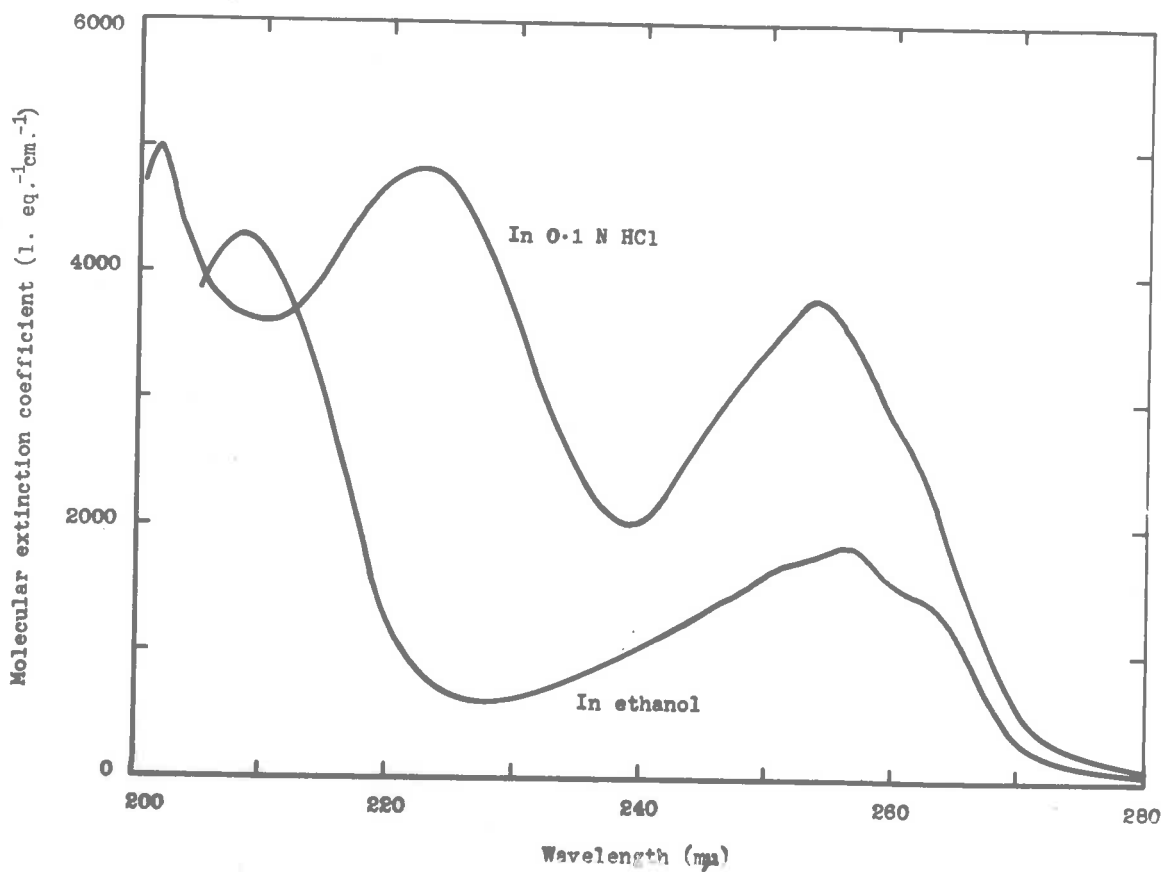


Fig. III-6. Absorption spectra of PVP in different solvents.

transition of high intensity ($\epsilon \sim 7500$) near $195 \text{ m}\mu$, and the ${}^1A - {}^1L_a$ transition producing benzenoid absorption in the $250 - 260 \text{ m}\mu$ region ($\epsilon \sim 2500$). In acidic solutions of pyridine, where the pyridinium ion is present, the intensity of the benzenoid band is increased ($\epsilon \sim 5300$) and the short wavelength band suffers a red-shift into the $225 \text{ m}\mu$ region. The spectrum of 4-ethylpyridine has been studied in less detail; it is similar to that of pyridine except that the intensity of the bands is somewhat reduced.³⁰

The spectra of aqueous solutions of PVP-80% HCl are shown in fig. III-7. At this degree of neutralization, the critical concentration, c_0 , is about $2 \times 10^{-5} \text{ g./ml}$. The spectra of the solutions below this concentration are seen to be identical down to $210 \text{ m}\mu$. The maximum present below this wavelength decreases in intensity and shows a red-shift with increasing polyelectrolyte concentration. These tendencies become more pronounced for the solutions with concentrations above c_0 and, in addition, the molecular extinction coefficient increases with increasing concentration in the $220 - 260 \text{ m}\mu$ region of the spectrum. A slight blue-shift of the peak near $255 \text{ m}\mu$ in the solutions above c_0 as compared with those below c_0 may also be observed. The spectral features shown by the more concentrated aqueous solutions are emphasised further on

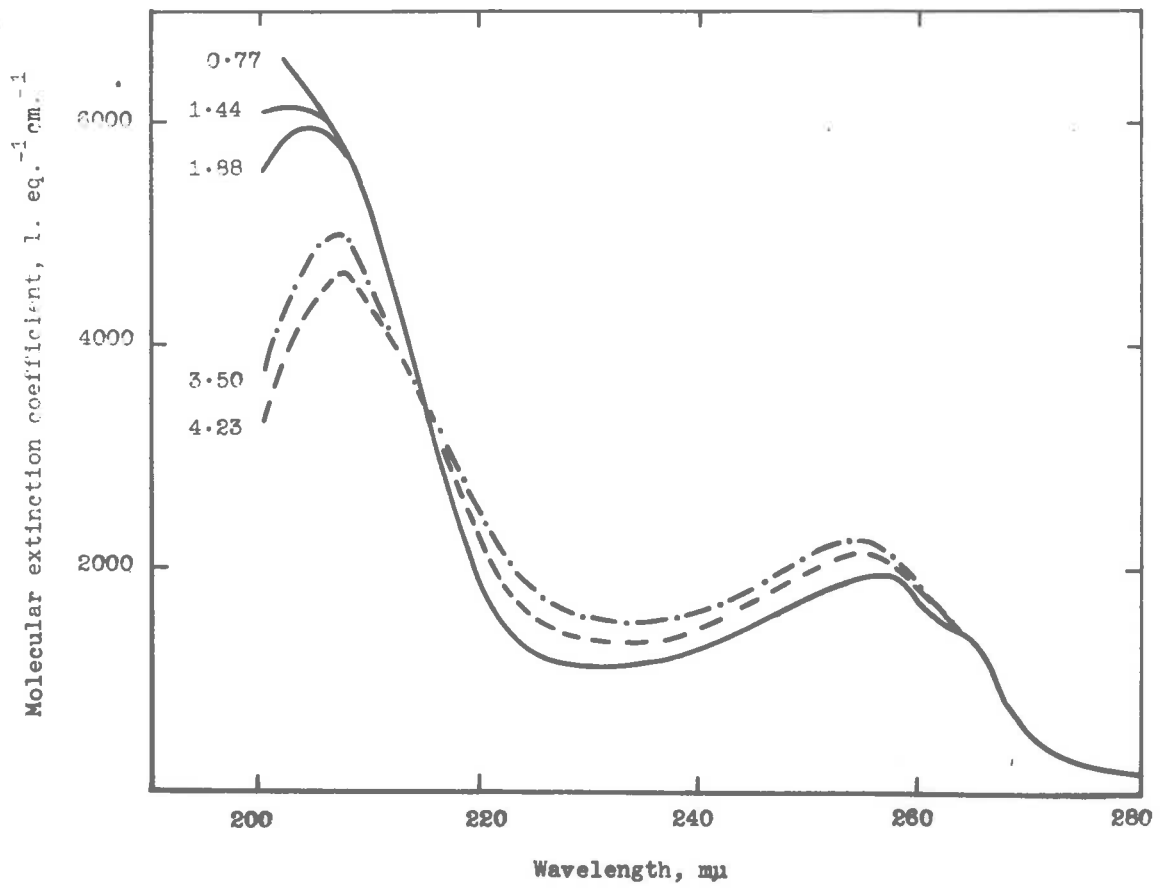


Fig. III-7. Absorption spectra of aqueous PVP-80% HCl.
 Numbers on curves are 10^5 c (g./ml.)

addition of sodium chloride, as shown in fig. III-8. In these spectra the presence of the 225 μ band is suggested by a shoulder.

Comparison of the spectra of the polymeric and monomeric absorbing species leads to a qualitative interpretation of the changes observed in the spectral activity of PVP-HCl solutions in terms of variation in the degree of hydrolysis of the pyridinium ions. If it is assumed that the absorption intensity at either 255 or 225 is a linear function of the fraction of pyridine groups which are ionized, the degree of hydrolysis of the polyions can be calculated as a function of concentration. Values obtained are shown in fig. III-3 (c), and they agree approximately with those obtained from pH and conductance measurements. The degree of hydrolysis appears to be constant below c_0 .

The observed concentration dependence of the degree of hydrolysis, and hence of the polyion charge, suggests the following interpretation of the anomalous viscosity behaviour of PVP-HCl: at very low concentrations, less than about 15% of the pyridine groups of the polyions are charged. Since water is a non-solvent for uncharged polyvinylpyridine, the polyion at low charge will be a very tightly coiled, essentially spherical structure, from the interior of which the solvent is excluded. The

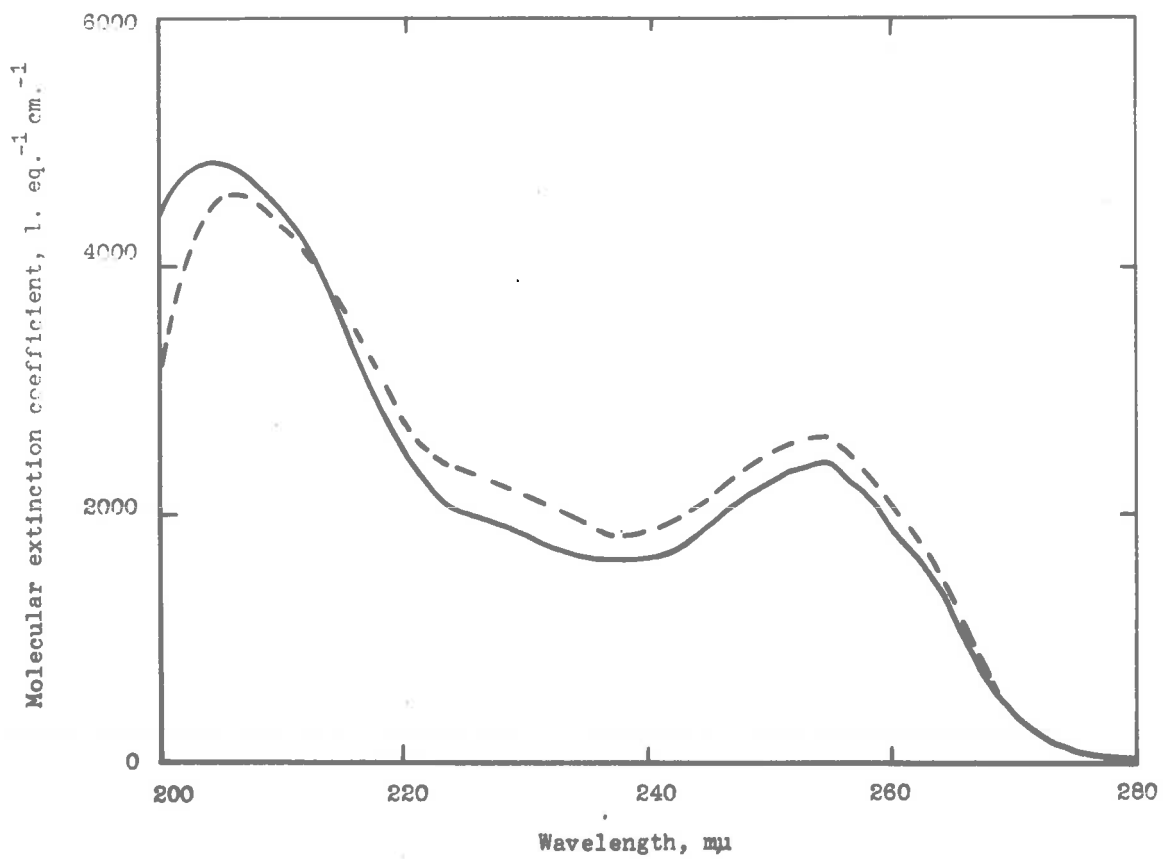


Fig. III-8. Absorption spectra of PVP-80% HCl in the presence of 0.02 M NaCl (————) and of 0.1 M NaCl (— — —).

Polymer concentration 2.3×10^{-5} g./ml.

stability of such a compact sphere may be enhanced by intramolecular $\text{NH}^+ - \text{N}$ hydrogen bonding; its size may be expected to be very sensitive to changes in its net charge. Since most of the ionized or ionizable groups of such a structure are inaccessible to the solvent, the degree of hydrolysis will not change much on dilution. Coagulation of this thermodynamically unstable system is prevented by the presence of charges on the particles. Thus although solutions of PVP-HCl below c_0 could not be prepared directly by dissolving solid PVP in a solution of HCl, such solutions, prepared by dilution from higher concentrations, appeared to be stable.

As the concentration of the solution is increased to approach c_0 , the charge may be assumed to increase slightly, resulting in expansion of the polyion. At a critical value of the net charge the compact structure is disrupted, solvent freely penetrates the coil interior, and the degree of hydrolysis decreases rapidly with increasing concentration, resulting in further expansion. Finally, at relatively high concentrations, the screening effect of the counterions becomes important, and the viscosity goes through a maximum.

The "hydrolysis hypothesis" presented above accounts in a satisfactory manner for most of the experimental observations on PVP-HCl. However, no decision between

this and the aggregation hypothesis is possible on the basis of existing data on PVP-HCl, since both predict an essentially similar variation of c_0 with change of conditions. Thus the increase in c_0 produced by an increase in temperature⁸³ is explained on the one hand as due to increased hydrolysis, or on the other hand as a weakening of the electrostatic attractive forces among the polyions due to the decreased charge density. The lower value of c_0 in the presence of added electrolyte is explained in terms of the lowering of the potential in the vicinity of the polyion,⁴³ resulting in an increase in the basic character of the pyridine groups, and hence a higher charge than at corresponding concentrations in the absence of salt. According to the aggregation hypothesis, this effect, together with the increased concentration of counterions available for triple ion formation, also results in an increased tendency to aggregate formation. The increase of c_0 produced by the addition of iodide counterions,⁸⁹ however, may be difficult to explain in terms of hydrolysis alone.

Evidently a conclusive test of the aggregation hypothesis may be obtained only by determination of the size of the kinetic units in the solution. The molecular weight of the uncharged (and therefore unaggregated) PVP may be obtained from measurements on ethanol solutions of

the polymer. To reduce difficulties in the interpretation of results, measurements on the charged polymer should be carried out in the presence of excess electrolyte; under such conditions aggregation should be favoured. Some unpublished results of Kurucsev⁹³ on PVP in ethanol and PVP-50% HCl in 0.5 M sodium chloride, in which solvents PVP has closely similar intrinsic viscosities, indicate that both the sedimentation coefficient and the amount of boundary spreading are not changed appreciably on ionization of the polymer. The possibility of aggregation is not entirely ruled out by this observation, however, and therefore light scattering measurements were made on PVP (sample B2) dissolved in ethanol, and on the same sample 56% neutralized with hydrochloric acid, dissolved in 0.2 M aqueous sodium chloride. The results are shown in figs. III-9 and III-10 respectively. Molecular weights (M_w) are compared below; values of the root-mean-square radius of gyration $\langle R_z^2 \rangle^{1/2}$, interaction coefficient B, and specific refractive index increment dn/dc are also shown (cf. section V-7).

	$10^5 \langle M_w \rangle$	$10^5 \langle R_z^2 \rangle^{1/2}, \text{cm.}$	$10^4 B$	$dn/dc, \text{ml./g.}$
PVP in ethanol	2.1	1.0	2	0.244
PVP-56% HCl in 0.2 M NaCl	1.6	1.1	2	0.302

The weight-average molecular weight of the polyelectrolyte appears to be some 30% lower than that of the

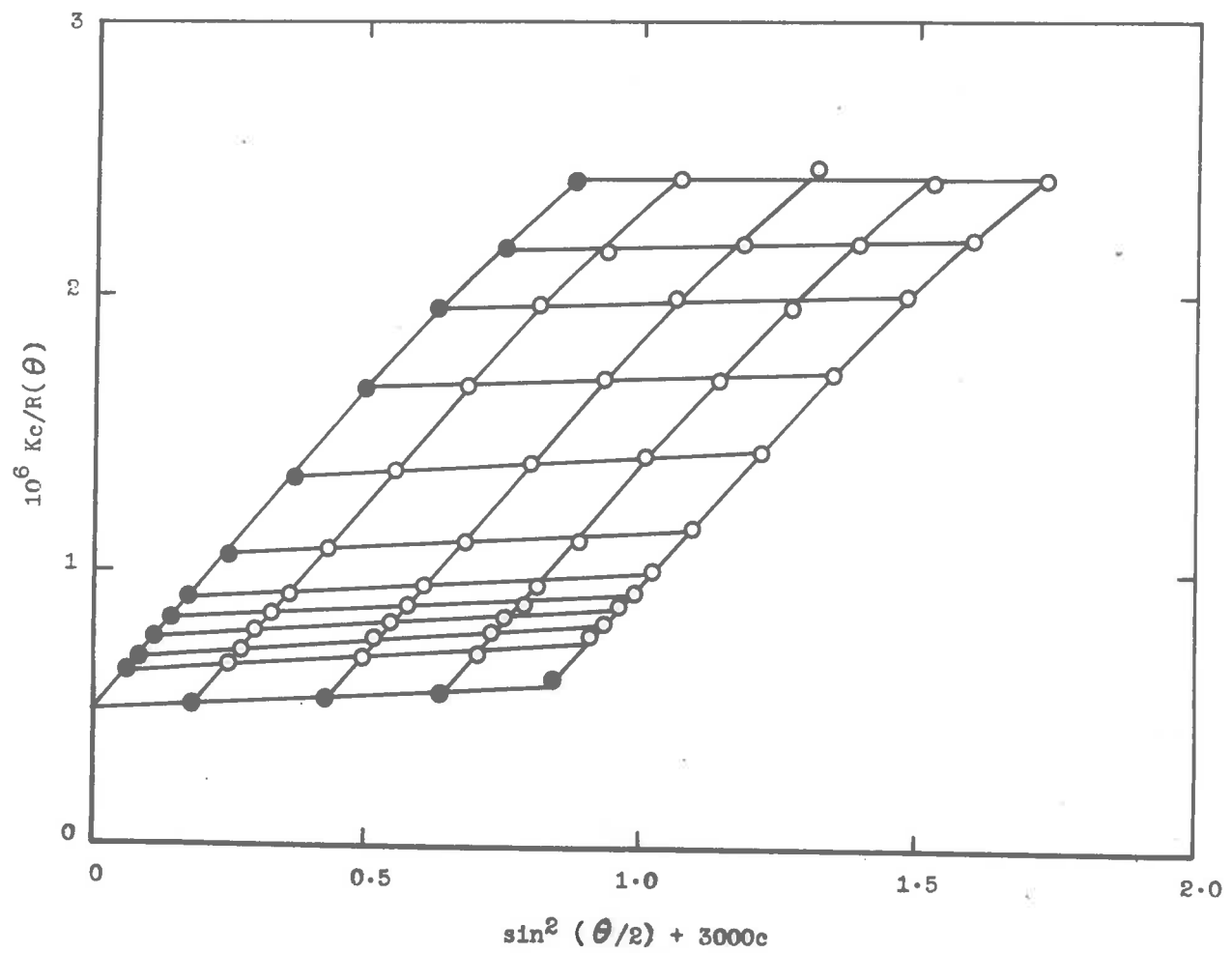


Fig. III-9. Zimm plot for PVP (sample B2) in ethanol.

