The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Effects of Ionic Spacing and Degree of Polymerization on the Stoichiometry of Polyelectrolyte Interaction in Dilute Aqueous Solutions

Stephen Hoi Tse

June, 1979

THE EFFECTS OF IONIC SPACING AND DEGREE OF POLYMERIZATION ON THE STOICHIOMETRY OF POLYELECTROLYTE INTERACTION IN DILUTE AQUEOUS SOLUTIONS

A thesis submitted by

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in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence University,
Appleton, Wisconsin

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TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	4
GENERAL ASPECTS OF POLYELECTROLYTE CHEMISTRY	5
General Structure of a Linear Polyelectrolyte	5
Solution Chemistry	6
Polyelectrolyte Reaction	9
A BRIEF ACCOUNT OF POLYELECTROLYTE COMPLEXATION RESEARCH	12
PRESENTATION OF THE PROBLEM AND THESIS OBJECTIVES	17
EXPERIMENTAL APPROACH	19
EXPERIMENTAL MATERIALS, EQUIPMENT AND PROCEDURES	23
Synthesis of N,N,N',N'-Tetramethylpentane-1,5-diamine	23
Syntheses of the Selected Symmetrical Ionene Bromides	24
Synthesis of Sodium Poly(vinyl sulfonate)	26
Structural Confirmation of the Synthesized Compounds	26
Fractionation of the Polyelectrolytes	28
Removal of Salts from the Polyelectrolyte Fractions	30
Determination of Molecular Weights by Ultracentrifugation	32
Determination of Partial Specific Volumes	33
Preparation of Solutions	35
Standardization of Sodium Poly(vinyl sulfonate) Solutions	35
Standardization of Bromide-containing Solutions	36
Polyelectrolyte Complexation Experiments	38
Preparation of the Control Solutions	40
Measurement of Conductance	44
Electrophoresis Experiments	45
Treatment of Secondary Data	46
A List of the Polyelectrolyte Complexation Experiments	46

	Page
EXPERIMENTAL RESULTS AND DISCUSSION	49
Structural Confirmation of Compounds	49
N,N,N',N'-Tetramethylpentane-1,5-diamine	49
3,3-Ionene Bromide	50
4,4-Ionene Bromide	50
5,5-Ionene Bromide	52
6,6-Ionene Bromide	52
Additional Comments on the Structures of the Ionenes	54
Sodium Poly(vinyl sulfonate)	54
Fractionation of the Polyelectrolytes	56
Ultrafiltration of Polyelectrolyte Fractions	56
Apparent Partial Specific Volumes of Polyelectrolytes	62
Molecular Weights of the Selected Polyelectrolytes	65
Standardization of Solutions	69
Sodium Poly(vinyl sulfonate) Solutions	69
Ionene Bromide and Sodium Bromide Stock Solutions	71
Polyelectrolyte Complexation Experiments	71
Criteria for Stoichiometry of Polyelectrolyte Interaction	71
Initial Complexation Reactions	73
Effect of Ionic Spacing	82
Effect of Degree of Polymerization	101
Effect of Polydispersity	113
CONCLUSIONS	120
ACKNOWLEDGMENTS	121
GLOSSARY OF SYMBOLS	122
LITERATURE CITED	126

Page

APPENDIX I. PROGRAM FOR STANDARDIZATION OF NaPVS SOLUTIONS 129

APPENDIX II. PROGRAM FOR DETERMINATION OF END POINT OF POTENTIOMETRIC TITRATION BY GRAN'S METHOD 131

APPENDIX III. PROGRAM TO CALCULATE THE TIMES OF DELIVERY OF POLYELECTROLYTE SOLUTIONS IN COMPLEXATION REACTIONS AND OF SOLUTIONS REQUIRED FOR PREPARING THE CONTROL SOLUTIONS 134

APPENDIX IV. PROGRAM FOR CALCULATION OF AVERAGE CORRECTED SPECIFIC CONDUCTANCE 136

APPENDIX V. PROGRAM FOR PLOTTING SPECIFIC CONDUCTANCE DATA AGAINST IONIC MOLE RATIO 138

APPENDIX VI. HYDROPHOBIC INTERACTION 140

APPENDIX VII. ESTIMATION OF COMPLETENESS OF POLYELECTROLYTE COMPLEXATIONS 141

APPENDIX VIII. PROGRAM FOR CALCULATION OF COMPLETENESS OF REACTION BETWEEN NaPVS AND IONENE BROMIDES WITH EQUAL DEGREE OF POLYMERIZATION 143

APPENDIX IX. PROGRAMS FOR CALCULATION OF COMPLETENESS OF REACTION BETWEEN HIGH DEGREE OF POLYMERIZATION NaPVS AND LOW DEGREE OF POLYMERIZATION IONENES 144

SUMMARY

The intentions of this thesis were to investigate the effects of ionic spacing and the degree of polymerization (DP) on the stoichiometry of polyelectrolyte interaction in dilute aqueous solutions and to delineate the various mechanisms involved.

Sodium poly(vinyl sulfonate) and 3,3-ionene bromide have equal ionic spacings. These polyelectrolytes and a homologous series of ionene bromides (4,4-, 5,5- and 6,6-ionene) with progressively larger ionic spacings were chosen for this research.

The polyelectrolytes were fractionated by gel permeation chromatography.

The concentrations of polyelectrolyte solutions were about 0.001M and the reactions were carried out at 25°C without stirring but with thorough mixing of the reagents. The conductance of each of the reaction mixtures and that of its corresponding control solution was recorded. The criteria of stoichiometry required the conductance of the reaction mixture to be identical to that of its control solution and the formation of an ionically neutral and hydrophobic complex.

The reactions between unfractionated sodium poly(vinyl sulfonate) (average DP = 100) and unfractionated 3,3-ionene bromide (average DP = 50) were stoichiometric whereas the reactions of the same polyanion with the other unfractionated ionenes (average DP = 10 to 20) were not. Three forms of complexes were obtained in these reactions, a soluble complex, a viscous fluid coacervate and a fine greyish precipitate that is similar in appearance to the one obtained in the stoichiometric reactions. The viscous fluid coacervate is proposed to have formed as a result of the hydration of unreacted ionic groups in a nonstoichiometric complex and the greyish complex was found to have an overall hydrophobic nature and was formed when the reaction completeness was high enough (ca. 90%).

The soluble complex was found to have formed as the result of a kinetic factor caused by vastly different electrostatic potentials among polyelectrolyte oligomers.

The stoichiometry of polyelectrolytes between fractions of approximately equal DP (ca. 170) was also found to be dependent upon the ionic spacings. The final complex of those reactions between polyelectrolytes with unequal ionic spacings is proposed to have formed in three successive stages while that of the reaction between polyelectrolytes with equal ionic spacings is proposed to have formed in only two stages. The completeness of reactions as predicted by the proposed complex structures are in excellent agreement with those calculated from experimental data.

When various molecular weight fractions of the selected polyelectrolytes (both high and low DP) were reacted, all of the reactions between sodium poly(vinyl sulfonate) and 3,3-ionene bromide were stoichiometric but those between it and the other ionene bromides were not. The mechanism of the formation of the final complex for the reaction between a low DP sodium poly(vinyl sulfonate) and a high DP ionene should closely parallel the 3-stage mechanism proposed for the reaction between polyelectrolytes with approximately equal DP. Meanwhile, the 3-stage mechanism was modified to a 3-step mechanism to explain the formation of the final complex for reactions between a high DP sodium poly(vinyl sulfonate) and a low DP ionene bromide. The completeness values as predicted by the proposed mechanism were again in excellent agreement with those calculated from experimental data. The chief effect of the degree of polymerization on the stoichiometry of polyelectrolyte interactions is that in the reactions between a low DP ionene and a high DP sodium poly(vinyl sulfonate) (unequal ionic spacings), the short length of the ionene polyions makes it possible for them to react with the polyanion through a more efficient 3-step mechanism. There-

fore, these reactions are more complete than those between a low DP sodium poly(vinyl sulfonate) and a high DP ionene bromide and those between polyelectrolytes with approximately equal DP.

INTRODUCTION

Linear polyelectrolytes, even in extremely dilute aqueous solutions, have regions of high charge density in the neighborhood of each polyion, as a simple consequence of structure. One could therefore expect a strong interaction between the electrostatic fields of polyanions and polycations, which would lead to complex formation. Investigations made in the areas of polyelectrolyte complexes and colloid titration have indeed verified the foregoing statement.

It was observed that under suitable conditions, mutual precipitation between two oppositely charged linear polyelectrolytes would lead to the formation of a neutral complex containing stoichiometric amounts of each polyion (1-3). In this context, stoichiometry refers to the one-to-one pairing of the ionogenic groups on the interacting polyions. This phenomenon was thought to have arisen from the equality of ionic spacing between the adjacent ionogenic groups on each polyion. Fuoss and Sadek (4) worked with polyelectrolytes with different ionic spacings but did not observe a stoichiometric interaction between the polyelectrolytes. Interestingly enough, stoichiometric reactions between a polycation and various polyanions with rather undefined structures were also reported in the area of colloid titration (5-17). It should be pointed out that the method of colloid titration was built entirely on the precarious assumption that all polyelectrolytes react stoichiometrically. Because most of the results were not confirmed by detailed analyses, the reported observations might just be artifacts.

Current knowledge of the stoichiometry of polyelectrolyte interactions is conflicting and inadequate. Hence, the clarification of the possible relation between ionic spacing and stoichiometry of polyelectrolytes in dilute aqueous solutions may greatly aid in understanding the interaction of polyelectrolytes in general.

GENERAL ASPECTS OF POLYELECTROLYTE CHEMISTRY

GENERAL STRUCTURE OF A LINEAR POLYELECTROLYTE

In this thesis, a linear polyelectrolyte is defined as being made up of a long backbone of repeating units that contains the ionogenic groups (Fig. 1). The backbone is generally referred to as the polyion. The ionogenic groups can be carried either in the polyion (integral type) or in side chains that are attached to the polyion (pendent type). In order to maintain electrical neutrality, there exist small ions that associate closely with the ionogenic groups on the polyion that are called counterions. These counterions only occupy a rather small volume of the water in the vicinity of the polyion.

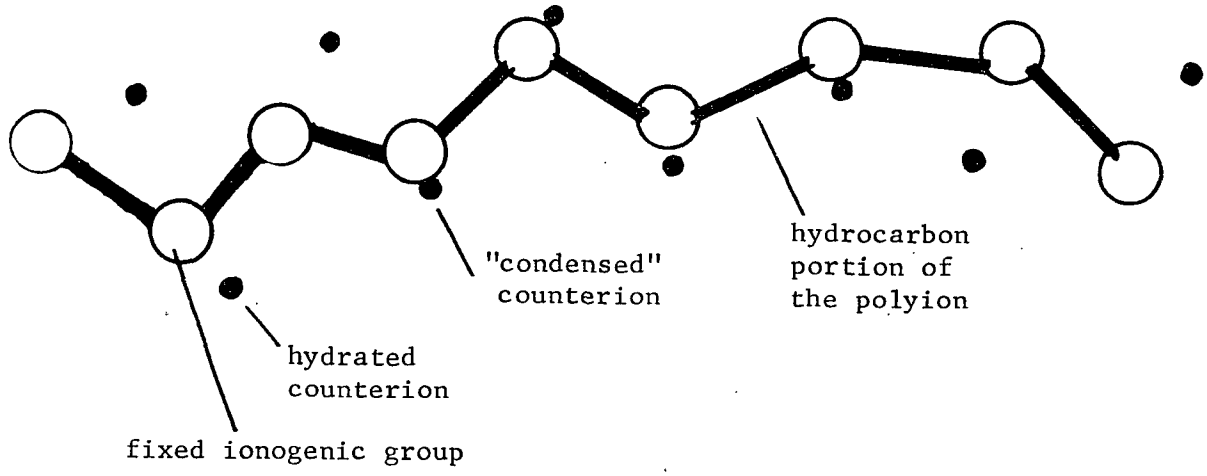
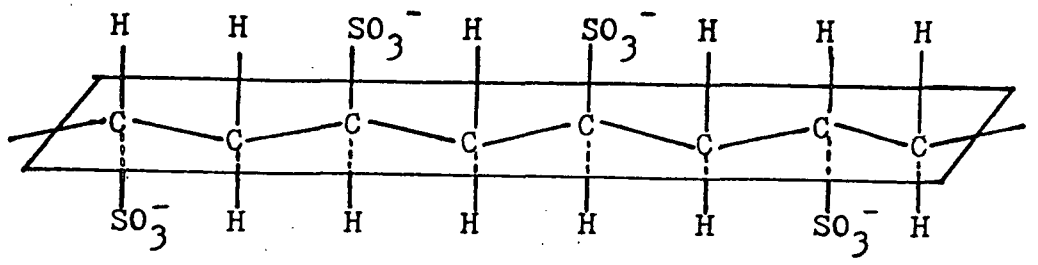


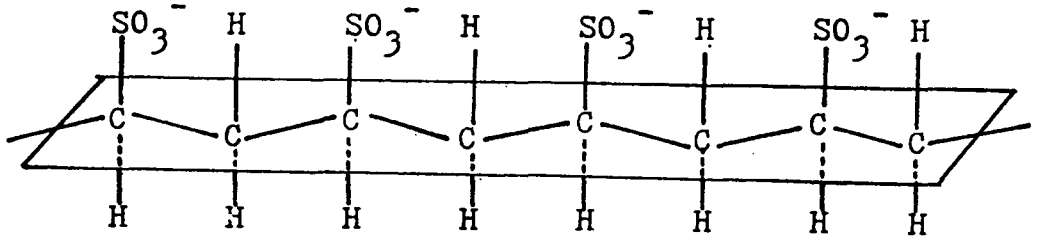
Figure 1. A Strong Polyelectrolyte in Salt-Free Water

In the pendent type polyelectrolytes produced by polymerizing any vinyl monomer, two stereoisomeric configurations are possible at every second carbon atom. Depending on the conditions of the polymerization, one may obtain a random sequence of the steric configuration of these centers or may obtain polyelectrolyte chains in which long sequences of these centers have either the same or regularly alternating configurations. These polyelectrolytes are termed atactic, isotactic, and syndiotactic, respectively. Using poly(vinyl sulfonate)

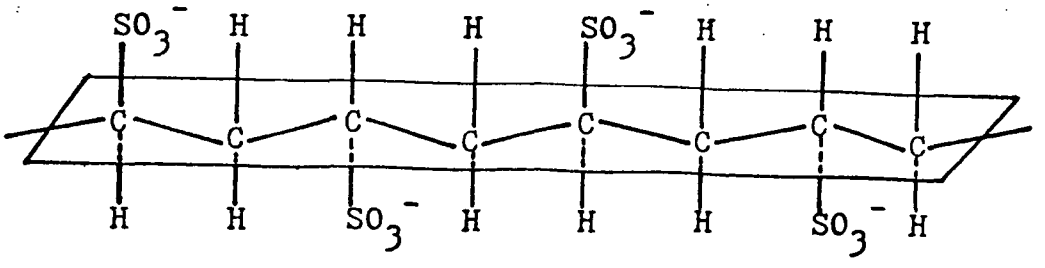
as an example, such polyelectrolyte configurations are represented schematically in Fig. 2.



Atactic chain



Isotactic chain



Syndiotactic chain

Figure 2. Diagrams Showing the Stereoregular Syndiotactic and Isotactic and the Irregular Atactic Configuration in a Vinyl Polyelectrolyte. The Main Carbon-Carbon Chain is Depicted in the Fully Extended (all trans) Planar Zigzag Conformation

SOLUTION CHEMISTRY

There are strong and weak polyelectrolytes. Very similar to the simple electrolytes, a strong polyelectrolyte dissolves and ionizes freely in aqueous solution. On the contrary, the dissociation of weak polyelectrolytes is governed mainly by the degree of neutralization.

When a strong linear polyelectrolyte is dissolved in water, there is interaction between the ionogenic groups on the polyion and the water molecules surrounding them. This causes the individual ions to hydrate and diffuse apart from one another, in attempting to distribute themselves homogeneously throughout the water. However, they are constrained from doing so by the covalent bonds holding the polymer chain together. As a result, in dilute solutions the polyion assumes a highly extended conformation which minimizes coulombic interactions among the ionic groups and some of their counterions. The expansion of the polyion to its fully stretched planar zigzag conformation in dilute solutions has been confirmed by the study of the conformation of strong vinyl polyelectrolytes in solution by small angle elastic neutron scattering (18). The same study also concluded that expansion of the polyelectrolyte chain increases when the charge density increases or when concentration and ionic strength decrease. Thus, if a simple electrolyte is added to a polyelectrolyte, the ions of the salt will shield the charges (Fig. 3). This shielding effect causes a reduction of electrostatic interaction among neighboring ionogenic groups which leads the polyion to "contract" to a less rigid and less extended conformation. When a large enough amount of salt is added to the system, the ionogenic groups on the polyion will be completely screened by small ions; the polyion will no longer be extended and the polyelectrolyte will exhibit a random coil conformation. In this case, the polyelectrolyte assumes its unperturbed dimension and it behaves as if it were an uncharged polymer. The solvent that brings about such conditions is a thermodynamically "poor" solvent and is called the "theta (Θ) solvent" for the polyelectrolyte.

In aqueous solutions, a strong polyelectrolyte exhibits transport properties such as electrical conductance and electrophoresis. Generally speaking, the specific conductance of a polyelectrolyte solution is lower than that of a simple

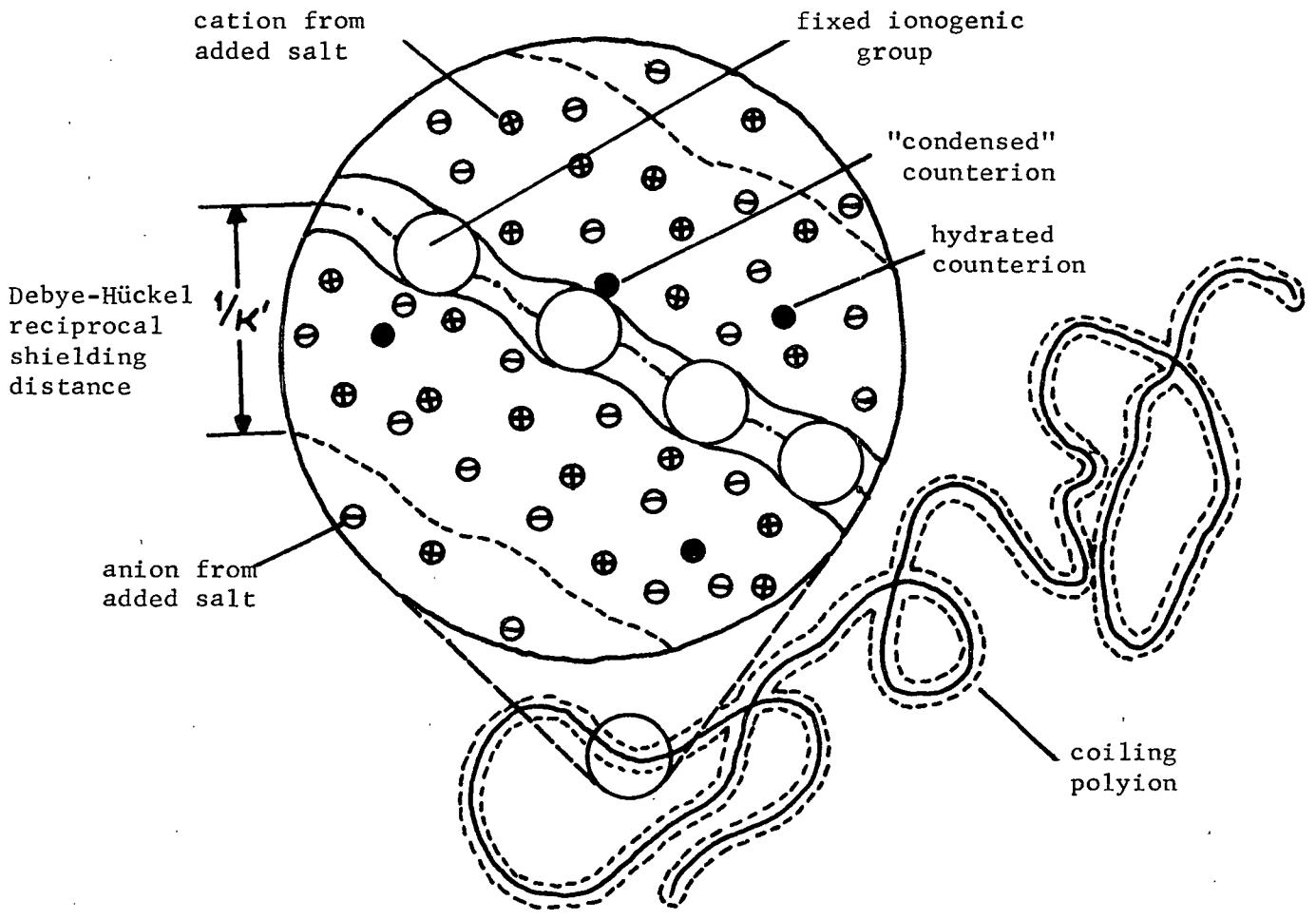


Figure 3. Polyelectrolyte in the Presence of a Simple Electrolyte

electrolyte solution of a comparable concentration. This is due to the counter-ion binding or condensation effect. This effect can be viewed as analogous to ion pair formation in simple electrolyte, and it has been demonstrated by the electrophoresis experiment on sodium poly(acrylate) (19). Results showed that some of the sodium ions did not move to the cathode but rather moved to the anode along with the polyion. This association effect is only observable at a degree of neutralization of over 60% for the polyacrylate. Therefore, counterion condensation is a function of charge density. That is to say, in extremely dilute solutions, even the strongest polyelectrolyte will not be 100% dissociated provided that its charge density is high enough. Conversely, the effect of counterion binding is less pronounced in a polyelectrolyte with a lower charge

density or in one whose ionogenic groups are spaced more widely. This is equivalent to saying that a polyelectrolyte with a lower charge density is more dissociated than one with a higher charge density. The conductivity of a polyelectrolyte solution is attributed to the polyion and to the "free" counterions. It is also true that the conductance of a polyelectrolyte solution with simple electrolytes in it is equal to the sum of the conductance of each individual species (20).

POLYELECTROLYTE REACTION

The interaction of two oppositely charged polyelectrolytes to form a single complex occurs in both natural and synthetic systems. Through the formation of a complex, the counterions (both free and condensed) achieve a state of maximum randomness and the electrostatic free energies of the ionogenic groups are minimized. Therefore, the principal driving forces for the interaction of two oppositely charged strong polyelectrolytes are probably both entropic and coulombic.

Michaels, et al. (1-3) were the first scientists in the field of polyelectrolyte research to propose a mechanism for the interaction of strong linear polyelectrolytes. Michaels' mechanism involves two pendent type polyelectrolytes with equal ionic spacings and each carrying ionic charges opposite in sign to the other. When they come into sufficient proximity, they will undergo ionic pairing with the simultaneous release of the counterions into the bulk of the solution (Fig. 4). Once an initial ionic reaction has occurred, the most probable points for further interaction are between the ions adjacent to the reacted site, and a "zippering" action thus results. The zippering of the polyions results in a highly ordered stoichiometric primary complex. Michaels claimed that this quantitative pairing of ionic groups relies heavily on the ability of long portions of the oppositely charged polyion chains to come into juxtra-

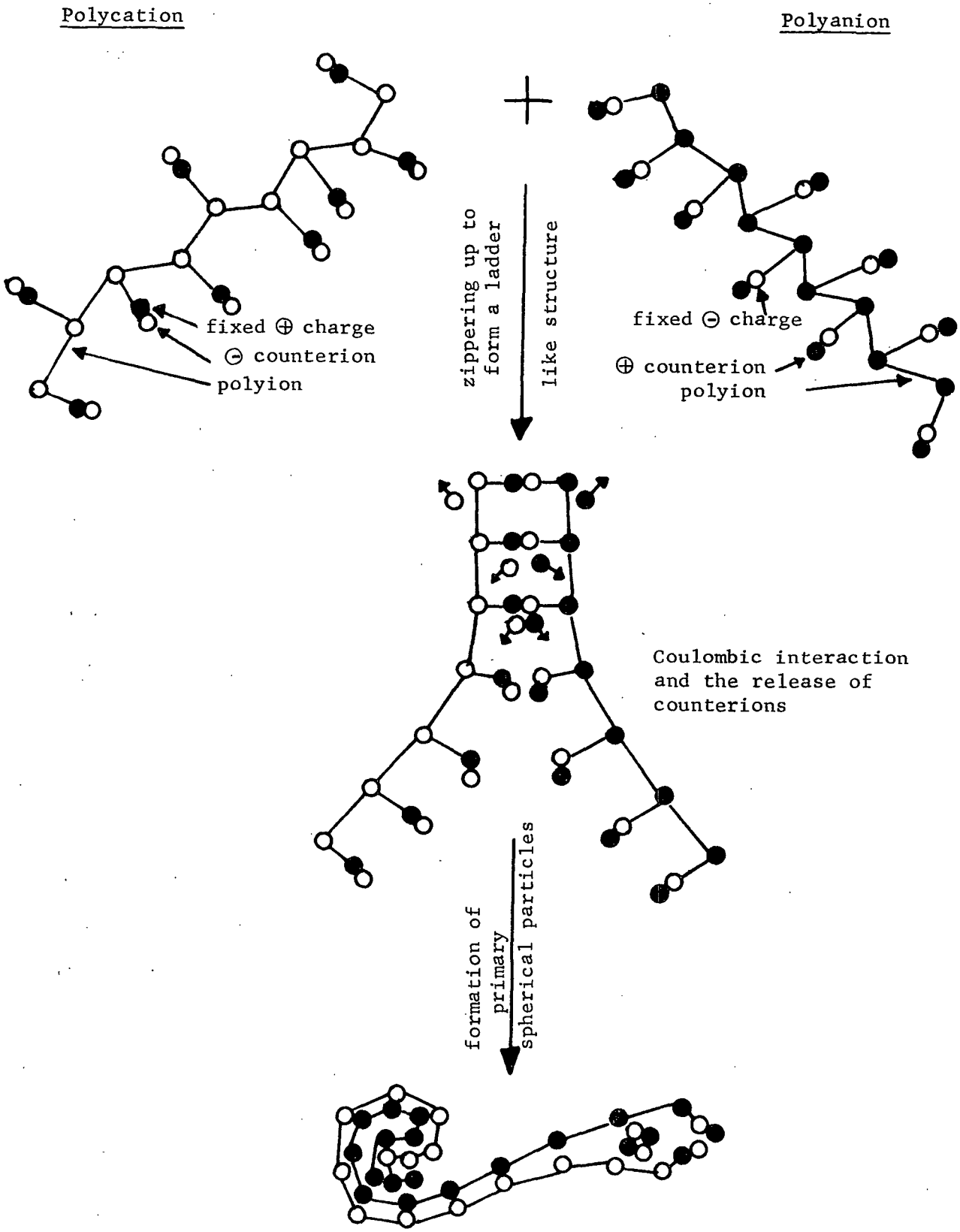


Figure 4. Possible Mechanism of Polyelectrolyte Interaction (After Michaels). All of the Counterions are Depicted as Bound to the Ionogenic Groups

position. This requirement is met by the stiff and extended conformation of the polyelectrolytes in salt-free solutions. As the zippering proceeds, the part that is already fastened starts to roll up into tiny spherical particles. This is probably due to hydrophobic interaction* between the hydrocarbon portions of the neutralized polyelectrolytes. These primary particles may later agglomerate into a precipitate.

Michaels found that this model is only valid for neutralized polybases and polyacids but does not apply to the free acids and bases. The reason for this is because the hydronium and hydroxyl ions are much more mobile ions than, for example, a sodium ion or a chloride ion. Therefore, the interaction between free polybases and polyacids involves much faster kinetics and the complex from such a reaction assumes a random structure which Michaels had called a "scrambled-salt." This mechanism is also invalid for the reaction of polyelectrolytes in solutions with a large amount of salt. The electrostatic shielding effect and the random coil conformation of the polyions make the formation of a complex with ordered structure impossible.

Michaels' mechanism was designed to explain the completeness of interaction between two polyelectrolytes with equal ionic spacings in the system he studied. In this thesis, similar ideas were used to propose mechanisms for the formation of complexes for strong polyelectrolytes with unequal ionic spacings.

*See Appendix VI for discussion of hydrophobic interaction.

A BRIEF ACCOUNT OF POLYELECTROLYTE COMPLEXATION RESEARCH

The earliest definitive studies of ionic interacting organic polymers could be attributed to those of Bungenberg de Jong, et al. (21,22) in the early 1930's. Out of their interest in biocolloidal systems, they found that the interaction between certain water-soluble polyelectrolytes, such as gelatin and gum arabic, resulted in the separation of two liquid phases, called "complex coacervation." Coacervation occurred when one of the polymers was negatively charged and the other positively charged; such reactions were found to be dependent upon the temperature, pH, and ionic strength of the solution phase.

Veis, et al. (23) studied gelatin interactions and they assumed that interaction between two oppositely charged polyions in salt-free solutions would result in the formation of aggregates of the component polyions. Their assumption is clearly justified by results obtained in the studies of complex formation involving oppositely charged polyelectrolytes.

In the 1940's, Fuoss and Sadek (4) showed that the yield of complex formation between poly(vinyl sulfonate) and poly(4-vinyl-N-n-butylpyridinium bromide) was dependent upon the order of mixing of the component polyelectrolytes and stoichiometric combination was not observed in this system. It was also observed that polyelectrolytes of low molecular weight or of low degree of polymerization (DP) did not interact to form a complex.

In the 1950's, Terayama (5), Okimasu (6,7), Senju (8-10), and Tanii (11) of Japan introduced an analytical method which proposed the quantitative determination of polyelectrolytes by titration with a standard polyionic material carrying opposite charges which they had called colloid titration. These investigations suggested that they were able to determine quantitatively various anionic polymers such as pectin, agar, tannin, sodium carboxymethyl cellulose,

lignosulfonic acid, alginic acid, gum acacia and chondroitin sulfuric acid and even amphoteric polymers such as proteins in their aqueous solutions. The structures of most of these polyanions are uncertain and the distribution of ionogenic groups in the polyions is unknown. The analysis involved the mixing of a known amount of an incompletely characterized "standard" polycation (glycol chitosan or trimethylglycol chitosan) and the unknown polyanion. The excess polycation and thus the amount of polyanion was determined by back titration with polyvinyl sulfate; the end point of which was determined by the color change of an indicator or by the sudden precipitation of the complex. In this case, the results obtained for the determination of pectin from colloid titration and from chemical analyses agreed quite harmoniously and a one-to-one combination between the polyions was inferred. However, a comparison between the results of colloid titration of the rest of the aforementioned polymers and detailed chemical analyses was not made. Nevertheless, it was believed that any two oppositely charged polyelectrolytes will react stoichiometrically in dilute solutions to produce a water-insoluble precipitate. With the establishment of colloid titration, these investigators became preoccupied with the extension of the applicability of this method to other colloidal systems. However, a systematic program to investigate the specificity of the stoichiometric combination between these oppositely charged polyelectrolytes or the mechanism of precipitation of the complex had never been undertaken. It is also unfortunate that the investigation of colloid titration seems to have faltered and not much progress has been published in recent times.

In the mid-60's, Michaels and Miekka (1) reported on the interaction between sodium poly(styrene sulfonate), NaSS, and poly(vinyl benzyltrimethylammonium chloride), VBTAC, and on the composition and properties of the resulting complex. These two polyelectrolytes have nearly equal ionic spacings, and their

polyion complex was found to be electrically neutral and contained almost exactly stoichiometric amounts of the component linear polyions and, furthermore, contained none of the counterions that were initially associated with the individual polymers. This phenomenon has been confirmed by conductometric studies carried out by Mir, et al. (2). Michaels' results also indicated that the polymers combined in some highly ordered fashion other than by random interaction between the polyions. In contrast to Fuoss' results, the yield of the complex and the stoichiometry of interaction were independent of the relative amounts of the polyelectrolytes or the order of mixing.

In this decade, research in the field of polyelectrolyte interaction has been dominated by the Japanese. Tsuchida, et al. (24) examined the reaction of NaSS and poly[(N,N,N',N'-tetramethyl-N-p-xylene)ethylenediammonium dichloride] and obtained a nonstoichiometric and soluble complex.

The formation of polyion complexes between a strong quaternary ammonium polycation carrying charges in the chain backbone and a weak polycarboxylic acid was also studied. Tsuchida, et al. (25) found that the compositions of the complexes were a function of the degree of dissociation of the polycarboxylic acid. Furthermore, it was found that in addition to coulombic forces, hydrophobic interaction played an important role in the complexation of these polyelectrolytes. The latter discovery was exemplified by the formation of higher structure by the polyelectrolytes (such as fibers) in an extremely concentrated salt solution (26,27). Abe, et al. (28) also studied the reaction of poly(methacrylic acid) and a quaternary ammonium polymer similar to that studied by Tsuchida (25). Abe found that the forms of the complex were variable. The polyion complex could assume either a soluble state, a coacervate form or a precipitate form upon changing such conditions as the polyion concentration, pH, degree of neutralization and the ionic strength.

Hosono, et al. (29) studied the interaction between a sulfated and an aminoacetylated derivative of poly(vinyl alcohol). Interestingly enough, it was found that the composition of the complex produced varied according to the rate of stirring.

Interest in the study of ionic polysaccharide interactions has been revived recently. Nakajima and Shinoda (30) investigated the formation of complexes between glycol chitosan and hyaluronic acid, chondroitin sulfate A, chondroitin sulfate C or sulfated cellulose. Their results indicated that the complexes formed were nonstoichiometric. Nakajima and Shinoda then concluded that the uneven distribution of ionizable groups along the polysaccharide chains might have been the cause of the formation of the nonstoichiometric complexes. Hara and Nakajima (31) studied the formation of a polyelectrolyte complex between heparin and aminoacetylated poly(vinyl alcohol). The complex obtained was also nonstoichiometric.

Fukuda and Kikuchi (32) reacted solutions of sodium dextran sulfate and chitosan under various conditions. They found that the complexes were grossly nonstoichiometric and that the mole ratio of nitrogen to sulfur in the complexes was dependent upon the pH and the mixing ratio of the complexing agents.

In a pair of papers, Abe and Tsuchida (33,34) discussed the complexation of poly(L-glutamic acid) with various strong polycations. They concluded that the conformation of the complexes varied with the structures of the component polycations. These structures referred to the position of active sites, ionic separation between adjacent ionic sites, rigidity and hydrophobicity. The interaction between DNA and the symmetrical and asymmetrical ionene polymers were studied by Mita, et al. (35). They found that the ratio of DNA to ionene polymer in the complex was dependent on the charge density of the DNA molecule.

Recently, Abe, et al. (36) have demonstrated the ability of a synthetic polyelectrolyte to react selectively with one component polymer out of three or more polyelectrolytes in a mixture to form an interpolymer complex as in many biological systems. This selectivity of the polyelectrolyte was realized only under very carefully controlled conditions of pH, ionic strength, temperature, solvents and interaction forces.

PRESENTATION OF THE PROBLEM AND THESIS OBJECTIVES

The Introduction and the brief review on polyelectrolyte complexation research suggests that our present knowledge concerning the effect of ionic spacing on the stoichiometry of polyelectrolyte interaction needs improvement. This suggestion is reflected by the conflicting views of Michaels (1) and Terayama (5) on this subject.

In the establishment of the method of colloid titration for the quantitative analysis of unknown biopolyelectrolytes, Terayama, et al. (5) based the method entirely on the assumption that all polyelectrolytes react stoichiometrically regardless of the ionic spacing or of the structure. Unfortunately, they were unable to present sufficient evidence to justify their assumption. As a result, the validity of this technique as an analytical procedure for polyelectrolytes is highly questionable.

Quite to the contrary, Michaels, et al. (1-3) carried out careful and rather extensive studies of the reaction between two well-defined synthetic polyelectrolytes. They suggested that the stoichiometry of polyelectrolyte interaction in their system may be attributed to the equality of ionic spacings in the interacting polyelectrolytes. Furthermore, the results of recent Japanese studies on the interactions between ionic polysaccharides and between other synthetic polyelectrolytes with unequal ionic spacings (24,25,29-34) tend to disagree with Terayama's assumption. However, the structures, the nature and the chemical compositions of most of the polyelectrolytes and the systems used in their studies were not characterized adequately.

Stemming from the above discussion, it is obvious that a satisfactory explanation for the specificity and completeness of the polycation-polyanion interaction is still lacking.

This thesis was proposed to evaluate the roles of ionic spacing, polydispersity and the degree of polymerization in determining the stoichiometry of polyelectrolyte interactions. By studying the reactions of well-characterized polyelectrolytes in a well-defined system, the mechanism(s) of polyelectrolyte interaction may be further understood.

EXPERIMENTAL APPROACH

In this thesis research, strongly ionized polyelectrolytes with well-defined structures and solution properties were chosen. In order to evaluate the effect of ionic spacing on the stoichiometry of polyelectrolyte interaction, the reactions of a polyanion with a homologous series of polycations with different ionic spacings were studied in salt-free solutions. The polycations selected were a series of ionene bromides. The ionene polymers were first described by Fuoss (4) as early as 1948 but were only successfully synthesized and fully characterized more recently by Rembaum, et al. (37-40). Ionenes are linear (integral type) copolymers of N,N,N',N'-tetramethyl-α,ω-diaminoalkanes and α,ω-dibromoalkanes. Symmetrical ionenes with controlled ionic spacings could be synthesized by selecting the diaminoalkanes and dibromoalkanes with an equal number of methylene groups. They are named ω,ω-ionene halides; ω being the number of methylene groups separating the ionogenic groups. The symmetrical ionenes are water soluble, and in the absence of added salts, the quaternary ammonium groups are dissociated and the polyions are essentially fully extended rods (39). Other advantages of the ionenes include the ease of their syntheses, the lack of chain branching and the ease in varying the ionic spacings.

The distance of separation of two ionogenic groups was measured by constructing scale models of the polyelectrolytes involved. This method gives a good approximation of the ionic spacing. The ionic spacing of 3,3-ionene bromide was found to be 5.0 A (Fig. 5a).

In a study of the intrinsic viscosities of the low molecular weight fractions of 100% neutralized poly(acrylic acid) it was found that this molecule assumes the rigid rod form in salt-free dilute aqueous solutions (41). Furthermore, in a recent conformational analysis of syndiotactic sodium poly(acrylate)

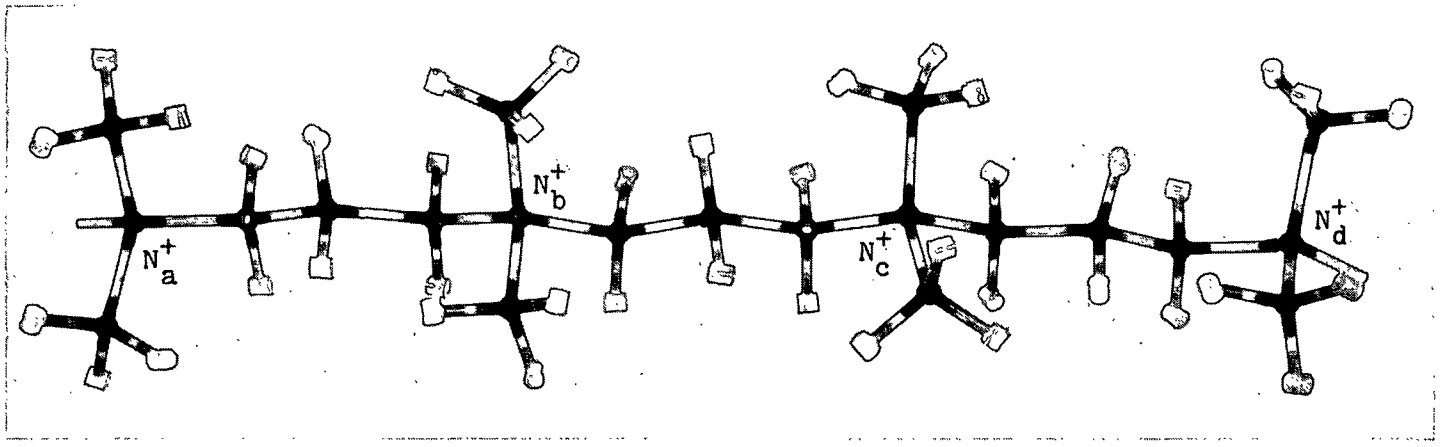


Figure 5a. Scale Model of 3,3-Ionene Bromide Tetramer. The Spacing Between Quaternary Ammonium Groups (Labeled) is 5.0 A. Two Methyl Groups are Attached to the Ammonium Ions. Adjacent Ammonium Ions are Separated by Three Methylene Groups

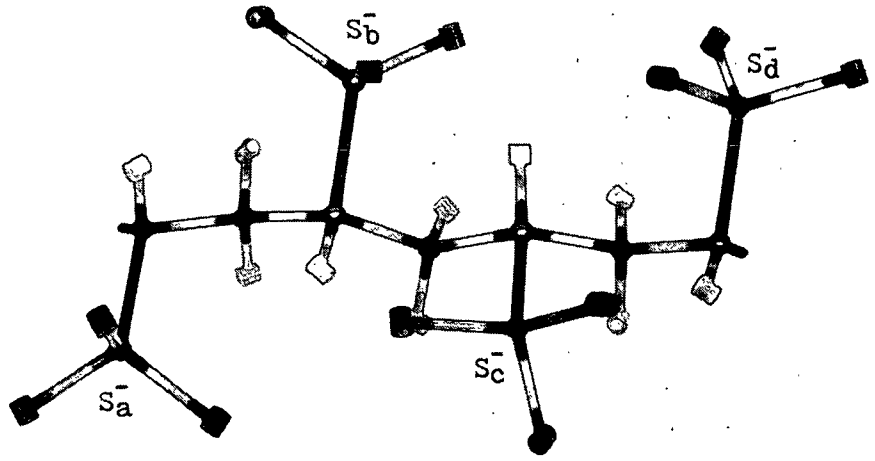


Figure 5b. Scale Model of Syndiotactic Poly(vinyl Sulfonate) Tetramer. The Ionic Spacings Between Adjacent and Alternate Sulfonate Groups (Labeled) are Both 5.0 A. Adjacent Sulfonate Groups are Separated by One Methylene Group

by rotational isomeric state approximation, Allegra, et al. (42) showed that the energy of the TT (trans,trans) diad (fully extended chain) is lower than that of the GG (gauche,gauche) diad by about 2.1 Kcal/mole. This indicates that the conformation of a syndiotactic polyelectrolyte similar to sodium poly(acrylate) would also assume a fully extended planar zigzag conformation. Syndiotactic sodium poly(vinyl sulfonate) is a pendent type vinyl polyelectrolyte and it is very similar to sodium poly(acrylate). Its fully extended polyion is found to have an average ionic spacing of 5.0 A between adjacent and alternate sulfonate groups (Fig. 5b). For these reasons, sodium poly(vinyl sulfonate) was chosen for this research.

The selected series of polycations was: 3,3-ionene, 4,4-ionene, 5,5-ionene and 6,6-ionene bromides, in ascending order of the ionic spacings. The ratios of the ionic spacings of these ionene bromides to that of the sodium poly(vinyl sulfonate) are: 1.0, 1.3, 1.6 and 1.8, respectively.

Various molecular weight fractions of the polyelectrolytes were reacted to study the effect of molecular weight on the stoichiometry of polymer interaction. In the assessment of the effect of polydispersity on the stoichiometry of polyelectrolyte interaction, an unfractionated sodium poly(vinyl sulfonate) was reacted with an unfractionated series of ionene bromides. These results were then compared with those on the fractions.

Since the selected polyelectrolytes assume a rigid rodlike conformation in their salt-free aqueous solutions, the excluded volume of these polyions is expected to be quite large. To avoid the adverse effect of intermolecular entanglement, the concentration of the polyelectrolyte solutions should be kept as low as possible. A polyelectrolyte concentration of 0.001M with respect to the monomer molecular weight was found to be appropriate. At this concentration, the polyelectrolyte molecules could be shown to be independent of one another by

comparing the excluded volume of the polyelectrolyte [as calculated by Zimm's (43) method] with the volume that is available to the polyelectrolyte in the solution.

The experimental program was divided into four major phases: (1) the syntheses of the selected ionene bromides and the sodium poly(vinyl sulfonate); (2) the fractionation of the selected polyelectrolytes by gel permeation chromatography; (3) the physical and chemical characterization of the various molecular weight fractions of the selected polyelectrolytes; and (4) the investigation of the effects of ionic spacing, the degree of polymerization and polydispersity on the stoichiometry of polyelectrolyte interaction by complexation experiments.

EXPERIMENTAL MATERIALS, EQUIPMENT AND PROCEDURES

SYNTHESIS OF N,N,N',N'-TETRAMETHYLPENTANE-1,5-DIAMINE

The title compound was synthesized according to the method published by Giumanini, et al. (44) on the exhaustive N-methylation of the primary α,ω-alkanediamines. A possible mechanism for the N-methylation of primary diamines by formaldehyde and sodium borohydride is depicted in Fig. 6. The mechanism is simplified by only taking into account the chemical reactions that are occurring at one of the two primary amine groups.

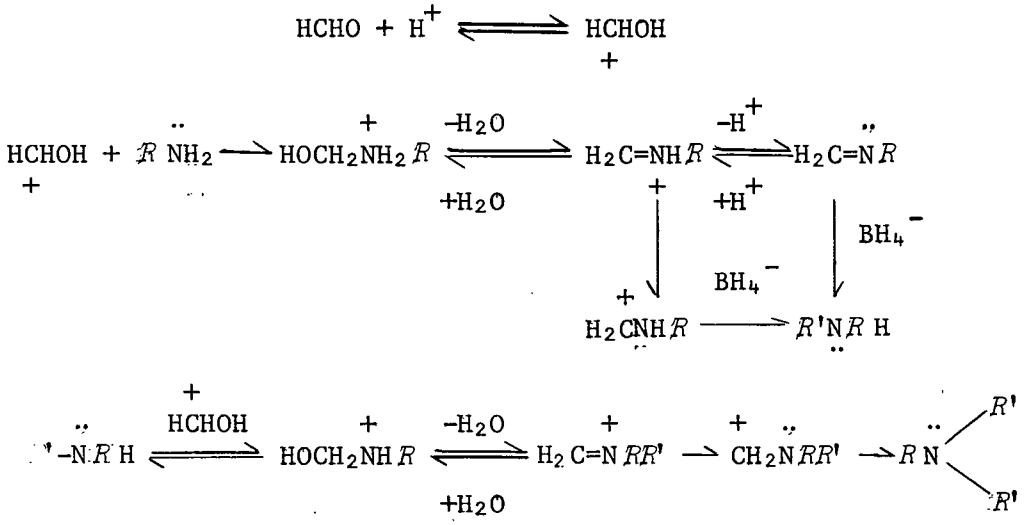


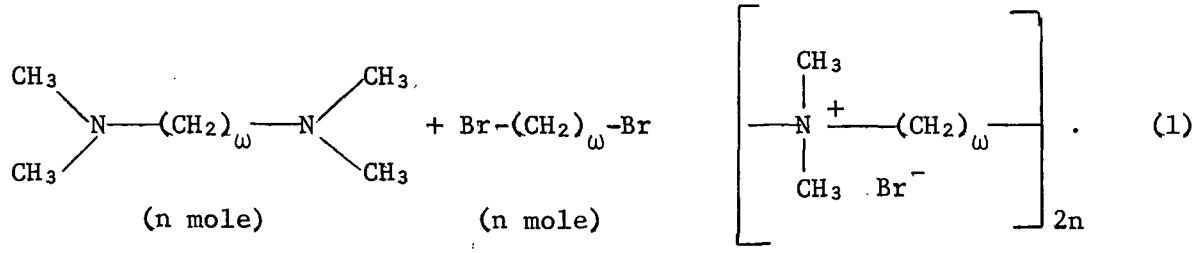
Figure 6. A Possible Mechanism of the N-Methylation of Diamines (After Giumanini). *R* Stands for the Alkyl Chain and *R'* Stands for a Methyl Group

Thus, 1,5-pentanediamine (5.05 g, 0.01 equiv. NH) was methylated with sodium borohydride (7.6 g/0.1 mole NH) in 3M sulfuric acid (18.3 mL) and 38% aqueous formaldehyde (28 mL), with control of temperature (0-20°C) under efficient stirring in an open flask. After the addition of sodium borohydride was completed, the mixture was made strongly acidic with concentrated sulfuric acid, extracted four times with ether and the ether extract was discarded. The acidic aqueous phases were rendered strongly alkaline with an excess of potassium hydroxide pellets and were extracted four times with ether. The crude product was

isolated by evaporating the ether. Distillation of the crude product through a semimicro column afforded the pure N,N,N',N'-tetramethylpentane-1,5-diamine. The final product was collected and dried over molecular sieve.

SYNTHESES OF THE SELECTED SYMMETRICAL IONENE BROMIDES

The ionenes are water-soluble linear copolymers of N,N,N',N'-tetramethylalkane-α,ω-dibromoalkanes, for which methods of synthesis have been well documented (37-40,45). Symmetrical ionenes are synthesized by selecting the diaminoalkanes and the N,N,N',N'-tetramethylalkanediamines with equal numbers of methylene groups. The formation of the ω,ω-ionene bromides (where ω stands for the number of methylene groups between two successive charges) is illustrated by Equation (1).



(n mole) (n mole) (1)

For the syntheses of the selected series of ionene bromides, all of the necessary reagents were obtained through commercial sources (Aldrich Chemicals, Inc.) except N,N,N',N'-tetramethylpentane-1,5-diamine, which was synthesized in this laboratory.

The ionene bromides were synthesized through the reaction of equimolar quantities of α,ω-dibromoalkanes and N,N,N',N'-tetramethylalkane-α,ω-diamines in a 4:1 (v/v) mixture of dimethylformamide (DMF) and absolute methyl alcohol. For example, in the preparation of 3,3-ionene bromide, 1,3-dibromopropane and N,N,N',N'-tetramethylpropane-1,3-diamine are required.

Two batches of each of the ionene bromides were synthesized according to the above standard method of preparation. Nevertheless, each of the ionene bromides was prepared a little differently than the others in terms of the

concentration, the reaction time and the reaction temperature, etc. By varying these parameters appropriately, the average molecular weights of the polymers could be controlled.

For brevity, the general procedures of the synthesis will be presented by using symbols for the variable parameters. The actual values of these parameters for each individual synthesis are presented in Table I.

TABLE I

REACTION CONDITIONS FOR THE SYNTHESIS OF IONENE BROMIDES

Batch	Ionene	Mass of DBA[a], a (g)	Mass of TMAD[b], b (g)	Concentration, d (molar)	Temperature, t (°C)	Time, W (hr)
1	3,3	6.18	3.95	0.2	80	163
2	3,3	20.60	13.15	2.0	25	340
1	4,4	6.54	4.46	0.2	72	163
2	4,4	14.54	9.58	2.0	25	340
1	5,5	6.90	4.75	0.2	72	166
2	5,5	5.03	3.47	2.0	25	340
1	6,6	5.03	3.48	1.0	25	260
2	6,6	16.77	11.61	2.0	25	340

[a]DBA stands for the dibromoalkane.

[b]TMAD stands for the N,N,N',N'-tetramethylalkane-diamine.

During the synthesis, about half of the volume of solvent that was required was added to a round-bottom flask. The solvent was then thermally equilibrated to a temperature of t°C in a water bath. The dibromoalkane, DBA (a gram), and the N,N,N',N'-tetramethylalkane-diamine, TMAD (b gram), were added simultaneously. The volume of the reaction mixture was adjusted with solvent such that a concentration of d M of each reagent was attained. The flask was stoppered and the reagents were allowed to react for a period of W hours. The crude product was separated by the evaporation of the solvent. The crude ionene bromide was then pulverized and washed with acetone. The washed ionene bromide was separated by centrifugation and was then dissolved in distilled water and freeze-dried.

SYNTHESIS OF SODIUM POLY(VINYL SULFONATE)

Sodium poly(vinyl sulfonate), NaPVS, was synthesized by the method of Eisenberg and Ram Mohan (46). This method involved the radical polymerization of sodium vinyl sulfonate in aqueous solution by ultraviolet irradiation without the aid of an initiator.

A 40% (w/w) aqueous solution of sodium vinyl sulfonate (60 mL) was concentrated to 75% on a rotary evaporator. The concentrated solution was polymerized under nitrogen in a quartz tube placed inside a photoreactor equipped with 16 mercury lamps (2573 A). The arrangement of the apparatus is shown in Fig. 7. After 24 hours, the viscous polyelectrolyte solution was diluted with a small volume of water for ease of removal from the quartz tube.

In order to obtain a polyelectrolyte with a higher molecular weight, a second batch of NaPVS was prepared in a similar fashion except the reaction time was extended to 80 hours.

The crude product was placed in a cellulose acetate bag and was dialyzed against distilled water. The purified polyelectrolyte solution was concentrated and was then freeze-dried.

STRUCTURAL CONFIRMATION OF THE SYNTHESIZED COMPOUNDS

The structures of the selected ionene bromides and of the sodium poly(vinyl sulfonate) (both Batch 1) and the N,N,N',N'-tetramethylpentane-1,5-diamine (TMPD) were confirmed by proton magnetic resonance spectroscopy at 60 MHz. A Varian Associates Model A60-A analytical NMR spectrometer was used in these studies. The TMPD was also sent to The Micro-Tech Laboratories, Inc., Skokie, Illinois for the elemental analyses of carbon, nitrogen and hydrogen contents. The TMPD was also analyzed for purity by gas chromatograph using an O.V. 17 column (6 ft

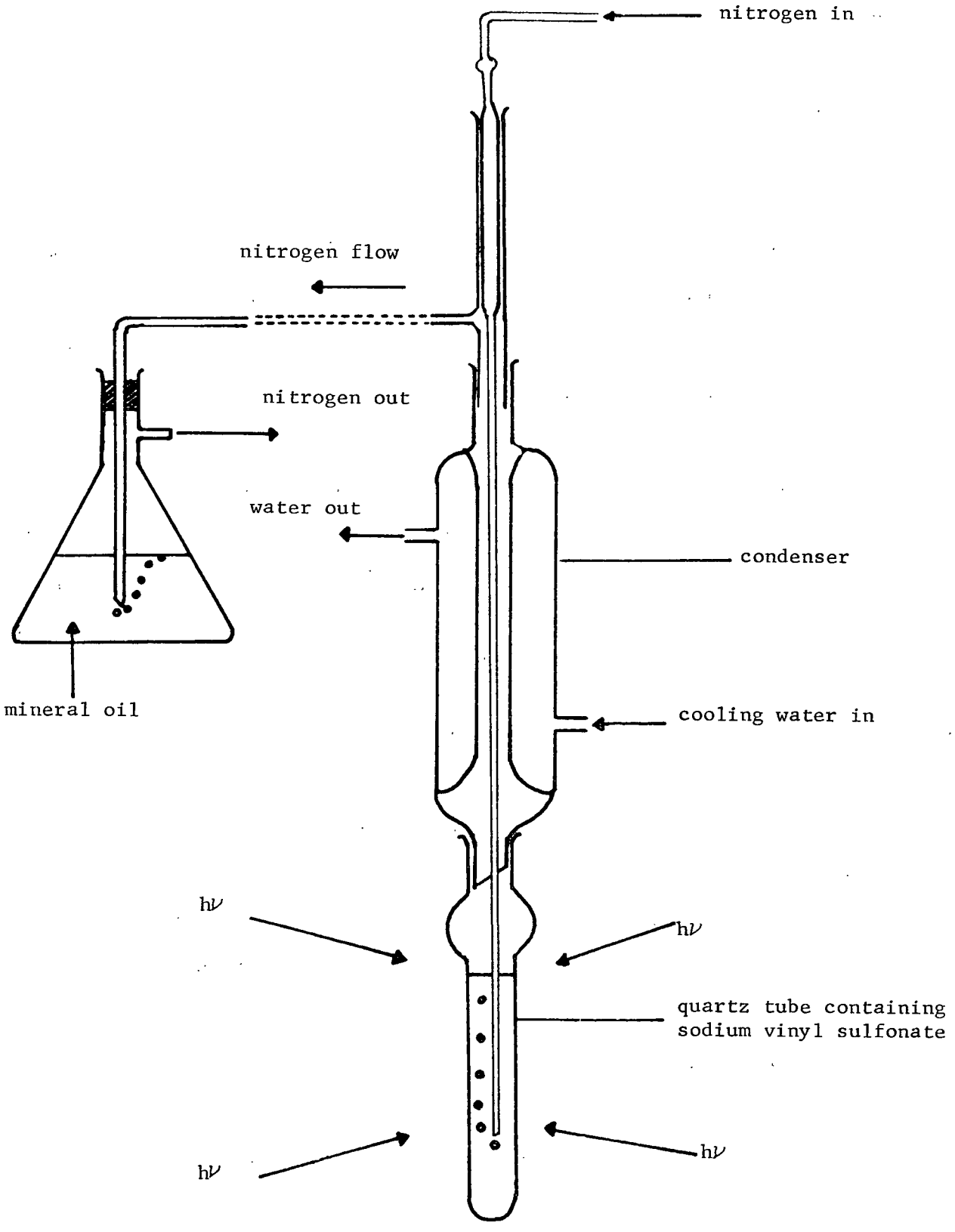


Figure 7. Apparatus for the Synthesis of Sodium Poly(vinyl sulfonate)

x 1/8 inch). The solvent used in this analysis was diethyl ether. The temperature of the column, injector and detector were set at 100, 200, and 230°C, respectively.