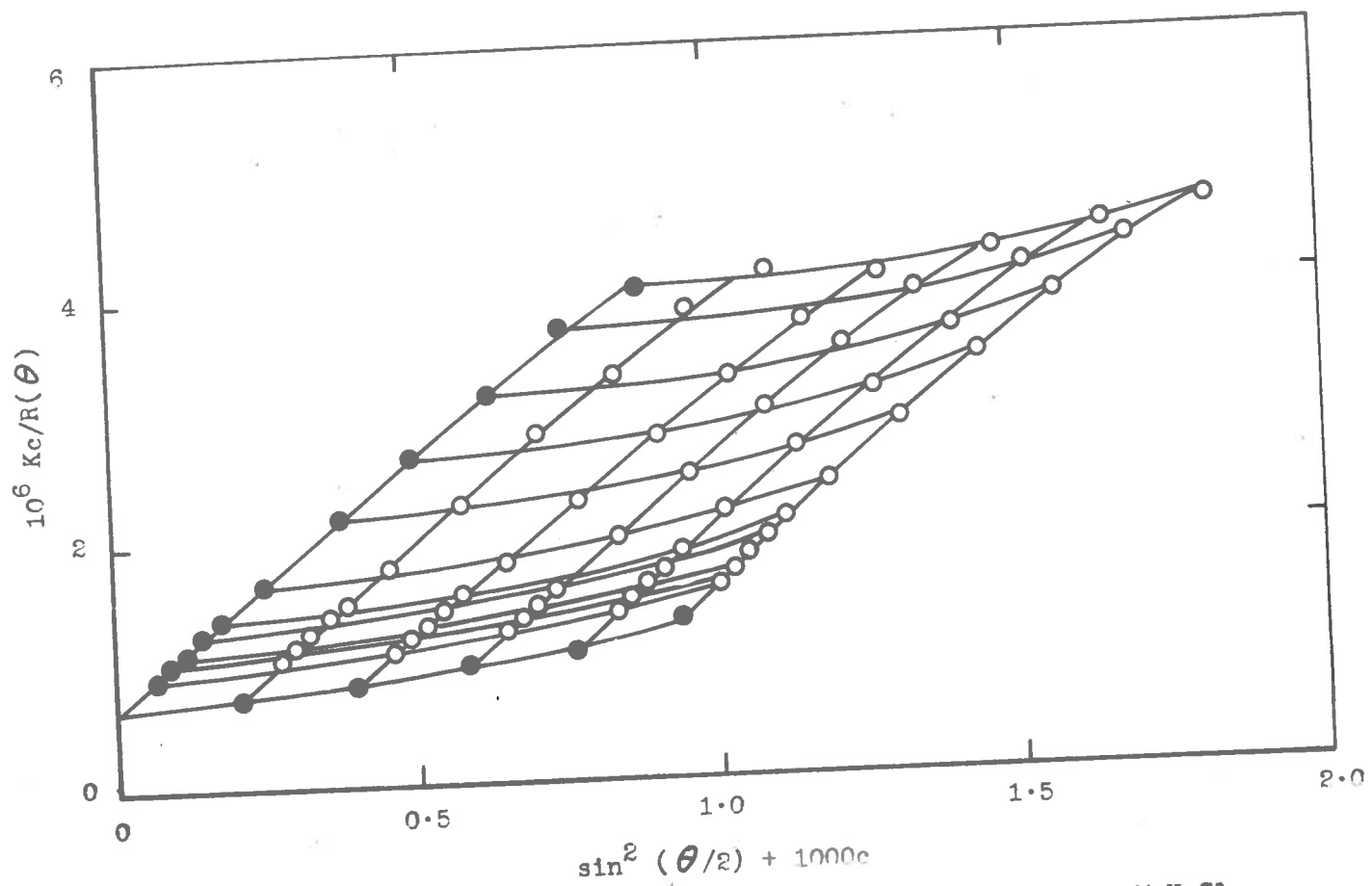


Fig. III-10. Zimm plot for PVP-56% HCl (sample B2) in 0.2 M NaCl

uncharged polymer; this discrepancy is believed to be due to neglect of the thermodynamic correction term required for a three-component system (cf. section V-7). These results are sufficient to show the absence of aggregation of PVP-HCl in the presence of sodium chloride, and suggest the same holds for the aqueous solutions above c_0 . It is possible that the peculiar concentration dependence of the viscosity in aqueous solution is caused by aggregation of the hydrolysed polyions below c_0 , instead of above c_0 as suggested by Jordan and Kurucsev. Measurements on sample B2, 50% neutralized, were made at two concentrations below c_0 . Values of $Kc/R(\theta)$ obtained at various angles θ are given below. The notation is defined in section V-7.

θ , degrees	30	45	60	75	90	105	120	135	140
$10^6 Kc/R(\theta)$, $c=1.8 \times 10^{-5}$ g/ml.	.40	.47	.52	.57	.58	.60	.61	.59	.61
$10^6 Kc/R(\theta)$, $c=2.9 \times 10^{-5}$ g/ml.	.43	.48	.53	.58	.59	.63	.64	.65	.65

The light-scattering constant K for these solutions was assumed to be the same as that for the solutions in sodium chloride. The correction for solvent scattering was relatively large; nevertheless the increase of $Kc/R(\theta)$ with increasing angle is believed to be significant, and is probably due to "external interference" of the scattered light, due to the presence of large repulsive

forces among the solute particles.³⁴ Approximate extrapolation to zero angle and concentration results in a value $\langle M_w \rangle \sim 3 \times 10^6$ for the molecular weight, in reasonable agreement with the molecular weight found in ethanol, considering the experimental difficulties involved. This shows that extensive aggregation does not occur under these conditions.

Application of the Einstein viscosity equation to the result $\eta_{sp}/c \leq 40$ ml./g. below c_0 , and using the molecular weight of B2 determined in ethanol, results in an estimate of the radius of the suspended particles as $r \leq 3.2 \times 10^{-6}$ cm. Evidently the observed dissymmetry of the scattered light cannot be due to internal interference,³⁴ since the particles are much smaller than the wavelength of the light.

On the basis of the results presented in this section, it appears that the viscosity maxima and other anomalies observed in dilute solutions of PVP-HCl are caused by changes in the degree of hydrolysis, and hence the shape, of the polyions in solution with changes in their environment. These effects are not, therefore, general properties of polyelectrolyte solutions, and were therefore not further investigated. The above explanation cannot, however, account for the appearance of viscosity maxima in most other polyelectrolyte solutions. Therefore viscosity

measurements were undertaken on polyelectrolytes for which the possibility of extensive hydrolysis cannot arise; an account of this work is given in the next section.

5. Viscosity Measurements at High Dilutions on Polyelectrolytes not Subject to Extensive Hydrolysis.

Initial measurements on quaternary salts of PVP were carried out in capillary viscometers. Provided the molecular weight of a polyelectrolyte is not very high, the effect of shear rate on its viscosity is relatively small,⁹⁵ and therefore at least the qualitative features of the reduced viscosity-concentration curve may be obtained using these convenient and precise instruments. At first, viscosity maxima were obtained for all polyelectrolytes studied. At this stage, distilled water with a specific conductance of $1 - 3 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ was used to prepare the solutions. These were always prepared by stepwise addition of concentrated solution to the solvent or dilute solution in the viscometer, as described in Chapter V, otherwise smooth curves could not be obtained. On plotting the relative viscosity against concentration, curves were generally obtained suggesting strongly the presence of a "discontinuity" at concentrations of the order 10^{-6} g./ml.

In subsequent work, carbon dioxide-free conductivity water (specific conductance $2 - 5 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$) was used as a solvent. The results obtained were in striking conflict with those of the earlier work, as

illustrated by the example in fig. III-11. Here the reduced viscosity of polyvinylbutylpyridinium bromide (PVP-Br, sample E3-Q) is shown as a function of polymer concentration. The lower curve, obtained with ordinary distilled water, has a flat maximum in the region $5 - 8 \times 10^{-5}$ g./ml., a result similar to that reported by previous authors^{77,78} for aqueous solutions of PVP-Br. The upper curve shows the results of two experiments in conductivity water: here the maximum, if present, is shifted to a concentration at least twenty times lower. In fig. III-12 similar results are shown for polyvinylbenzyltrimethylammonium chloride (PBTA-Cl). The sequence of the curves could not be correlated exactly with the solvent conductance, partly because this was measured before transference to the viscometer, and partly because the nature of the ionic impurities present is of importance as well as their conductance. There can be no doubt, however, that the effects observed are due to variations in the purity of the solvent. The results indicate that such variations become less important as the polyelectrolyte concentration is increased. Another polyelectrolyte briefly studied was polyvinylimidazole neutralized to 5% and 40% with HCl. No maximum could be detected with either sample to the lowest concentrations (ca. 10^{-5} g./ml.) allowed by

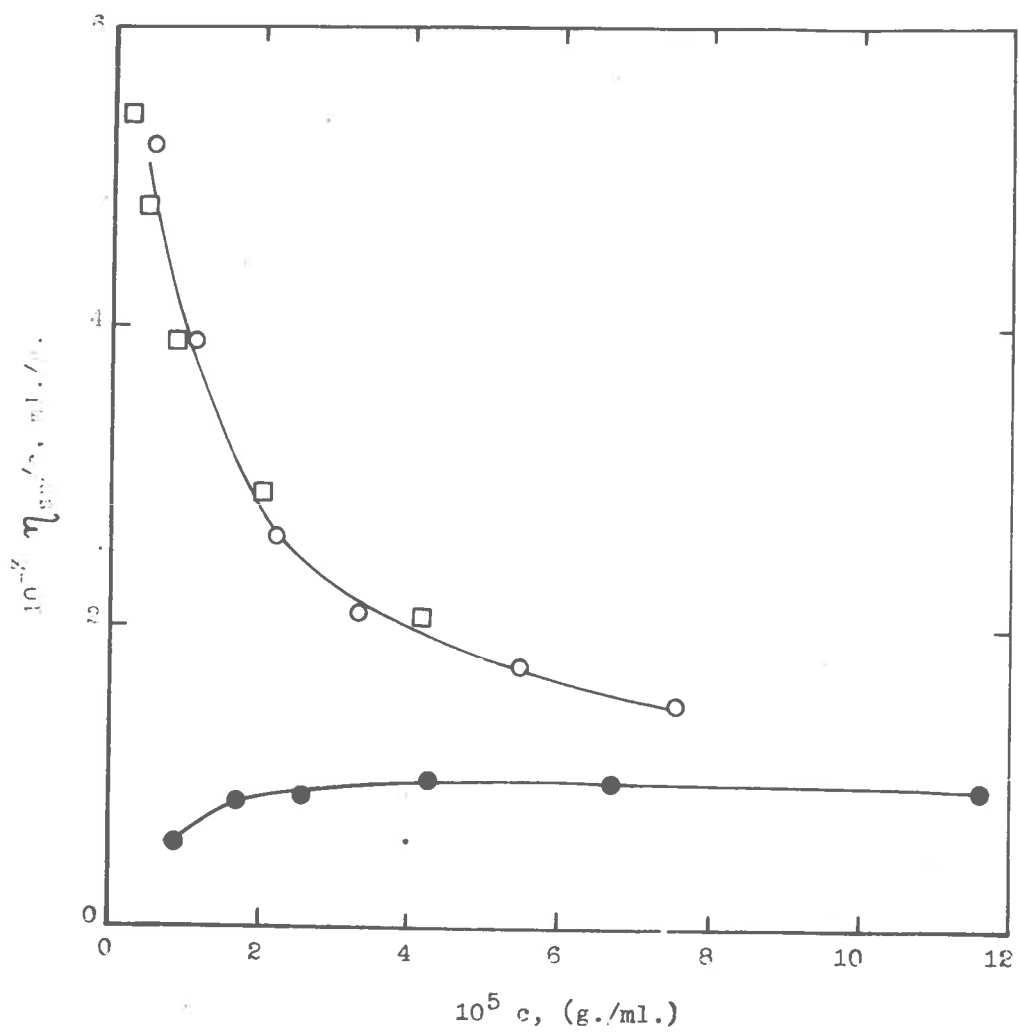


Fig. III-11. Viscosity of PVP-Br (sample E3-Q, Ostwald No. 1 viscometer).

○ and □ : in conductivity water.
 ● : in distilled water.

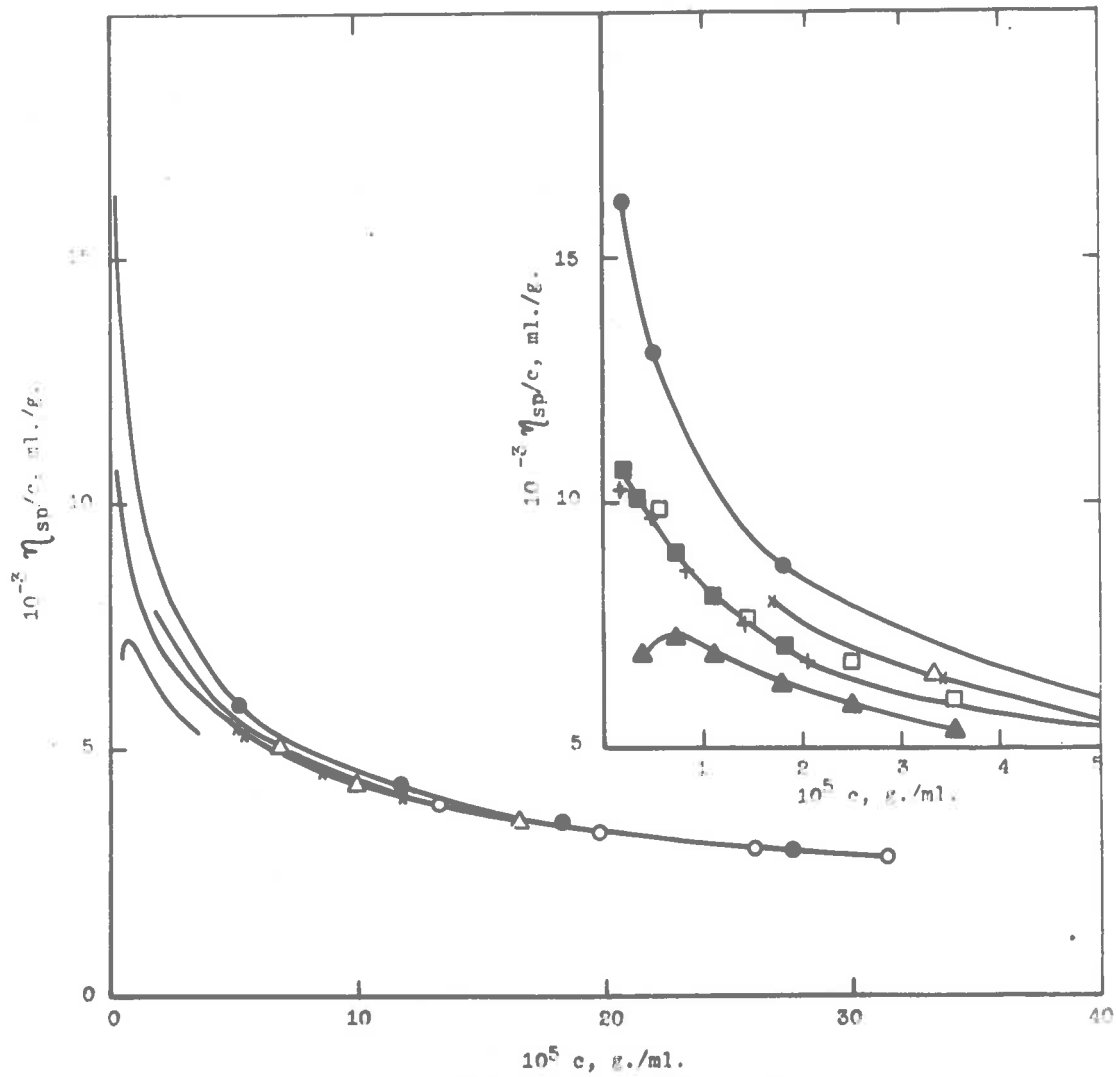


Fig. III-12. Viscosity of PBTA-C1 (Ostwald No. 1 viscometer).

○, ▲, × : in distilled water.
 Other points: in conductivity water.

experimental precision.

When a sample of PVP-Br of high molecular weight (sample A1-Q) was studied in capillary viscometers, a maximum was always observed even in the purest water used. This behaviour is thought to be an effect of shear rate: on expansion of the polyions, the shear dependence of the viscosity increases, and if measurements are carried out at high rates of shear, the observed viscosity may decrease although the extension of the polyion increases. The curves obtained were similar to those reported⁷⁴ for sodium carboxymethylcellulose of high molecular weight at high rates of shear.

The above view was confirmed by measurements at low rates of shear in a Couette-type viscometer. A disadvantage of the instrument used, apart from its relatively low sensitivity, is the danger of contamination of the solutions with ionic impurities. Thus at first the viscosity curves obtained invariably showed maxima even when conductivity water was used. The concentration of ions produced by atmospheric carbon dioxide is too small to account for this effect. It was eventually found that the conductance of water increased considerably on standing in the viscometer for times comparable to those required for viscosity measurements. On coating the stainless steel surfaces

in contact with the solution with a film of polymethyl methacrylate, this contamination was considerably reduced, and the viscosity maxima, when present, were displaced to much lower concentrations. In fig. III-13 results of measurements on PVP-Br (sample A1-Q) in conductivity water are shown. The reproducibility of the results is seen to be satisfactory except at the lowest concentrations, and there is an indication of the presence of a maximum just below 10^{-5} g./ml. This curve should be compared with those of Eisenberg and Pouyet⁷⁷ and of Jordan, Mathieson, and Porter.⁷⁶ Evidently the maxima reported by these authors are due to traces of ionic impurities. To illustrate the pronounced effect of small amounts of electrolyte on the viscosity behaviour, the viscosity of PVP-Br in 4.8×10^{-5} M potassium bromide is also shown in fig. III-13.

The low concentrations at which these viscosity maxima occur makes their investigation difficult. Several authors⁷⁰⁻⁷² have reported maxima in the viscosities of sodium polyacrylate and polymethacrylate at relatively high concentrations ($1-5 \times 10^{-4}$ g./ml.). Therefore viscosity measurements were made on a sample of polymethacrylic acid (PMA) 90% neutralized with sodium hydroxide. Fig. III-14 shows the results obtained. The effect of shear may be seen, by comparison of the curves obtained with the Couette and Ostwald viscometers respectively, to

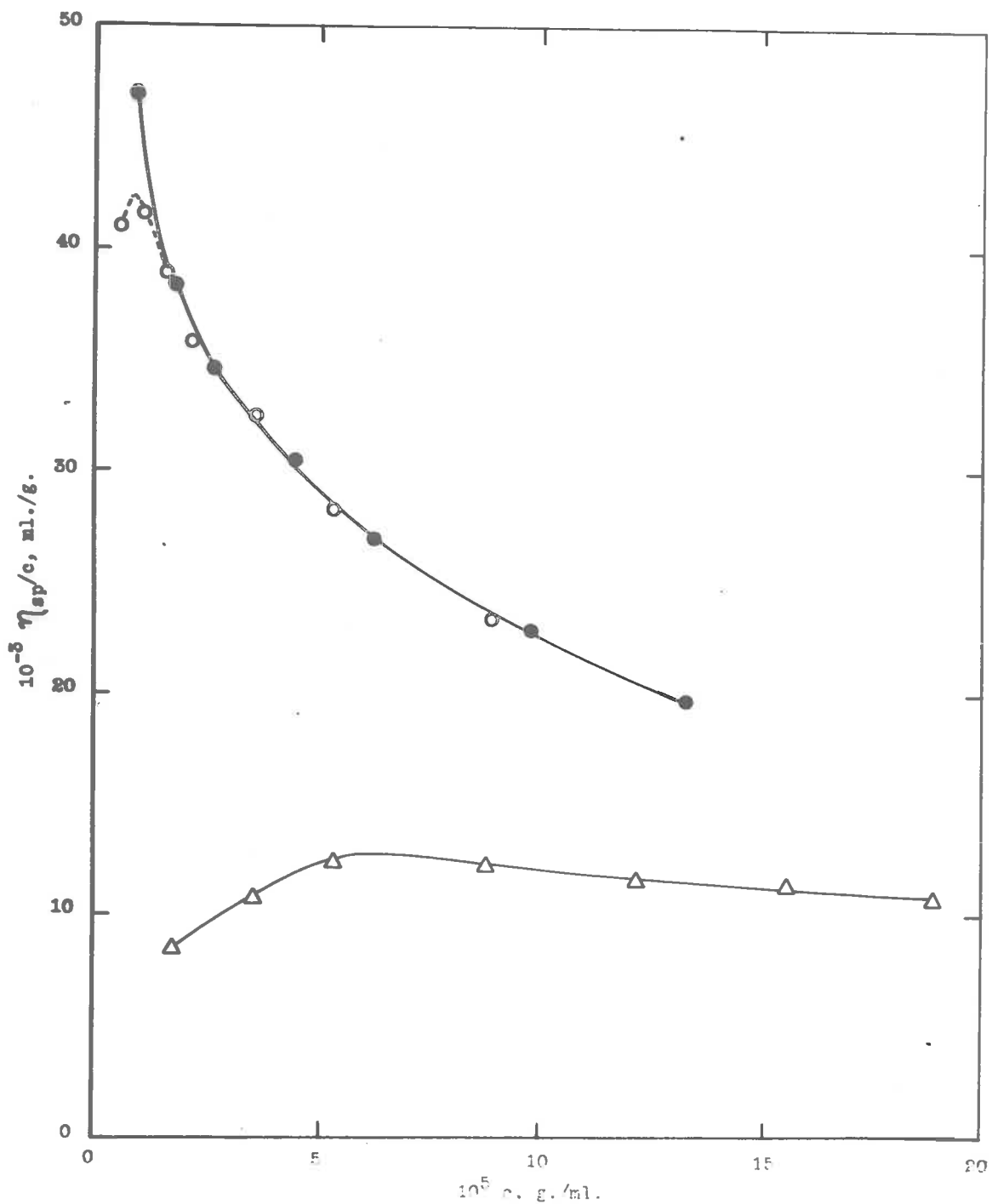


Fig. III-13. Viscosity of PVP-Br (sample Al-Q, Couette viscometer).

○ and ● : in conductivity water.
 △ : in 4.8×10^{-5} N KBr.

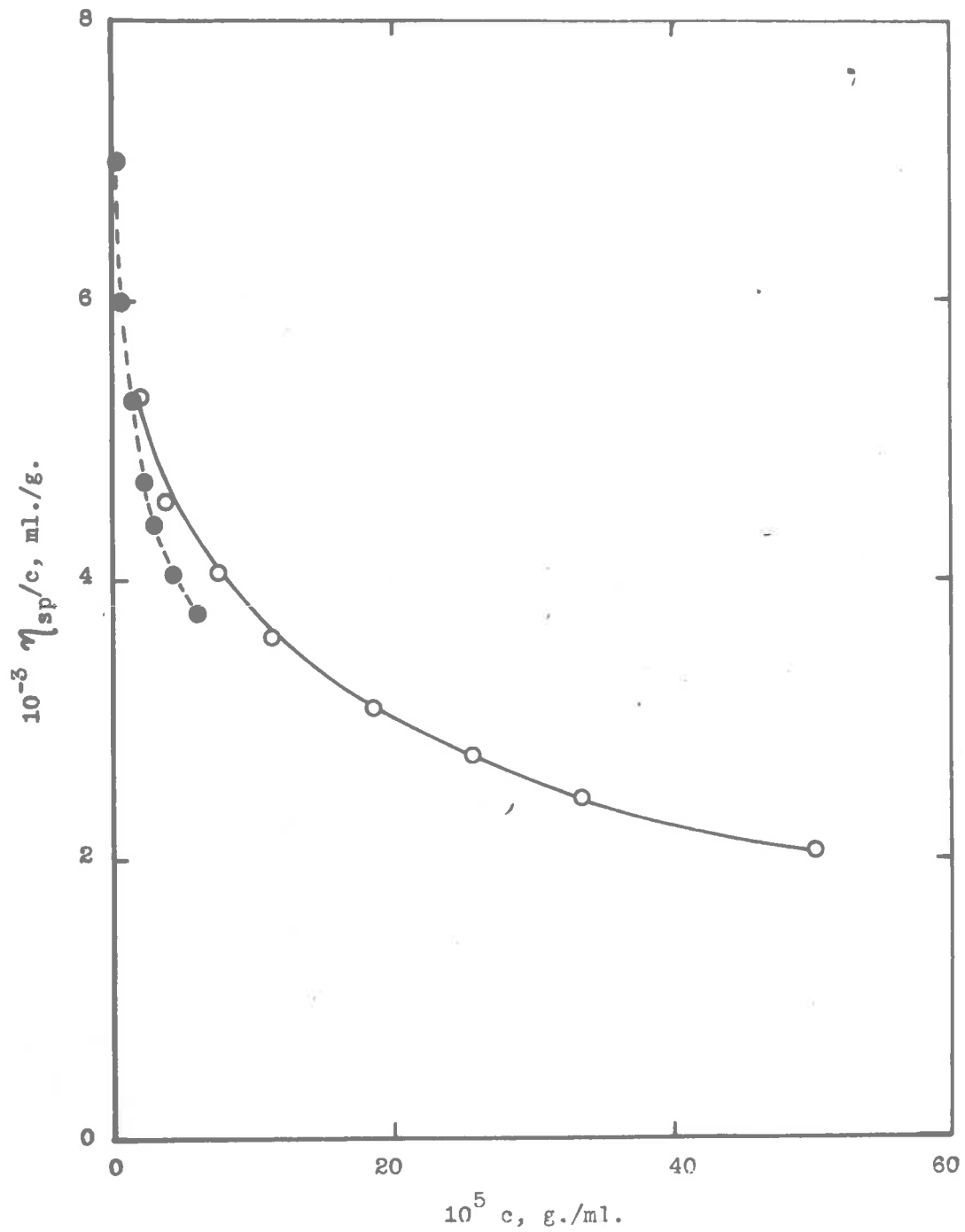


Fig. III-14. Viscosity of PMA-90% Na.

- : Couette viscometer.
- : Ostwald No. 1 viscometer.

be relatively small in this case. The viscosities obtained at the lowest concentration studied (4×10^{-6} g./ml.) were reproducible ($\pm 10\%$) since the specific conductance of the water used (2×10^{-7} ohm $^{-1}$ cm. $^{-1}$) did not change from sample to sample. The precaution of excluding carbon dioxide proved to be essential at this concentration: when it was not observed, the measured value of η_{sp}/c was too low by a factor of ~ 5 . It may be concluded, therefore, that the positions of the viscosity maxima previously reported for similar materials in salt-free solution are in error.

Viscosity curves with no maxima at low concentrations have been published by Oth and Doty⁹⁶ for sodium polymethacrylate (lower limit of concentration $\sim 7 \times 10^{-5}$ g./ml.), Eisenberg and Mohan⁹⁵ for polyvinylsulphonic acid ($\sim 2 \times 10^{-5}$ g./ml.), and Gregor and Gold^{96a} for polyvinylmethylimidazolium salts ($\sim 10^{-5}$ g./ml.). These results were obtained using relatively pure water. The purity of the solvent used has not been established in any study where a maximum was found.

The maxima in the viscosity curves generally occur when the polyelectrolyte concentration, in equivalents per litre (cf. Chapter IV), is of the same order as the concentration of simple electrolyte in the solvent.

Conductivity water of specific conductance 2×10^{-7} ohm⁻¹ cm.⁻¹, which was the purest solvent used in the present investigation, contains about 2×10^{-6} eq./l. of ionic impurities, whereas the lowest polyelectrolyte concentration investigated was of a similar magnitude. It is not surprising, therefore, that the reproducibility of viscosity measurements on polyelectrolytes at low concentrations is poor. The intrinsic viscosity in the complete absence of simple ions is therefore difficult to determine unambiguously, except perhaps by extrapolation of data obtained in the presence of low concentrations of added salt to zero concentration of both salt and polyelectrolyte.⁶⁰

The intrinsic viscosity. The viscosity data obtained on the polyelectrolyte solutions in conductivity water generally could be extrapolated to infinite dilution by means of the Fuoss equation (III-8), although in some cases the graphs obtained were slightly curved. The intrinsic viscosities so obtained proved to be somewhat dependent on the purity of the solvent used; the highest values obtained for a given sample were therefore taken as being closest to the ideal case of a salt-free solution.

Some of the extrapolations of viscosity results by previous authors from relatively high concentrations are

of doubtful validity owing to the great length of the extrapolations (in terms of η_{sp}/c) and, in some cases, the very low intercepts obtained, which may result in large errors on taking the reciprocal to obtain the intrinsic viscosity. The latter source of error may be eliminated by reversing slope and intercept of the graph, i.e. by plotting $(\eta_{sp}/c)^{-1}c^{-\frac{1}{2}}$ vs. $c^{-\frac{1}{2}}$. Extrapolated values of the viscosity of some polyelectrolytes are listed in table III-1. For comparison, values calculated on the basis of a fully extended, all-trans⁴⁴ configuration are also shown; these were obtained by the use of Simha's equation (III-1) for cylindrical rods, in the manner suggested by Yang.⁹⁷ The final expression for the intrinsic viscosity is

$$[\eta] = \frac{\pi N M^2 b_0^3}{4 M_0^2} \left[\frac{14}{15} + \frac{1}{15(\ln 2p - 1.80)} + \frac{1}{5(\ln 2p - 0.80)} \right]$$

where N is Avogadro's number, M the molecular weight of the polyelectrolyte, and M_0 and b_0 are respectively the molecular weight and the length of the repeating units. The axial ratio p was obtained from the calculated length of the extended chain and its diameter, estimated by the use of Courtauld's molecular models; the calculated value of $[\eta]$ is insensitive to p . The value $b_0 = 2.5 \times 10^{-8}$ cm. was used.

Table III-1.

Intrinsic Viscosities of some Polyelectrolytes.

Sample	PVP-Br(A1-Q)	PBTA-Cl	PMA-90%Na	PMA-100%Na**	PVSA*
Degree of polymerization	6700	2100	720	500	320
Axial ratio	800	250	170	120	70
M_0	242	198	108	108	108
$10^3[\eta]$ observed, ml./g.	~ 80	~ 25*	~ 10	~ 1.3*	~ 12*
$10^3[\eta]$ calculated, ml./g.	59	8.7	2.0	1.1	0.51

* Measured at high shear

** Sodium polymethacrylate, data of Oth and Doty.⁹⁶* Polyvinylsulphonic acid, data of Eisenberg and Mohan.⁹⁵

The calculated values of $[\eta]$ are all lower than those obtained by extrapolation; this discrepancy has been pointed out by previous authors.^{95,96} It may be explained, at least in part, by the polydispersity of the samples as follows. Since the Simha equation can be approximated by equation (III-3) with the exponent $a \sim 1.7$, the viscosity-average

molecular weight is higher than the weight-average, which was used in the calculations. The calculated values of $[\eta]$ are therefore too low by the factor $y = (\langle M_v \rangle / \langle M_w \rangle)^2$. For a "most probable distribution" of molecular weights,⁴⁵ where the ratio of number-average to weight-average molecular weight is 1 : 2, $y = 1.36$. Since the molecular weight distribution of the samples used is not known, this correction cannot be applied. It is significant, however, that in the two cases where fractionated materials were used (sample A1-Q and the PMA sample of Oth and Doty⁹⁶), the best agreement between observed and calculated values of $[\eta]$ is obtained, whereas the largest discrepancy occurs for the very heterogeneous polyvinylsulphonic acid sample of Eisenberg and Mohan.⁹⁵

The intrinsic viscosities obtained by extrapolation according to the Fuoss method are probably somewhat lower than would be obtained in pure water. Shear effects may result in similar errors. On the other hand, the calculated values of $[\eta]$ are upper limits, since the highest possible extension of the macromolecules is assumed. Thus the discrepancy between calculated and observed intrinsic viscosities may be greater than is apparent from table III-1.

Discussion. According to current interpretation, the value of η_{sp}/c at finite concentrations is due largely to polyion

interactions. If the ascending part of the viscosity curve is extrapolated to infinite dilution, a value of $[\eta]$ should therefore be obtained which is increasingly in error as the molecular weight of the polyelectrolyte becomes larger. No such trend is apparent from the data in table III-1. By extrapolating the intrinsic viscosities of sodium carboxymethylcellulose (obtained in the presence of sodium chloride by the isonic dilution technique) to zero ionic strength, Pals and Hermans⁹⁸ obtained values of $[\eta]$ which are also higher than those calculated on the basis of the fully extended length of the chain. Their extrapolation does not contain the uncertainty of the possible appearance of a maximum at low polyelectrolyte concentrations. Evidently, then, the high observed values of $[\eta]$ cannot be used as evidence for the current "interaction hypothesis."

It is possible that the importance of interaction terms in the viscosity of dilute polyelectrolyte solutions has been overestimated by some authors. Thus the polyions in solutions of flexible polyelectrolytes, although having a charge density similar to that of the spherical particles studied by Harmsen et al.,⁶⁴ are too large to exhibit a significant secondary electroviscous effect. Further, interaction terms large enough to

produce a maximum in the reduced viscosity curve would be expected to be very shear-dependent. Shear dependence of the viscosity of very dilute polyelectrolyte solutions is only observed, however, for polyions large enough to be oriented in the field of flow, and increases on dilution, contrary to the behaviour expected on the basis of the interaction hypothesis.

The viscosity behaviour of polyelectrolytes can be accounted for in terms of configurational changes alone,⁹⁹ although the mechanism proposed for these configurational changes, namely a changing degree of counterion binding,^{68, 99} must be amended (cf. Chapter IV). Consider an isolated polyion in an infinite volume of solvent containing a very low concentration m of 1 : 1 electrolyte. The bulk counterion concentration is therefore m , but in the vicinity of the polyion the local counterion concentration will be much larger than m , say m' . At a low finite polyelectrolyte concentration, such that the bulk counterion concentration is still essentially m , each polyion now has only a finite volume from which to draw counterions, and m' therefore decreases. Since the screening of the polyion charges is determined by m' , and not by m , the polyion expands. This expansion continues with increasing polyelectrolyte concentration until the concentration of

counterions supplied by the polyelectrolyte becomes an appreciable fraction of m , whereupon contraction occurs on further increase in concentration. These changes in shape are reflected in the familiar viscosity maxima. The high values of k' sometimes reported for isoionic dilution curves of polyelectrolytes may thus be due also to a contraction of the polyions on dilution.

CHAPTER IV

ELECTROCHEMICAL PROPERTIES OF STRONG POLYELECTROLYTES

1. Counterion Binding

(i) Methods of measurement

- (a) Transference methods
- (b) Tracer diffusion method
- (c) Thermodynamic methods
- (d) Hydrodynamic methods

(ii) Review of previous work

(iii) Experimental results and discussion

(a) Charge fraction

- (1) Effect of electrode reactions
- (2) Effect of field and time of electrolysis
- (3) Effect of sintered-glass partition
- (4) Concentration dependence of degree of association
- (5) An attempted absolute determination of charge fraction

(b) Activity coefficients

2. Electrophoretic Mobility

3. Conductance

4. Effect of Change in Temperature and Dielectric Constant on Electrochemical Properties

5. General Discussion

1. Counterion Binding.

(i) Methods of Measurement.

The fraction $1 - \alpha$ of associated counterions may be defined as the ratio of the number of counterions moving in the same direction as the polyions in an electric field, to the total number of counterions resulting from complete ionization of the polyelectrolyte. With this definition, no distinction is made among various states of binding which may exist. The quantity α may be termed the charge fraction of the polyelectrolyte.

A number of methods for the experimental determination of the charge fraction are available. The theoretical basis of some of these methods is outlined below. Since the combination of conductance and transference data is the most precise method available at present, it was used extensively in the present work, and is therefore discussed in greater detail.

(a) Transference methods. The equivalent conductance Λ of a polyelectrolyte may be defined as

$$\Lambda = 10^3(K - K_s)/C \quad (\text{IV-1})$$

where K is the total specific conductance of the solution, and K_s the specific conductance of simple electrolyte in

the solution, including solvent conductance. The concentration C is expressed as equivalents per litre of solution, where the equivalent weight of the polyelectrolyte is defined as the weight containing one equivalent of counterions.

The equivalent ionic conductances of the polyion (subscript p) and of the free (i.e., unbound) counterions (subscript c) are defined as

$$\lambda_p = 10^3 K_p / C \quad (\text{IV-2})$$

and

$$\lambda_c = 10^3 K_c / C_c \quad (\text{IV-3})$$

where $C_c = \alpha C$ is the concentration of free counterions.

Introducing the definition of α , one may write

$$\Lambda = \lambda_p + \alpha \lambda_c \quad (\text{IV-4})$$

It is readily shown that the relation between equivalent conductance and electrophoretic mobility of the polyion is

$$\lambda_p = \alpha F u_p \quad (\text{IV-5})$$

where u_p is expressed in $\text{cm.}^2 \text{ sec.}^{-1} \text{ volt}^{-1}$ and F is the Faraday constant. Combination of (IV-4) and (IV-5) gives

$$\alpha = \Lambda / (F u_p + \lambda_c) \quad (\text{IV-6})$$

an equation first derived by Hartley and Robinson.¹⁰⁰

Equivalent expressions are given by Huizenga et al.¹⁰¹ and by Schindewolf.¹⁰²

Equation (IV-4) may be criticized on two grounds. First, since the conductance is generally measured in an alternating field, movement of the bound ions parallel to the polymer backbone¹⁰³ could result in a significant amount of surface conduction.¹⁰⁴ Second, another possible contributing mechanism to the high-frequency conductance is the independent motion of the polyion segments due to the flexible nature of the polymer chain.¹⁰⁵ These criticisms may be dismissed by realizing that the presence of these effects would produce a region of frequency dispersion in the conductance. Since no frequency dispersion is observed for polyelectrolytes in the low frequency range (10 - 50,000 sec.⁻¹), it is unlikely that the D.C. conductance will differ appreciably from the value obtained at these frequencies.¹⁰⁶ This conclusion was verified by the D.C. conductance measurement described in section V-4, and thus the use of equation (IV-4) is justified.

Two further assumptions are required in the calculation of the charge fraction. First, at present no method is known for the determination of K_s in equation (IV-1), since the conductance of a simple electrolyte may be altered by the addition of polymeric ions to the solution.¹⁰⁷

In the present work this difficulty did not arise since only salt-free systems were studied by the transference method. Here K_s is the solvent conductance, which is generally small compared to the overall conductance.

Second, the conductance λ_c of the free counterions (equation IV-3)) is not known, and requires careful consideration. (1) Measurements of conductance¹⁰⁸ and tracer diffusion coefficients¹⁰⁹ in electrolyte solutions containing uncharged polymers have shown that the ionic mobility is not significantly affected even by considerable increases in the macroscopic viscosity coefficient, provided the volume fraction occupied by the polymer segments is small. This conclusion is also expected to be valid in solutions of charged polymers.

(2) The free counterions in a polyelectrolyte solution are subject to electrical retardations about which little is known. According to Hartley,⁸ the electrophoretic effect is the dominant retardation in solutions of multivalent ions. Qualitatively one may predict that the electrophoretic effect will influence polyions and counterions to a different extent. Thus since the inner part of the ionic atmosphere moves with the polyion, only the more distant parts of the atmosphere contribute to the electrophoretic retardation of the polyion. Considering that these distant counterions are surrounded only by ions

of like charge, moving in the same direction as themselves, it may be possible that the net electrophoretic contribution to the velocity of the counterions of retardation due to the polyion, and acceleration due to each other, is small. Relaxation, on the other hand, will cause the same fractional reduction in the velocities of both polyion and counterions. Experimentally, Möller et al. observed a significant decrease of λ_c from its value in solutions of simple salts at infinite dilution, λ_c^0 , in the presence of highly charged proteins, and attributed this result to the electrical retardations mentioned above. However, Doremus and Johnson¹¹¹ prefer to interpret similar observations in terms of association of counterions with protein ions.

(3) Since no method is known for the independent determination of λ_c in systems where binding occurs, it is generally assumed that λ_c has the same value (λ_c') as in a solution of a 1 : 1 electrolyte at a concentration corresponding to that of the free counterions in the polyelectrolyte solution.¹⁰¹ At present the only possibility of testing this assumption lies in the comparison of the results obtained with those given by other methods utilizing different assumptions.

Accepting the above assumption regarding λ_c' , the use

of equation (IV-4) enables the calculation of the charge fraction in certain favourable cases from conductance data alone.¹⁰⁴ For this purpose, measurements are made on a series of polysalts having a common polyion, but different counterions. If both u_p and α are independent of the nature of the counterion (which would be nearly true for a purely electrostatic, non-specific association), a plot of Λ vs. λ_c at constant concentration should be linear with slope α and intercept λ_p . Kern¹⁰⁴ and Eisenberg¹⁰⁶ successfully applied this method to alkali metal salts of polyacrylic and polymethacrylic acids; however conductance data on salts of polyvinylsulphonic acid⁹⁵ and of polyvinylmethylimidazolium hydroxide^{98a} cannot be interpreted in this manner.