FRACTIONATION OF THE POLYELECTROLYTES

The technique of preparative gel permeation chromatography (GPC) was employed to fractionate the polyelectrolytes into narrow molecular weight fractions. The column used was a glass column (3 ft x 1 inch). The column packing material was a Bio-Gel P-series (Bio-Rad Laboratories) chromatographic gel which was previously hydrated and swollen in a buffer solution. The suspension was vacuum degassed. The ionic strength buffer solutions for the ionene bromides and for the sodium poly(vinyl sulfonate) were 0.4M KBr and 0.5M NaCl, respectively. The 0.4M KBr solution is a Θ-solvent for the ionenes (39). The salts screen the charges on the polyelectrolytes and prevent their adsorption onto the glass walls and onto the gel during fractionation. The swollen gel was allowed to settle in the column by gravity (Fig. 8a). The column was then flushed with 2 liters of solvent. The eluant stream of the column was connected to a control unit consisting of an optical unit and a refractive index monitor unit (both Pharmacia Fine Chemicals Company). The control unit was in turn connected to a chart recorder (Speedomax Model H) which traced the chromatograms. During each fractionation run, a fixed volume (25 mL) of a buffered solution of the polyelectrolyte was carefully loaded on top of the column packing with a syringe equipped with a long needle. The fractions were collected in numbered glass culture tubes arranged on an automatic rotating fraction collector (Fig. 8b). The like fractions from all of the runs were combined and were stored in polyethylene bottles at 4°C. The fractionation of the selected polyelectrolytes is summarized in Table II.

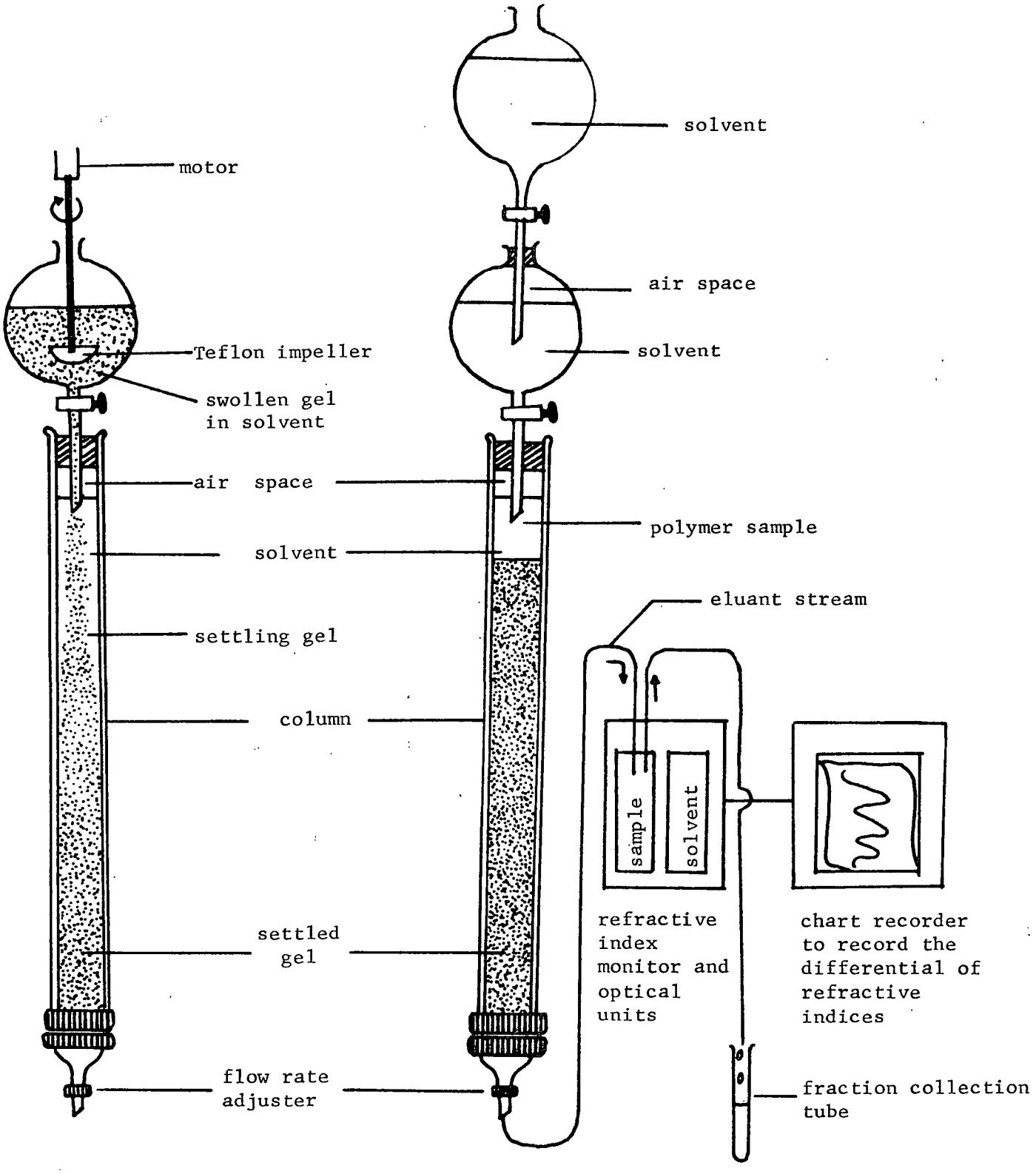


Figure 8a. The Preparation of GPC Column by the Gravitation Settling of Swollen Gels

Figure 8b. A Fractionation in Progress

TABLE II

CONDITIONS FOR THE GPC FRACTIONATION OF THE POLYELECTROLYTES

Polyelectrolyte[a]	Column Packing	Concentration of Solution (%)	Number of Fractionations	Flow Rate (mL/Hr)
NaPVS	P60/P100[b]	2.6	10	34
3,3-Ionene	P100	2.5	16	38
4,4-Ionene	P100	2.5	18	44
5,5-Ionene	P100	1.5	10	46
6,6-Ionene	P100	2.5	19	40

[a]The second batch of the polyelectrolyte was fractionated.

[b]The ratio by weight of the gels was unity.

REMOVAL OF SALTS FROM THE POLYELECTROLYTE FRACTIONS

Since the stoichiometry of polyelectrolyte interactions was to be studied in low ionic strength conditions, it became necessary to remove the added salts in the various polyelectrolyte fractions. This was accomplished by continuous dialysis against distilled water using an Amicon Ultrafiltration System. The system (Amicon stirred cell Model 202) consisted of a pressure source, a reservoir, a concentration/ultrafiltration selector, the stirred cell membrane and the magnetic stirrer. The following diagram (Fig. 9) illustrates the essential components of the system. The instructions for operation are described in the manual supplied by the manufacturer (47).

In the removal of salts from the polyelectrolyte fractions, a UM-2 membrane was used for those with lower molecular weights (<5,000) and a UM-10 membrane was used for the fractions with molecular weights that exceeded this lower limit. Thus, a combined fraction was first concentrated to about 1 dL. The pressure was set at 45 psig such that a flow rate of about 1 mL/min was attained. The ultrafiltration was considered complete when no salt could be detected in the solution.

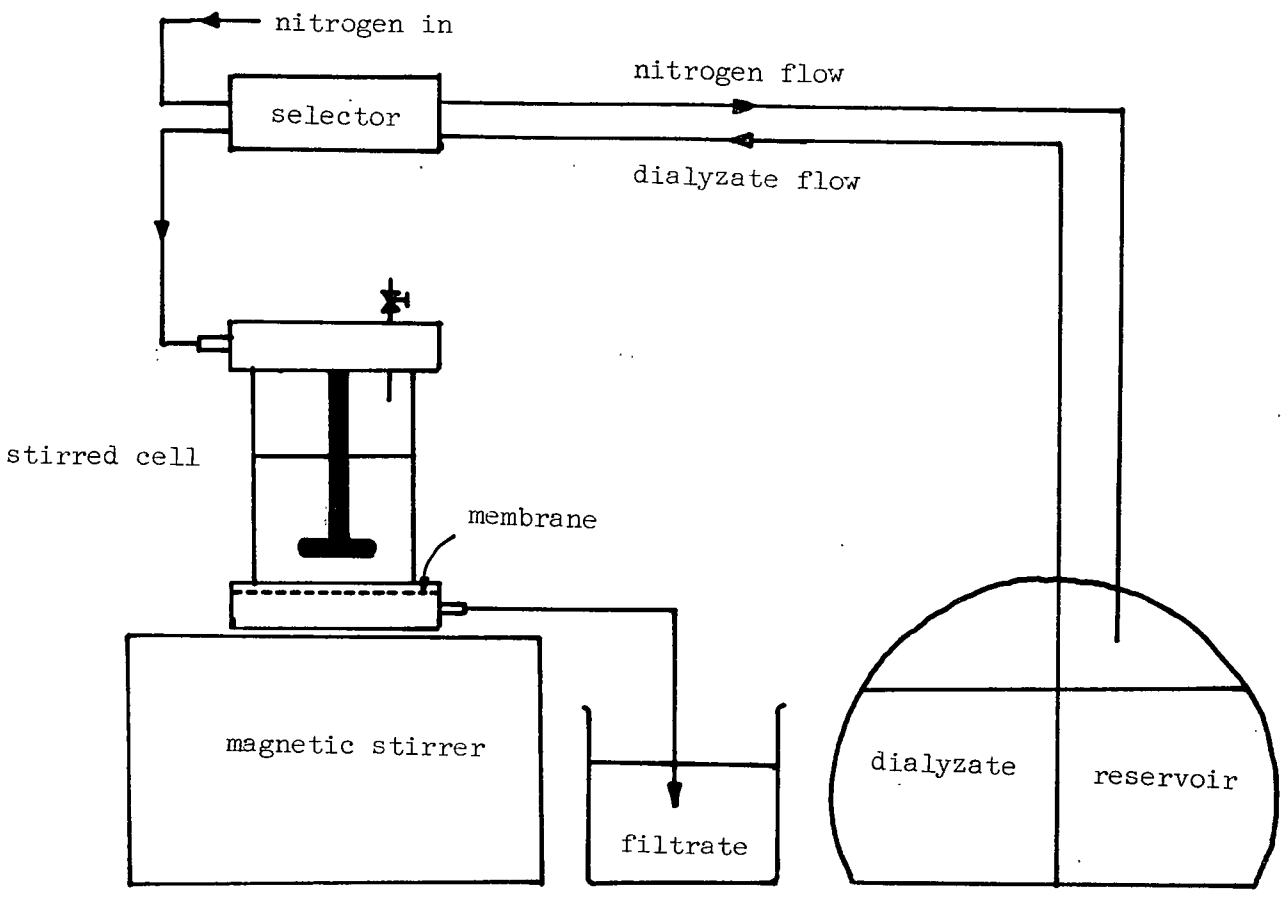


Figure 9. Amicon Stirred Cell Ultrafiltration System

In order to determine the completeness of diafiltration, the sodium ion content in the filtrate was determined at intervals by flame photometry on a Beckman Model DU spectrophotometer. The diafiltration of the NaPVS fractions was completed when no sodium could be detected in the filtrate.

The amount of residual potassium bromide in the ionene bromide fractions was determined by an analysis of the potassium ion content on a Perkin-Elmer flame emission spectrophotometer. The diafiltration was considered complete when no potassium ion ($[K^+] < 1$ ppm) was detected in the polyelectrolyte solution in the stirred cell. Depending on the size of the combined fraction before the initial concentration, the complete removal of salts usually occurred within a range of 10 to 100 sample volume turnovers. The purified polyelectrolyte fractions were concentrated and freeze-dried.

DETERMINATION OF MOLECULAR WEIGHTS BY ULTRACENTRIFUGATION

When a suspension is left to stand, the suspended particles gradually sink to the bottom under the influence of gravity and the mass of the particles can be calculated from the sedimentation rate. Macromolecules behave in a similar fashion but their sedimentation may only be observed in a very strong centrifugal field. Omitting the discussion of the complex theory and the derivation of lengthy equations, the apparent weight average molecular weight, $M(w)_{app}$, is calculated from the concentration distribution of the macromolecules in the centrifugal field by the sedimentation equation (48):

$$M(w)_{app} = [2RT/\Omega^2(1-\bar{v}_2^*\rho)][d(\ln C_x)/d(x^2)], \qquad (2)$$

where R = gas constant

T = absolute temperature

Ω = angular velocity of the rotor

ρ = density of the solution (whereas in the case of an extremely dilute solution, the density of the solvent is frequently used)

$\bar{v}_2^*$ = apparent partial specific volume of the polymer

C_x = concentration in fringes at distance x from the axis of rotation

From a plot of $\ln(C_x)$ *versus* x^2, the slope, $d(\ln C_x)/d(x^2)$, is proportional to the apparent weight average molecular weight.

The molecular weights of the unfractionated ionene bromides (Batch 1) and the unfractionated NaPVS (Batch 1) were determined by the sedimentation equilibrium method. Meanwhile, the molecular weights of the polyelectrolyte fractions were determined by the so called "Short Column Sedimentation Equilibrium Method" on the ultracentrifuge. The instrument used was a Beckman/Spinco Model E analytical ultracentrifuge equipped with a Rayleigh optical system. All of the measurements were made at 25°C. The experiments were performed at a rotor speed

of 30,000 rpm. The solvent for the ionene bromides was a 0.40M KBr solution and that for the NaPVS fractions was a 0.50M NaCl solution. The sample concentration was kept low at 0.1%. The theory and practice of sedimentation equilibrium has been reviewed extensively by Hostetler (49) and Kindler (50) and therefore will not be discussed. The theory of the "Short Column Sedimentation Equilibrium Method" is identical to that of the sedimentation equilibrium method; the only difference is that a sample cell with short columns was used so that equilibrium could be attained at a much shorter period of time. The practice and application of this technique were also discussed elsewhere (48).

During a run, Rayleigh optics were used to record C_x. Fringe numbers and their positions were determined from film negatives of the interference patterns with an x-y microcomparator. The concentration across the sample cell in fringes was used to evaluate Equation (2) with the aid of an IBM 360/44 computer using the sedimentation equilibrium analysis program "MOLWT." This program was originally written by Teller (51) and was later modified by the Institute staff to be run on the Institute computer.

DETERMINATION OF PARTIAL SPECIFIC VOLUMES

In the calculation of the weight average molecular weight of a polyelectrolyte from ultracentrifugation data its partial specific volume, $\bar{v}_2$, must be known. Theoretically, the specific volume (reciprocal density) $\bar{v}$, of any two-component system can be represented precisely by the equation (52):

$$\bar{v} = (\bar{v}_2^* - \bar{v}_1^o)w_2 + \bar{v}_1^o \quad , \qquad (3)$$

where w_2 = weight fraction of the polyelectrolyte

$\bar{v}_1^o$ = specific volume of the solvent

$\bar{v}_2^*$ = apparent partial specific volume of the polyelectrolyte

The quantity $\bar{v}_2^*$ is independent of the polyelectrolyte molecular weight and it contains the parameters of nonideal mixing of both the solvent and the polyelectrolyte. Generally, $\bar{v}_2^*$ does not differ much from $\bar{v}_2$ if the polyelectrolyte solution is lower than 1% and if $\bar{v}_2^*$ is assumed to be independent of concentration. Therefore, the values sought in this method were $\bar{v}_2^*$ values rather than $\bar{v}_2$ values.

The apparent partial specific volumes of the ionene bromides and of the sodium poly(vinyl sulfonate) were determined in 0.40M KBr and 0.50M NaCl solutions, respectively. The densities of the solvents and of the polyelectrolyte solutions were determined pycnometrically at 25°C. A Lipkin type pycnometer (4.5 mL) was used. It was cleaned with chromic acid and was thoroughly rinsed with distilled water and then dried with absolute methanol before and after the experiment. The pycnometer was calibrated with various volumes of triple-distilled water and a calibration curve was constructed. The calibration curve enables one to determine accurately the volume of the solution being held in the pycnometer. The mass of the solution was recorded and the density was calculated. For each polyelectrolyte, the densities of its solutions at various weight fractions were determined. In all cases, the mass of the solutions was corrected for the buoyancy of air. All of the calculations involved have been reviewed in detail by Weissburger and Rossiter (52) and will not be discussed here.

When the specific volume of the solutions was plotted against the weight fractions, the quantities $(\bar{v}_2^* - \bar{v}_1^o)$ and $\bar{v}_1^o$ are the slope and intercept of the equation of the straight line obtained by performing a least squares linear regression on the two dimensional variables $(w_2, \bar{v})$ in Equation (3). The apparent partial specific volumes for the polyelectrolytes were therefore obtained by substituting $\bar{v}_1^o$ into the term $(\bar{v}_2^* - \bar{v}_1^o)$.

PREPARATION OF SOLUTIONS

In this research, triply distilled water was used as the solvent for all of the required solutions. It was boiled to get rid of dissolved carbon dioxide. While it was still hot, the distilled water was poured into clean polyethylene bottles and was tightly capped. Adsorption of the polyelectrolytes onto the glass surfaces was prevented by pretreating the glassware with a 1% aqueous solution of polyethylene glycol-20M (Union Carbide Corp.). The expression of the ionic molar concentration of the polyelectrolyte solutions was based on the molecular weight of the monomeric repeating unit, assuming that one counterion is associated with one ionic group per monomer unit.

The standard silver nitrate (0.1M) solution was prepared as precisely as possible by dissolving an accurate amount of oven-dried (110°C, 2h) analytical grade silver nitrate crystals in distilled water. The sodium bromide stock solution was prepared at a concentration of about 0.004M while the polyelectrolyte solutions were prepared at a concentration of about 0.001M. Other concentrations of these solutions were obtained by dilution of the stock solutions. The exact concentrations of the sodium bromide stock solution and of the polyelectrolyte solutions were determined quantitatively by the methods described as follows.

STANDARDIZATION OF SODIUM POLY(VINYL SULFONATE) SOLUTIONS

The sodium poly(vinyl sulfonate) solutions were standardized by measuring the sodium ion contents of the polyelectrolyte solution with a sodium ion electrode (Orion Research). A reference double junction electrode with lithium aluminum acetate as the outer filling solution was used in conjunction with the specific ion electrode. These electrodes were connected to a pH meter with digital readout and an expanded scale in millivolt response. A series of standard

sodium solutions (0-100 ppm Na^+) was prepared. Sodium ion electrodes are particularly subject to pH interference by the presence of the hydrogen ion. Therefore, to each deciliter of standard and sample solution, 2 mL of an ionic strength adjuster (25 g of ammonium chloride and 4 mL of concentrated ammonium hydroxide dissolved in 1 dL of water) was added. The electrode potential of the standard solutions and of the unknown NaPVS sample solutions were measured alternately at 25°C, allowing 3 minutes of stirring before taking each reading. The electrode potential of the standard solutions was plotted against the logarithm of the concentration. A computer program was written to facilitate the automatic processing of the experimental data and the plotting of the calibration curve for the sodium ion electrode. A section of the program also evaluates the concentrations of the NaPVS solutions. A listing of the computer program is given in Appendix I.

STANDARDIZATION OF BROMIDE-CONTAINING SOLUTIONS

The argentometric titration method was adopted for the standardization of the ionene bromide solutions and of the sodium bromide solutions. This method involves the measurement of the change in electrode potential with the precipitation of silver bromide by silver nitrate in an aqueous solution containing bromide ions. The titration of the bromide solutions with the silver nitrate solution was carried out at 25°C with stirring. The change in the electrode potential of the system was monitored with a Ag/AgCl indicating electrode and a glass reference electrode. The determination of the end point of the titration was accomplished by the so called "Gran's Method." The following is a brief discussion of the method based on an article by Liberti and Mascini (53).

When a Ag/AgCl electrode is immersed in a solution containing a known quantity of silver ions, according to the Nernst equation, the potential of the indicator electrode is:

$$E = E_o - S \log_{10}[(C_oV_o + CV')/(V_o + V')] - S \log_{10}\gamma + E_j \,, \qquad (4)$$

where V_o = initial volume of the unknown

C_o = initial concentration of the unknown

V' = volume of titrant (Ag^+ ions) added

C = concentration of the titrant

E = measured electrode potential

E_o = standard electrode potential

E_j = junction potential

S = 2.303 RT/F

R = gas constant

T = absolute temperature

F = Faraday constant

γ = activity coefficient of the silver ion

To facilitate end-point determination, all of the potentiometric titration data were analyzed according to a rectified form of the Nernst equation or the "Gran's" equation:

$$(V_o + V')10^{-E/S} = 10^{-(E_o + E_j)/S}(C_oV_o + CV') \qquad (5)$$

Under constant conditions of pH and ionic strength, a plot of $(V_o + V')10^{-E/S}$ versus V' gives rise to two rectilinear portions which intercept at the equivalence point. Being a linear function, only a few points are needed to determine the end point of the titration unequivocally without going through the end point where the electrodes are most sluggish. This method therefore also cuts down on analysis time. A computer program was written to analyze the potentiometric titration data according to Equation (5), to plot the titration curve and to determine the equivalence point of the titration and finally, to calculate the

concentrations of the unknown ionene bromide and sodium bromide solutions. A listing of the computer program is provided in Appendix II.

POLYELECTROLYTE COMPLEXATION EXPERIMENTS

In the polyelectrolyte complexation experiments, each of the four ionene bromides was reacted with the sodium poly(vinyl sulfonate) in dilute aqueous solutions. These polyelectrolyte solutions, being approximately equal in concentration, were mixed in predetermined ionic mole ratios of polycation to polyanion. Therefore, in each group of complexation experiments, unless otherwise stated, an ionene bromide was reacted with sodium poly(vinyl sulfonate) at the following eight ionic mole ratios (cationic/anionic): 0.20, 0.50, 0.70, 0.90, 1.00, 1.20, 1.45, and 2.00. The volume of sodium poly(vinyl sulfonate) (8 mL) in each experiment was kept constant. Hence, by changing the volume of the ionene bromide solution appropriately, a series of reaction mixtures with the above mole ratios could be obtained.

The two polyelectrolyte solutions were each held in a disposable polyethylene syringe with Luer-Lok™ tip mounted on a syringe pump (Sage Instruments Model 351). The syringes were connected to a delivery device by Teflon™ female Luer™ adapters, couplings and spaghetti tubings. A Cheminert™ on-off valve was installed between each delivery device and the syringe.

The design of the delivery device was such that the two polyelectrolyte solutions were mixed thoroughly at the point where the two streams meet. A modified version of this device was also made for those experiments in which no initial mixing of the solutions was desired. These delivery devices are illustrated diagrammatically in Fig. 10.

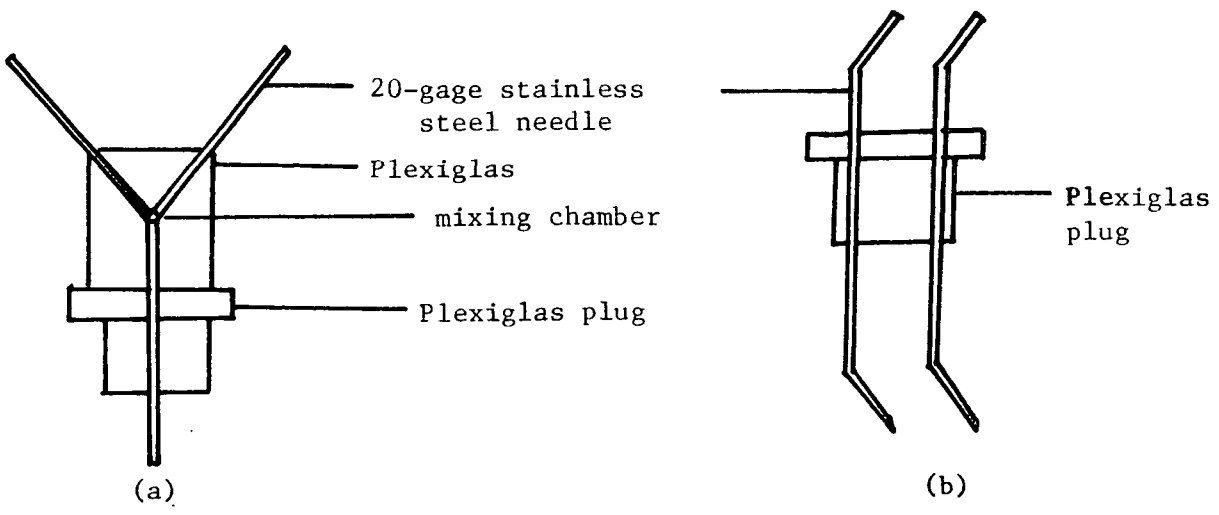


Figure 10. Polyelectrolyte Solution Delivery Devices: (a) With Mixing Chamber; (b) Without Mixing Chamber

During an experiment, the polyelectrolyte solutions were delivered drop by drop to a polycarbonate centrifuge tube that was placed in a constant temperature bath (25°C) rather than by titrating one polyelectrolyte into the other. This practice helped prevent adsorption of excess polyelectrolyte onto the primary complex. The solutions were delivered at constant and approximately equal rates that were controlled by the two calibrated syringe pumps. Each syringe pump was connected to a Gralab^{TM} electric timer which would turn off the pump automatically at any preset time. The time required for the deliveries was calculated from the flow rates and ranged from 3 to 27 minutes. A computer program was written to aid in the calculations. A listing of the computer program is given in Appendix III.

The complexation reaction at unit mole ratio of polycation to polyanion was performed by mixing equimolar quantities of the polyelectrolyte solutions. The complexation reaction at any other ionic mole ratio was performed in a similar fashion, and the excess polyelectrolyte solution was added to satisfy the predetermined condition.

The arrangement of the various apparatus required for carrying out the complexation experiments is shown in Fig. 11.

After the prescribed volumes of the polyelectrolyte solutions had been delivered, the reaction mixtures were capped and shaken mechanically for 48 hours or longer to ensure complete mixing of the polyelectrolyte solutions and to allow for any transitory phenomena.

The polyion complexes which formed a second phase were separated from the reaction mixtures by centrifugation on a preparative ultracentrifuge (Sorvall Co., Model RC2-B) at 15,000 rpm (27,600 x g) for 30 minutes.

The conductance of the supernatant solutions and that of their corresponding control solutions were measured.

The study of the stoichiometry of polyelectrolyte interaction in dilute aqueous solution is summarized in the flow diagram as shown in Fig. 12.