(4) The assumption regarding λ_c may be avoided if diffusion potential measurements are carried out in addition to transference measurements. The diffusion potential dE across a concentration increment dC of an electrolyte solution is given by the Nernst equation¹¹²

$$-dE = (RT/F) \sum_i (t_i/z_i) d \ln(f_i C_i) \quad (\text{IV-7})$$

where t_i , z_i , and f_i are respectively the electrical transport number, valency, and activity coefficient of the i -th species, R is the gas constant, and T the absolute temper-

ature. Assuming univalent counterions and a polyion of very high valency ($z_p > 100$ say), equation (IV-7) reduces to^{113,114}

$$\pm dE = (RT/F)t_c d \ln(f_c C) \quad (IV-8)$$

with the positive sign referring to a polycation. Both E and f_c can be measured directly. Thus the counterion transport number t_c , and hence the polyion transport number t_p , can be obtained, assuming the concentration dependence of the liquid junction potential to be the same in measurements of both f_c and E . Transference experiments on polyelectrolytes give in general the transference number of the polyion constituent,¹¹⁵ t' , defined in section IV-2 (equation (IV-12)). The two transference numbers can be shown to be related by the equation

$$t_p = \alpha t'$$

The determination of α by this method has not yet been attempted; however, transport numbers in some polyelectrolyte solutions have been measured by the diffusion potential method.^{113,114} At present, the experimental accuracy of such measurements is low, especially at low concentrations.

(b) Tracer diffusion method. Assuming that, as is generally true, the self-diffusion coefficient D_c of the free counterions is much larger than that of the polyions, it can be

shown¹⁰⁸ that

$$D = \alpha D_c \quad (\text{IV-9})$$

where D is the observed overall self-diffusion coefficient of the counterions in the polyelectrolyte solution. The definition of α used in the derivation of (IV-9) is probably essentially identical with that used in the transference method; however, no theoretical or experimental information on this subject is available.

The limiting self-diffusion coefficient D_i^0 of an ion in a simple electrolyte solution is given by the equation⁵¹

$$D_i^0 = RT\lambda_i^0/F \quad (\text{IV-10})$$

where R is the gas constant. As the electrophoretic effect is absent in self-diffusion, the variation of D_i with concentration is considerably smaller than that of λ_i .⁵¹ Nevertheless, Huizenga et al.¹⁰⁸ used the assumption, analogous to that made in the transference method, that $D_c = RT\lambda_c'/F$. The difference between λ_c' and λ_c^0 is small at low concentrations, so that no serious error is introduced by the above inconsistency.

(c) Thermodynamic methods. The activity coefficient of the counterions in a polyelectrolyte solution can be

determined by E.M.F. measurements on suitable electrochemical cells. The most satisfactory procedure is to calibrate the electrode system used by measurements on a simple electrolyte containing the required counterion. A calibration curve is constructed by plotting the E.M.F. against the logarithm of the single-ion activity. By using this curve together with E.M.F. data on the polyelectrolyte solution, the counterion activity coefficient can be calculated, with the assumption that the liquid junction potential is either negligible or has the same value both in the polyelectrolyte and in the reference electrolyte solution. This assumption was recently discussed by Overbeek.¹¹⁵

The osmotic coefficient g of the solvent may be determined from the colligative properties of the solution by simple modification of the classical methods. The reasonable assumption is made that polyions with a high degree of polymerization do not contribute significantly to the colligative properties of the solution.

The significance of the thermodynamic properties in terms of ion binding is discussed in section II-3. Clearly, even if f_c and g are directly related to α , the charge fraction obtained by thermodynamic methods need not correspond to that defined in terms of a transference

experiment. This uncertainty must be borne in mind whenever comparisons are made between values of α determined by the two general methods.

(d) Hydrodynamic methods. Pedersen's theory of the primary salt effect in sedimentation¹¹⁷ has been used by Kraut¹¹⁸ to interpret the data of Howard and Jordan¹¹⁹ on the sedimentation velocity of sodium polymethacrylate. Several assumptions are made to obtain the result $\alpha \approx 0.37$ at 100% neutralization of the polyacid, which may be compared to the values $\alpha \approx 0.37$ obtained by other methods (cf. table IV-1).

Since there does not appear to be any relationship between viscosity and charge fraction in polyelectrolyte solutions (cf. section IV-5), the viscosity method proposed by Terayama and Wall⁸⁵ for the determination of α may not be justified (cf. section III-3).

(ii) Review of Previous Work.

According to the theories of binding outlined in Chapter II, the degree of binding and the thermodynamic functions are independent of the molecular weight of the polyelectrolyte, provided this is not too low. Several workers have reported results confirming this view.^{102,104,106,120-122} In particular, Schindewolf¹⁰² studied the transition from simple condensed phosphates

to polyphosphates by measurements of membrane potential and transference numbers. Both α and f_c were found to decrease with increasing degree of polymerization, and appeared to approach constant values asymptotically at degrees of polymerization above about 100.

The absence of covalent binding or other strong specific polyion-counterion interactions in solutions of polystyrene sulphonic acid has been demonstrated recently by the methods of Raman and proton magnetic resonance spectra.^{123,124} By analysis of partial specific volume data, a similar conclusion was reached¹²⁵ for solutions of ammonium and potassium polyvinylsulphonates. Nevertheless, a small effect of the nature of the counterion on the values of α , g , and f_c is generally observed. It is not known to what extent these variations are due to size effects. The only reported instances of non-specificity appear to be solutions of the alkali metal polyacrylates and polymethacrylates.^{104,106}

The dependence of binding (and of f_c and g) on the nature of the polyion backbone parallels the behaviour observed on changing the counterions, i.e., the species dependence is not pronounced. The degree of binding appears to be governed almost solely by the overall charge density along the polymer backbone. As expected,

the binding increases with increasing charge density; at high values of the charge density parameter q (equation (II-4)), the proportionality α (or f_c or g) $\propto q^{-1}$ is obeyed approximately.¹²⁶ This makes it possible to compare data on polyions having slightly different values of q .

In addition to its effect on the absolute magnitude of f_c , the charge density may influence the variation of f_c with concentration. When q is high, f_c is generally found¹²² to be insensitive to C , or to decrease on dilution,¹²⁰ although an increase of f_c with dilution has also been observed.¹²⁷ On the other hand, when q is low the activity coefficient rises at low concentrations and approaches unity.¹²⁸

Most investigations of the concentration dependence of α and g have been made on polyelectrolytes of high charge density. It is generally agreed that the osmotic coefficient decreases with decreasing concentration in the concentration range generally investigated.^{104,128,129} Huizenga et al.^{101,109} found the charge fraction of sodium polyacrylate to be essentially constant over the limited concentration range investigated by the transference and diffusion methods. This result is confirmed by the conductance data of Eisenberg,¹⁰⁶ which indicate that

the charge fraction of salts of polyacrylic acid is constant over a wide range of concentrations, at all charge densities studied. A different conclusion was reached by Martin and van Winkle,¹⁰⁷ who obtained an increase in α with dilution for polyvinylbutylpyridinium bromide.

There are many possible sources of error associated with the investigation of the electrochemical, thermodynamic and hydrodynamic properties of polyelectrolytes, especially in very dilute solutions. Some of the discrepancies referred to above may be due to such errors. Therefore it is of interest to compare some results for α , f_c , and g obtained by different authors for sodium polyacrylate and sodium polyphosphate. Some relevant data are shown in table IV-1, where the degree of neutralization of the polyacrylic acid is denoted by r .

Table IV-1.

Some literature values of charge fraction, osmotic coefficient, and counterion activity coefficient in polyelectrolyte solutions at 25°.

(a) Sodium polyacrylate.

Method	r, %	C, eq./l.	αr	$f_c r$	gr	ref.
(1) Λ and u_p	98	.015 - .038	.37			101
(2) Λ and u_p	99.5	.05	.22			36
(3)* Λ	65	.04	.36			104
(4) Λ	68	$2 \times 10^{-4} - 5 \times 10^{-3}$.35			106
(5)** Λ	68	" "	.38			106
(6)** Λ	90	" "	.40			106
(7) D_c	98	.015 - .038	.38			109
(8) E	100	.007 - .03	.43			113
(9) f_c	100	.005 - .05		.23		122
(10) g	80	.02 - .5			.11 - .20	128
(11)* g	100	.01			.14	132

* Measurements at 20°. ** Sodium polymethacrylate.

(b) Sodium polyphosphate.

Method	C, eq./l.	α	f_c	ref.
(12) and u_p	.04, .03	.299, .292		133
(13) and u_p	.01	.25		102
(14) E	.008 - .045	.36 ^a , .27 ^b		113
(15) f_c	.005 - .05		.22	122
(16) f_c	$10^{-5} - 10^{-2}$.9 - .22	102, 134

^aCalculated using data from ref.133

^bData from ref.102

The quantities to be compared are αr , $f_c r$, and $g r$. Examination of the values of the charge fraction obtained by the conductance, and conductance plus transference methods (entries 1 - 6 in the table) reveals good agreement among the various values of αr , with the exception of entry 2. The latter value was obtained by certain extrapolation procedures,³⁶ the validity of which is somewhat doubtful (see section IV-1-(iii)-a). On these grounds one may take the concordant set of values $\alpha r \sim 0.36$ to be correct.

An important point is the approximate agreement between this set of values and the values determined by tracer diffusion¹⁰⁹ (entry 7) and from the diffusion potential data of Botre et al.¹¹³ (entry 8). Such agreement shows that the contribution of both the electrophoretic and the relaxation effects to the conductance of the free counterions may be neglected at the concentrations studied, within the error of these experiments. Thus the assumption $\lambda_c \sim \lambda'_c$ appears to be justified.

A further point evident from table IV-1 is that no two of the quantities α , f_c , and g may be considered to be equal. Work on other polyelectrolytes confirms this result.⁴³ Of particular interest are the values of the counterion activity coefficient (0.44) and charge fraction (0.386) obtained by Mock et al.¹³⁰ for a sample of poly-(styrene-

vinyltoluene) sulphonic acid. The latter value was obtained from conductance data assuming the conductance to be due exclusively to hydrogen ions; making a reasonable allowance for the polyion conductance would reduce this value by 10 - 20%.

A decrease in α when the dielectric constant D of the solvent is lowered has been inferred from the marked dependence of equivalent conductance of polyelectrolytes on dielectric constant.⁵³ According to the theories of non-specific binding, the temperature dependence of α should¹⁰⁶ involve only the product DT , which in the case of water is insensitive to temperature over a limited range. The results of Wall and Hill,¹³¹ obtained in the range 20 - 35°C, and those of Eisenberg¹⁰⁶ over the wider range 0 - 50°C, are in qualitative agreement with the theoretical predictions.

(iii) Experimental Results and Discussion.

(a) Charge fraction. The polyelectrolytes used in this investigation were poly-4-vinyl-*N*-*n*-butylpyridinium bromide (PVP-Br, sample A1 - Q) and polyvinylbenzyltrimethylammonium chloride (PBTA-Cl), both fully quaternized and of high molecular weight. Their source and characterization is described in section V-1. Unless otherwise stated, values of α have been obtained in aqueous solution at 25° using silver-silver halide electrodes, as described in section V-5.

The calculations were carried out as suggested in section IV-1-a, using the assumption $\lambda_c = \lambda'_c$. Values of λ'_c were taken from the literature;⁵¹ they were always within 2% of λ_c^0 .

(1) Effect of electrode reactions. Most previous transference measurements on polyelectrolytes have been made using bright platinum electrodes.¹³⁵ It was therefore of interest to determine the magnitude of the error introduced as a result of the production of OH^- and H^+ ions at the electrodes. In fig. IV-1 are plotted the results of several measurements with platinum electrodes on PBTA-Cl, together with the results obtained by the use of reversible electrodes. Since all points fall on a common curve within about $\pm 1\%$, it may be concluded that no detectable error results from the use of irreversible electrodes, at least under the present experimental conditions. This is the result expected for conditions where no H^+ or OH^- ions produced at the electrodes reach the vicinity of the sintered glass frit. Conversely, the presence of such an error, as claimed by Wall and Hill¹³¹ for solutions of sodium polyacrylate, means that either an excessive proportion of the polyelectrolyte has been transferred (ca. 20% or more), or that the solution has been subject to stirring caused by mechanical vibration or inadequate temperature control.

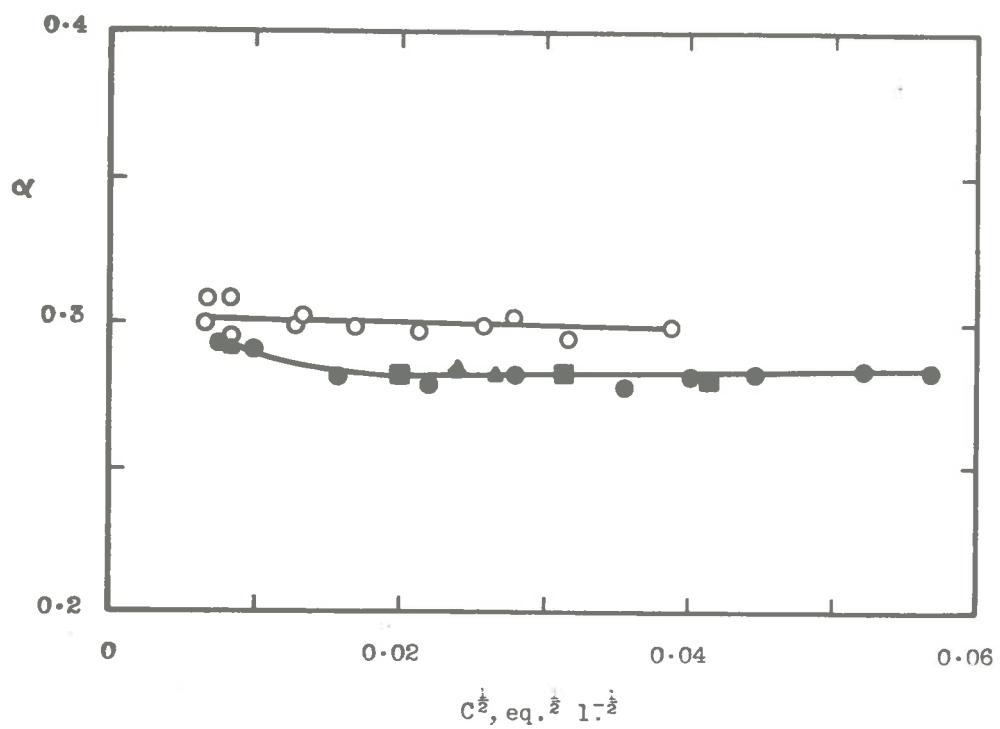


Fig. IV - 1. Charge fraction, transference method.

- PVP-Br. ● PBTA-Cl, reversible electrodes.
- ▲ PBTA-Cl, platinum electrodes.
- PBTA-Cl, 3-compartment cell.

(2) Effect of field and time of electrolysis. Since the conductance of the polyelectrolyte solutions is independent of field in the range 0.1 - 20 volts/cm. (section V-4), a dependence of α on field in this range is unlikely. This conclusion was confirmed by transference measurements on PBTA-Cl, which showed that α was constant within $\pm 1\%$ when the applied field was varied from 0.3 to 20 volts/cm. As discussed in section II-3, this result is expected on theoretical grounds. When the relative amount of polyelectrolyte transferred from anode to cathode compartment was varied between 5% and 25%, the value of α was found to remain constant within $\pm 1\%$, i.e. no effect of time of electrolysis could be observed.

These findings are at variance with previously published results on sodium polyacrylate,^{38,131} where a decrease of α with both decreasing field strength and time of electrolysis was noted when these variables decreased below certain limits. It was suggested³⁶ that the true degree of binding could be obtained by extrapolating the results to zero field and time of electrolysis. However, it is possible that the above effects are anomalies, such as may occur in the determination of small concentration differences as required by this method. The almost constant values of α obtained at relatively high fields and times are expected to be more

reliable in this respect.

(3) Effect of sintered glass partition. The presence of a sintered glass partition between anode and cathode compartments in the transference cells used in this and in previous work could conceivably lead to erroneous results, owing to electrokinetic or other undesired effects occurring in the capillary pores. This possibility was investigated by the use of a conventional three-compartment Hittorf cell, without a sintered glass partition. These results are also included in fig. IV-1, and show that the use of the convenient divided cell is justified under the present experimental conditions. Some anomalous results were obtained, however, with a cell having a glass sinter of finer porosity (Pyrex No. 3) than the cell described in section V-5. These results are not reported here.

(4) Concentration dependence of degree of association. The values of α obtained by the transference method are reported in table IV-2 and also in fig. IV-1. The charge fraction of PVP-Br was found to be nearly independent of C in the range investigated. Below a concentration of about 10^{-4} eq./l., however, the accuracy of the method decreases owing to the increasing importance of the correction for solvent conductance. Above about 2×10^{-4} eq./l. the charge fraction of PBTA-Cl appears to rise slightly with

increasing concentration, but this trend may be within experimental error. From fig. IV-1 and table IV-2 an increase in charge fraction of PBTA-Cl on dilution below about 2×10^{-4} eq./l. is apparent. This difference from the behaviour of PVP-Br may be due to the presence of a greater proportion of material of relatively low molecular weight in the sample of PBTA-Cl.

Table IV-2 (a)

Conductance and transference data, PVP-Br

$10^4 C, \text{ eq./l.}$.459	.467	.685	.692	1.68	1.76	2.87	4.49	6.71	7.75	10.0	15.1
$\Lambda, \text{ cm.}^2 \text{ ohm}^{-1} \text{ eq.}^{-1}$	44.1	44.0	43.0	43.0	41.3	41.2	40.6	40.0	39.5	39.3	39.0	38.4
$u_p, \text{ cm.}^2 \text{ ohm}^{-1} \text{ volt}^{-1}$	6.6 ₃	7.2 ₀	6.4 ₀	6.8 ₉	6.2 ₅	6.1 ₄	6.1 ₃	5.9 ₆	5.6 ₈	5.5 ₁	5.7 ₆	5.4 ₀
α	.308	.299	.308	.294	.299	.301	.298	.296	.299	.301	.294	.299
t_p	.44 ₈	.47 ₀	.43 ₉	.46 ₅	.43 ₅	.44 ₃	.43 ₀	.42 ₅	.41 ₅	.40 ₅	.42 ₀	.38 ₄

Table IV-2 (b)

Conductance and transference data, PBTA-C1

$10^4 C$, eq./l.	.580	.655*	.973	2.53	4.00*	4.91	5.77*	5.95*
Λ , cm. ² ohm ⁻¹ eq. ⁻¹	47.3	46.5	45.6	41.3	40.6	39.6	39.3	39.0
u_p , cm. ² ohm ⁻¹ volt ⁻¹	8.8 ₅	8.6 ₈	7.8 ₂	7.3 ₆	6.8 ₅	6.9 ₂	6.5 ₀	6.4 ₈
α	.293	.291	.290	.281	.284	.278	.284	.282
t_p	.50 ₆	.51 ₃	.49 ₆	.48 ₉	.46 ₈	.46 ₇	.45 ₇	.44 ₅
$10 C$, eq./l.	7.80	9.79*	12.6	16.1	17.2*	20.1	27.1	32.5
Λ , cm. ² ohm ⁻¹ eq. ⁻¹	38.5	38.2	37.8	37.5	37.4	37.2	36.8	36.6
u_p , cm. ² ohm ⁻¹ volt ⁻¹	6.3 ₅	6.1 ₆	6.3 ₅	5.9 ₉	6.0 ₃	5.9 ₂	5.6 ₅	5.6 ₁
α	.281	.283	.277	.281	.280	.281	.284	.283
t_p	.44 ₆	.44 ₂	.45 ₀	.43 ₃	.43 ₈	.43 ₆	.43 ₀	.41 ₆

* Platinum electrodes.

* 3-compartment cell, platinum electrodes.

The results of Martin and van Winkle¹⁰⁷ for the charge fraction of PVP-Br differ considerably from those of the present work. Part of the discrepancy may be due to the higher concentrations studied by the former authors; further, their experimental method is of relatively low accuracy.

(5) An attempted absolute determination of the charge fraction. For counterions bound only by electrostatic forces, the rate of exchange with free counterions is expected to be high. Exchange rates may be measured in principle by passing an electric current through two polyelectrolyte solutions in contact at a sintered glass partition, the solutions being identical except that one is labelled with radioactive counterions.¹³⁶ Consider for example a solution of PBTA-Cl divided into two parts by the sintered glass frit of a transference cell, the anode compartment containing tagged chloride ions. If the exchange is slow compared with the time of electrolysis, then $1 - \alpha$ equivalents of labelled chloride will be dragged into the cathode compartment, in opposition to the "normal" movement of chloride ions, for each equivalent of polyelectrolyte transferred. As the polyion, with its bound radioactive counterions, moves into the tracer-free side of the cell, however, some of the labelled counterions are freed by exchange and begin to move in the opposite direction, thus reducing the net flow of



tracer from the fraction $1 - \alpha$ expected on the basis of zero exchange rate. A highly simplified theory of this effect has been given by Wall and Grieger.¹³⁷ On the basis of this theory and of measurements on sodium polyacrylate solutions, it was concluded that the half-life of the second order exchange reaction is roughly 5 minutes at a concentration of .03 eq./l.¹³⁶ This result suggests that in principle the total fraction of bound ions can be found by conducting this experiment at sufficiently short times, and employing a suitable extrapolation to zero time, in order to avoid effects due to exchange of bound ions. The value of α thus obtained would be free from the assumptions made in the methods previously described.

The results of such an experiment on PBTA-Cl are given in table IV-3. The apparent charge fraction α' , calculated from the transference results assuming negligible rate of exchange, was found to be independent of time within the error of the radioactive counting technique used. Similar behaviour is found on inspection of the results reported by Wall et al.,¹³⁸ although these were obtained at much longer times. Even at a polyelectrolyte concentration 70 times lower than that employed by these authors, the expected decrease of α' with decreasing time could not be observed in this work. Therefore these experiments cannot be used

for the determination of charge fraction.

Table IV-3.

Values of α' for PBTA-Cl at various concentrations and times.

time, sec.	13	20	60	72	120	240
$C = 1.55 \times 10^{-2}$ eq./l.				.74	.75	.73
$C = 1.55 \times 10^{-3}$ eq./l.	.59		.61			.66
$C = 4.2 \times 10^{-4}$ eq./l.		.64	.62			.60

The approximate independence of α' to time may be explained, without assuming a slow rate of exchange, as follows. As the polyions with their bound tagged counterions enter the cathode (non-radioactive) compartment, exchange of counterions takes place, and the originally bound tracer ions move back towards the anode compartment. Therefore polyions which subsequently enter the cathode compartment find themselves in a region already containing tracer ions, and exchange of counterions does not therefore eliminate tracer flow towards the cathode.

The observed values of α' are much larger than those of α . Clearly the former cannot represent the true polyion charge fraction since on combination with transference data they yield polyion transport numbers t_p (cf. section IV-2) equal to or close to unity.

(b) Activity coefficients. Values of the counterion activity coefficients of PBTA-Cl and PVP-Br, obtained by the method described in section V-6, are shown as a function of concentration in fig. IV-2. A gradual decrease of f_c with increasing concentration is evident from both curves. Comparison of these curves with those of α (fig. IV-1) shows that the difference between α and f_c is outside the limits of random error of these measurements, at least in the case of PBTA-Cl. Owing to the possible presence of a systematic error (due to the liquid junction potential) in the values of f_c , however, the present results are insufficient to show conclusively a difference between f_c and α . Similarly, the minimum in the $f_c - C^{\frac{1}{2}}$ curve of PBTA-Cl at relatively high concentrations may be an artifact caused by the same source of error. The values of f_c obtained at the lowest concentrations studied are also somewhat uncertain because of the presence of low concentrations of impurities in the solvent.

Although the values of f_c and α were obtained at different temperatures, a comparison is possible since neither of these quantities is expected to be appreciably temperature-dependent.

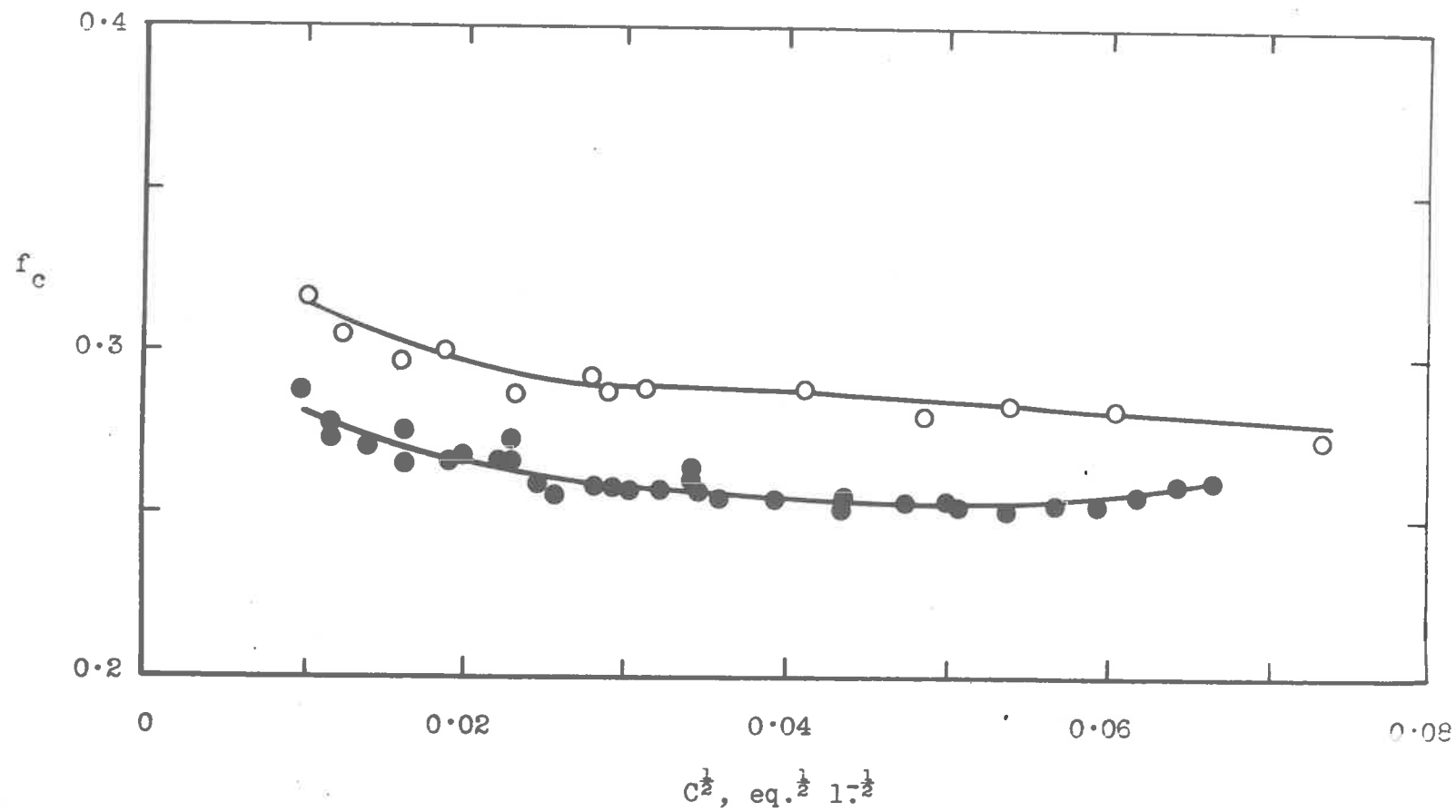


Fig. IV-2. Counterion activity coefficients.

○ PVP-Br, 22°. ● PBTA-Cl, 19°.

2. Electrophoretic Mobility of the Polyions.

The theoretical treatment of the electrophoresis of flexible polyions is very difficult, and has been attempted only for the case of solutions containing added salt, without consideration of the effects of ion binding. Theoretical and experimental results in this field have been reviewed recently.^{43,138} Few mobility data on salt-free polyelectrolyte solutions have been reported, although in principle the most reliable results should be obtained under these conditions.

The simplest method for the measurement of polyion mobilities is the Hittorf method, which is especially suitable if the concentration of added salt is low or zero. It may be shown that the mobility of, e.g., the polyion constituent is given by¹³⁹

$$u_p = 10^3 K Q_p / C F n \quad (\text{IV-11})$$

if the mobility u_p is expressed in the units $\text{cm.}^2 \text{ volt}^{-1} \text{sec.}^{-1}$. Here Q_p is the number of equivalents of the polyion constituent traversing any fixed plane in the solution on the passage of n Faradays.

The above method was employed in the present work since it can be used at low polyelectrolyte concentrations, where

the moving boundary method fails owing to convectional instability of the boundaries and difficulty in their accurate location.

An adaptation of the moving boundary method especially suitable for polyelectrolytes and for low concentrations is the "analytical boundary" method.¹⁴⁰ Some preliminary studies on solutions of PBTA-Cl were carried out using this technique, but the method was abandoned because of the necessity of finding a new indicator electrolyte concentration for each different polyelectrolyte solution used, and because of the possibility of error due to the contamination of the polyelectrolyte solution with the indicator electrolyte.

In any transference experiment, the mobilities and transference numbers obtained are those of the ion constituents.¹¹⁵ The transference number t' of the polyion constituent is given by

$$t' = (Q_p/n)/(1 - K_s/K) \quad (\text{IV-12})$$

where the term $(1 - K_s/K)^{-1}$ is the correction for the current carried by simple electrolytes in the solution. The quantity t' , also known as the material transference number of the polyion, may be greater than unity; it is related to the electrical transport number t_p by the

equation $t_p = \alpha t'$.

The mobility data are reported in table IV-2. These values have been used in the calculations of the charge fraction. Values of the transport number t_p are also given in the table. In fig. IV-3 the polyion mobilities are plotted, for convenience, as a function of $C^{1/2}$. Despite the low charge fraction of the polyions, their mobilities are higher than those expected for their monomeric analogues. The polyion mobilities decrease with concentration in the same manner as the equivalent conductances, and no extrapolation to infinite dilution could be made. The limiting mobility u_p^0 can be calculated from the relation $u_p^0 = \alpha Ze/f$, where Z is the total number of fixed charges on the polyion, and f is the frictional coefficient for translation. Assuming a fully stretched configuration for the polyion at infinite dilution, the factor f may be calculated using Simha's equation⁵⁴ for randomly oriented cylinders of length l and axial ratio p

$$f = 2 \pi \eta_0 l / (2 \ln 2p - 0.22) \quad (\text{IV-13})$$

On substitution of the values of l and p for the two polyions studied (cf. section III-5) and setting $\alpha = 0.3$, the following values of u_p^0 are obtained: PBTA-Cl, $3.8 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$; PVP-Br, $5.0 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$. Although these calculations are not expected to be accurate, they show that,

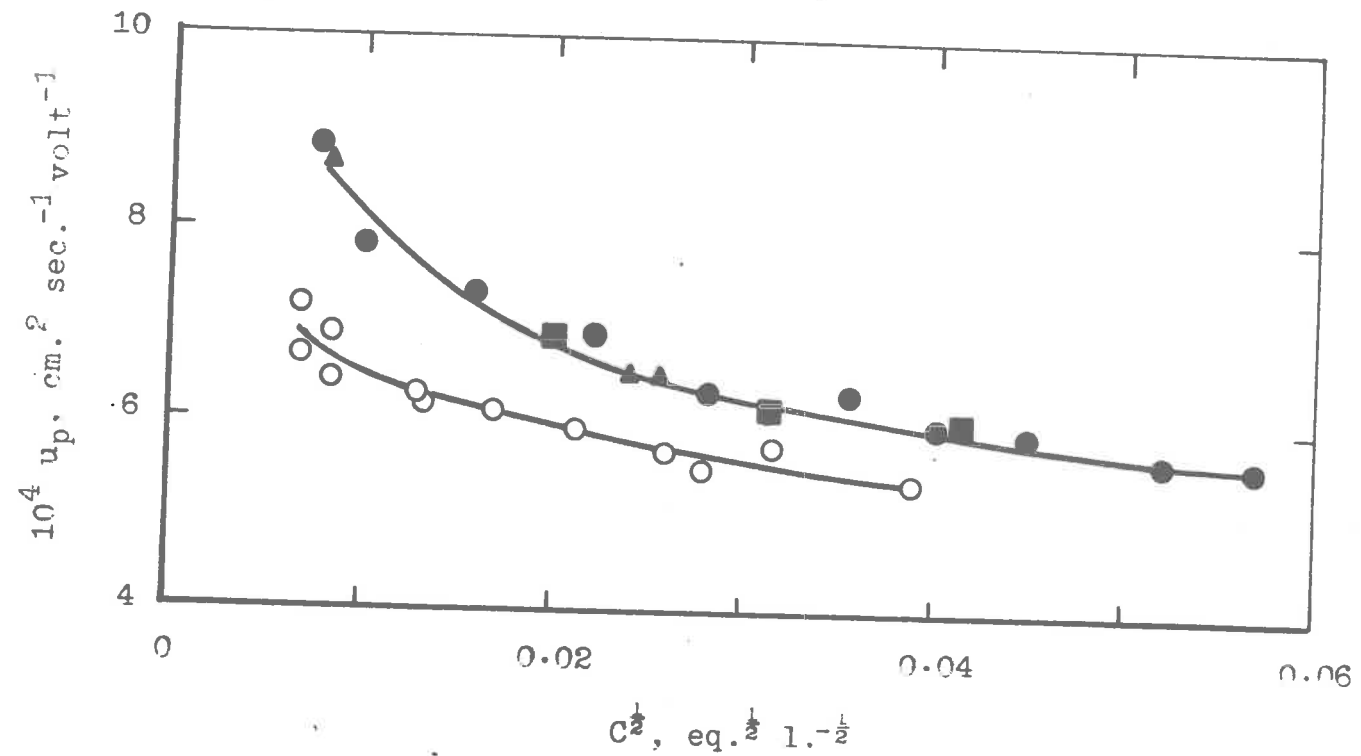


Fig. IV-3. Polyion constituent mobility.

- PVP-Br.
- PBTA-Cl, reversible electrodes.
- ▲ PBTA-Cl, platinum electrodes.
- PBTA-Cl, 3-compartment cell.

even when allowance is made for the low charge fraction of the polyions, the mobility at finite concentrations is much lower than u_p^0 . From similar observations on bovine serum albumin,¹¹⁰ where the dimensions of the macroion are independent of concentration, it may be inferred that the major effect contributing to the decrease in polyion mobility is the electrostatic braking due to the counterions. The effect of polyion interactions may also be significant.

The generally observed insensitivity of polyion mobility or equivalent conductance to molecular weight may be explained by the approximate constancy of α , together with the form of eq. (IV - 13), which predicts an approximate proportionality between f and molecular weight. This "free-draining" property may be expected to persist at finite concentrations provided the degree of coiling is low. According to the theories of polyion mobility, however, polyions are free-drained only in the presence of excess salt.¹³⁸

3. Conductance.

As can be seen from equation (IV-4), a theoretical description of the conductance behaviour of polyelectrolytes should involve treatments of polyion mobility, counterion mobility, and counterion binding. Attempts have been made to treat the conductance of salt-containing polyelectrolytes, with neglect of ion binding, but the theory does not apply to salt-free solutions.^{43,138} Despite the lack of theory, numerous experimental investigations of polyelectrolyte conductance have been made, and a number of qualitative conclusions about the nature of polyelectrolyte solutions have been drawn from the results obtained.³³

The curves of equivalent conductance vs. $C^{\frac{1}{2}}$ (fig.IV-4) obtained for the polysalts studied in this work are similar to those previously published.¹⁴¹ Evidently an extrapolation of these curves to infinite dilution is not possible. Considering the complex nature of polyelectrolyte solutions it would be entirely fortuitous if a simple analytical expression could be used to represent the dependence of Λ on C . The empirical representations of polyelectrolyte conductance proposed in the past do not fit the present data, with the possible exception of an expression used by Gregor and Gold^{36a}

$$\Lambda^{\circ} - \Lambda = C^{\frac{1}{2}} / (A + BC^{\frac{1}{2}}) \quad (\text{IV-14})$$

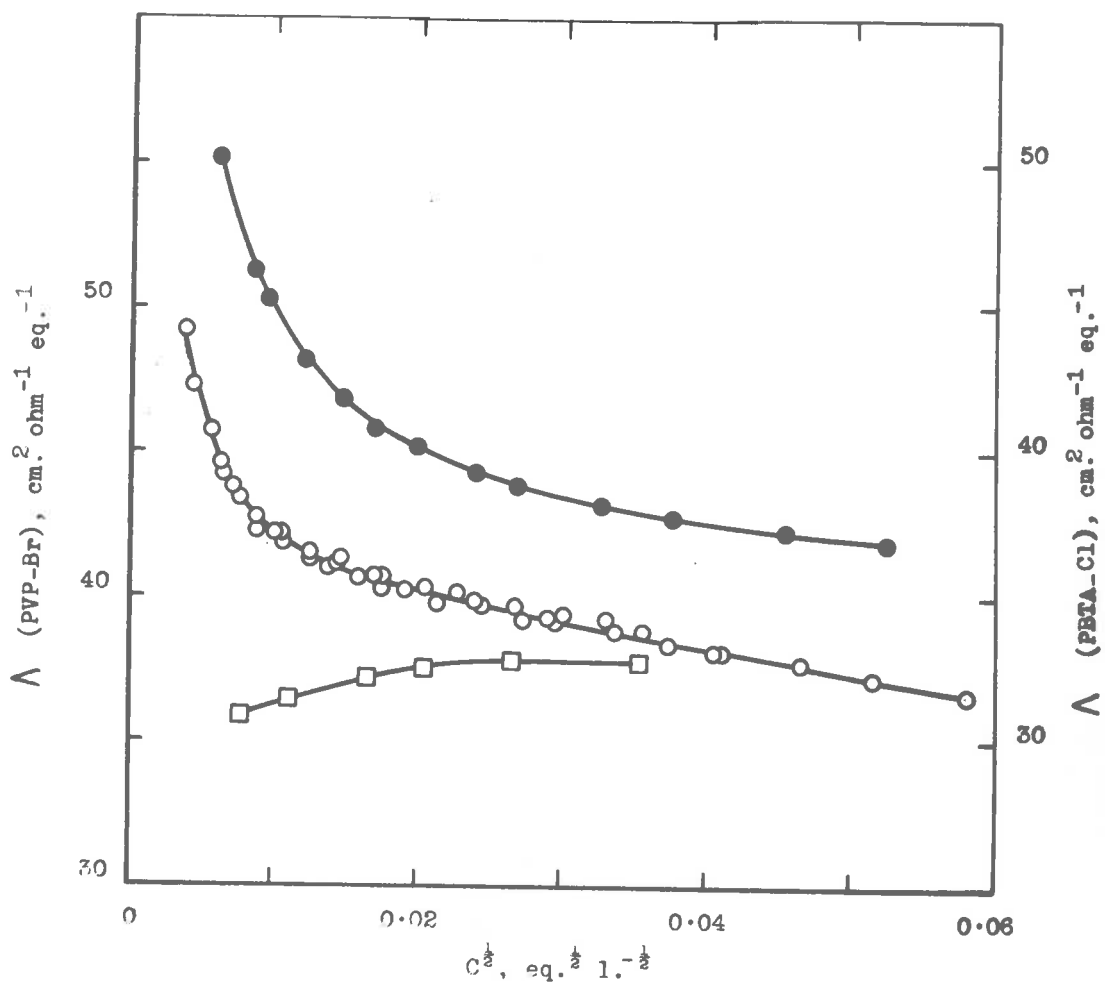


Fig. IV-4. Equivalent conductances of PVP-Br and PBTA-Cl.

● PBTA-Cl. ○ PVP-Br. □ PVP-Br in $4.8 \times 10^{-5} \text{ M KBr}$.

where A, B, and Λ° are constants. Plots of $(\Lambda^{\circ} - \Lambda)^{-1}$ vs. $C^{-\frac{1}{2}}$ were made for a series of assumed values of the parameter Λ° . Straight lines were obtained for PBTA-Cl with Λ° in the range 90 - 130, but no value of Λ° could be found to fit the data for PVP-Br over the whole concentration range studied. The significance of the parameter Λ° is open to doubt.

Such empirical extrapolations can yield the correct limiting conductance Λ° only if the observed functional dependence of Λ on C persists to zero concentration. One source of error in this connection is the increasing magnitude of the solvent correction as C approaches zero. It was found that measurements made with conductivity water of varying quality give slightly different values of Λ , the difference increasing with dilution. To confirm this finding, measurements were made on PVP-Br in 4.8×10^{-5} M potassium bromide. The resulting curve, shown in fig. IV-4, appears to pass through a flat maximum and to approach the curve obtained in conductivity water at higher concentrations. It should be noted that the position of this maximum is quite different from that found in the reduced viscosity curve of this material at the same salt concentration (fig. III-13).