PREPARATION OF THE CONTROL SOLUTIONS

When an ionene bromide and the sodium poly(vinyl sulfonate) react stoichiometrically, all of the counterions will be released into the bulk of the solution. Therefore, if equimolar quantities of the polyelectrolytes are allowed to react, the conductance of the reaction mixture (with the polyion complex already removed) would be identical to that of an aqueous solution containing the stoichiometric amount of pure sodium bromide (if stoichiometry of the reaction prevails). Similarly, if unequal molar quantities of the polyelectrolytes were mixed, the conductance of the reaction mixture in this case would be equal to the sum of the conductance of an aqueous solution containing the stoichiometric amount of pure salt and that of the excess polyelectrolyte. The following example will illustrate how the control solutions for the upcoming polyelectrolyte interactions were prepared.

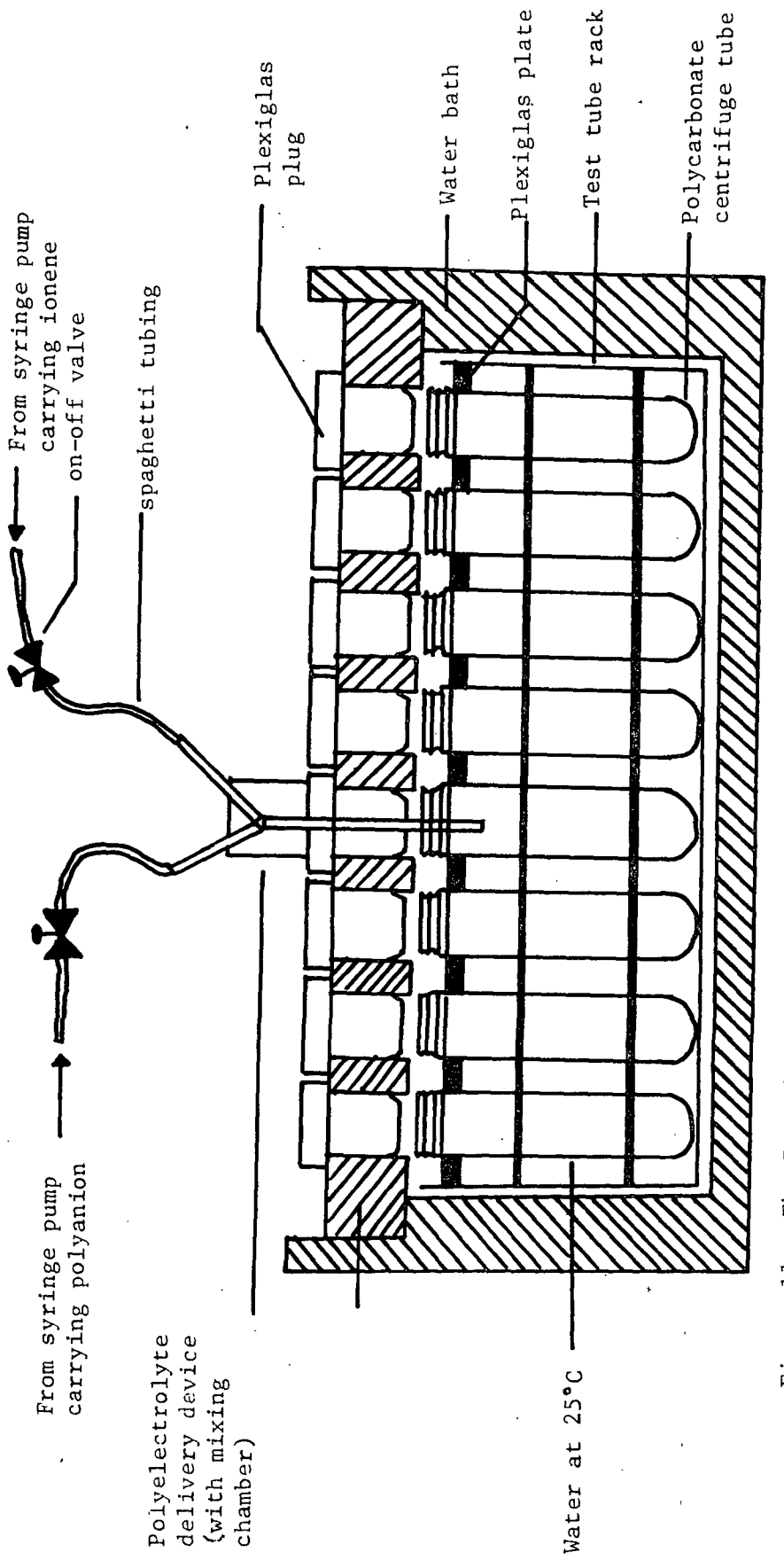


Figure 11. The Reaction Vessels and the Arrangement of the Various Apparatus

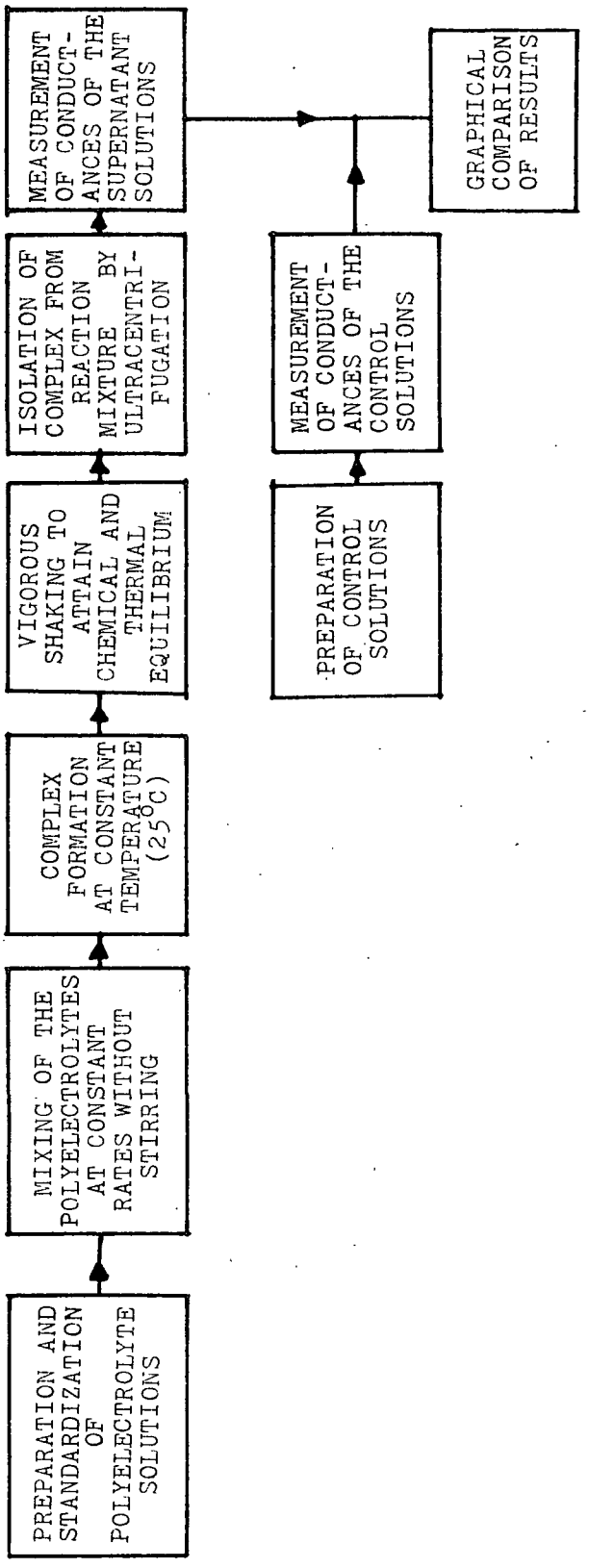


Figure 12. A Schematic Diagram Representing the Stoichiometric Study of Polyelectrolyte Interactions

Example

Concentration (M) of ionene bromide = P_1
Concentration (M) of NaPVS = P_2
Concentration (M) of NaBr stock solution = S'
Volume (mL) of NaPVS used in each reaction = 8
Volume (mL) of control solution required = 25

Case I: When the ionic mole ratio is unity

Volume (mL) of ionene required for this reaction = $8P_2/P_1$
Total volume (mL) of reaction mixture = $8 + 8P_2/P_1$
Amount (mmole) of NaBr formed = $8P_2$
Concentration (M) of NaBr in the reaction mixture = $P_2/(1 + P_2/P_1)$
There was no ionene bromide or NaPVS left unreacted
Volume (mL) of NaBr stock solution required = $25 \times [P_2/(1+P_2/P_1)]/S'$

Case II: When the ionic mole ratio is 2.00

Volume (mL) of ionene required for this reaction = $16P_2/P_1$
Total volume (mL) of mixture = $8 + 16P_2/P_1$
Amount (mmole) of NaBr formed = $8P_2$
Amount (mmole) of ionene left unreacted = $16P_2 - 8P_2 = 8P_2$
Amount (mmole) of NaPVS left unreacted = 0
Concentration (M) of the NaBr formed = $P_2/(1 + 2P_2/P_1)$
Concentration (M) of the ionene left unreacted = $P_2/(1 + 2P_2/P_1)$
Volume (mL) of NaBr stock solution required = $25 \times [P_2/(1+2P_2/P_1)]/S'$
Volume of ionene required for the control would be the same as that of the NaBr stock solution required in this special case

The volumes of the various stock solutions required to prepare the control solutions for reaction mixtures at ionic mole ratios lower or greater than unity could be calculated in a similar fashion. A computer program was written to handle these calculations. A listing of this program is given in Appendix III. Incidentally, this program also calculates the time required to deliver stock solutions to make up the control solutions.

MEASUREMENT OF CONDUCTANCE

The conductance of the supernatant solution of the reaction mixtures and of their corresponding control solutions was measured at 25°C in a modified Shedlovsky research type conductance cell (Leeds and Northrup Company) (Fig. 13). The cell was equipped with bright platinum electrodes. The electrodes were cleaned with warm aqua regia and were then rinsed thoroughly with triple-distilled water (average specific conductance nearly equals 1.0 μmho/cm). The conductance was measured with a General Radio Company Type 1603-A Z-Y bridge. A Hewlett Packard frequency generator was used in conjunction with the bridge. The null point of the bridge circuit was detected by an oscilloscope. To avoid polarization effects, the conductance measurements were made at 5 kHz. The theory and the details of operation of the conductance bridge are described in the instruction manual supplied by the manufacturer (54). For each solution, the conductance

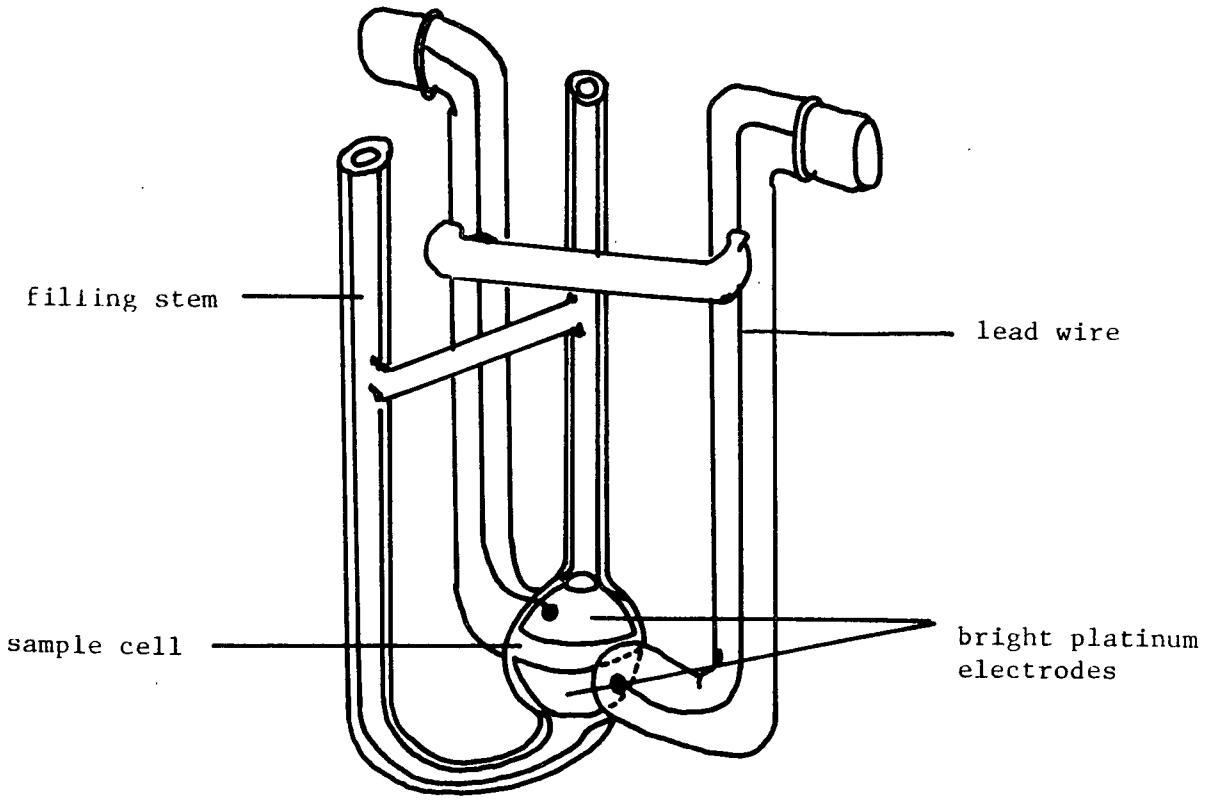


Figure 13. Modified Shedlovsky Research Conductance Cell

of the solvent (water) was also measured and the net conductance was determined by difference. The instruction manual also describes the method of the calculation of the correction factor for the conductance.

The specific conductance of a solution is defined as $\kappa = L\theta$, where L is the conductance and θ is the cell constant characteristic of the geometry of the cell. The cell constant of a particular conductance cell was obtained experimentally by measuring the conductance of a solution with a known specific conductance. Thus, the cell constant of the modified Shedlovsky cell was determined to be 1.0144 with a 0.020M KCl solution (κ = 2,767 μmhos/cm).

A computer program was written to calculate the corrected conductance and the specific conductance, G_x, of the solution. A listing of this program is provided in Appendix IV.

ELECTROPHORESIS EXPERIMENTS

Electrophoresis experiments were performed in the Beckman Spinco Model H electrophoresis apparatus by the moving boundary method. The theory and application of the moving boundary method had been demonstrated by Bier (55) and will not be included here.

The electrophoresis of the supernatant solution of the reaction mixtures and of the pure polyelectrolyte solutions was performed on 0.040M KCl at 10°C. In order to make the sample solution to be 0.040M KCl, 1 mL of a 2.00M KCl solution was added dropwise to every 49 mL of the sample solution. The salt solution will carry much of the electric current and therefore helps to maintain a sharp boundary. The displacements of the boundaries were monitored by Schlieren optics.

TREATMENT OF SECONDARY DATA

The secondary data in this research were: the specific conductance of the supernatant solution of the reaction mixtures and of their corresponding control solutions. These data from each group of complexation reactions were plotted against the ionic mole ratio. In this manner, the stoichiometry of the complexation reactions could be evaluated. A computer program was designed to plot the specific conductance data as described. A listing of the computer program is given in Appendix V.

A LIST OF THE POLYELECTROLYTE COMPLEXATION EXPERIMENTS

The reactions of the sodium poly(vinyl sulfonate) and the ionene bromides amounted to six major sets of complexation experiments. Unless otherwise stated, each set of experiments was made up of four groups (corresponding to the four ionene bromides) of eight complexation reactions; in each group, the NaPVS was reacted with one of the ionene bromides at the selected eight ionic mole ratios. All of the complexation reactions were done in duplicate. The six sets of complexation reactions that were performed in this research are listed in Fig. 14. Each group of reactions was given a group number, and each individual reaction within a group was also given an identification number. For example, the alpha-numeric sequence, 4HNB-LOX, is a group number. The series of alphabets after the dash sign (-) of the group number is merely a reaction set number reminder which is of little importance (see Fig. 14). For instance, "LOX" refers to the reactions in Set 4 where a high molecular weight NaPVS is reacted with a series of low molecular weight ionene bromides. The group number 4HNB-LOX represents collectively all of the eight complexation reactions between fraction B of NaPVS and fraction H of 4,4-ionene bromide. By the same token, each of these eight reactions within the same group could be

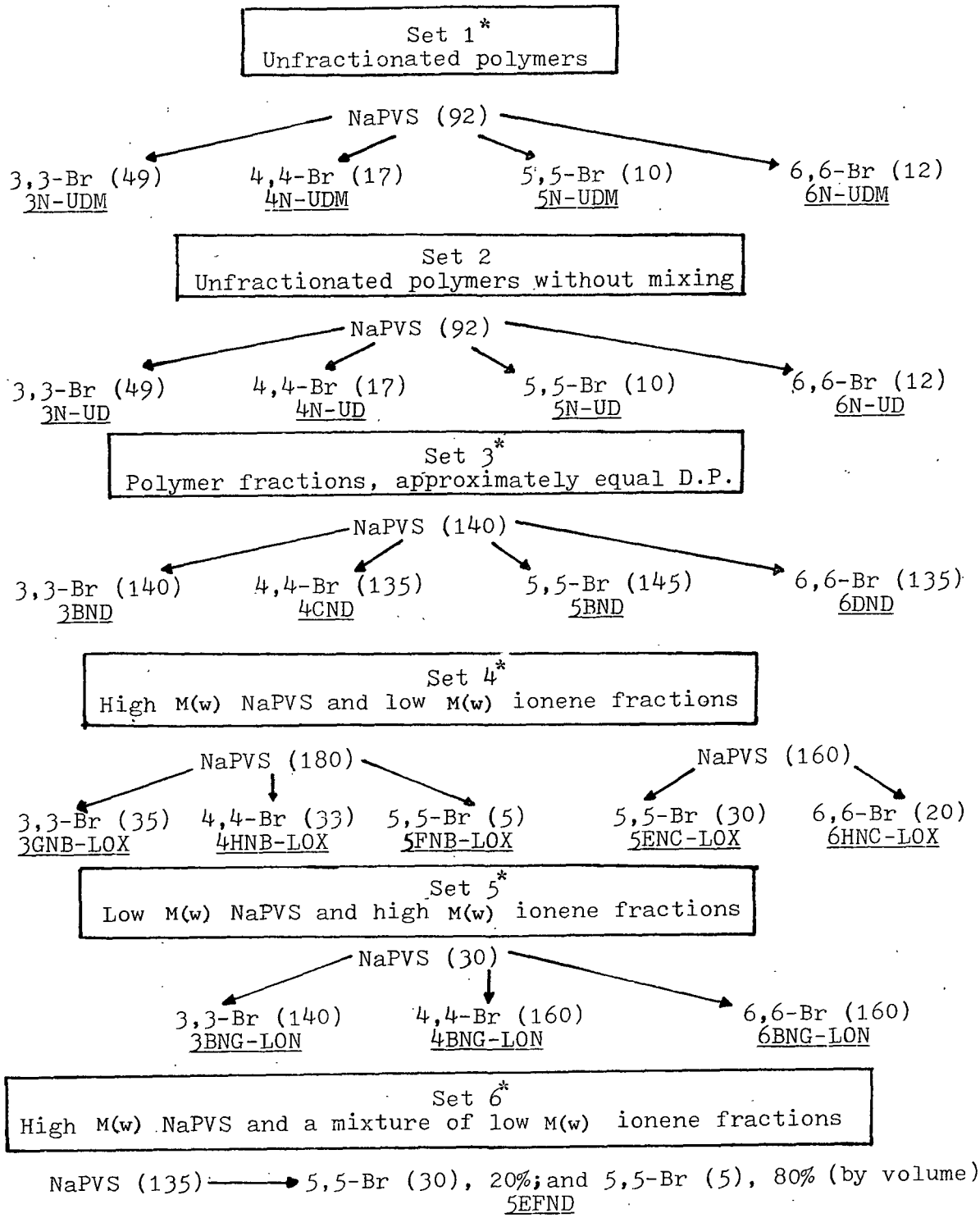


Figure 14. A Summary of the Six Sets of Complexation Reactions Between the Selected Ionene Bromides and the NaPVS. The Numbers in the Parentheses are the DP of the Polyelectrolytes and the Underscored Alphanumeric Sequence are the Group Numbers. Arrows are Pointing at the Ionene Bromide with Which the NaPVS was Reacted in Each Group of Experiments

*With initial mixing of the polyelectrolyte solutions.

identified by tagging on a specification number (from one to eight) after the group number. The selected series of ionic mole ratios increases numerically with the specification number. Thus, the number, 4HNB-LOX1 corresponds to the reaction carried out at an ionic mole ratio of 0.20. Similarly, 4HNB-LOX2 and the other numbers refer to the reactions at ionic mole ratios of 0.50, etc.

EXPERIMENTAL RESULTS AND DISCUSSION

STRUCTURAL CONFIRMATION OF COMPOUNDS

N,N,N',N'-TETRAMETHYLPENTANE-1,5-DIAMINE

The crude title compound was purified by vacuum distillation. The yield of the pure tetramethyl diamine was close to 40%. The product is a faint-smelling colorless liquid. Its molecular structure was confirmed by its NMR spectrum (Fig. 15). The interpretation of the spectrum is as follows.

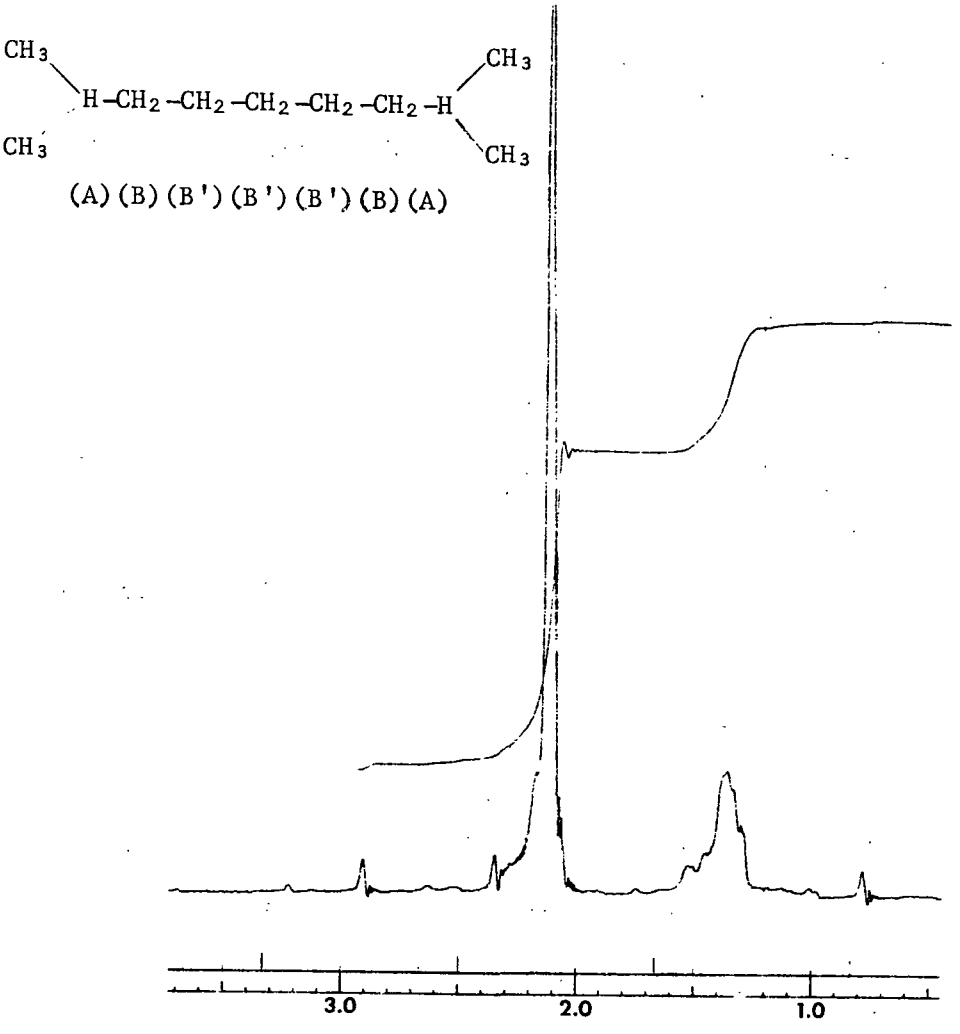


Figure 15. NMR Spectrum of N,N,N',N'-Tetramethylpentane-1,5-diamine

The strong absorption peak at 2.12δ is assigned to the protons (A) of the dimethylamino groups at either end of the molecule and to the protons (B) on the adjacent methylene groups. The peak at 1.32δ is then assigned to the internal methylene protons (B'). Integration of peak areas showed that the assignment of protons was consistent with the structure of N,N,N',N'-tetramethylpentane-1,5-diamine as shown in the inset of Fig. 15.

The percentages of the elements calculated for the molecule of the title compound ($C_9H_{22}N_2$) were: C, 68.3; H, 14.0; N, 17.7. The elemental percentages of the purified product as obtained by elemental analyses were: C, 67.7; H, 14.1; and N, 18.0.

The gas liquid chromatographic study showed that the N,N,N',N'-tetramethyl-pentane-1,5-diamine was of high purity.

3,3-IONENE BROMIDE

The freeze-dried 3,3-ionene bromide has a white, fluffy and fibrous appearance and it is hygroscopic. It is also very tacky when being ground. For this reason no infrared spectrum was obtained. The yield was 31%. In its NMR spectrum (Fig. 16), the strong absorption peak at 3.28δ is assigned to the protons (A) of the dimethylammonium ion and those peaks at 3.45δ to 3.62δ and 2.35δ to 2.55δ are assigned to the methylene protons (B) and the internal methyl-ene protons (C), respectively. Integration showed that the numbers of (A), (B) and (C) protons are 6, 4 and 2, respectively. This is consistent with the monomeric structure of 3,3-ionene bromide depicted in the inset of Fig. 16.

4,4-IONENE BROMIDE

The structure of the reaction product was identified by NMR spectroscopy (Fig. 17). The peaks at 3.20δ, 3.48δ and 1.88δ are assigned to the protons (A)

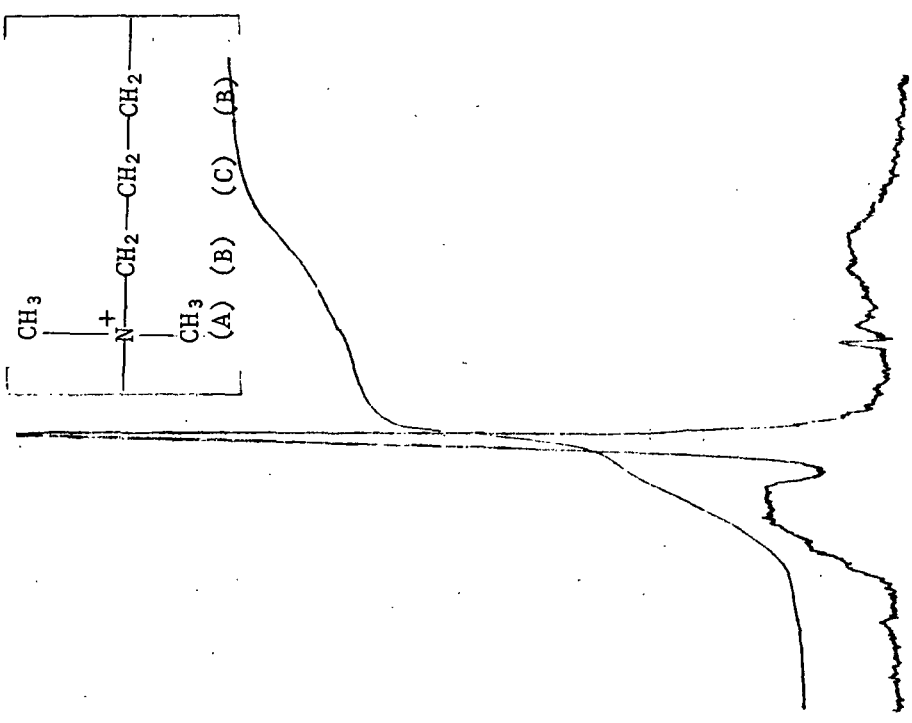


Figure 16. NMR Spectrum of 3,3-Ionene Bromide

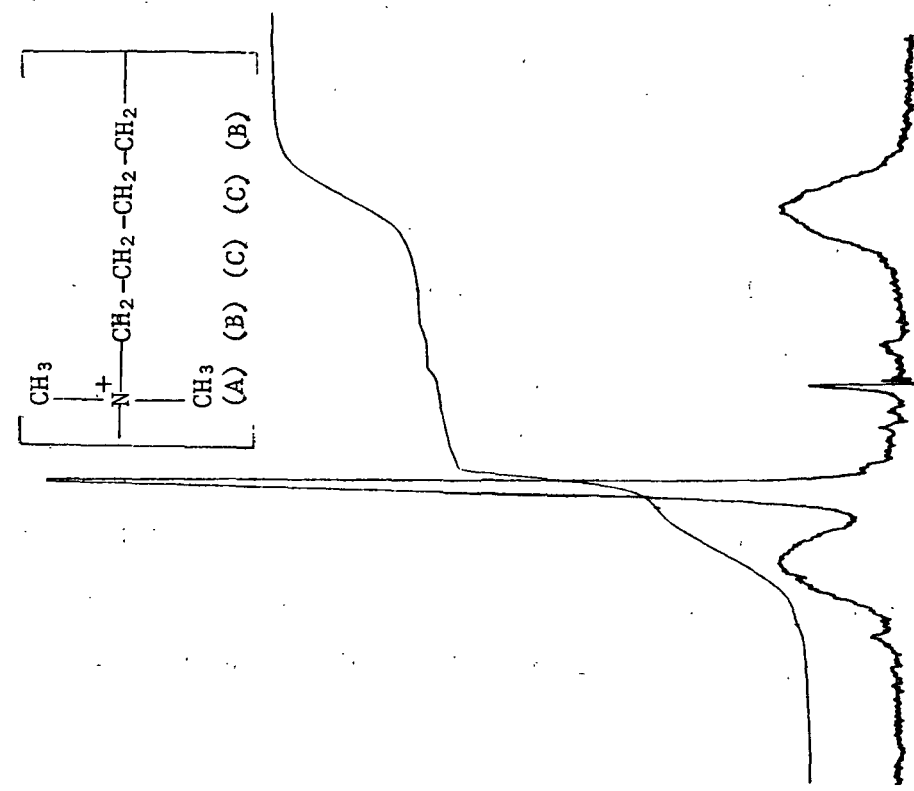


Figure 17. NMR Spectrum of 4,4-Ionene Bromide

of dimethylammonium ion, the methylene protons (B) adjacent to the ammonium ion and the internal methylene protons (C), respectively. Integration showed that there are six (A) protons, four (B) protons, and four (C) protons, which is indicative of the structure depicted in the inset of the NMR spectrum.

The freeze-dried 4,4-ionene bromide is a white, fluffy and fibrous material. The yield was about 91%. The polyelectrolyte is hygroscopic and it is also tacky when being ground.

5,5-IONENE BROMIDE

Among the ionene bromides, 5,5-ionene bromide is the most hygroscopic one. It would form a solution if left standing in a very humid place. The 5,5-ionene bromide is a powder with a yellowish tint to it. The yield of the polyelectrolyte was 67%.

The NMR spectrum of 5,5-ionene bromide is shown in Fig. 18. The spectrum shows that the six protons (A) of the two methyl groups on the ammonium ion absorb at 3.10δ, while those four methylene protons (B) adjacent to the ammonium ion absorb at 3.20δ to 3.35δ. The broad peak at 1.73δ is assigned to the six internal protons (C). Integration and proton counting confirmed that the reaction product is indeed 5,5-ionene bromide.

6,6-IONENE BROMIDE

The 6,6-ionene bromide is similar in appearance to 3,3- and 4,4-ionene bromides. It is also quite hygroscopic. The yield of the polyelectrolyte is close to 100%.

With reference to the NMR spectrum of 6,6-ionene bromide (Fig. 19), the peak at 3.05δ is assigned to the six (A) protons, while those peaks at 3.15δ to 3.30δ

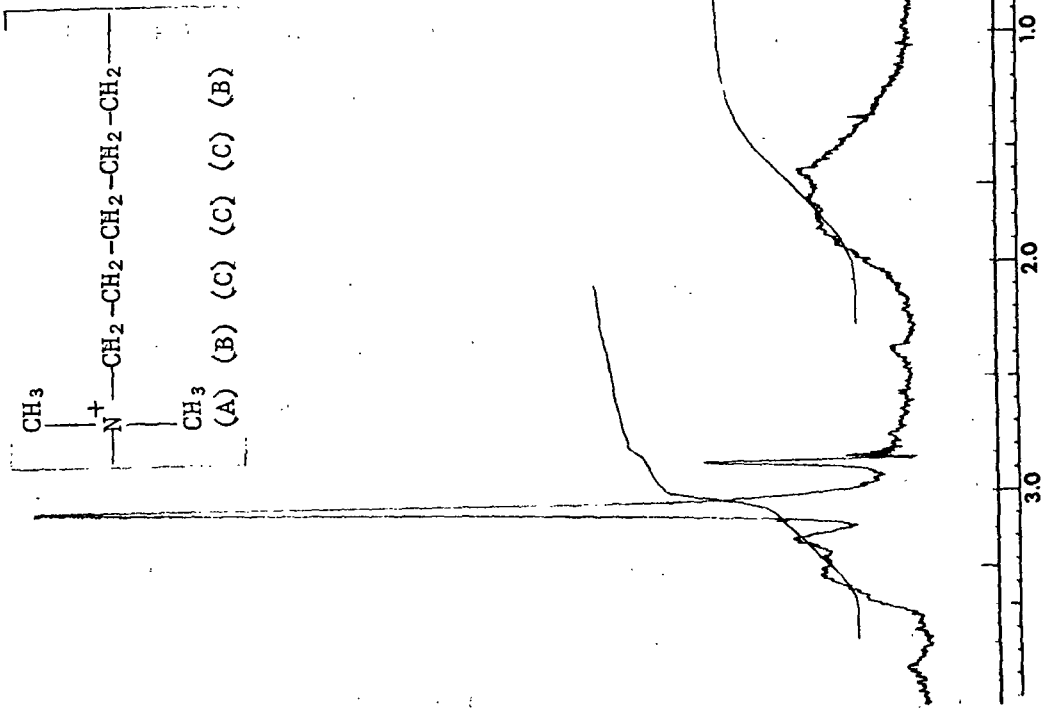


Figure 18. NMR Spectrum of 5,5-Ionene Bromide

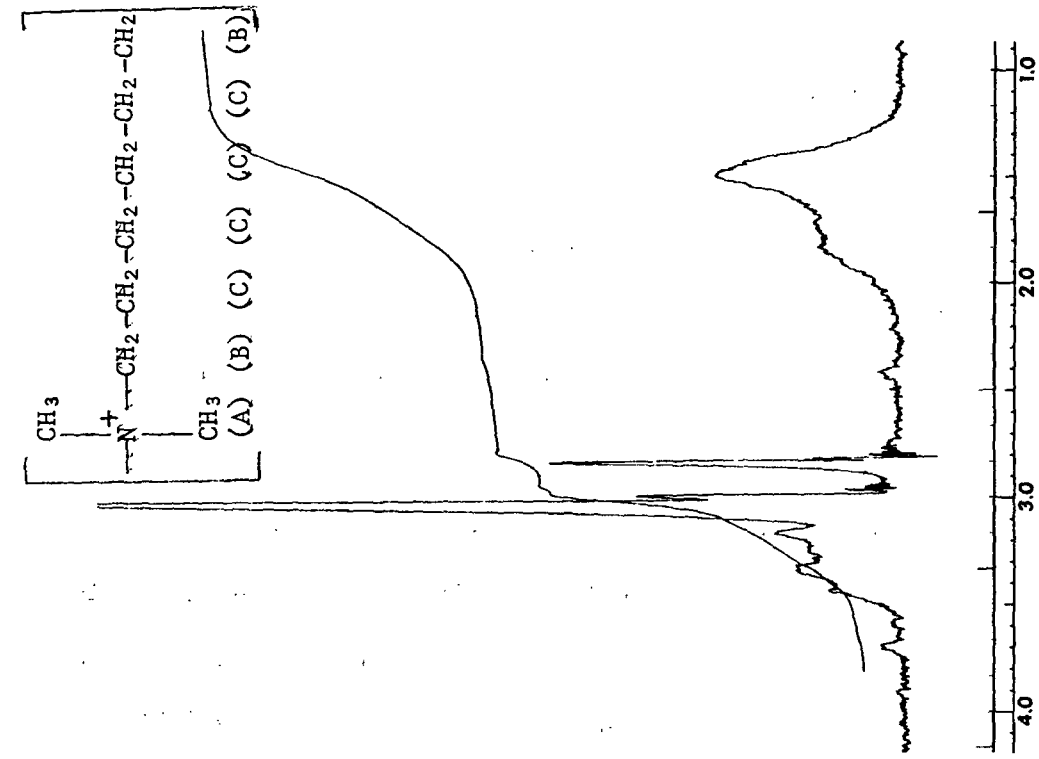


Figure 19. NMR Spectrum of 6,6-Ionene Bromide

and at 1.50δ to 1.75δ are assigned to the four (B) protons and eight (C) protons, respectively. Results of proton integration confirmed the reaction product to be 6,6-ionene bromide.

ADDITIONAL COMMENTS ON THE STRUCTURES OF THE IONENES

With reference to the NMR spectra of the ionene bromides, the absorption of the protons of the dimethylammonium ion moves progressively to higher field as the number of methylene groups in the ionene bromide is increased. This phenomenon is due chiefly to the shielding effect of the internal methylene groups.

The sharp, narrow spikelike peak immediately to the right of the strong ammonium ion peak is probably due to the terminal dimethylamino groups. It is indeed possible to observe such a peak since the NMR spectra of the 4,4-ionene, 5,5-ionene and 6,6-ionene bromides were taken of very low molecular weight samples (DP nearly equals 15). This explanation is further supported by the fact that this spikelike peak is much less conspicuous in the 3,3-ionene bromide spectrum since the 3,3-ionene bromide sample used in obtaining this NMR spectrum is relatively higher in molecular weight (DP nearly equals 50).

SODIUM POLY(VINYL SULFONATE)

The dialyzed and freeze-dried sodium poly(vinyl sulfonate) is a white solid and is only slightly hygroscopic. The yield of this polyelectrolyte was quantitative before dialysis. However, an overall recovery of about 40% of the polyelectrolyte was obtained.

It has been reported by several investigators (56-58) that ionization of the asymmetric group of the monomer consistently favors syndiotactic addition since syndiotactic placements are favored by electrostatic repulsion between

sulfonate groups. Therefore, it is expected that the polymerization of sodium vinyl sulfonate in aqueous solution should yield a polyelectrolyte with a high content of syndiotactic triads.

In the NMR spectrum of sodium poly(vinyl sulfonate) (Fig. 20), the broad peak from 1.40δ to 2.60δ is assigned to the methylene protons (A) while that peak at 3.20δ to 4.00δ is assigned to the methine proton (B). This spectrum is identical to an NMR spectrum of a syndiotactic sodium poly(vinyl sulfonate) sample obtained by Blumstein, et al. (59). Integration showed that the numbers of methylene and methine protons are two and one, respectively. This confirms that the polyelectrolyte obtained has a syndiotactic configuration and it has the structure as depicted in the inset of Fig. 20.

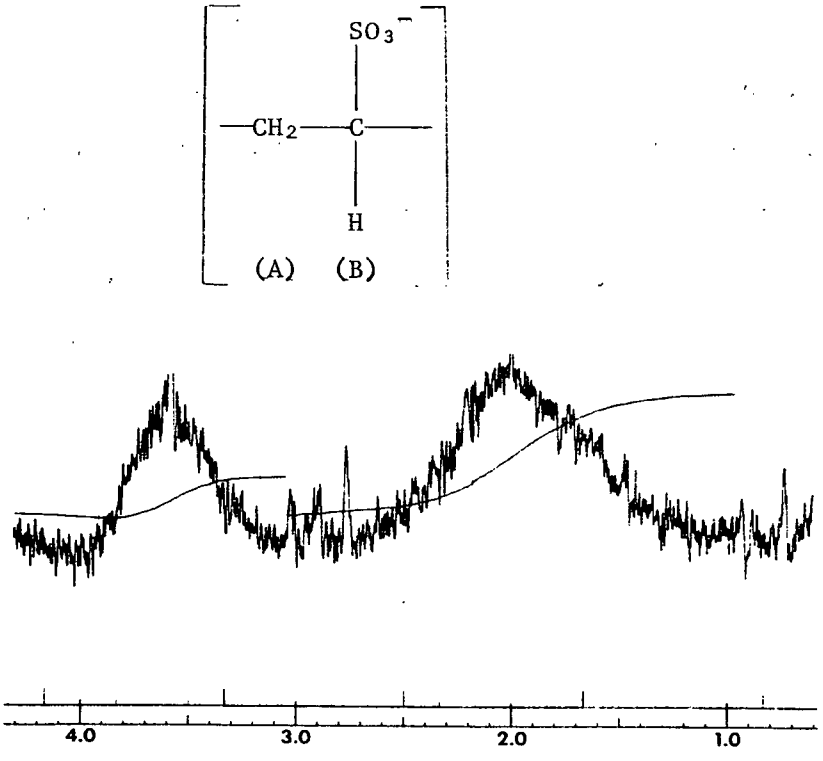


Figure 20. NMR Spectrum of Sodium Poly(vinyl sulfonate)

FRACTIONATION OF THE POLYELECTROLYTES

The selected ionene bromides and sodium poly(vinyl sulfonate) were separated into various molecular weight fractions by gel permeation chromatography. The chromatograms of these fractionations are shown in Fig. 21 to 25.

Throughout the fractionation experiments, relatively constant and desirable flow rates were maintained. There were only slight changes in the chromatograms from one fractionation to the next. Thus, the values plotted in each chromatogram are the average values for the combined fractions for all of the fractionation runs. In some of the runs, a slight compression of the column packing was observed. However, this effect was considered negligible, since the molecular weight distributions of the polyelectrolyte fractions were shown to be quite narrow.

ULTRAFILTRATION OF POLYELECTROLYTE FRACTIONS

The salts in the polyelectrolyte fractions were removed by ultrafiltration technique. In almost every case, the recovery of polyelectrolyte was excellent and loss through the membrane was almost nil. However, in the ultrafiltration of the low molecular weight fractions, the recovery of polyelectrolytes was not as efficient. For instance, the loss due to ultrafiltration of the lower molecular weight fractions of 5,5-ionene bromide (5F, 5G and 5H) was most severe. The selection of an ultrafiltration membrane of smaller pore size seemed to remedy this predicament. However, the time required for the ultrafiltration was increased tremendously. This disadvantage far outweighs the membrane's retention ability; therefore, the recovery of low molecular weight polyelectrolyte fractions was extremely difficult. The overall recoveries of the sodium poly(vinyl sulfonate), 3,3-ionene, 4,4-ionene, 5,5-ionene and 6,6-ionene bromides are: 87%, 57%, 59%, 52%, and 63%, respectively.

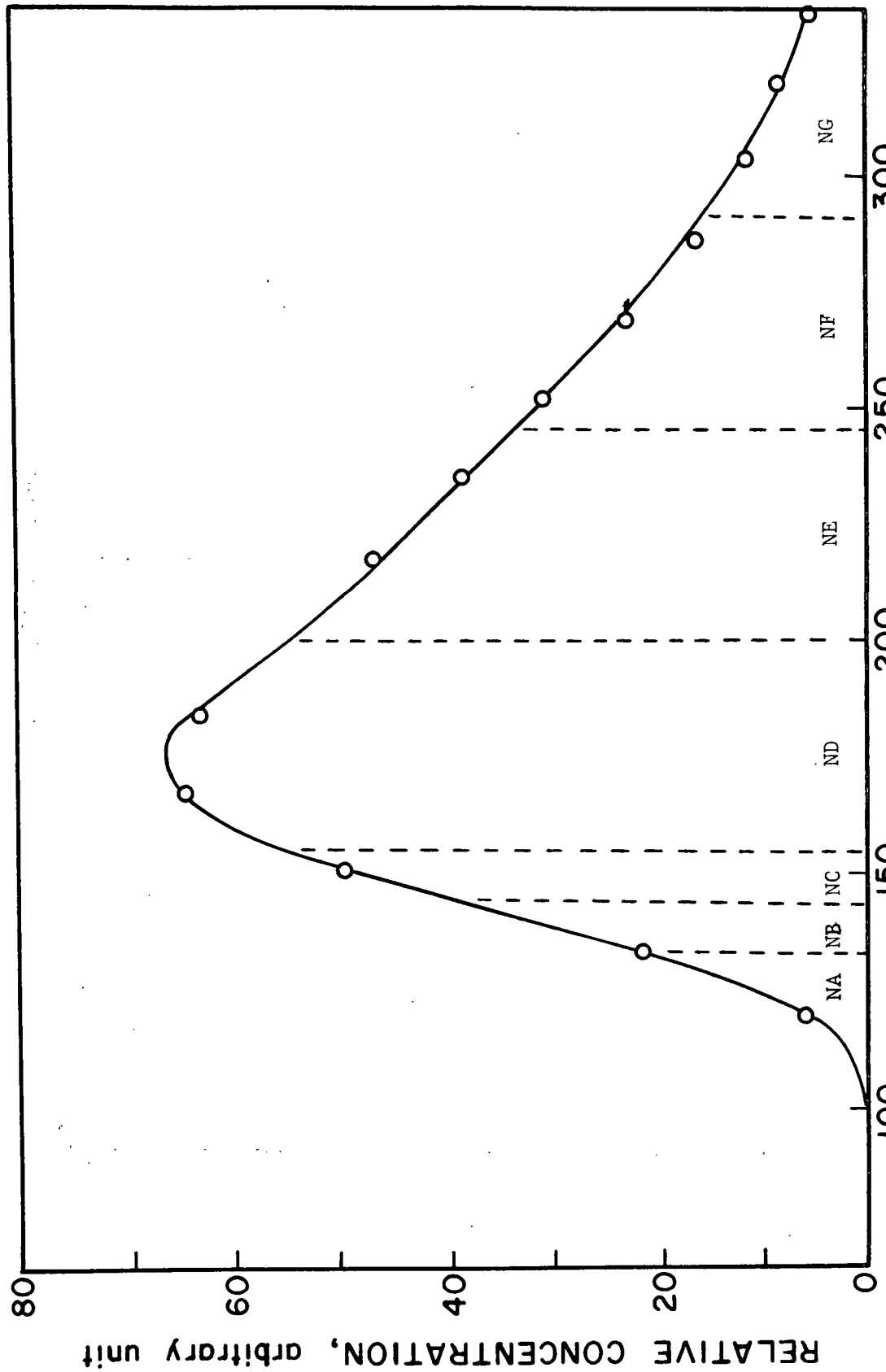


Figure 21. Gel Permeation Chromatogram of Sodium Poly(vinyl sulfonate). The Alphabetic Sequences are Fraction Numbers

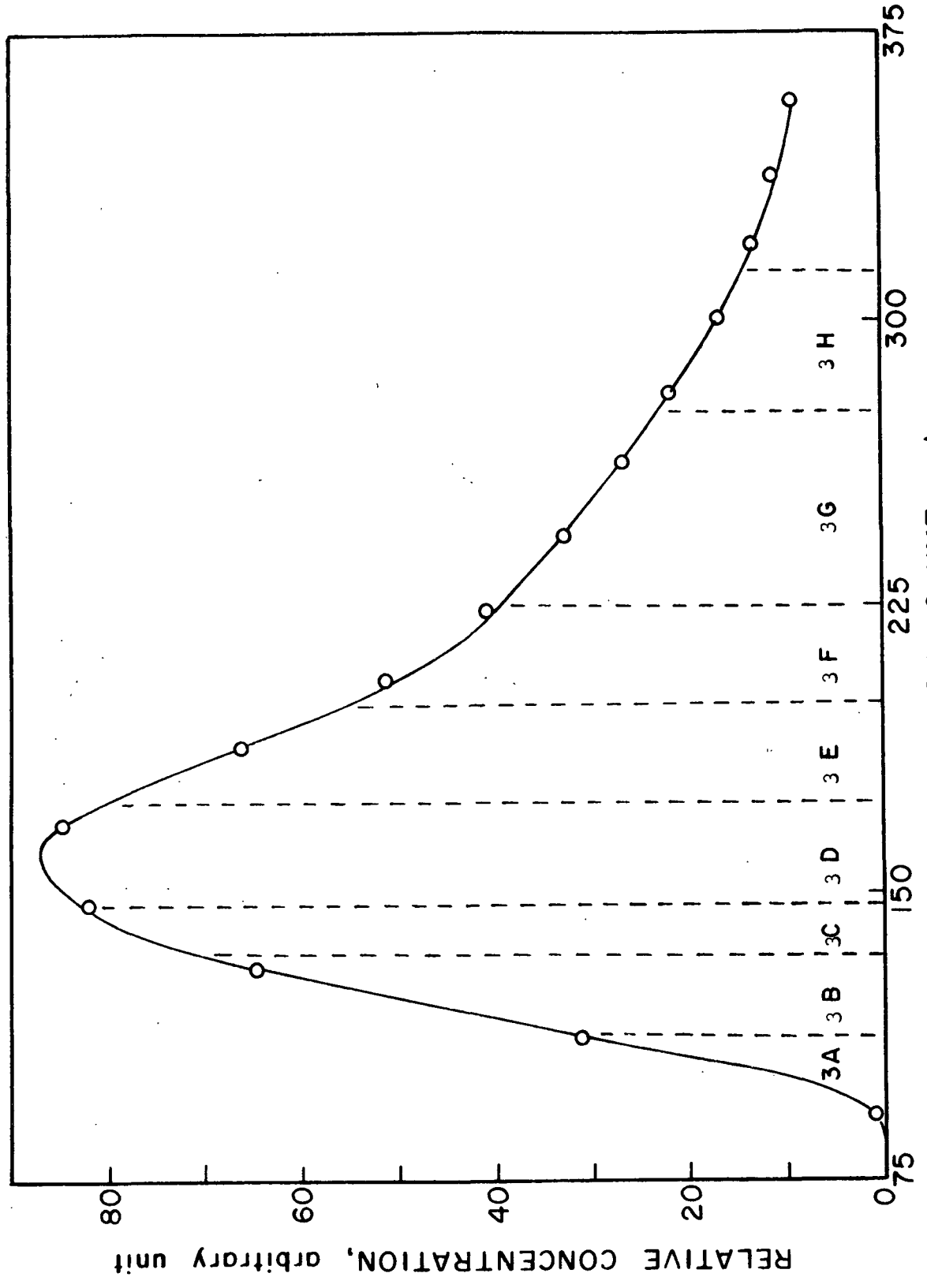


Figure 22. Gel Permeation Chromatogram of 3,3-Ionene Bromide. The Alphanumeric Sequences are Fraction Numbers

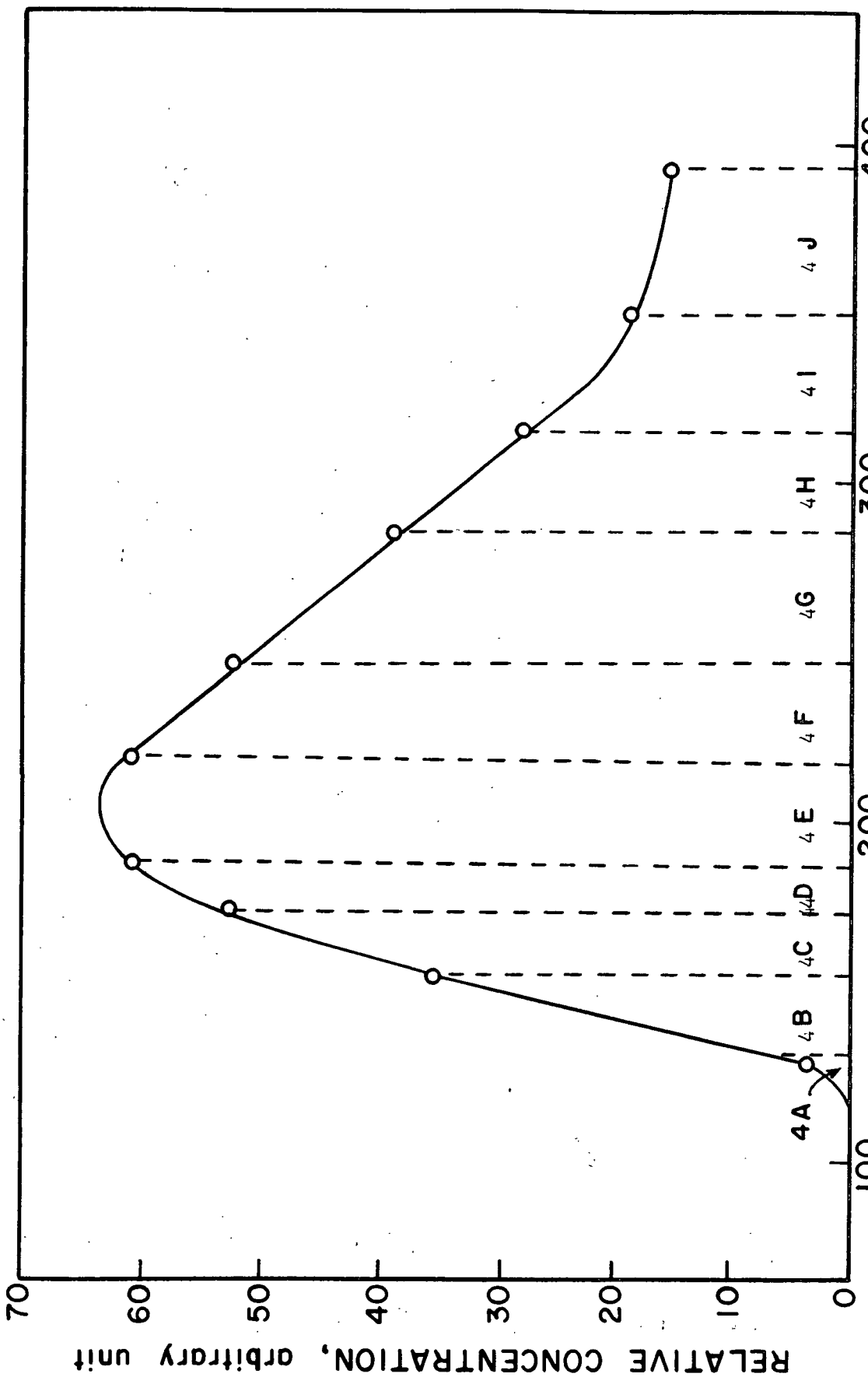


Figure 23. Gel Permeation Chromatogram of 4,4-Ionene Bromide. The Alphanumeric Sequences are Fraction Numbers