Since α is not appreciably affected by the presence of

low concentrations of salt,¹⁴³ the dependence of Λ on solvent quality is probably due to a slight decrease of the polyion mobility caused by the increased ionic strength. Thus to obtain very accurate values of Λ at low concentrations ($C < 10^{-4}$ eq./l.), the results should be extrapolated to zero solvent conductance.

The conductance behaviour of polyvinylbenzyltrimethylammonium hydroxide (PBTA-OH) shown in fig. IV-5 is different from that of the polysalts in that a minimum appears in the $\Lambda - C^{\frac{1}{2}}$ curve at a concentration of about 4×10^{-4} eq./l. The variation of Λ in the range investigated is only about 5%; the absolute magnitude of the increase at low concentrations, however, is about the same as for PBTA-Cl. A possible explanation of this effect is given in section IV-5.

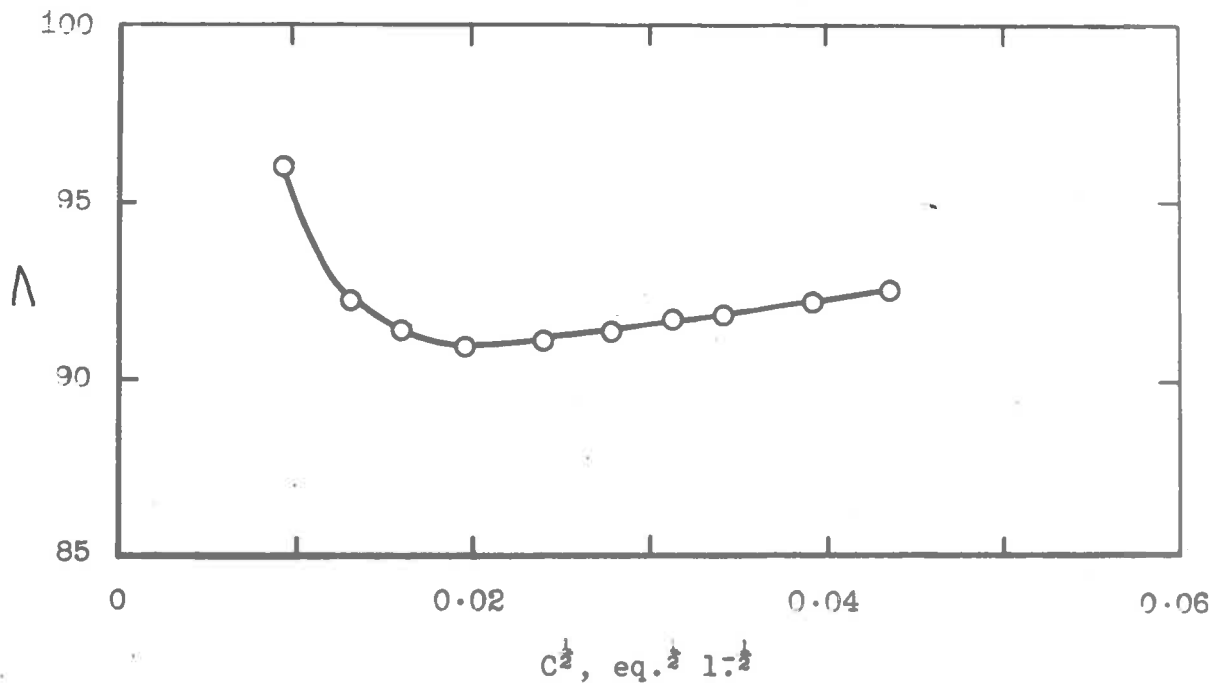


Fig. IV-5. Conductance of PBTA-OH.

4. Effect of Change in Temperature and Dielectric Constant
on Electrochemical Properties.

Previous studies have shown that both the equivalent conductance¹⁴⁴ and the osmotic coefficient¹⁴⁵ of polyelectrolytes are greatly reduced when the dielectric constant of the solvent is lowered. This effect was assumed to be due to an increase in the fraction of bound ions at the lower dielectric constant. The validity of this interpretation was confirmed by transference measurements on PVP-Br dissolved in absolute ethanol at 25° (D = 24.2); relevant data are given below.

C, eq./l.	$u_p, \text{cm.}^2 \text{sec.}^{-1} \text{volt}^{-1}$	$\Lambda, \text{cm.}^2 \text{ohm}^{-1} \text{eq.}^{-1}$	α	t_p
4.6×10^{-4}	$1.5_0 \times 10^{-4}$	2.6_4	$.06_9$	$.39_5$

The value $\lambda_c = \lambda_c^0 = 23.6$ was used in the calculations.¹⁴⁶

The decrease in α from the value observed in aqueous solution (D = 78.5) can be qualitatively accounted for by various theories of binding; e.g. the theory of Cosawa²⁹ predicts $\alpha \sim 0.11$ in ethanol.

The limiting mobility calculated with $\alpha = .069$ is $1.1 \times 10^{-3} \text{ cm.}^2 \text{ sec.}^{-1} \text{ volt}^{-1}$. The relative difference between u_p^0 and u_p is roughly the same as that for the aqueous solutions. It should be noted that although the net charge is lower in ethanol solution, the electrical

effects per unit charge are correspondingly higher, and the solution still shows typical polyelectrolyte behaviour.

The temperature dependence of equivalent conductance, mobility, and charge fraction of PBTA-Cl was investigated at a concentration of 1.61×10^{-3} eq./l. Results are given below.

Temperature	5	15	25	35	45	55°C
Λ/λ_c^0	·480	·488	·490	·493	·496	·496
α	·282	·2835	·281	·277	·276	·278
$10^5 \eta_0 u_p$	5·34	5·30	5·35	5·49	5·49	5·29

Conductances are reported in terms of the ratio Λ/λ_c^0 ; this increases with rising temperature, indicating a change in α or λ_p/λ_c^0 , or both. The variation is small, however, confirming Eisenberg's¹⁰⁶ observation that the temperature dependence of polyelectrolyte conductance can be reduced to a good first approximation to the variation in counterion conductance alone.

The charge fraction decreases by about 3% in the range 5 - 55°; this change is believed to be outside the experimental error. In the same interval, the product DT decreases by about 6%. The variation of the polyion mobility-solvent viscosity product, $u_p \eta_0$, is within the limits of experimental error.

5. General Discussion.

Validity of the results. The existence of counterion binding in solutions of polyelectrolytes, and of colloidal electrolytes in general, is proved conclusively by two well-established observations, namely, the movement of radioactive counterions in the same direction as the polyion on electrolysis, and the negative values obtained for the transport number of the counterion constituents. The numerical values of α obtained by the transference method are, however, uncertain owing to the assumption made regarding the mobility of the free counterions. Although the maximum concentration of free counterions in the present work was about 10^{-3} eq./l., at which concentration the mobilities in 1 : 1 electrolytes are within a few percent of their limiting values, the high charge on the polyion may cause significant electrostatic retardation of the counterions. The rapid decrease of polyion mobility with C shows that such retardations are operative at least on the polyions.

It may therefore appear to be unjustified to assume an essentially constant value, $\lambda_0 = \lambda_0'$, for the mobility of the counterions. It is possible, however, as discussed in section IV-1-(1)-(a), that in a polyelectrolyte solution the electrical effects on the polyion are much larger than

those acting on the free counterions. Such asymmetry of behaviour has been observed for salts of bovine serum albumin,¹¹⁰ where the decrease of u_p from its limiting value was about three times greater than the corresponding decrease for the counterions. Since the synthetic polyelectrolytes are generally of a much more asymmetric valency type than the above protein, the difference between the conductivity behaviour of polyions and counterions may also be much greater.

The main justification for the assumption $\lambda_c = \lambda'_c$ is the approximate agreement of values of α for sodium polyacrylate and polyphosphate obtained by the transference method with those derived from diffusion potential measurements (cf. table IV-1). Similar agreement with results of diffusion measurements indicates that the electrophoretic retardation of the counterions is small and probably negligible at the much lower concentrations employed in the present work. Unfortunately the diffusion measurements referred to were made with the diaphragm-cell method, which may be subject to error at low concentrations.¹⁴⁷ The capillary method has been applied to the measurement of the tracer diffusion coefficient of strontium ions in polystyrene sulphonic acid,¹⁴⁸ but no transference data are available for comparison.

Comparison with theory. Some measured values of the charge fraction and activity coefficient are compared below with those calculated on the basis of the rod-like model of polyions.

$10^4 C$, eq./l.	1.0	5.0	10	30
α (PVP-Br, obs.)	.296	.296	.293	
α (PBTA-Cl, obs.)	.284	.270	.271	.274
α (Oosawa, calc.)	.368	.370	.372	.375
α (Mock, calc.)	.175	.175	.175	.175
f_c (PVP-Br, obs.)	.32	.30	.30	.29
f_c (PBTA-Cl, obs.)	.29	.27	.26	.26
f_c , eq. II-5	.218	.226	.249	.253

Except for the increase of α at low concentrations of PBTA-Cl, the concentration dependence of α is well represented by Oosawa's theory,²⁸ although the calculated values are 25 - 40% too high. These theoretical values agree well with the results of previous work on sodium polyacrylate, where the binding appears to be completely non-specific. Such agreement seems surprising in view of the approximate nature of the theory.

Mock's theory²⁸ also predicts correctly the observed constancy of α , but gives values which are about 50% lower than those observed. When the charge fraction is calcul-

ated as the fraction of counterions with $|e\psi| < kT$, the result $\alpha \sim 0.38$ at 10^{-3} eq./l., and increasing slightly with increasing concentration, is obtained. It appears, therefore, that all the above theories give a good qualitative representation of the present data, including the effects of temperature and dielectric constant on α . The observed independence of α to C at low charge densities,¹⁰⁶ however, cannot be explained on the basis of Oosawa's theory, whereas it follows from Mock's theory.

Owing to the uncertainty introduced by possible variations of the liquid junction potential, the result of section IV-1-b, that $f_c \neq \alpha$, is not conclusive, although it appears to be supported by previous data⁴³ where the difference between the two quantities is much larger. Further work, both theoretical and experimental, is required on this topic.

The observed concentration dependence of f_c does not agree with that predicted by equation (II-5). Except at the lower concentrations studied, however, the difference between calculated and observed values of f_c is small. Although the correct variation of osmotic coefficient with concentration is reproduced by this equation, the calculated values are generally too high. An attempt to overcome this discrepancy has been made²⁹ by adjusting the

polyion charge density to allow for deviations of the polymer configuration from the stretched form. This procedure may be criticized on the grounds that if the rod-like model is applied to a coiled polyion, the equation for the potential would be expected to be valid only at distances from the chain backbone small compared to its radius of curvature. Therefore the local charge density, i.e., the value used for the stretched rod, should be used instead of the overall "effective" charge density.

A knowledge of the degree of association in polyelectrolytes is useful in the discussion of their electrochemical properties. In early work it was assumed, by analogy with associated simple electrolytes, that the fraction of free counterions increases with dilution.³³ The characteristic increase of both equivalent conductance and reduced viscosity with dilution could thus be explained. Recently Botre et al.¹²² pointed out that, whereas the reduced viscosity of sodium polyacrylate increases considerably on dilution, the charge fraction, assumed to be given by the activity coefficient, remains constant in the same range of concentration. The comparison of viscosity and transference measurements on the polyelectrolytes studied here leads to the same result, and further shows that the conductance variation is not due to a change in the charge fraction.

The current explanation of the characteristic viscosity and conductance behaviour does not, however, rely on assumed changes in degree of association, but on changes in counterion distribution (the effect of the counterions on the viscosity is discussed in section III-3). On the basis of the assumption regarding counterion mobility and the derived result that α is constant, the variation of Λ is due almost wholly to variations in polyion mobility, which is determined by the distribution of counterions about the central polyion as well as by the net charge on the kinetic unit.

The conductance behaviour of strong polyacids and polybases can be explained on the above basis as follows. Owing to the high value of $\lambda_{\text{O}}^{\ominus}$, the equivalent conductance of these materials consists largely of the constant contribution $\alpha\lambda_{\text{O}}^{\ominus}$ of the free hydrogen^{OR} hydroxyl ions, which swamps the variation in the polyion mobility, and one would expect Λ to be almost independent of concentration. Such constancy of Λ has been reported for polystyrene sulphonic acid,¹³⁰ PBTA-OH (fig. IV-5) and polyvinyl sulphonic acid⁹⁵ show minima in the conductance curves. As expected, the magnitude of the increase in Λ at low concentrations is about the same as that for the corresponding polysalts. The slight increase at concentrations above about 5×10^{-4} eq./l. may indicate a corresponding increase in charge fraction.

Since the behaviour of α for non-specific association is in semi-quantitative agreement with theory, an approximate estimate of the linear charge density of an unknown polyelectrolyte may be made by means of transference measurements. Deviations from expected behaviour may indicate the presence of unusual effects such as strong specific interaction or a change in structure with concentration. For example, the increase of charge fraction¹⁴⁹ and of counterion activity coefficient¹⁵⁰ on dilution of sodium deoxyribonucleate below a critical concentration has been explained in terms of denaturation of the polyion at low concentration to give a new polyion with a lower charge density.

The effects on the charge fraction of added salts having a common ion may be mentioned here. The charge fraction of sodium polyacrylate has been shown to be little affected by the addition of sodium chloride.¹⁴⁴ A similar conclusion was reached by a number of authors for the behaviour of the counterion activity coefficients.^{43,12} The latter result has been interpreted with some success in terms of the rod-like polyion model.¹²

If an excess of a salt not having a common ion is added, one may expect a rapid exchange of bound and free counterions (provided the binding is mainly of electrostatic

origin), resulting in an increase in the activity coefficient of the original counterions. The difference in the titration curves of strong polyacids in the presence and absence of added electrolyte⁹⁵ may be explained on this basis.

The reversibility of nonspecific binding is readily deduced from a number of observations, for example the agreement of chloride and bromide analyses of PBTA-Cl and PVP-Br obtained by the Parr bomb method with those determined in solution by titration with silver nitrate (cf. section V-1). The identity of the end points obtained in the titration of strong polyacids and polybases in the presence and absence of salt^{95,96a} shows that the exchange of bound ions is completed during the time required for the titration.

CHAPTER V

EXPERIMENTAL

1. Materials

- (i) Poly-4-vinylpyridine
- (ii) Poly-N-vinylimidazole
- (iii) Polymethacrylic acid
- (iv) Poly-4-vinyl-N-n-butylpyridinium bromide
- (v) Polyvinylbenzyltrimethylammonium chloride
- (vi) Polyvinylbenzyltrimethylammonium hydroxide
and polyvinylbenzyltrimethylammonium nitrate
- (vii) Solvents
 - (a) Conductivity water
 - (b) Other solvents
- (viii) Solutions

2. Viscosity Measurements

- (i) Capillary viscometers
- (ii) The Couette viscometer
- (iii) Time dependence of the viscosity

3. Spectrophotometry

4. Conductance Measurements

5. Transference Experiments

- (i) Measurement of mobility
- (ii) Exchange determinations

6. Potentiometric Measurements

- (i) Counterion activity coefficients
- (ii) Measurement of pH

7. Light Scattering

- (i) Light-scattering apparatus
- (ii) Scattering cell
- (iii) Calibration and measurements
- (iv) Clarification
- (v) Refractometer
- (vi) Treatment of data

1. Materials.

(i) Poly-4-vinylpyridine (PVP). The various samples of PVP used in this work are listed in table V-1, together with their intrinsic viscosities in ethanol at 25°, determined in an Ostwald B.S.S. No. 1 viscometer.¹⁵¹ The molecular weights (M) shown are approximate values calculated from viscosity-molecular weight relations given in the literature.^{152,153}

Table V-1. Characterization of PVP samples.

Designation	RA	R1	RD	E6	A1	B2
$[\eta]$, ml./g.	270	~1000	~3000	120	230*	410*
Purity %	88	91.7	88.5	90	89.5	88.6
$10^5 M$	8	-	-	2.5	5.8	15

* Measured in 92% ethanol.

Samples R1 and RD were prepared by a method similar to that of Fitzgerald and Fuoss.¹⁵⁴ The monomer (Light and Co., London) was distilled twice under reduced pressure of nitrogen immediately before use. Benzoyl peroxide (B.D.H. Laboratory Reagent) was dissolved in the monomer to give an approximately 0.03% solution, which was emulsified in about 10 volumes of water containing 1% of the non-ionic

detergent Alcol V.I. (J. Beith and Co., Sydney). Polymerization was carried out, under the exclusion of atmospheric oxygen, by shaking the mixture for three days at room temperature (ca. 22°). The resulting polymer, which had separated in granular form, was washed with distilled water over a period of several days, and then air dried. After solution in tert-butanol and removal of insoluble material by centrifugation, about two-thirds of the polymer was precipitated by slow addition of benzene. The precipitate was redissolved in tert-butanol; part of this solution was freeze-dried and subsequently vacuum-dried at 60° and 0.01 mm. for 12 hours. The product, designated R1, represents the whole polymer from which some of the species of lower molecular weight had been removed. From the rest of the above solution, a high-molecular weight fraction RD was obtained by the addition of benzene. The precipitate obtained was dissolved in tert-butanol and dried as above.

The preparation of sample RA was similar to that of R1, except that Mannoxol OT (B.D.H. Laboratory Reagent) was used as emulsifying agent, and the polymerization was carried out at 50° for 3½ hours with an initiator concentration of 0.05%.

Samples E6 and E3 are those described by Jordan, Mathieson and Porter.¹⁵⁵ Samples A1 and B2 were obtained by B.C. Simpson¹⁵⁶ by polymerization at 60° for 15 hours,

using azobis-isobutyronitrile as initiator and Alcol V.I. as emulsifier. A1 and B2 are two of a series of fractions obtained from the methanol-toluene solvent-precipitant system by the method of Berkowitz, Yamin, and Fuoss.¹⁵²

The complete drying of the samples could not be achieved even by heating at 60° under high vacuum for several days. Therefore the purity of the polymer fractions was determined by potentiometric titration of the basic pyridine groups with p-toluene sulphonic acid, using a silver-silver chloride reference electrode and a glass indicator electrode. Steady potentials were obtained when the titrations were carried out under an atmosphere of dry, CO₂-free nitrogen; accurate analysis is made possible by the break of about 200 mV. in the titration curves at the equivalence point. Satisfactory end points ($\pm 1\%$) could also be obtained visually with crystal violet indicator. The toluene sulphonic acid was standardized with anhydrous sodium carbonate.

Similar methods of analysis of PVP have been developed by Burleigh, McKinney and Barker,¹⁵⁶ and by Iwakura et al.¹⁵⁸ The advantage of the present method is that the products of the titration remain in solution without the addition of a second solvent component.

Some of the potentiometric purity determinations were

compared with results of Kjehldahl nitrogen analyses. Provided the analytical procedure was carefully specified,¹⁵⁷ the agreement was found to be satisfactory.

The percentage purities of the samples used in this work are included in table V-1. The impurity present was assumed to be water. This assumption is consistent with results of elementary analyses, and with the observed slightly hygroscopic nature of the polymer. Residual water or organic solvent is unlikely to cause a significant error in any of the measurements on PVP, provided proper allowance is made in the calculation of polymer concentration.

(ii) Poly-N-vinylimidazole was obtained through the courtesy of the Badische Anilin- und Soda-Fabrik A.G. Ludwigshafen, Germany. The material was dried to constant weight at 60° and 0.01 mm.; according to Gregor and Gold,^{96a} this procedure gives the pure polymer. The intrinsic viscosity in water was found to be 58 ml./g.

(iii) Polymethacrylic Acid (PMA). The polymethacrylic acid used was a sample prepared by polymerization in aqueous solution initiated by benzoyl peroxide. The polymer was recovered from solution by precipitation with HCl and vacuum drying. By titration with NaOH, the equivalent weight was found to be 100; the formula weight is 86. The intrinsic viscosity in 0.005 M HCl at 25° was found to be

0.164 dl./g., corresponding¹⁵⁹ to a molecular weight of 62000.

(iv) Poly-4-vinyl-N-n-butylpyridinium bromide (PVP-Br).

Two samples of PVP-Br were used. The first, designated E3-Q, was prepared by heating PVP (fraction E3) with n-butyl bromide in nitromethane solution at 85° for 10 days. The PVP-Br was recovered from the solution by vacuum drying, and was purified by precipitation from ethanol solution with diethyl ether. The precipitate was vacuum dried giving a red powder. Analysis showed that 97% of the nitrogen in the sample was quaternized with butyl bromide, the remainder with HBr.