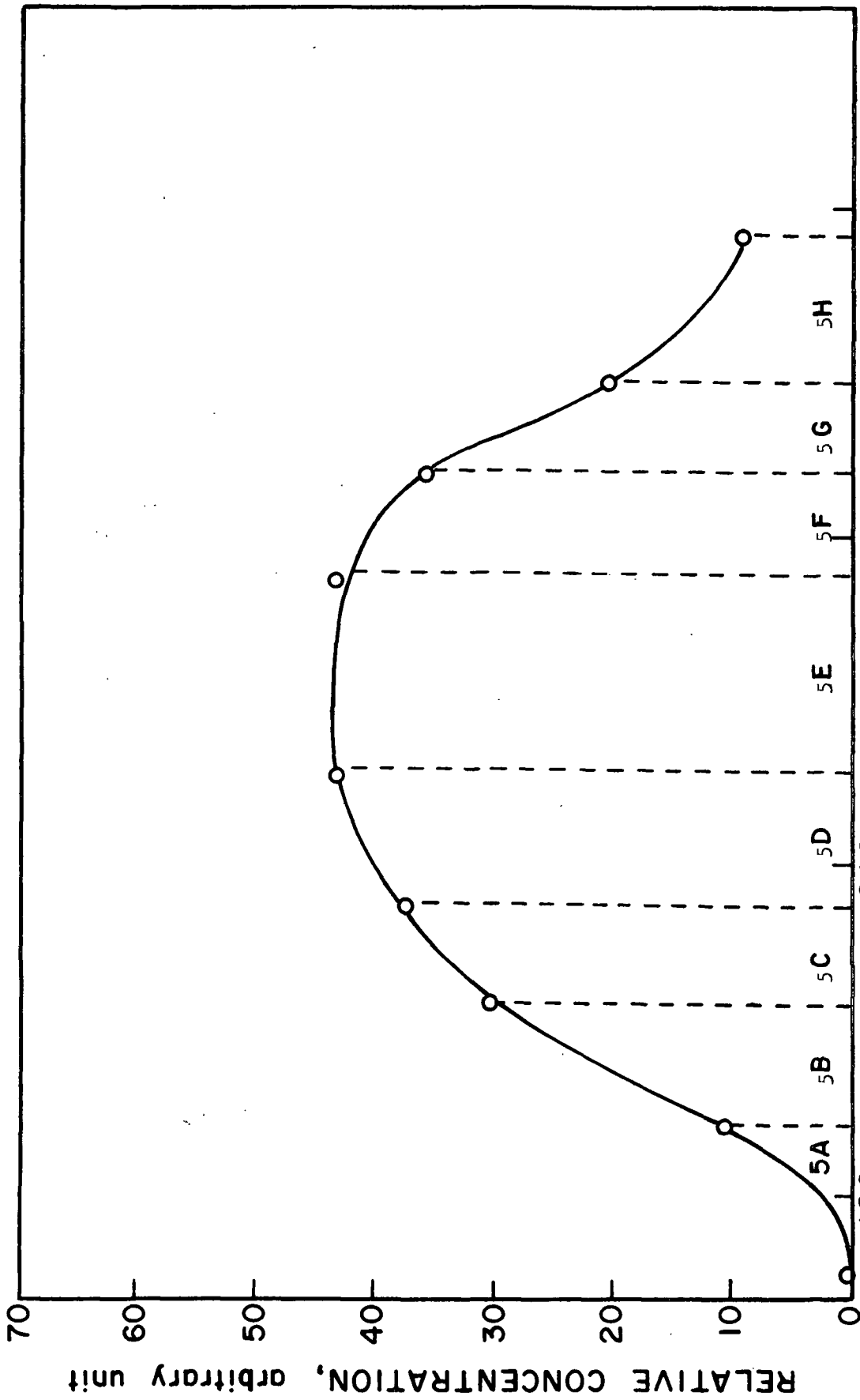


Figure 24. Gel Permeation Chromatogram of 5,5-Ionene Bromide. The Alphanumeric Sequences are Fraction Numbers

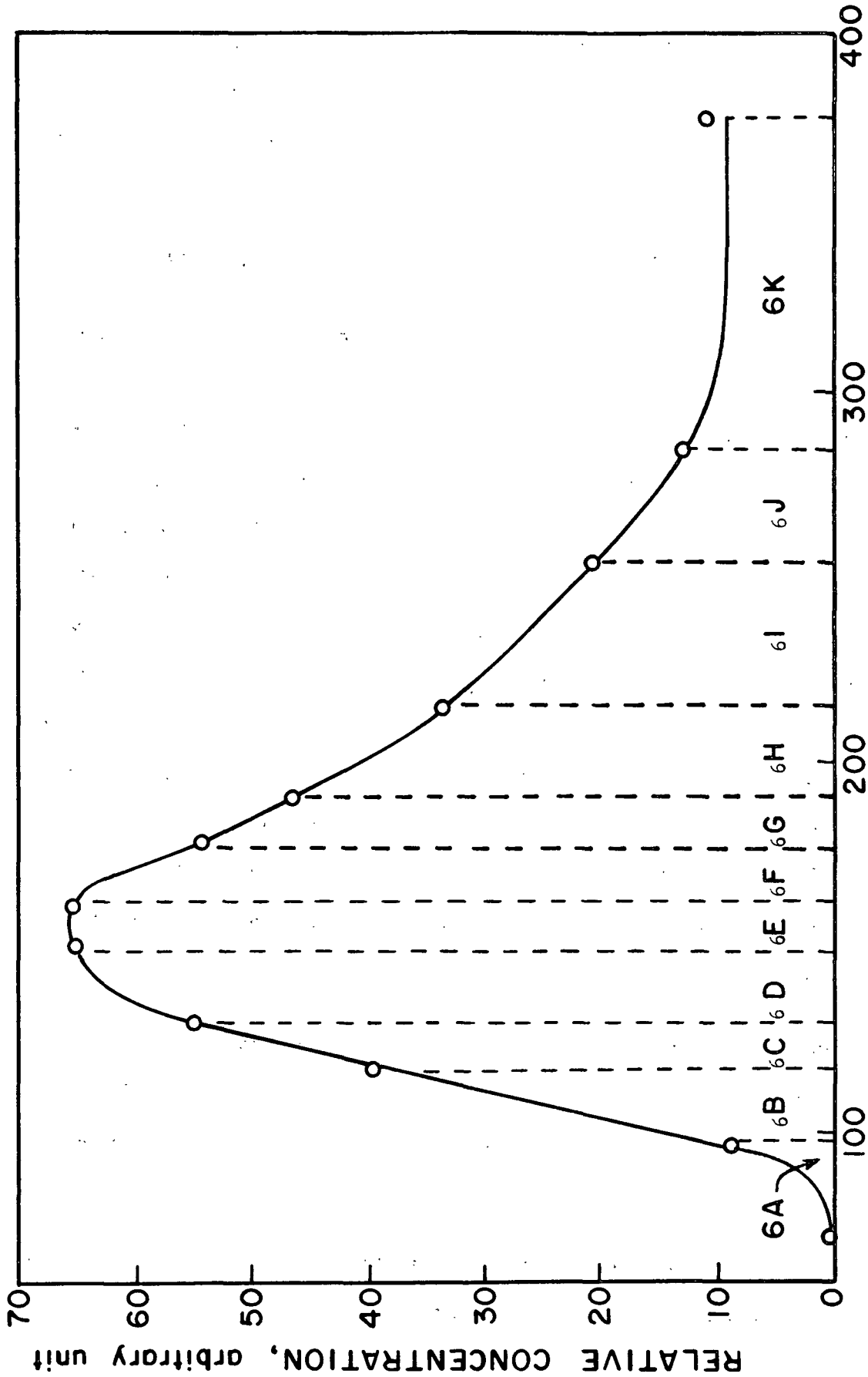


Figure 25. Gel Permeation Chromatogram of 6,6-Ionene Bromide. The Alphanumeric Sequences are Fraction Numbers

The quality of the polyelectrolytes fractions was carefully controlled. The results from the analyses for potassium and sodium ions by flame emission spectrophotometry indicated that no excess salt remained in the polyelectrolyte fractions.

APPARENT PARTIAL SPECIFIC VOLUMES OF POLYELECTROLYTES

The solvents for the sodium poly(vinyl sulfonate) and ionene bromides were 0.50M NaCl and 0.40M KBr, respectively. The densities of these solvents at 25°C were determined to be 1.0309 g cm^{-3} and 1.0173 g cm^{-3} for the 0.40M KBr and the 0.50M NaCl, respectively. These numbers are in excellent agreement with literature values (60). The densities of the polyelectrolyte solutions were determined at various weight fractions. The specific volume (reciprocal density) of the polyelectrolyte solution was plotted against the weight fraction. The graph for sodium poly(vinyl sulfonate) is shown in Fig. 26. The graphs for the ionene bromides are shown in Fig. 27. These diagrams show that the data points fit very well to the least-squares regression lines. The intercept represents the specific volume, $\bar{v}_1^o$, of the solvent. The $\bar{v}_1^o$ values for the 0.40M KBr and the 0.50M NaCl solutions obtained by extrapolation are 0.970$_2$ cm^3 g^{-1} and 0.983 cm^3 g^{-1}, respectively; which are identical to the reciprocals of the solvent densities determined in separate experiments.

The apparent partial specific volume $\bar{v}_2^*$ of the polyelectrolyte solutions is calculated from the slope and intercept of the regression line. The $\bar{v}_2^*$ values of the selected polyelectrolytes in their appropriate solvents are tabulated in Table III.

As would be expected, the ionene bromides showed a gradual increase in the apparent partial specific volume as the monomer molecular weight increases. The $\bar{v}_2^*$ value of 0.415 cm^3 g^{-1} for NaPVS is identical to that determined by Dialer and Kerber (61).

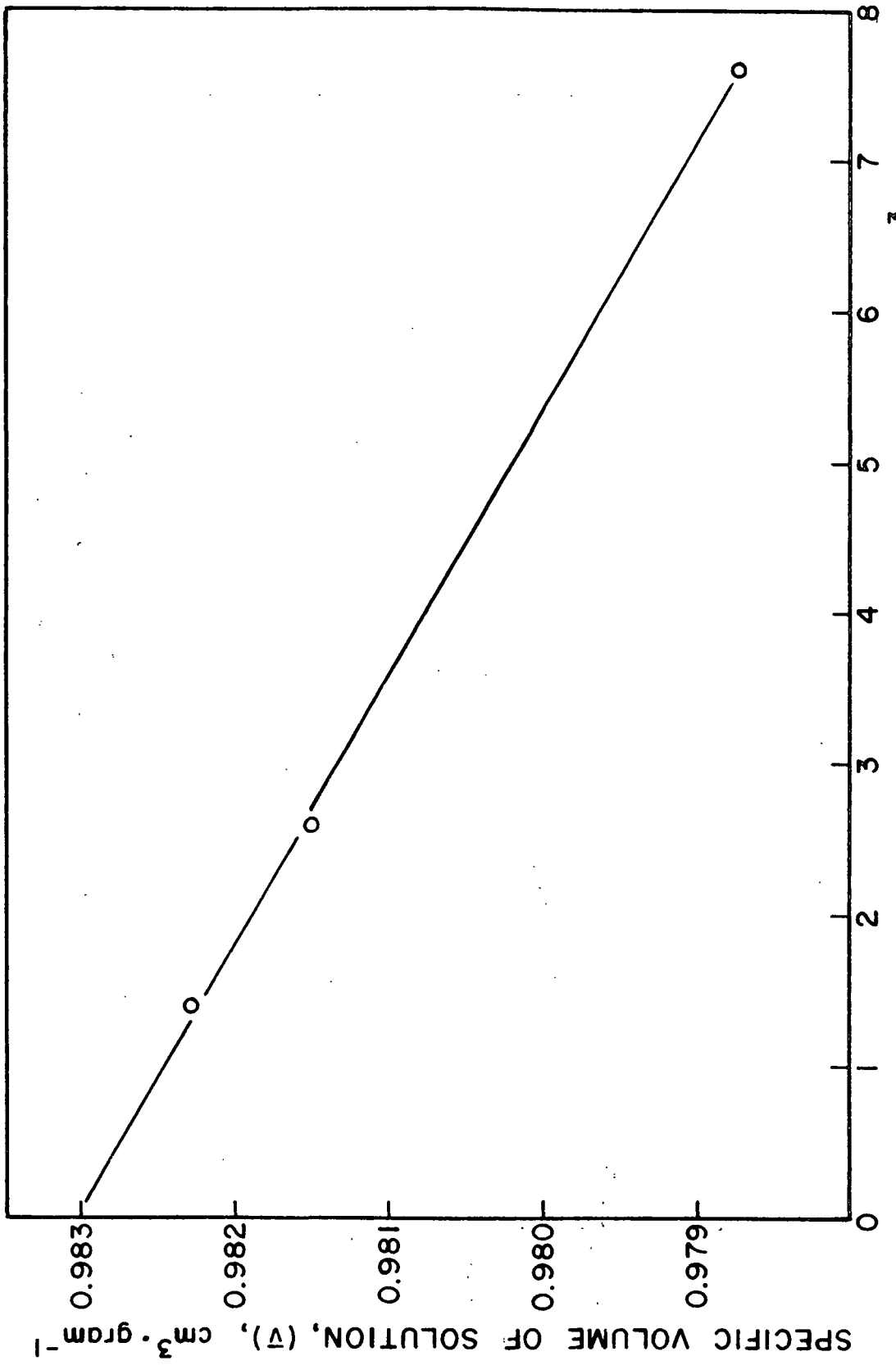


Figure 26. Specific Volume Versus Sodium Poly(vinyl sulfonate) Weight Fraction

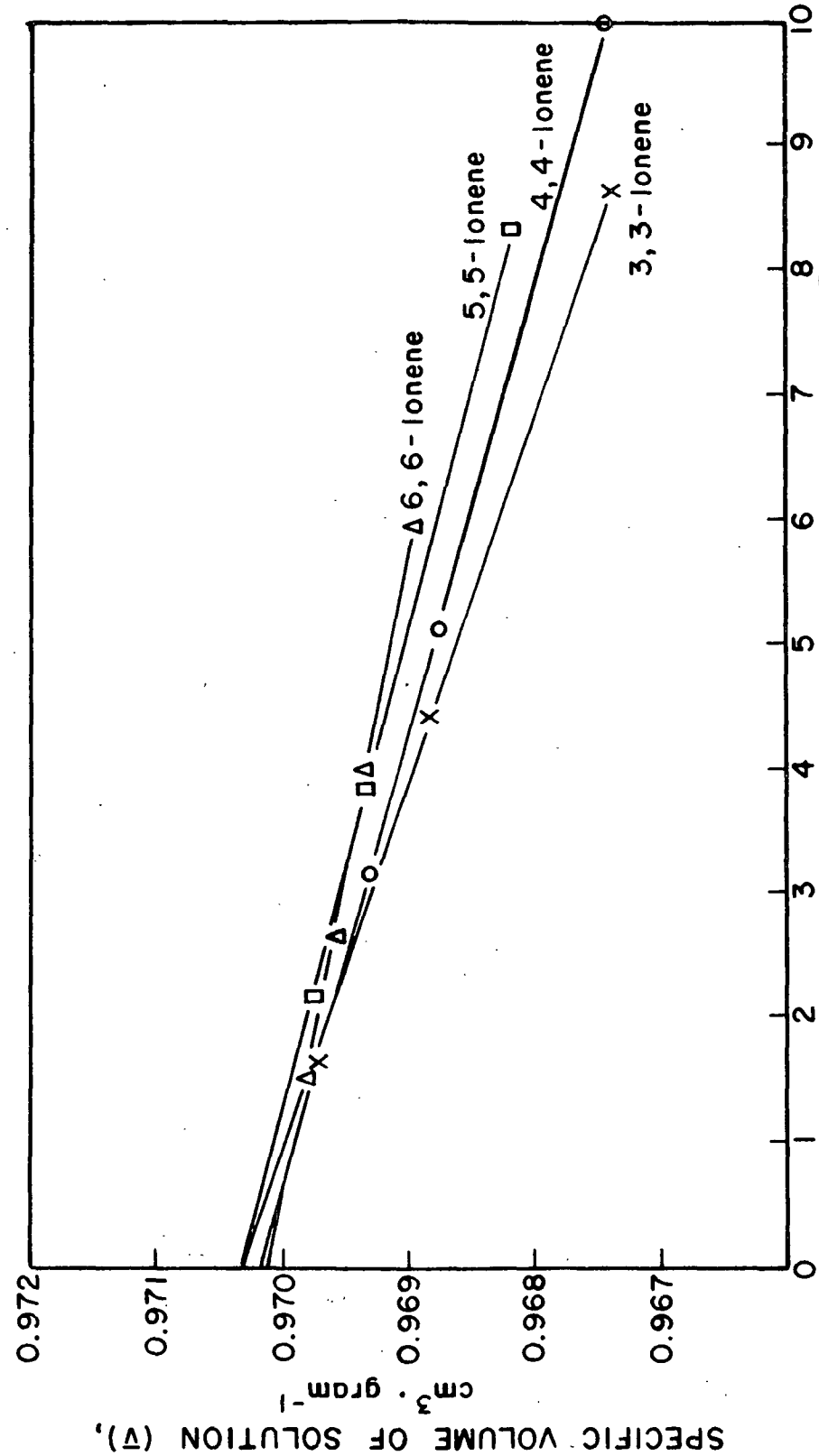


Figure 27, Specific Volume Versus Ionene Bromide Weight Fraction

TABLE III

APPARENT PARTIAL SPECIFIC VOLUMES OF POLYELECTROLYTES AT 25°C AS CALCULATED FROM THE SLOPES AND INTERCEPTS OF THE REGRESSION LINES

Polymer	Slope	Intercept	$\bar{v}_2^*$ ($cm^3\ g^{-1}$)
NaPVS	-0.567_7	0.983	0.415_3
3,3-Ionene	-0.334_3	0.970_3	0.636
4,4-Ionene	-0.270_4	0.970_1	0.699_7
5,5-Ionene	-0.253_9	0.970_3	0.716_4
6,6-Ionene	-0.191_7	0.970_1	0.778_4

MOLECULAR WEIGHTS OF THE SELECTED POLYELECTROLYTES

The absolute molecular weight of a polymer is usually obtained by determining the weight average molecular weight at various concentrations on the ultracentrifuge and then by extrapolating a plot of the reciprocal weight average molecular weight against concentration to infinite dilution. In this thesis research, a large number of polyelectrolyte samples was to be run on the ultracentrifuge. Therefore, it was impossible to determine the absolute molecular weight for all of them. Instead, the apparent weight average molecular weight, $M(w)_{app}$, was determined for the selected polyelectrolytes at one common concentration (0.001 g/mL) and rotor speed (30,000 rpm). Figures 28 and 29 are the typical d $\ln(C_x)$ versus x^2 graphs for the unfractionated and the fractionated polyelectrolytes, respectively.

For a monodisperse and ideally behaved polyelectrolyte, the molecular weight does not change with the radial distance. Thus, the resulting d $\ln(C_x)$ versus x^2 plot will be a straight line. The slope of this straight line is used in Equation (2) to calculate the molecular weight.

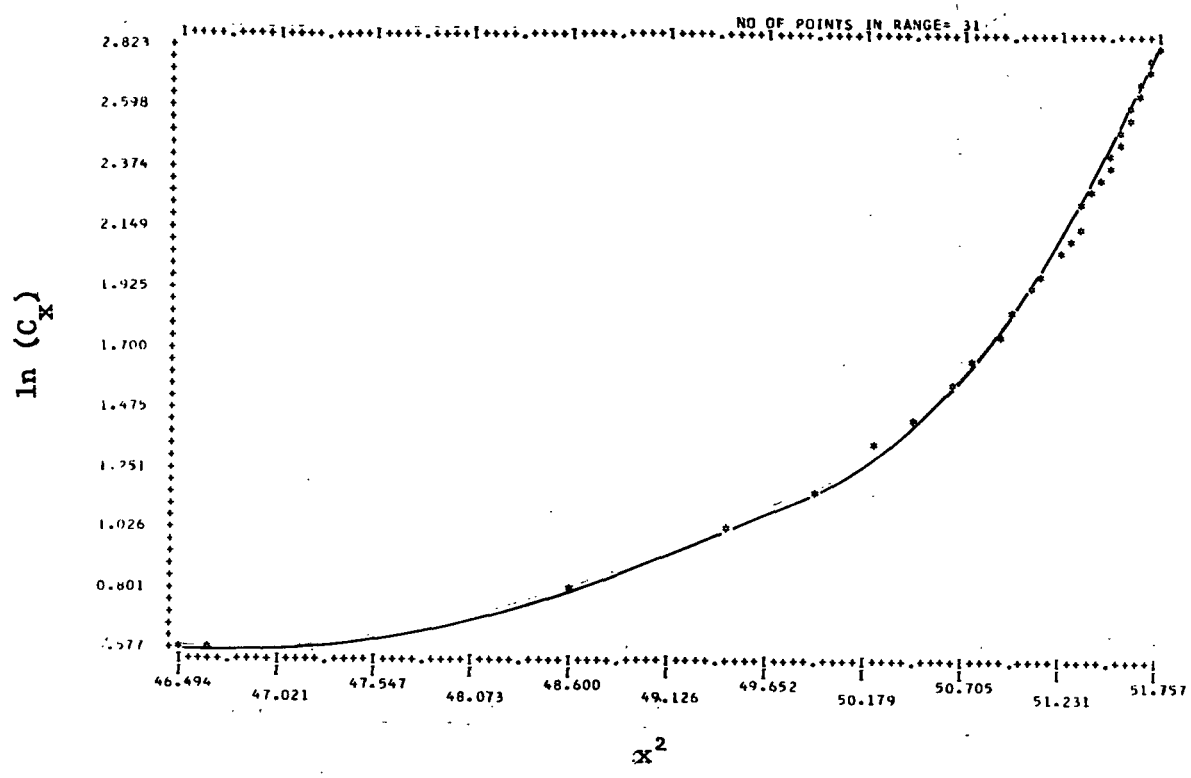


Figure 28. A Typical ln (C_x) Versus x^2 Curve for Unfractionated Polyelectrolytes (taken from NaPVS Batch 1)

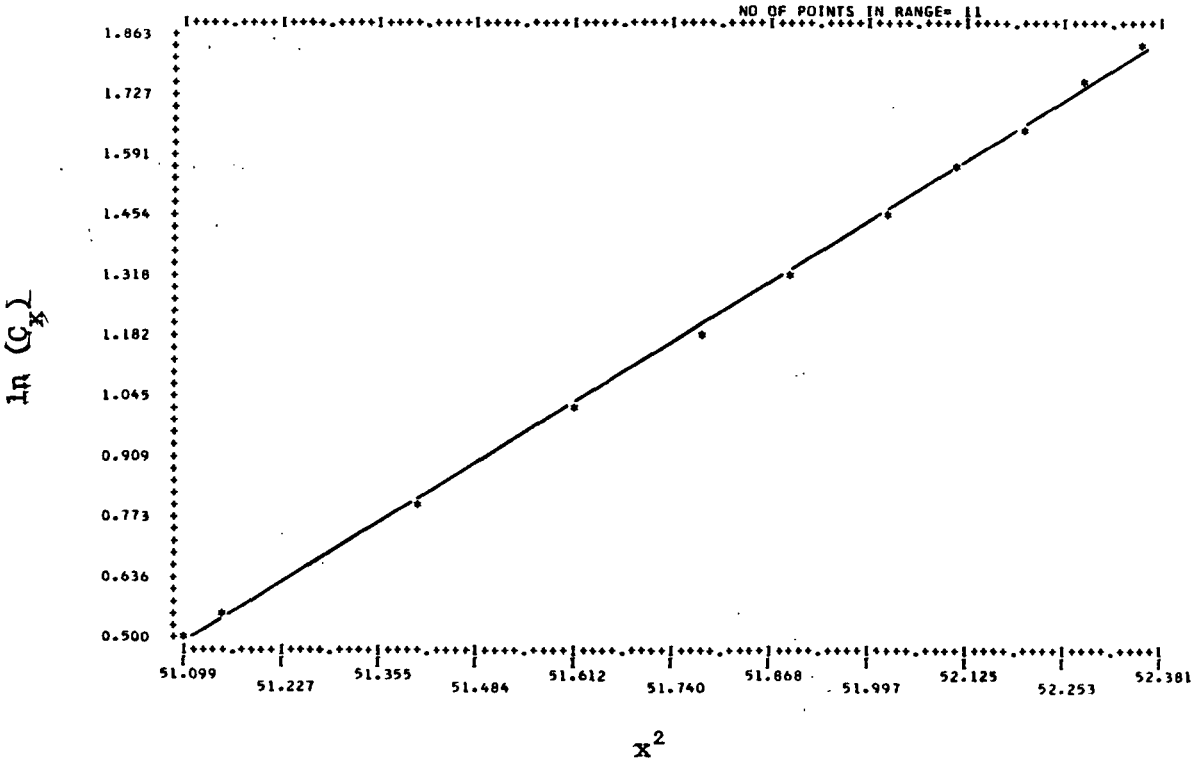


Figure 29. A Typical ln (C_x) Versus x^2 Curve for Fractionated Polyelectrolytes (taken from 6,6-Ionene Fraction D)

It is also possible to obtain nonlinear plots. According to Equation (2), the slope at any point on such a plot is still proportional to the average molecular weight at a corresponding radial position in the cell. If the plot curves downward, meaning the molecular weight decreases with increasing concentration, the general indication is that the polymer solution is nonideal. On the contrary, an upward curvature, as in Fig. 28, means that the molecular weight increases as the radial distance increases, indicating that the polyelectrolyte is polydisperse.

One should be extremely cautious in drawing conclusions on the basis of a run at a single concentration yielding a straight line plot. Care must be taken to avoid a subtle pitfall: the sample may exhibit concentration dependence of molecular weight and at the same time be polydisperse (48). Thus it is possible for a plot of d $\ln(C_x)$ versus x^2 to be straight as a result of fortuitous mutual cancellation of the two effects. In this case, however, the polyelectrolyte fractions were obtained from very meticulous fractionation procedures. Therefore, it is believed that the straight line plots they produced may indeed infer that the polyelectrolyte fractions are of very narrow molecular weight distribution.

A list of the apparent weight average molecular weights of the selected polyelectrolytes and of their fractions is given in Table IV. For the unfractionated polyelectrolyte the value represents the molecular weight averaged over the cell. Because of the strong curvature (see Fig. 28), this value gives only rough approximations of $M(w)_{app}$.

TABLE IV

APPARENT WEIGHT AVERAGE MOLECULAR WEIGHT AND DEGREE OF POLYMERIZATION OF THE SELECTED POLYELECTROLYTES

Polymer	Fraction	$M(w)_{app}$	DP
3,3-Ionene	Unfractionated[a]	8,200	49
	B	24,000	140
	C and D	18,000	110
	E and F	9,000	50
	G	6,000	35
	H	4,000	25
4,4-Ionene	Unfractionated[a]	3,000	17
	B	29,000	160
	C and D	24,000	135
	E	17,000	90
	F	13,000	70
	G	9,000	50
	H	6,000	33
	I	4,000	20
5,5-Ionene	Unfractionated[a]	1,900	10
	B	28,000	145
	C	19,000	100
	D	14,000	70
	E	6,300	30
	F	900	5
6,6-Ionene	Unfractionated[a]	2,400	12
	B	34,000	160
	C	30,000	145
	D	28,000	135
	E	23,000	110
	F	18,000	90
	G	14,000	70
	H	4,400	20
NaPVS	Unfractionated[a]	12,000	92
	B	23,000	180
	C	20,000	160
	D	18,000	140
	E	11,000	90
	F	7,000	50
	G	4,000	30

[a]Batch 1 polyelectrolyte.

STANDARDIZATION OF SOLUTIONS

SODIUM POLY(VINYL SULFONATE) SOLUTIONS

The concentrations of the sodium poly(vinyl sulfonate) solutions were determined by direct potentiometry. A typical calibration curve for the sodium ion electrode is presented in Fig. 30. If the electrode potential of the unknown solution is measured, its sodium concentration could be interpolated from the curve. An alternative method of solution is by obtaining the equation of the least-squares linear regression line passing through the data points of the standard solutions and then solving the equation for the sodium concentration of the unknown polyelectrolyte solution at its electrode potential. The latter method was adopted in this research because it eliminates the human errors and bias involved in direct graphical procedures.

Throughout the experiments, the sodium ion electrode had behaved ideally. The change in the electrode potential per decade change in sodium ion concentration was always about 58 mv, which was in close agreement with the theoretical value of 59 mv as predicted by the Nernst equation. The electrode also gave drift-free response to all of the solutions. The average concentrations (from three determinations) of the various aqueous solutions of sodium poly(vinyl sulfonate) used in the complexation experiments are listed in Table V.

TABLE V

CONCENTRATIONS OF SODIUM POLY(VINYL SULFONATE) SOLUTIONS

NaPVS	Experiment	Concentration, $\underline{M} \times 10^3$
Unfractionated	Sets 1 & 2	0.97 ± 0.03
Fraction D	Sets 3 & 6	1.00 ± 0.01
Fraction B	Set 4	0.90 ± 0.01
Fraction C	Set 4	1.00 ± 0.01
Fraction G	Set 5	1.00 ± 0.01

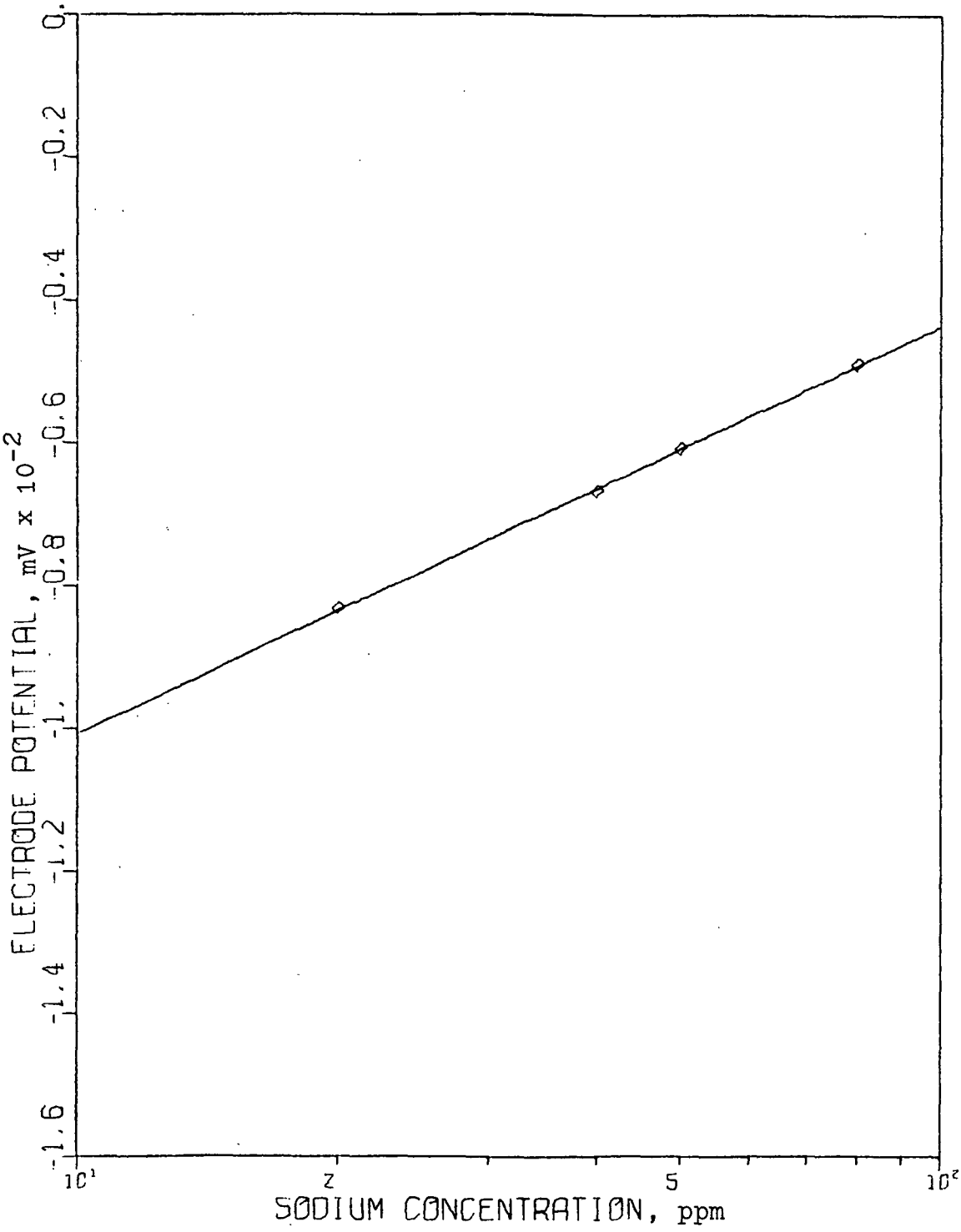


Figure 30. A Typical Calibration Curve for the Sodium Electrode

IONENE BROMIDE AND SODIUM BROMIDE STOCK SOLUTIONS

The bromide containing solutions were standardized by titration with silver nitrate solution. Figure 31 is a typical Gran's Titration curve. The end point of titration was determined by solving the set of two simultaneous equations of the least-squares regression lines passing through the data points preceding and beyond the end point. To simplify the calculations, the end point was assumed to lie at the intersection between the abscissa and the regression line with the steeper slope. This simplification is valid because the ordinate values preceding the end point are lower than those beyond by many orders of magnitude as a result of the abrupt steepening of the slope immediately beyond the end point. The difference between the end points as calculated by the standard method and by the simplified method was found to be negligible. The average concentrations (from two determinations) of the sodium bromide stock solutions and the ionene bromide solutions used in the preparation of the control solutions and in the complexation experiments are tabulated in Table VI.

POLYELECTROLYTE COMPLEXATION EXPERIMENTS

CRITERIA FOR STOICHIOMETRY OF POLYELECTROLYTE INTERACTION

The specific conductance of the supernatant solution of the polyelectrolyte reaction mixtures was compared to that of their corresponding control solutions graphically. The control solution for a reaction at a particular ionic mole ratio contained the stoichiometric amount of each component that would be present in the supernatant solution if stoichiometry prevails. When the specific conductance of the reaction mixture and that of its control solution are identical, the reaction is considered stoichiometric. Consequently, stoichiometry of reaction also calls for the formation of a hydrophobic, electrically neutral and precipitable polyion complex. These are the criteria for the stoichiometry

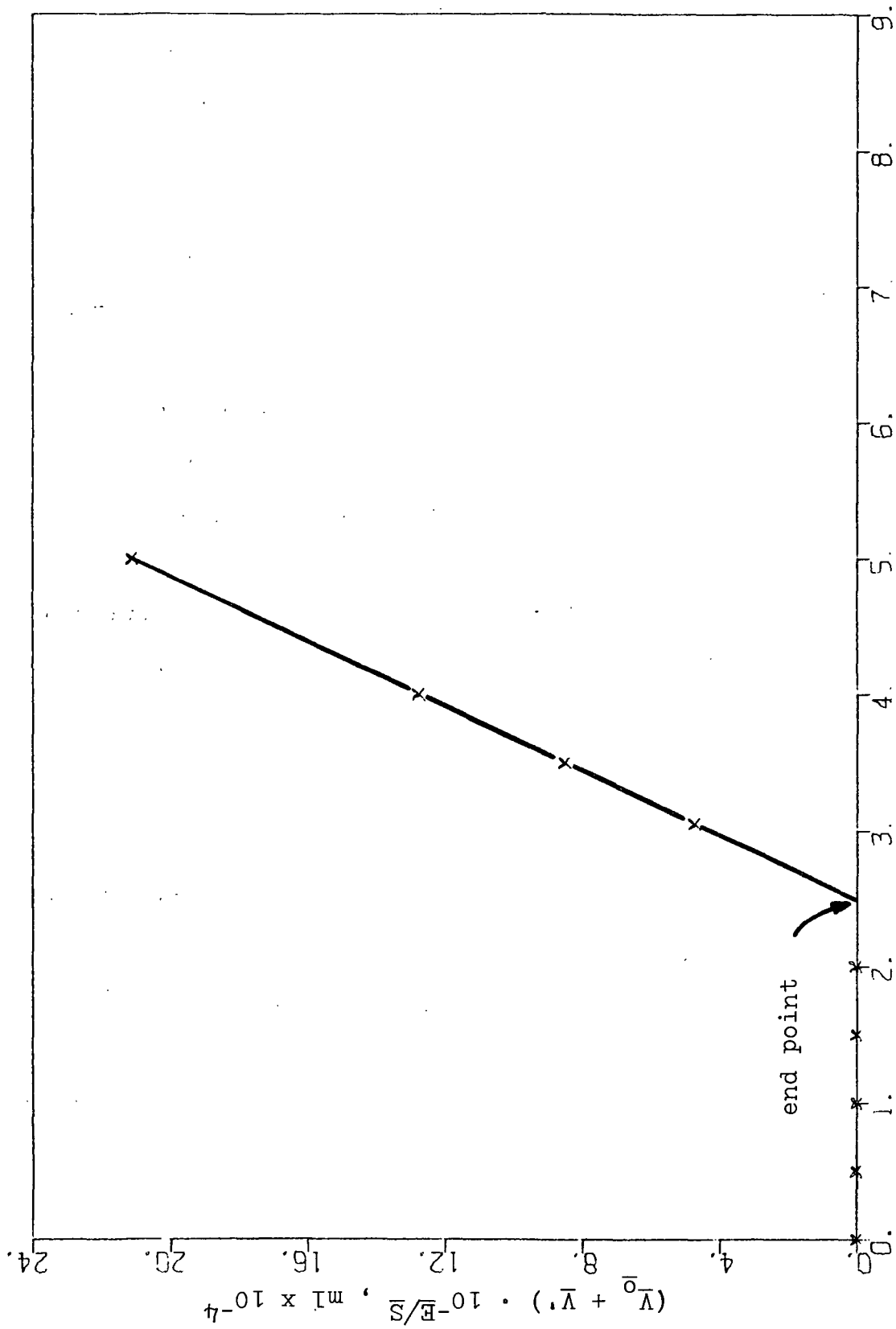


Figure 31. A Typical Gran's Titration Curve (Taken from 3,3-Ionene Fraction B)

of polyelectrolyte interaction. If any of the above conditions is not satisfied, stoichiometry of complexation can not be inferred from these measurements.

TABLE VI

CONCENTRATIONS OF BROMIDE-CONTAINING SOLUTIONS

Solution	Fraction	Experiment	Concentration, $\underline{M} \times 10^3$
3,3-Ionene	Unfractionated	Sets 1 & 2	1.09 ± 0.02
	B	Sets 3 & 5	1.07 ± 0.01
	G	Set 4	1.10 ± 0.02
4,4-Ionene	Unfractionated	Sets 1 & 2	1.07 ± 0.01
	B	Sets 3 & 5	1.01 ± 0.02
	H	Set 4	0.97 ± 0.02
5,5-Ionene	Unfractionated	Sets 1 & 2	1.08 ± 0.01
	B	Set 3	1.11 ± 0.01
	E	Sets 4 & 6	1.11 ± 0.01
	F	Sets 4 & 6	0.96 ± 0.01
6,6-Ionene	Unfractionated	Sets 1 & 2	1.04 ± 0.01
	B	Sets 3 & 5	1.06 ± 0.01
	H	Set 4	1.10 ± 0.01
NaBr stock	--	Sets 1 & 2	4.38 ± 0.02
	--	Sets 3 to 6	4.35 ± 0.01

INITIAL COMPLEXATION REACTIONS

Initial complexation studies were conducted using unfractionated polyelectrolytes. The results of these complexation reactions are shown in Fig. 32. In the group 3N-UDM, 3,3-ionene bromide was reacted with sodium poly(vinyl sulfonate). The specific conductance of the reaction mixture was identical to that of its control solution throughout the entire range of interest. The reaction mixtures had turned turbid when inspected after the reagents were completely delivered. The turbidity persisted until it was centrifuged. The turbid solution indicated that reaction had taken place and that a complex was formed. By visual inspection, the turbidity increased as the mole ratio was increased, up to and including a mole ratio of one. This simply meant that the amount of insoluble complex

formed was gradually increasing as the amount of available polyelectrolyte (3,3-ionene) was increased. Beyond the ionic mole ratio of one, a slight and gradual decrease in turbidity of the reaction mixture was observed. The decrease in turbidity was due to dilution by the excess 3,3-ionene bromide solution.

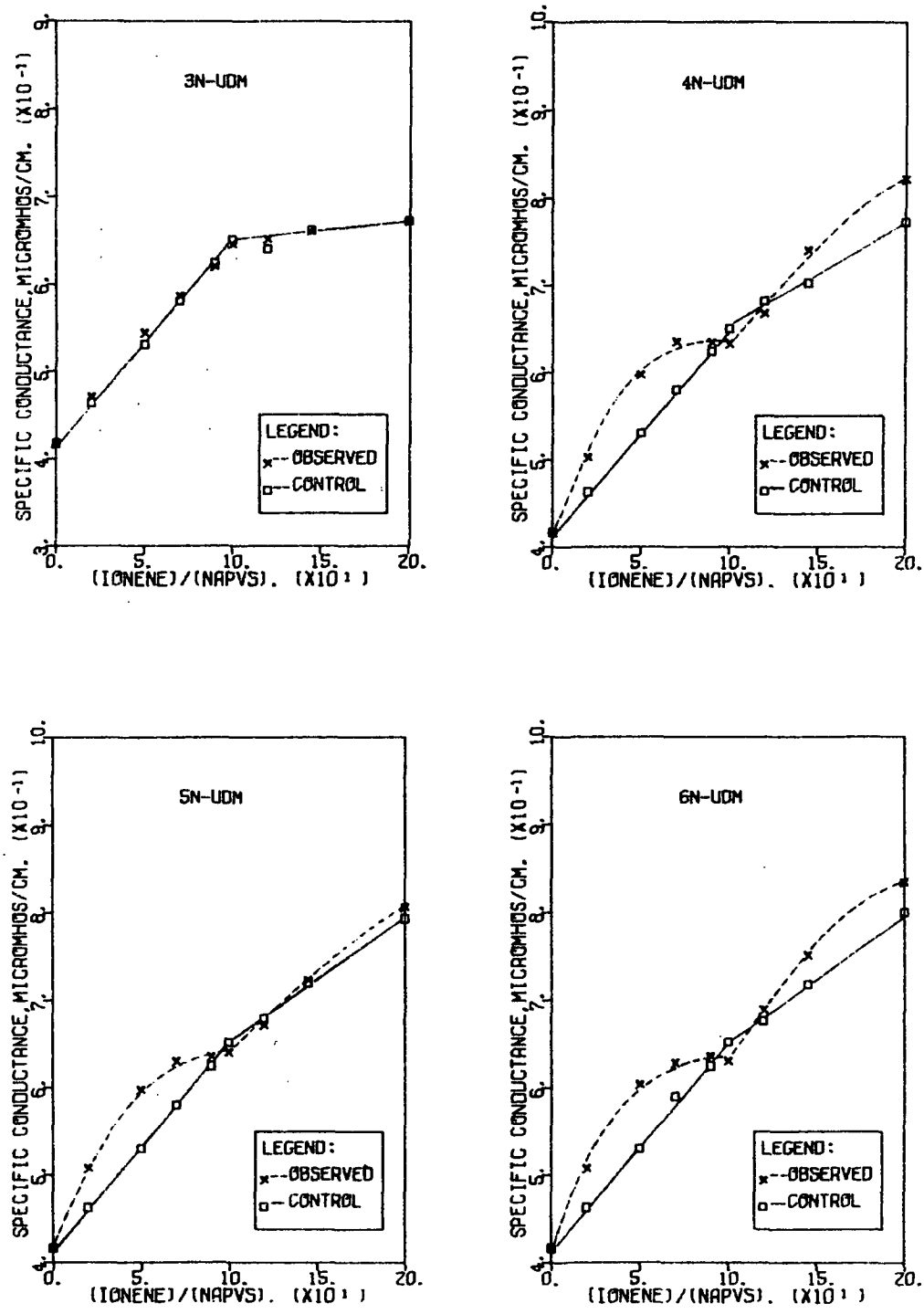


Figure 32. Specific Conductance Versus Ionic Mole Ratio of Reactions Between Unfractionated Polyelectrolytes

Upon centrifugation, a fine greyish complex was obtained. Some of this complex was also observed to be precipitable from the reaction mixtures on standing. The easy precipitability and equality of conductivity between the reaction mixture and the control solution indicate that the greyish complex is hydrophobic and electrically neutral. These results satisfied the criteria for stoichiometry of complexation. Thus, it was concluded that 3,3-ionene bromide and sodium poly(vinyl sulfonate) had reacted stoichiometrically and that polydispersity had no effect on the reaction of polyelectrolytes with equal ionic spacings.

Before proceeding to the presentation and discussion of the reactions between sodium poly(vinyl sulfonate) and the rest of the ionene bromides, let us discuss a plausible complex structure which two oppositely charged polyelectrolytes with markedly different ionic spacings might form. This structure is depicted in Fig. 33. When the two extended strands of polyions are "zippered" together, in all likelihood, a nonstoichiometric primary complex is formed. If this complex would coalesce to form a precipitate, then the unreacted ionogenic groups would not contribute to the conductivity of the supernatant solution. Since fewer than stoichiometric amounts of counterions are released, the specific conductance of the supernatant solution of such a reaction should be lower than that of its control solution.

Unlike the 3N-UDM system, the equality of the specific conductance of the reaction mixture to that of the control solution was not at all realized in the other three groups of reactions (Fig. 32, b-d). Since the ionic spacings of the other ionene bromides are higher than that of the sodium poly(vinyl sulfonate), they are not expected to form stoichiometric complexes. In these systems, the conductance of the reaction mixture was always higher than that of its control solution except at unit mole ratio. Interestingly enough, this

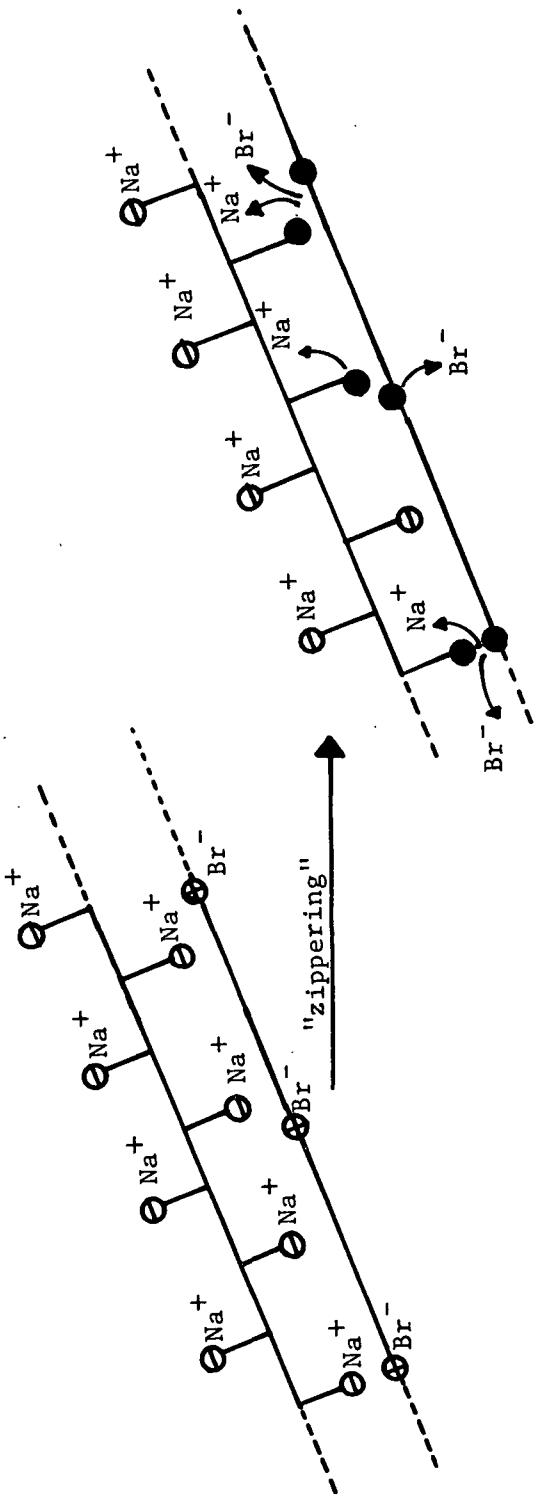


Figure 33. Primary Complex Formation. A Plausible Structure of the Nonstoichiometric Primary Complex Through the Interaction of a Polycation Whose Ionic Spacing is Larger than that of the Polyanion

phenomenon is the exact opposite to what is expected for a nonstoichiometric reaction as discussed in the previous paragraph. The anomalous conductivity effect exhibited by the nonstoichiometric reaction mixtures will be discussed in greater detail later.

The reaction mixtures of groups 4N-, 5N- and 6N-UDM were quite clear, and a more turbid solution was only obtained at an ionic mole ratio of one. By visual comparison, the turbidity of the reaction mixtures of these three groups of reactions was lower than that of the reaction mixture in the group 3N-UDM at unit mole ratio. In addition, the forms of the polyion complex were variable. Their appearances ranged from a viscous fluid coacervate embedding a smaller amount of fine precipitate to just a viscous fluid coacervate. Due to the small quantities involved, no convenient means was available to measure the yield of complexations. Thus, no weight was recorded of the precipitates. However, by visual inspection, the amounts of precipitable complexes seemed to decrease in descending order of the DP of the ionene bromides. With reference to Table IV, the DP of the polycations used in this set of experiments (Set 1) decreases in the order: 3,3-ionene, 4,4-ionene, 6,6-ionene and 5,5-ionene. On the other hand, at unit ionic mole ratio the amounts of precipitate formed were about the same for every experiment. Scanning electron micrographs of the two forms of precipitates are shown in Fig. 34 and 35.

The phenomenon of complex coacervation was subjected to extensive studies by Bungenberg de Jong (62) and Kruyt (63). They concluded that complex coacervation represents a less intimate interaction of the ionogenic groups on the interacting polyions and/or the constituents of the complex, since polyelectrolyte coacervates are generally dissolved on addition of electrolytes. In this investigation, as Fig. 33 depicts, the complexes of 4,4-, 5,5-, and 6,6-ionene bromides may indeed be less closely associated with the sodium poly(vinyl

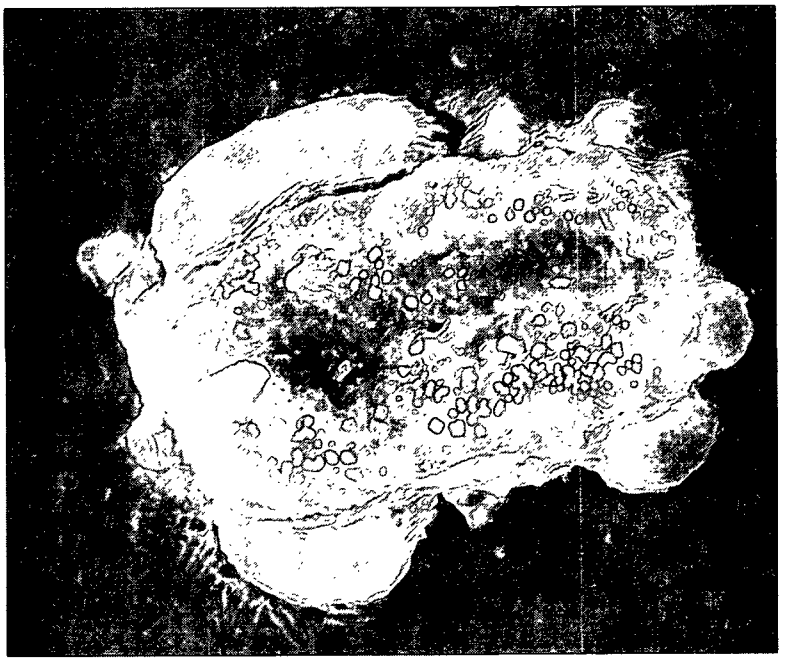


Figure 34. Scanning Electron Micrograph of the Fine Precipitate from Group 3N-UDM. The Precipitate Dried as a Film Which the Micrograph Shows. The Light Spots on the Film Bubble are Sodium Bromide Crystals. Magnification: 3,000X

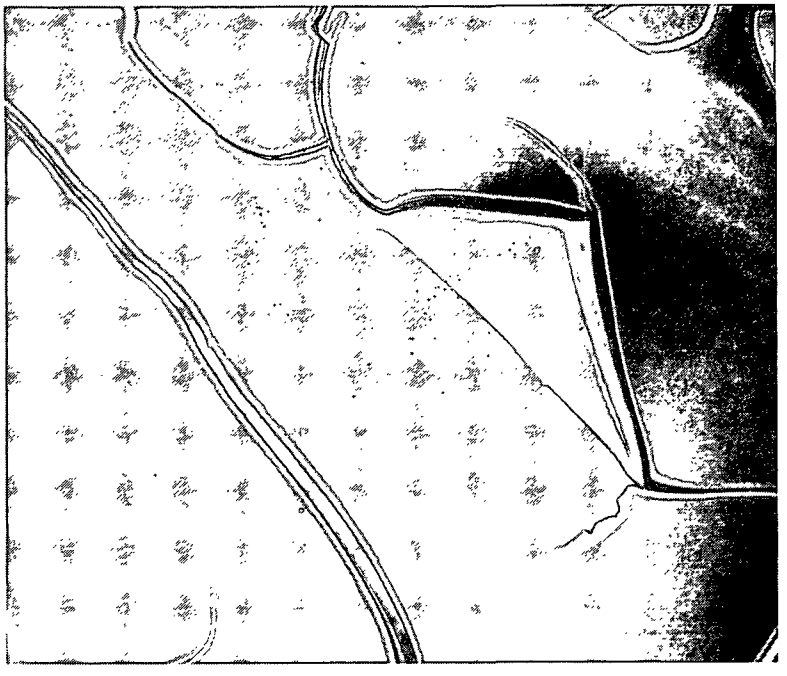


Figure 35. Scanning Electron Micrograph of the Viscous Fluid Coacervate from Reaction 6N-UDM7. Cracks on the Micrograph are Formed as a Result of Shrinkage on Drying. Magnification: 100X

sulfonate) than the 3,3-ionene bromide since not all of their ionic groups were expected to have taken part in the complexation. Meanwhile, the viscous fluid coacervate also suggests that it has acquired a somewhat hydrophilic character through the hydration of the exposed unreacted ionogenic groups in the complex. Therefore, the presence of a viscous fluid coacervate may also be an indication of nonstoichiometry.

When a small amount of sodium chloride crystals were added to the clear supernatant solution of those reactions that yielded a viscous fluid coacervate, the solution turned turbid immediately and the coacervate disappeared. The dissolution of the coacervate was consistent with Kruyt's and Bungenberg de Jong's expectation. Upon ultracentrifugation, the solution turned clear once again and an additional amount of viscous fluid coacervate was precipitated. Further addition of salt to this supernatant solution did not change its clarity. Interestingly enough, the addition of salt to those supernatant solutions at unit mole ratio seemed to have only slight but observable effects on the clarity and the amounts of coacervate. Since none of the selected polyelectrolytes could be salted out by electrolytes, the second viscous fluid coacervate could not be the excess polyelectrolyte. This simple experiment has then shown that in addition to the greyish complex and the viscous fluid coacervate, a third kind of polyion complex exists in either a dissolved or colloidal form in the supernatant solution of these reaction mixtures. In order for this complex to remain dissolved, it must have an excessive amount of unreacted ionogenic groups.

The electrophoresis experiment on the supernatant solution of Reaction 4N-UDM2 revealed a negatively charged species with an electrophoretic mobility of -1.98×10^{-4} cm^2/V sec. However, in the electrophoretic pattern, only one sharp band was observed. Therefore, it was concluded that no excess NaPVS (electrophoretic mobility = -4.26×10^{-4} cm^2/V sec) was present in the super-

natant solution. At an ionic mole ratio of 0.5, there should be twice as many sulfonate groups as ammonium groups. The absence of NaPVS in the supernatant solution means that all of the excess NaPVS molecules must have taken a role in the formation of the dissolved complex. Besides, no ionene bromide was detected. This means that all of the reactions between unfractionated NaPVS and 4,4-, 5,5- and 6,6-ionene bromide are nonstoichiometric. Meanwhile, the existence of a dissolved complex is also confirmed. Since this dissolved complex is negatively charged, it may have been the culprit of the anomalous specific conductance effect that was observed. Unfortunately, the results from electrophoresis offered no definitive explanation of this anomaly.

In order to find out whether reacting the polyelectrolytes without good initial mixing would affect the outcome, the above four groups of experiments were repeated, using the delivery device without a mixing chamber. The results are shown in Fig. 36. The diagrams show that there is practically no difference between the specific conductance and the forms of the polyion complexes whether or not they had initial mixing. This suggests that the concentrations used here were dilute enough so that mixing of the solutions is not an important factor.