In order to avoid extensive degradation of the polymer and the introduction of HBr, a different method was used for the preparation of the sample (A1-Q) of PVP-Br used in the electrochemical studies described in Chapter IV. 2.3 g. PVP (fraction A1) was dissolved in 30 ml. dimethylformamide, and 15 ml. n-butyl bromide added. The mixture was boiled under vacuum to remove atmospheric oxygen, and heated under nitrogen for 12 hours at 50°. The precipitate obtained was vacuum dried, dissolved in 5 ml. water, and re-precipitated by the addition of 50 ml. of acetone. The polymer was freeze-dried from a solution in tert-butanol, and vacuum dried at 60° and 0.01 mm for 5 hours.

Analysis: C 48.63%, H 7.05%, N 5.18%, O 9.79%, Br 29.7%.

By titration with silver nitrate, Br = 29.5%. Titration with NaOH, as well as pH measurements on dilute aqueous solutions of A1-Q, showed the absence of HBr from the sample. These results are consistent with the presence of $(10.8 \pm 0.5)\%$ water in the sample, all the nitrogen of which is quaternized with butyl bromide. The equivalent weight was taken as 271; the monomer formula weight is 242.2. The weight-average molecular weight of the sample, determined by light scattering measurements (cf. section V-7), was found to be 1.65×10^6 .

(v) Polyvinylbenzyltrimethylammonium chloride (PBTA-Cl) was kindly provided by Dr. G. D. Jones, of the Dow Chemical Company, Midland, Michigan, U.S.A., and was used as supplied. It was stated to be a copolymer containing the para and ortho isomers of the monomer in the ratio of about 2 : 1, and to be completely ammoniated. The latter statement is confirmed by the following analytical data: C 56.25%, H 8.93%, N 5.56%, Cl 13.8%. By titration with silver nitrate, Cl = 13.9%. From these results, an equivalent weight of 257 is calculated, compared to the monomer formula weight 197.7; the purity of the sample is thus 76.9%. According to the manufacturers, the material has been resin treated to remove ionic impurities, precipitated with

acetone, and dried to a water content of 14.5%. The remaining 6.4% of impurity is probably acetone. The weight-average molecular weight (cf. section V-7) was found to be 4.1×10^5 .

(vi) Polyvinylbenzyltrimethylammonium hydroxide (PBTA-OH) and Polyvinylbenzyltrimethylammonium nitrate (PBTA-NO₃) were prepared from the chloride by ion exchange, using Amberlite resins in the appropriate forms. The preparation of PBTA-OH was carried out under purified nitrogen. No precipitate could be detected on the addition of a high concentration of silver nitrate to the acidified solutions, even when the mixtures were allowed to stand for several weeks in the dark, indicating the absence of residual chloride. The concentration of the PBTA-OH was determined by titration; that of the nitrate from the original concentration of PBTA-Cl, assuming that the polyelectrolyte was completely removed from the column by rinsing with water.

(vii) Solvents.

(a) Conductivity water. Rain water was de-ionized, distilled, and distilled again from alkaline KMnO₄ in an all-glass still. It was then passed slowly through a mixed-bed ion exchange column, and collected in a seasoned vessel of Pyrex glass. The specific conductance of the water, measured under nitrogen, was in the range $1.5 - 4 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Water prepared by such a method may contain colloidal material leached from the resin.¹⁶⁰ To prevent possible contamination, the columns were rinsed with large quantities of distilled water before use. Several samples of the conductivity water were examined by electron microscopy, with a negative result. Further, no anomalous behaviour in the $\Lambda - \sqrt{c}$ curve of KCl was detected down to a concentration of 10^{-5} M. This observation excludes the possibility that resin particles were present in the water in significant amount. When conductance or mobility measurements on polyelectrolyte solutions were repeated using conductivity water prepared by distillation only, agreement was obtained with values determined in resin-treated water, if allowance for the small effect of solvent conductance on the results was made (section IV-5).

(b) Other solvents were purified by standard methods.

Ethanol, dimethylformamide, and n-butyl bromide were distilled immediately before use.

(viii) Solutions: Stock solutions of polymers were prepared by dissolving a known weight of polymer in a small amount of solvent, and then making up to the required volume. In the case of PVP, solution generally required several days. No significant amount of moisture was absorbed by the samples while being weighed, provided they

were transferred quickly. Concentrations were calculated on the basis of the known purity of the samples. The stock solutions were kept in the dark at 5° when not in use; they were used within one or two weeks of preparation.

Aliquots of stock solutions were measured with an "Agla" Micrometer Syringe (Burroughs Wellcome Ltd., London) having either a glass or stainless steel (Luer fitting) needle.

2. Viscosity Measurements.

(1) Capillary viscometers. Data for the capillary viscometers used are listed below.

Viscometer	Ostwald No.0	Ostwald No.1	Ubbelohde
Length of capillary, cm.	12	12	11.5
Flow time for water, sec.	381	157	269
Approx. working volume, ml.	7	7	20

The Ostwald viscometers were of British Standards Specification¹⁵¹ design, except for the No. 1, which had an additional bulb above the solution reservoir to allow dilutions to be made within the viscometer. The dimensions of the viscometers were such that the kinetic energy and end effect corrections were negligible for the purpose of the present work.

The viscometers were suspended, with the capillaries vertical, in a water bath at 25° thermostated to $\pm .005^\circ$. Flow times were determined visually to within 0.1 sec. with a stopwatch; several readings of each flow time were taken. Measurements in an inert atmosphere were carried out by connecting the arms of the viscometer to a supply of purified nitrogen, and flushing the system thoroughly with nitrogen.

(ii) The Couette viscometer used has been described previously;^{76,88} several minor modifications were made to give greater stability. For the later work, the stainless steel surfaces in contact with the solution were coated with a thin film of polymethyl methacrylate (Perspex, I.C.I. Ltd.) deposited from chloroform solution. The film was thin enough to show interference colours. Relative viscosities were generally measured at mean velocity gradients of $5 - 15 \text{ sec.}^{-1}$ to a precision of $\pm \frac{1}{2}\%$ or better.

Solutions of successively higher concentrations were generally prepared in the viscometer by the addition of a small aliquot of stock solution to the solvent contained in the outer cylinder, mixing well, and removing the same volume of the final solution. By this procedure, a viscosity-concentration curve was obtained using a single sample of solvent, a procedure which is necessary for dilute salt-free polyelectrolyte solutions if smooth curves are to be obtained.

(iii) Time dependence of the viscosity. The solution viscosities of the samples R1 and RD decreased rapidly with time in all solvents studied, both in the Couette and the capillary viscometers. This time effect became more pronounced as the solutions were diluted, and no accurate intrinsic viscosity values could be assigned to the above

materials. Concentrated solutions appeared to be little affected. A time effect was observed for most of the other polymer samples also, but it was much less pronounced.

In view of this difficulty, viscosity measurements were carried out as rapidly as possible, since it proved impracticable to perform all operations in an oxygen-free atmosphere, or to extrapolate the viscosity of each solution to zero time. The viscosities of the quaternary salts, and of the sodium polymethacrylate, varied only slowly with time, and solutions of the samples E6 and PBTA-C1 appeared to be stable.

The instability of PVP and PVP-Br solutions has been noted previously, and explanations in terms of adsorption,⁷⁷ bacterial attack,¹⁶¹ or degradation due to the presence of peroxides in the polymer chain,^{152,162} have been given. No decrease in polymer concentration due to adsorption on to the viscometer walls could be detected in the present work by measurements of ultraviolet absorption (section V-3). Evidence that the phenomenon may be due to autoxidation is shown in fig. V-1, where the viscosity of a solution of PVP (sample R1) in 0.1 N HCl, followed simultaneously in two Ostwald No. 1 viscometers, is plotted against time. One of the solutions was freed from oxygen and kept in an atmosphere of nitrogen, the other was exposed to air. The

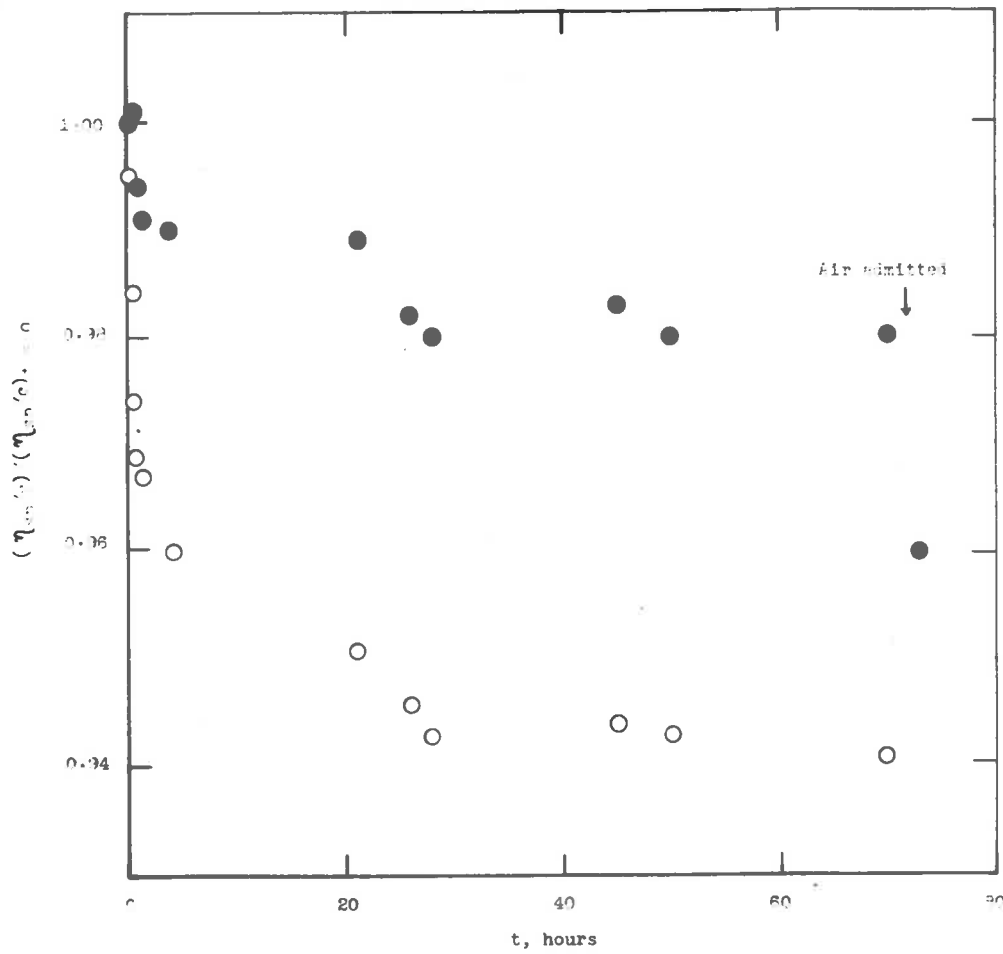


Fig. V-1. Dependence of viscosity on time (sample R1 in 0.1 N HCl).

○ Open to air. ● Under nitrogen.

results indicate that the time effect is accelerated by the presence of oxygen. It should be pointed out that the viscosity decrease observed in other solvents was much more rapid than in either of the cases in excess HCl shown in fig. V-1.

3. Spectrophotometry.

The wavelength scale of the Unicam SP-500 instrument employed was checked as recommended by the manufacturers. The photoelectric response was tested by measurements of the extinction coefficient¹⁶³ of a standard potassium chromate solution¹⁶⁴ in the wavelength range 215 - 500 m μ ; all values were within 3% of the tentative results of Gibson¹⁶⁵. The extinction coefficient at 275 m μ was found to be 0.784, compared to the values 0.780 and 0.793 found for Carey¹⁶⁶ and Beckmann¹⁶⁴ spectrophotometers respectively.

When necessary, a constant temperature attachment, consisting of a cell holder with a jacket through which thermostated water could be circulated, was employed. Some measurements were repeated on an Optica recording spectrophotometer in order to check the positions of the absorption maxima. Extinction coefficients of solutions were measured in silica cells of suitable length (2, 5, 10, 20 or 40 mm.). In studies of the concentration dependence of the extinction coefficient, solutions were prepared in the cells by adding successive increments of stock solutions and mixing with a platinum stirrer. The accuracy of this procedure was verified by measurements on separately prepared solutions.

The extinction coefficients of the solutions studied were found to be independent of time, and in general the reproducibility of the measurements was good, except for aqueous solutions of polyvinylpyridinium chloride (PVP-HCl) in the absence of excess HCl. Here the slopes of separate determinations of the extinction coefficient-concentration curves showed a variation of up to $\pm 5\%$, so that the reproducibility of the point of intersection c_0 of the linear regions was poor. These errors may be due to variations in the degree of hydrolysis of the polyions, caused by the absorption of atmospheric carbon dioxide, or the leaching of alkali from the volumetric glassware. This variation was eliminated by the addition of excess HCl.

Variations in the extinction coefficient of PVP-Br were also observed, but they were about ten times smaller. These solutions could also be stabilized by adding HCl or a buffer solution.

4. Conductance Measurements.

The bridge used for conductance measurements has been described previously,¹⁴⁹ The conductance cell, shown diagrammatically in fig. V-2, was designed to avoid errors due to adsorption of solute on the electrodes; it is similar in some respects to those described by Eisenberg¹⁰⁶ and by Longworth and Hermans.¹⁶⁷ The electrodes, bright platinum discs 2.5 cm. in diameter and spaced ca. 1 mm. apart, were sealed into Pyrex glass via a tungsten seal. The cell was cleaned occasionally with hot chromic-sulphuric acid mixture followed by steaming for 12 hours. When not in use it was filled with conductivity water. The cell constant (0.0125 cm.^{-1}) was determined with 0.001 N potassium chloride (B.D.H. Analytical Reagent, dried to constant weight). Redetermination from time to time showed a variation of less than $\pm 0.1\%$.

Measurements were generally made at a series of polymer concentrations, starting with a known volume (25 - 100 ml.) of pure solvent. The latter was freed from dissolved carbon dioxide by bubbling purified, solvent saturated nitrogen through it until the conductance reached a constant value. Stock solution (0.1 - 1.0 ml.) of polymer was then added to the solvent through the ball-joint A (fig. V-2) while nitrogen was passed over the surface of the liquid in the

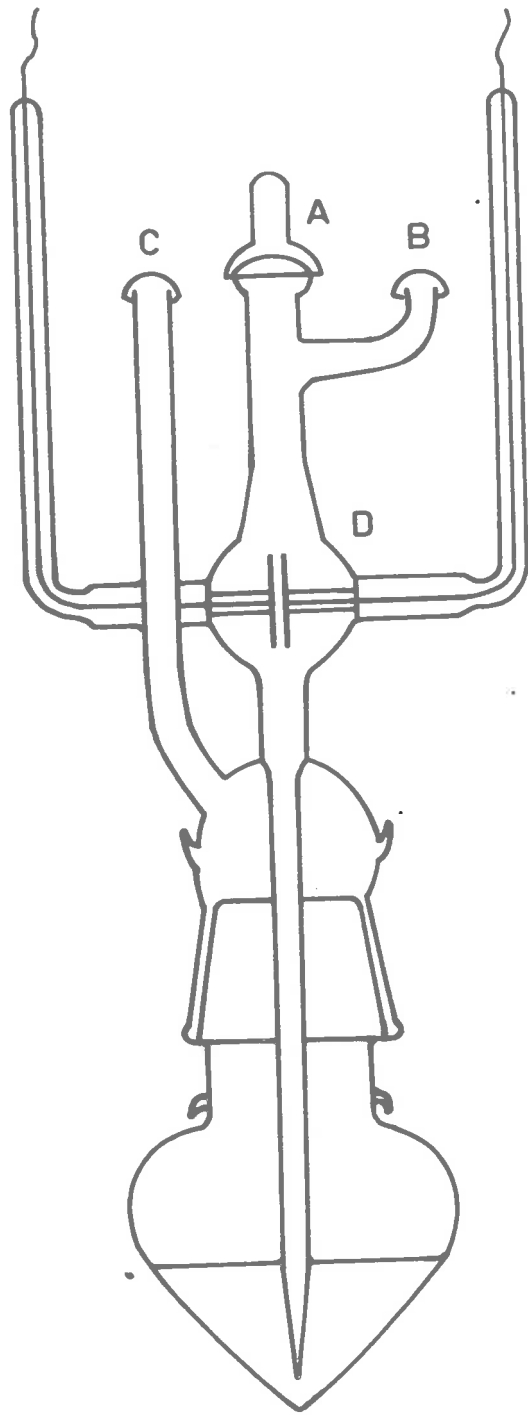


Fig. V-2. Conductance Cell.

cell through B. After thorough mixing of the solution, the electrode compartment C was filled, taking care that no small gas bubbles were present, and the resistance measured. Further additions of stock solution were then made as required.

The resistances of the polyelectrolyte solutions generally increased with time. This increase was most rapid for very dilute solutions, especially those of PVP-Br in ethanol, whereas it was very slight for all solutions of PBTA-Cl, and absent in the case of simple electrolytes. Since the original value of the resistance could be restored, to within 0.1% or better, by renewing the solution between the electrodes, it was assumed that the above effect was caused by adsorption of polymer on the platinum. Adsorption on the glass parts of the cell was shown to be unimportant (except for solutions of PVP-HCl) by the constancy of the resistance, measured by the above method, over a period of several hours, and by several spectrophotometric concentration measurements. Such constancy of resistance could not be obtained with PVP-HCl, and measurements were therefore made as rapidly as possible. The error produced by this effect is unlikely to exceed 1% except perhaps at the lowest concentrations studied. The specific conductance-concentration plots,

although always linear at low concentrations of PVP-HCl, usually were found to extrapolate to a small positive value c' on the c axis (cf. fig. III-2). The values of Λ for this substance were calculated using $c - c'$ as the polyelectrolyte concentration.

Resistance measurements were made with the cell immersed in a water bath at 25° regulated to $\pm .02^\circ$, at frequencies of 1, 2.5, 5, and 10 kc./sec. The resistance was found to be a linear function of the reciprocal frequency (fig. V-3(a)), and was extrapolated to infinite frequency to eliminate polarization errors. The resistance was found to be independent of the applied field in the range 0.13 - 30 volts/cm.; the lowest fields were obtained by the use of a cell with electrodes 7.5 mm. apart.

After subtraction of the solvent conductance, specific conductances of PBTA-Cl and PVP-Br solutions were reproducible to $\pm 0.5\%$ from run to run, except at the lowest concentrations studied, where systematic deviations of up to $\pm 1.5\%$ occurred. This effect is discussed in section IV-3. The overall reliability of the method used was verified by measurements on KCl solutions in the same range of specific conductance. The results (fig. V-3(b)) show that the accuracy is sufficient for the present purposes.

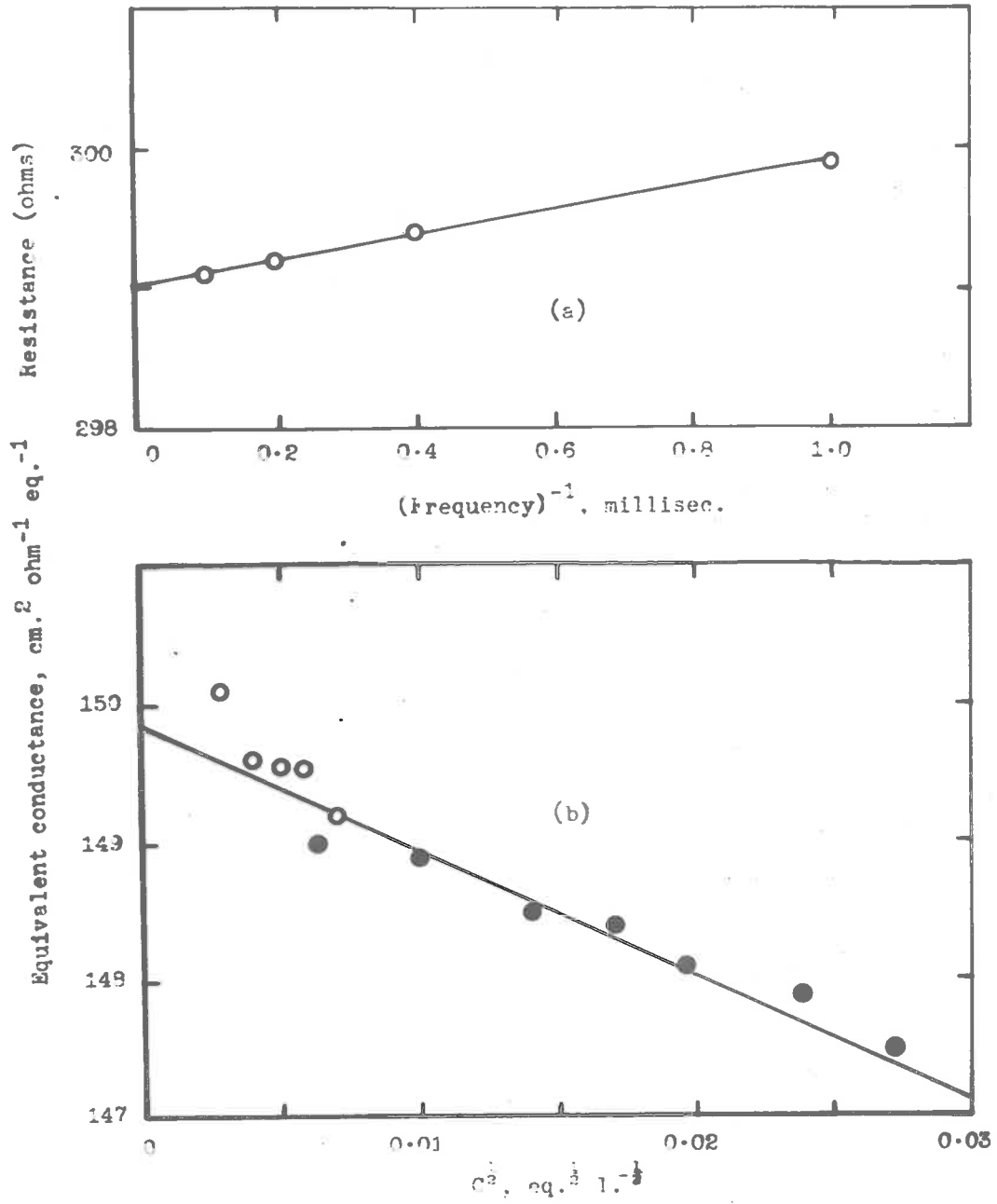


Fig. V-2. (a) frequency dependence of resistance.
 (b) Equivalent conductance of KCl. The curve drawn represents the literature values.

The temperature dependence of the conductance of PBTA-Cl was investigated by varying the temperature of the water bath. Readings taken with increasing and decreasing temperatures agreed within 0.1%. The cell constant was assumed to be independent of temperature. A correction for the change in density of the solvent was applied to the equivalent conductance.

Direct-current measurements were made in a cell consisting of two electrode compartments connected by a tube of 0.5 cm. bore and 16 cm. length. The solution in this part of the cell contributed almost the total resistance observed. A stabilized, accurately known current could be passed through the cell via two silver-silver chloride electrodes. The potential difference between the same electrodes was measured with a potentiometer. The measurements could be made within about ten seconds of switching on the current; the potential difference remained almost constant for several minutes. Currents used were in the range 40 - 400 μ A, resulting in potential differences up to 250 volts. Resistances were independent of current passed when this was sufficiently high. The specific conductance obtained by this method for a 10^{-3} eq./l. solution of PBTA-Cl at 25° was $(40.4 \pm 0.3) \times 10^{-6}$ ohm⁻¹ cm.⁻¹, compared with the value 40.6×10^{-6} ohm⁻¹ cm.⁻¹ obtained for the same solution by

the previously described A.C. method.

5. Transference Experiments.

(1) Measurement of mobility.

The transference cell used¹⁰¹ consists of two compartments, each of about 50 ml. capacity, separated by a coarse sintered-glass disc (Pyrex No. 2). The electrodes, spaced 18 cm. apart, are platinum discs coated with silver and the appropriate silver halide; in some experiments, however, the uncoated electrodes were used.

Solutions for study were prepared under nitrogen in CO₂-free conductivity water. They were transferred, avoiding contact with air, to the dry transference cell, which was rinsed several times before the final filling. At lower concentrations the solutions were prepared in the conductance cell, to which they were temporarily returned after filling the transference cell, in order to detect any increase in conductance due to, e.g., solution of silver halide. This increase was usually slight and always less than 4%; it was incorporated in the solvent correction (equation IV-12). In preliminary experiments, large errors were caused by incomplete removal of CO₂ from solutions. It was found that CO₂ was not removed effectively by boiling the solutions at room temperature under reduced pressure. Solutions having a concentration above about 10⁻³ eq./l.

were generally not made CO_2 -free, and a contribution of $8 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$ to the solvent conductance was assumed.

The filled transference cell was immersed in a water bath at 25° regulated to $\pm .01^\circ$ or better. Current from an electronically regulated power supply (Electronic Instrument and Lighting Co., Toorak Gardens, South Australia) was passed through the cell for about 15 mins., sufficient to transfer 10 - 20% of the polymer from the anode to the cathode compartment. The quantity of electricity passed was found from measurements of time and current. The latter was automatically kept constant to within 0.1%. Leakage currents were shown to be insignificant by measurements of the resistance between the electrodes and thermostat liquid.

During electrolysis of aqueous solutions, a colloidal precipitate of AgCl or AgBr appeared around the anode; in such cases, only the solutions from the cathode compartment were kept for analysis. No precipitate was formed in ethanol solution. No electro-osmotic flow was observed in this work.

The change in concentration was determined spectrophotometrically by the transmission ratio method.¹⁶³ The difference in optical density between the original and electrolysed solutions, diluted if necessary, was measured

directly at a number of suitable wavelengths, viz. 220 (7700) and 225 (6900) μ for PBTA-Cl, and 245 (3500), 257 (3800), and 260 μ (3550) for PVP-Br. The corresponding molecular extinction coefficients (in l. eq.⁻¹cm.⁻¹) are given in parentheses; they were found to obey Beer's law. The solutions of PVP-Br were buffered before analysis by the addition of 1% by volume of 1 M, pH 7 phosphate buffer, or of 5 M HCl.

The more recent experiments on PBTA-Cl were carried out by diluting the original and electrolysed solutions by weight in the ratios expected to reduce them to the same concentration. The difference in optical density was then very small and not subject to errors caused by stray light.¹⁶³ Both methods gave the same results provided the optical density was less than about 1.3; only results of experiments for which this condition was satisfied are reported. The change in concentration determined by the above methods is expected to be accurate to within 1% for PBTA-Cl, and within 2% for PVP-Br.

(ii) Exchange Determinations. 20 ml. of a 2% aqueous solution of PBTA-Cl was made radioactive by the addition of about 0.3 ml. of a 2 N solution of HCl containing Cl³⁶ at a specific activity of 100 microcuries/gm. (suppliers Radiochemical Centre, Amersham, U.K.).

After allowing the solution to stand for an hour, it was dialysed against distilled water at 5° for 48 hours with repeated changes of dialysate. No polymer passed through the membrane. pH measurements on the diluted solution showed the complete removal of HCl.

For the most dilute solution studied, a higher specific activity was required. This was attained by passing 10 ml. of a 2% solution of PBTA-Cl through a mixed-bed ion-exchange column into 0.15 ml. of 2 N radioactive HCl, allowing to stand at 5° for 5 hours, and dialysing as above.

A cell similar to that described in the previous section was used. The anode compartment was first filled with a radioactive solution (A), and several ml. was allowed to seep through the frit. Small air bubbles were removed from the frit, and the stopper containing the silver-silver chloride anode inserted. The anode compartment was thus completely closed to prevent streaming of solutions through the frit. The cell was clamped in a 25° water bath controlled to $\pm 0.001^\circ$. The solution (B) to be introduced into the cathode compartment was also thermostated. This solution was identical to solution A except that it was not radioactive. The radioactive solution was then removed from the cathode side of the frit with a syringe. Several ml. solution B was added

and also removed. After repeating this operation, the compartment was filled with solution B, the electrode inserted, and the current turned on immediately. When sufficient current had been passed, the cell was removed from the bath, and the cathode compartment was immediately drained into a tared flask. It was rinsed with two small portions of solution B; these were also added to the flask, which was then reweighed. The contents of the flask were counted in a 10 ml. liquid Geiger-Müller tube (20th Century Electronics, type M6) using an automatic scaler (EKCO Electronics Ltd., type N 530.D). The original solution A, diluted if necessary, was also counted for comparison. The change in polymer concentration in solution B was then measured by the method described in the previous section. Several blank experiments showed that no radioactive chloride passed into the cathode compartment by diffusion or convection.

6. Potentiometric Measurements.

(i) Counterion activity coefficients. The following electrochemical cells were set up: (1) $\text{Ag, AgCl} \mid \text{PBTA-Cl}_{\text{aq}} \parallel \text{KCl}(\text{sat.}) \mid \text{Hg}_2\text{Cl}_2, \text{Hg}$; (2) $\text{Ag, AgBr} \mid \text{PVP-Br}_{\text{aq}} \parallel \text{KCl}(\text{sat.}) \mid \text{Hg}_2\text{Cl}_2, \text{Hg}$. The liquid junction was a fine asbestos thread sealed into glass.¹⁶⁸ Contamination of the test solutions with KCl from the saturated calomel reference electrode was thus prevented. The E.M.F.s of the cells were measured at various polyelectrolyte concentrations at room temperature, using a Cambridge pH-meter. No precautions against absorption of CO_2 were considered necessary. Similar measurements were made on solutions of KCl and KBr using the same electrodes. The E.M.F.s for these reference solutions were plotted vs. $\log f_{\text{C}}$, with $\log f_{\text{C}}$ calculated from the Debye-Hückel limiting law. The observed values of E.M.F. for the polyelectrolytes were interpolated on these calibration curves to yield $\log f_{\text{C}}$, and hence f_{C} .

(ii) Measurement of pH. The electrodes and measuring device were the same as above, except that the silver halide electrode was replaced with a Cambridge "Alkacid" glass electrode. The system was standardised with 0.05 M phthalate buffer and checked with .05 M borate buffer. Solutions were thermostated at 25° if required. For

measurements on PVP-HCl, water was first introduced into a Pyrex polarograph cell directly from a mixed-bed column under an atmosphere of nitrogen. The pH of the water was in the range 5.8 - 6.5. Stock solution of polymer was added, nitrogen was bubbled through the solution for one minute, and then passed over the surface of the solution while the pH was measured. No drift was observed. The concentration of H^+ ions was obtained from a calibration graph constructed for dilute HCl solutions.

7. Light Scattering.

(i) Light-scattering apparatus. A commercially available P.C.L. - Peaker light-scattering apparatus^{169,170} was modified to eliminate the large fluctuations in signal caused by the wandering of the mercury arc used as light source. Only the modified parts of the apparatus are described.

Light from a high pressure, compact-source mercury vapour lamp (Mazda 250 watt type ME/D), run from a 50-cycle A.C. supply, is focused on a narrow spectrometer slit. The image of the slit is focused in the centre of the scattering volume, giving a beam of width 2 mm. and height 10 mm., with a divergence of 0.47° and 0.78° in the horizontal and vertical directions respectively. Stray light is reduced by four apertures, each slightly larger than the incident beam, in front of the scattering cell. The 436 m μ line of the mercury spectrum is isolated by means of an interference filter (Schott u. Gen., Mainz). The components of the optical system were aligned with the aid of a cathetometer.

The photocurrent measuring device was designed and built by the Electronic Instrument and Lighting Co., Toorak Gardens, South Australia. A block diagram of the circuit is shown in fig. V-4. The ratio of the photocurrents due

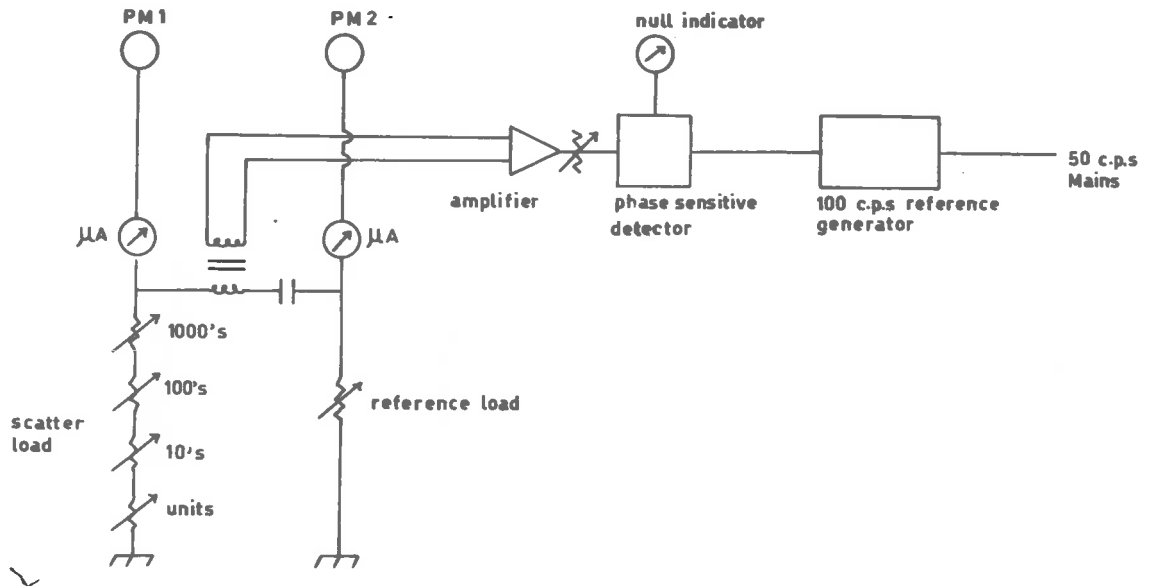


Fig. V-4. Block diagram of electronic detector.

to the incident and scattered light can be measured directly as the ratio of two variable resistances, adjusted to give a null reading on the detector. The two photomultiplier tubes have a common supply of high tension. The D.C. component of the dark current has no effect on the results obtained, since the measuring device is tuned to receive only the 100 c.p.s. component of the photocurrent.

(ii) Scattering Cell. Solutions for scattering determinations were contained in rectangular cells, inside dimensions 4 mm. x 33 mm. (length) x 46 mm. (height), constructed from glass 3.5 mm. thick. About 4 ml. of solution was used to fill the cell, which could be covered with a piece of microscope cover glass. The cell was held in an outer cell of blackened brass containing distilled water. After traversing the scattering cell, the primary beam is absorbed by a piece of red glass. With this arrangement the Fresnel correction⁹⁴ is rendered negligible. The scattered light is observed through a semicircular glass window cemented to the outer cell. The range of angles accessible to observation is 27° - 140° .

(iii) Calibration and Measurements. The symmetry of the system was checked by measuring the fluorescence from dilute solutions of sodium dichlorofluoresceinate, using a

yellow cutoff filter to eliminate scattered light. The values of $r(\theta) \sin \theta$, where $r(\theta)$ is the ratio of the photo-currents due to scattered and incident light at the angle θ , showed a slight dependence on θ . Since these values were reproducible, even when the optical system was realigned, they were used to determine correction factors, $x(\theta)$, to the usual $\sin \theta$ volume factor.⁹⁴ Values of $x(\theta)$ are given under (1) in table V-2.

Table V-2.

θ	30°	35	40	45	60	75	90	105	120	140
(1) $x(\theta)$	1.02 ₀	1.02 ₄	1.02 ₄	1.02 ₇	1.03 ₀	1.01 ₀	- .98 ₆	.99 ₄	.99 ₅	
(2) $10^6 R(\theta)$	11	7.6	5.7	5.0	4.2	3.6	3.5	3.1	3.3	3.8

The apparatus was calibrated using purified, dust-free benzene (obtained by distillation). The value $R(r) = 47 \times 10^{-6} \text{ cm.}^{-1}$ for the reduced scattering intensity of benzene was used.^{94,171} Since high absolute accuracy was not required in the present work, this procedure was considered to be satisfactory.

The reduced scattering intensities, $R(\theta)$, of unknown solutions were obtained using the equation

$$R(\theta) = F n^2 r(\theta) x(\theta) \sin(\theta) / (1 + \cos^2 \theta)$$

where F is the calibration factor, and n the refractive index of the solution. In the case of highly scattering solutions, a neutral filter was placed in the primary beam.

(iv) Clarification. Solutions and solvents were centrifuged for one hour at 20,000 g in 1 inch x 3 inch polypropylene tubes using a Servall SS - 1 angle-head centrifuge. The solutions were transferred to the scattering cell by means of a pipette. The pipette and cell were first rinsed thoroughly with the clarified solvent. The cell was then rinsed twice with clarified solution before the final filling. The presence of large particles, e.g. dust, could be detected by visual inspection of low-angle scattering in a darkened room. The interference filter was removed for this purpose.

The efficiency of clarification and elimination of stray light can be assessed by examination of the scattering pattern obtained from aqueous solvents.¹⁷² Typical results are listed under (2) in table V-2. These values should be compared with the value $R = 2.3 \times 10^{-6}$ for pure water,¹⁷³ almost independent of θ . In the present work, solution scattering was usually sufficiently high to render the correction for solvent scattering small.

The above clarification procedure proved to be unsatisfactory for solutions of PVP-HCl, and "striations" like

those reported by Huque et al.¹⁷² were sometimes observed. Solutions of PVP-HCl were therefore centrifuges in an SW-39 swinging-bucket rotor for 2 hours at 20,000 g, using a Spinco Model E ultracentrifuge. The rotor was stopped with minimum braking.

(v) Refractometer. Specific refractive increments were determined with a double-prism differential refractometer of the type described by Cecil and Ogston.¹⁷⁴ The instrument was calibrated with solutions of NaCl. The standard deviation of a refractive increment was 2×10^{-6} . Measured increments were always greater than 2.5×10^{-4} . This corresponded to polymer concentrations above 0.1%. The values of specific refractive increment were found to be independent of polymer concentration in the range studied.

(vi) Treatment of Data. Light-scattering data were plotted as $Kc/R(\theta)$ vs. $\sin^2(\theta/2) + kc$, as proposed by Zimm.¹⁷⁵ Here k is an arbitrary constant chosen for convenience, and K is given by

$$K = 2\pi^2 n^2 (dn/dc)^2 / (N \lambda^4) \quad (V-1)$$

where λ is the wavelength of the light, and N is Avogadro's number. The weight-average molecular weight $\langle M_w \rangle$ is obtained using the equation

$$\frac{Kc}{R(\theta)} = \frac{1}{\langle M_w \rangle P(\theta)} + 2Bc \quad (V-2)$$

where $P(\theta)$ is the particle scattering factor,⁹⁴ and B is related to the second virial coefficient. By definition, $P(0) = 1$. The mean square z-average radius of gyration, $\langle R_z^2 \rangle$, is obtained from the ratio of the initial slope of the $c = 0$ line to its intercept from the relationship

$$\text{slope/intercept} = 16\pi^2 \langle R_z^2 \rangle / 3\lambda^2 \quad (V-3)$$

No correction for depolarization was applied; this is expected to be less than 5% for all the samples studied.

For polyelectrolytes in the presence of added salt (component 3), equation (V-2) must be multiplied on the right-hand side by the term¹⁷⁶ $(1 - D)^{-2}$, where $D = M_3 \delta (\partial n / \partial c_3) / (\partial n / \partial c_2)$. The quantity δ , which can be obtained by membrane equilibrium studies,¹⁷⁷ is a measure of the thermodynamic interaction between components 2 and 3. Assuming the behaviour of PBTA-Cl and PVP-Br to be similar to that of some other polyelectrolytes,^{177,178} the value of δ for the solution used in the present work is estimated as about 5×10^{-4} , giving values of $(1 - D)^2$ in the vicinity of 1.05. Since this correction is small, and in the opposite direction to that for depolarization, no serious error is incurred by neglecting both these corrections. For PVP-HCl,

the thermodynamic correction is probably somewhat larger than that for other polyelectrolytes. Because of the possibility of membrane hydrolysis, the value of δ for PVP-HCl in the presence of neutral salt cannot be determined by membrane equilibrium measurements.

Characterization of PVP-Br (sample A1 - Q) and PBTA-Cl.

Light-scattering measurements on the above polyelectrolytes were carried out in the presence of excess simple electrolyte at 27° C. The results are summarized below.

Sample	Solvent	dn/dc	$\langle M_w \rangle$	$10^4 B$	$\langle R_z^2 \rangle^{1/2}$, A.U.
A1 - Q	0.2 N KBr	0.247	$1.6_5 \times 10^6$	0.7	980
PBTA-Cl	0.2 N KCl	0.261	4.1×10^5	2	450

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