Now, it is clear that there exist two types of viscous fluid coacervate, viz., one which is precipitable purely by mechanical means and another that is separable by mechanical means only with the aid of excess salt. In the separation of the former viscous fluid coacervate by ultracentrifugation, the ionic repulsion due to excess charges on the coacervate is overcome by the high gravitational force developed at high speed and the system is destabilized. It was assumed that when the system is destabilized, hydrophobic interaction follows and the hydrocarbon portions of the complex coalesce; a viscous fluid coacervate is formed. Apparently, a very delicate balance of ionic repulsion and hydrophobic

interaction exists. Therefore, if the ratio of the unreacted charges to the hydrophobic portions (Hp) exceeds a certain critical value (Hp_c), the coacervate will remain dissolved in the bulk of the supernatant solution and no complex will be precipitated.

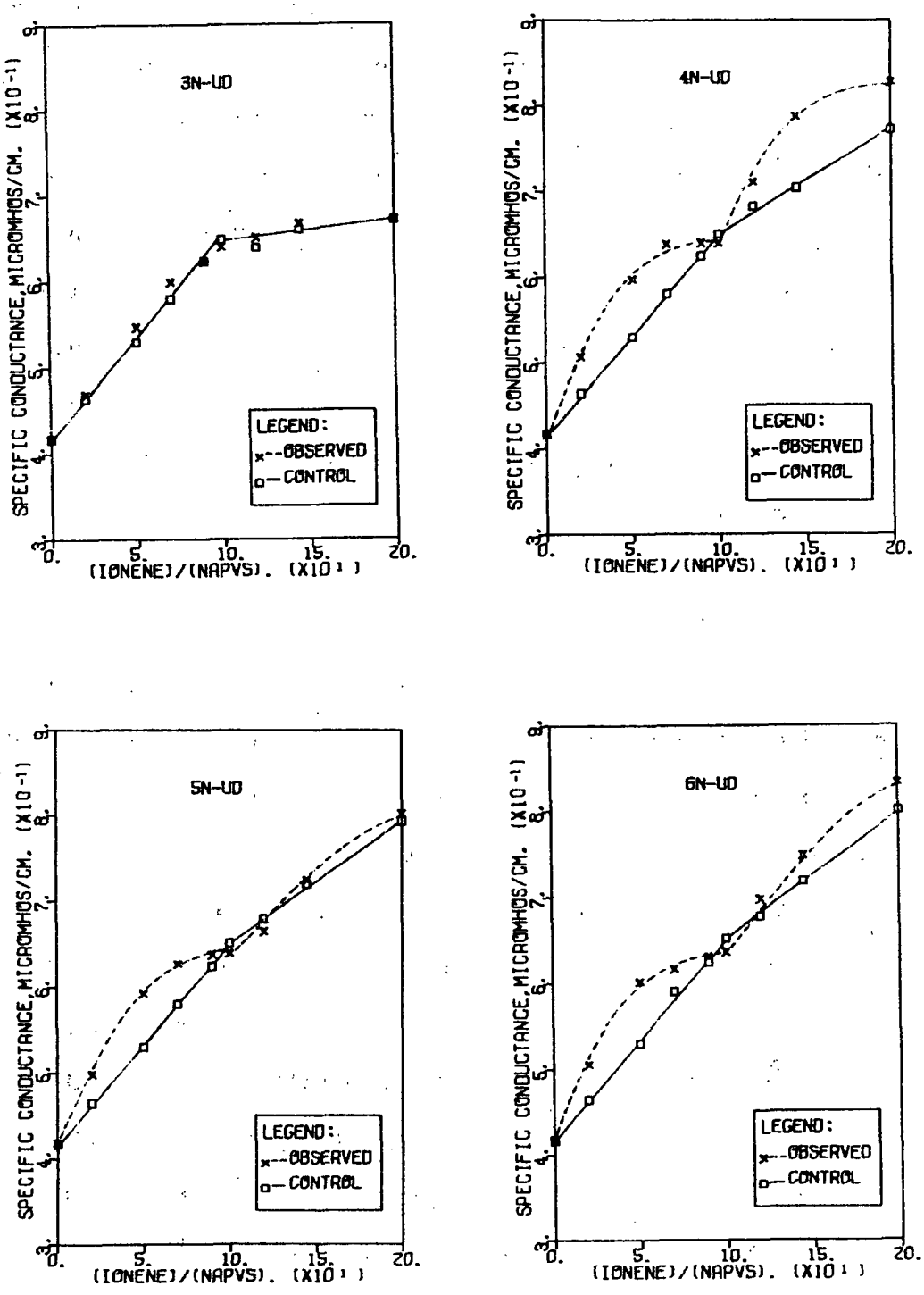


Figure 36. Specific Conductance Versus Ionic Mole Ratio of Reactions Between Unfractionated Polyelectrolytes Without Initial Mixing

With such limited information at hand, it is extremely difficult to offer a satisfactory explanation for the formation of the dissolved and fine polyion complexes at this stage. Since these polyelectrolytes are unfractionated, they represent a blend of high, medium and low DP polymer chains. The relative amount of each kind of chain is dependent upon the average molecular weight, and each kind of chain may react quite differently with the others. Since a mixture of polyion complexes had been obtained in the reactions mixtures of Groups 4N-UDM, 5N-UDM and 6N-UDM, their coexistence suggests that these phenomena may be molecular weight dependent. Therefore, the easily precipitable hydrophobic fine complex (whether stoichiometric or not) may be viewed as formed by the reaction of high DP polymer chains. On the contrary, the dissolved complex may be a product of the complexation between a low DP polyion with a high DP polyion. The validity of this hypothesis will be tested when the reactions of the narrow polyelectrolyte fractions are studied.

EFFECT OF IONIC SPACING

The effect of ionic spacing on the stoichiometry of polyelectrolyte interaction was studied by the reactions of a high molecular weight NaPVS fraction and ionene bromide fractions with comparable degrees of polymerization. The results of these experiments are illustrated graphically in Fig. 37. The reaction mixtures were turbid and a greyish fine precipitate was formed. In addition, a minute but noticeable amount of a viscous fluid coacervate was also found in the precipitates of the reaction mixtures of Groups 4CND, 5BND and 6DND. The fine precipitate showed that the complex had an overall hydrophobic character. As expected, 3,3-ionene bromide reacted stoichiometrically with NaPVS but the other ionenes did not. It is also encouraging to note that the specific conductance of the supernatant solutions of the nonstoichiometric reaction mixture was less than that for the control at all mole ratios, suggesting the absence of a

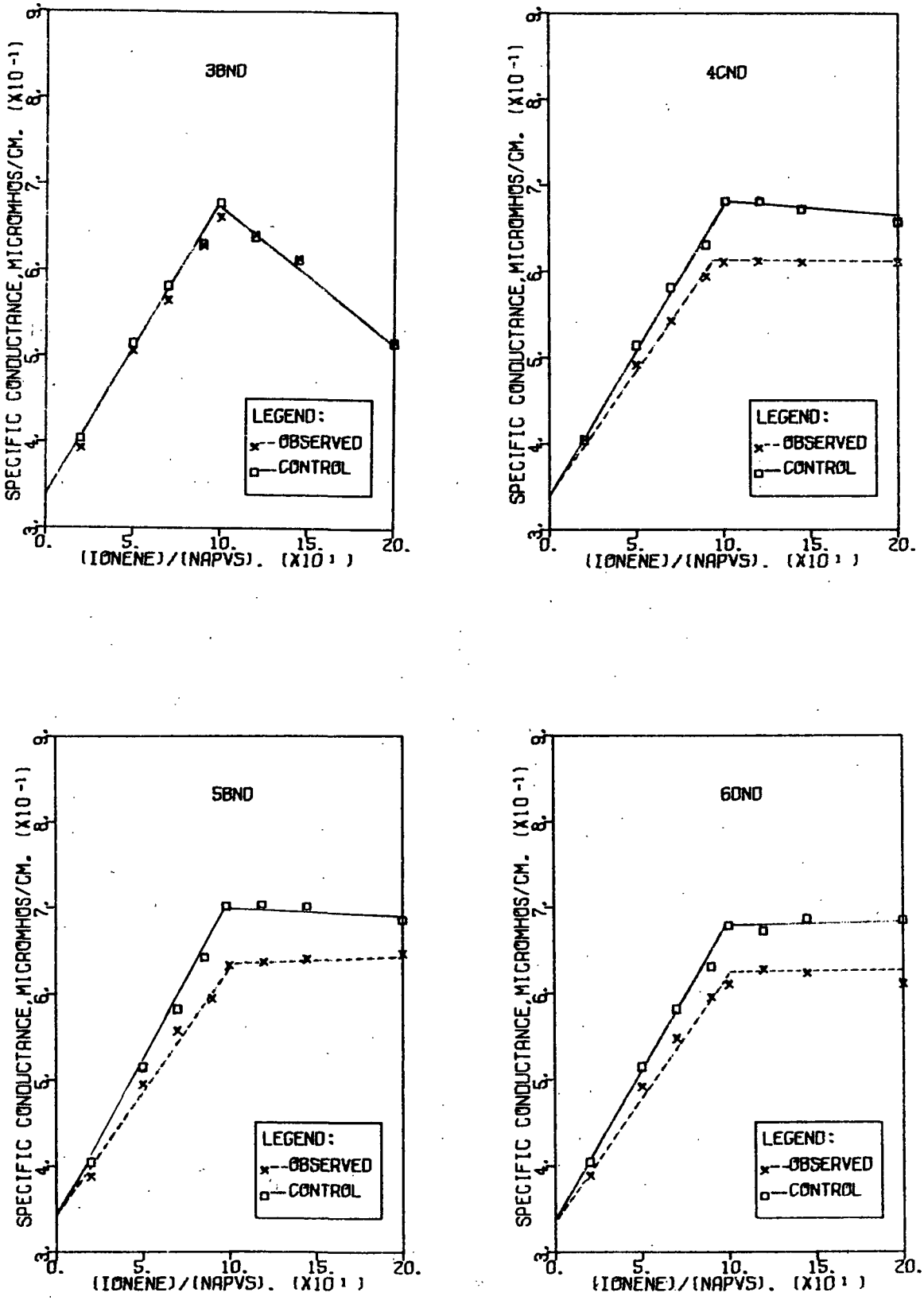


Figure 37. Specific Conductance Versus Ionic Mole Ratio of Reactions Between Polyelectrolytes of Similar DP

dissolved complex which gave an anomalously high conductance to the supernatant solution . The absence of the dissolved complex was later confirmed by the negative result from the qualitative test for this complex by salt addition.

The positive difference between the specific conductances of the control solution and of the reaction mixture represents the difference in the amounts of sodium bromide in the two solutions. With the knowledge of the concentration-specific conductance relationship for pure sodium bromide aqueous solution, the amounts of sodium bromide formed in the reactions (or conversely, the amounts of unreacted ionogenic groups) could be estimated. The methods of calculations are given in Appendix VII. The results of these computations are tabulated in Table VII.

TABLE VII

THE COMPLETENESS OF POLYELECTROLYTE COMPLEXATION AT UNIT IONIC MOLE RATIO

Reaction	NaBr in Control Solution, $\underline{M} \times 10^4$	Unreacted Ionic Groups, $\underline{M} \times 10^4$	Completeness of Reaction, %
3BND5	5.36	0.00	100.0
4CND5	5.36	0.57 ± 0.03	89.4 ± 0.6
5BND5	5.57	0.48 ± 0.01	91.4 ± 0.2
6DND5	5.40	0.44 ± 0.01	92.0 ± 0.2

We now turn to the discussion of the formation of the polyion complexes of these reactions. Bear in mind that the configurational difference between the ionene bromides and the NaPVS is that the former are an integral type polyelectrolyte and that the latter is a syndiotactic pendent type of polyelectrolyte. This means the ionogenic groups on the NaPVS are distributed in an alternating fashion on either side of the polyion. In dilute aqueous solutions, these polyelectrolytes are fully extended rigid rods. Thus, even though 3,3-ionene bromide and NaPVS have the same ionic spacing and the same DP, the length of the ionene polyion is twice as long as that of the NaPVS (Fig. 38). As for the other ionenes,

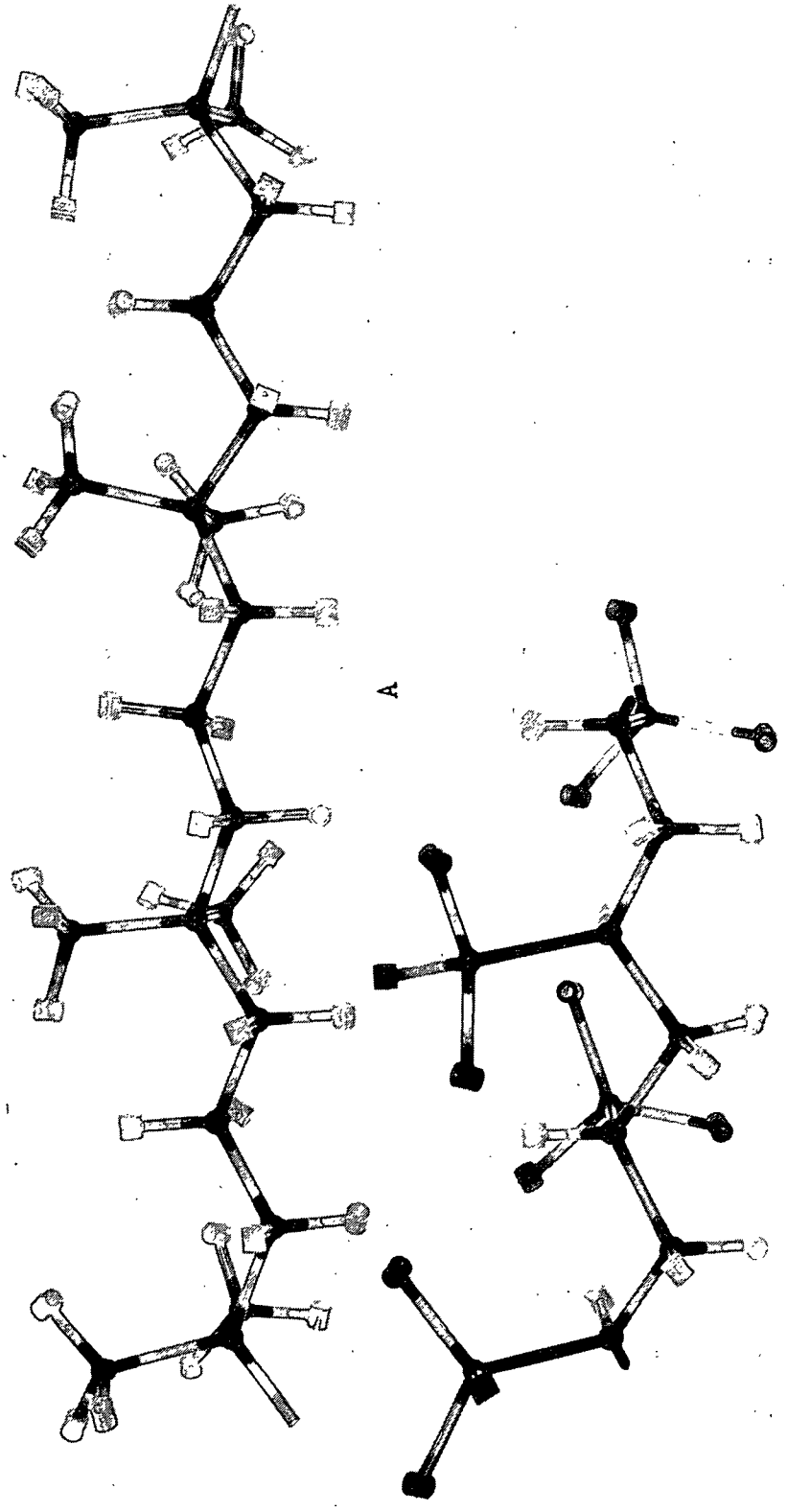


Figure 38. Scale Models of Tetramers of (A) 3,3-Ionene and (B) Syndiotactic NaPVS. The Polyelectrolytes are Depicted in Their Fully Extended (Zigzag) Conformation

since their ionic spacings are much larger than that of the NaPVS, the overall length of the polycation would be even longer than that of a 3,3-ionene bromide with an equal DP.

In an earlier section, it was mentioned that these polyions assume a rigid and fully extended conformation in water. The much restricted rotation of the carbon-carbon bonds causes the quaternary ammonium groups on the polycations to always seek to react with those sulfonate groups that are closest to themselves. Therefore, an ionene polyion is expected to react exclusively with the sulfonate groups on one side of the NaPVS polyion rather than crossing over to react with those on the other side.

During the formation of a primary complex in dilute solutions, the numbers of polycation and polyanion molecules were kept approximately equal at all times. Therefore, the primary complex is a complex formed by the interaction of only two oppositely charged polyions. A proposed structure of these primary complexes is illustrated in Fig. 39. Such a primary complex structure was evolved as a result of the consideration of the idealized case when the polyelectrolytes react.

It is clear in Fig. 39a that the side of the NaPVS polyion that is available for reaction had "zippered up" nicely with the 3,3-ionene bromide polyion as a consequence of equal spacing. On the other hand, due to the stereochemistry of the NaPVS polyion, the sulfonate groups on the other side of the polyion are not available to the same 3,3-ionene bromide polyion for further reaction. Therefore, such a primary complex is nonstoichiometric and it contains unreacted anionic groups and a "long tail" of unreacted quaternary ammonium ions. As for the other ionene bromides, since their ionic spacings are larger than that of the NaPVS, the reactions between these ionenes and the NaPVS would be similar to the fastening of a zipper with an unequal number of evenly spaced interlocking tabs or teeth on either edge; except the tabs on one edge are spaced wider than

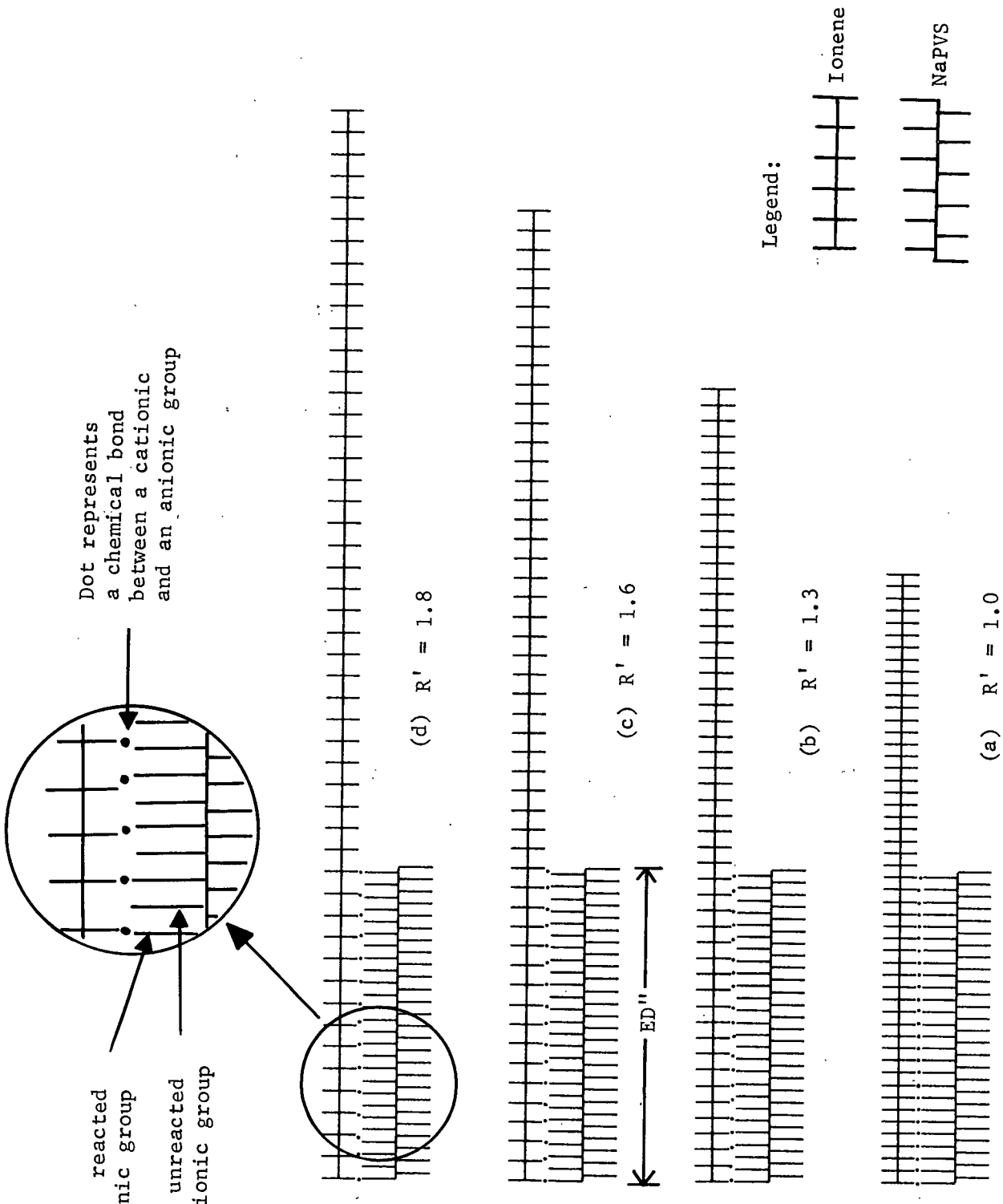


Figure 39. Scale Diagrams of the Proposed Structure for Primary Complexes of Syndiotactic NaPVS and Ionene Bromides with Similar Degree of Polymerization (DP = 50). (a) 3,3-Ionene, (b) 4,4-Ionene, (c) 5,5-Ionene and (d) 6,6-Ionene. Each of the Vertical Lines Represent an Ionogenic Group on the Polyion (Horizontal Line)

those on the other. The inequality of ionic spacing causes an imperfection in the "zippering" process and the resulting primary complexes are nonstoichiometric. These complexes consist of a partially reacted portion with some residual anionic groups from the side of the NaPVS chain that had reacted with the ionene polyion, an unreacted side of the NaPVS chain full of sulfonate groups and a "long tail" of unreacted cationic groups from the ionene polyion whose length increases as the ionic spacings of the ionene increases. Such a complex is most vividly illustrated by Fig. 39d. The diagram inscribed in the larger circle directly above Fig. 39d is a magnified view of a portion of a nonstoichiometric primary complex representative of those primary complexes from reactions of the NaPVS with ionenes with larger ionic spacings. In Fig. 39, those ionic groups that had reacted as a result of coulombic interaction were connected by a dot. This is a convenient bookkeeping device to account for the reacted ionogenic groups and to distinguish them from the unreacted ones.

In reality, other structures are also possible for these primary complexes. Two additional models for the primary complex are given in Fig. 40.

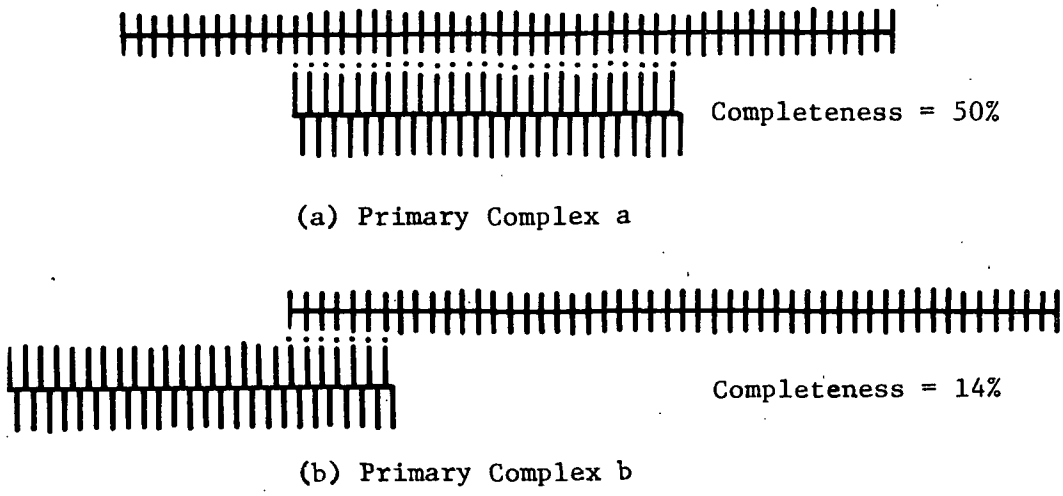


Figure 40. Two Additional Scale Diagrams of the Proposed Structures of Primary Complex of NaPVS and Ionene Bromide (3,3-Ionene) with Similar Degree of Polymerization

The reckoning of reacted and the total number of ionogenic groups of the entire complex depicted in Fig. 39 by counting dots revealed that the maximum fraction of reacted ionogenic groups in the primary complex of 3,3-ionene bromide with NaPVS is 50%. Similarly, the fraction of reacted ionogenic groups in primary complex (a) as depicted in Fig. 40a is also found to be 50%. Thus, it is concluded that the model depicted in Fig. 39a and that in Fig. 40a may be equally probable. On the contrary, in the primary complex depicted in Fig. 40b, the maximum percentage of ionic groups that have taken part in the complexation is merely 14%. Since a part of the driving force of polyelectrolyte interaction is the achievement of minimum electrostatic energy and potential, the formation of such a primary complex is not favored and the probability should be extremely low.

When the polyelectrolytes involved are of high DP and when the ionic spacing of the ionene bromides gets progressively larger than that of the NaPVS, the reckoning of reacted groups by dot counting becomes extremely tedious and impractical. Therefore, general mathematical expressions for the estimation of the completeness of complexation between polyelectrolytes with similar DP are to be developed as follows.

Let us consider the idealized reaction of a molecule of NaPVS with a molecule of an ionene bromide that has a larger ionic spacing than itself. The degrees of polymerization of the two polyionic species are to be quite similar. To simplify the calculation slightly, the NaPVS is considered to assume an ionic spacing of unit length. Thus, the ionene bromides assume an ionic spacing of R', where R' is the ratio of the ionic spacing of the ionene to that of the NaPVS. Denoting the degree of polymerization (or the number of ionic groups per molecule) of NaPVS by DPN, and that of ionene bromide by DPI, the length of the syndiotactic NaPVS polyion, ED" (as depicted in Fig. 39c),

is calculated by the equation:

$$ED'' = 0.5* DPN - 1$$

Meanwhile, the quaternary ammonium groups in an equal length of the polycation would react with the sulfonate groups within the length ED". In Fig. 39 it is obvious that all of the cations in this length are used up in the interaction. The number of cations (also anions) that has taken part in the reaction is given by the equation:

$$NPCRX = (0.5* DPN - 1)/R' + 1 \quad (6)$$

Since NPCRX is also equal to the number of reacted sulfonate groups, the total number of ionogenic groups reacted in the formation of a primary complex is:

$$NTOTP = 2* [(0.5* DPN - 1)/R' + 1] \quad (7)$$

The total number of ionic groups in the primary complex is given by N = DPN + DPI. The completeness of complexation in the primary complex is thus expressed by the equation:

$$P_p = 100* NTOTP/N \quad (8)$$

The completeness of the reactions in the primary complexes as predicted by Equation (8) is tabulated in Table VIII.

TABLE VIII

PREDICTED REACTION COMPLETENESS FOR PRIMARY COMPLEXES AT UNIT IONIC MOLE RATIO

Reaction	DPN	DPI	P_p, %
3BND5	140	140	50.0
4CND5	135	140	39.3
5BND5	145	140	31.0
6DND5	135	140	28.6

When the predicted completeness of polyelectrolyte interaction in the primary complexes was compared to that as calculated from experimental data, it was found that the former values are much lower than those of the latter. It is evident that the decrease in reaction completeness is brought about by an increase in the ionic spacing. All of the nonstoichiometric primary complexes discussed above are highly charged. In order to yield the final greyish complex with an overall hydrophobic character, these primary complexes must have undergone some sort of interprimary complex reaction. One may expect the first result of such a reaction is the formation of a secondary complex. Eventually when the formation of the secondary complex is completed, they may further interact and/or aggregate by hydrophobic forces to yield the greyish complex in which Hp is much less than Hp_c.

Fig. 37, b-d, show that the specific conductance values for the reaction mixtures beyond an ionic mole ratio of one were nearly parallel to those of their corresponding control solutions. In the polyelectrolyte complexation experiments, the excess polyelectrolyte solution was always added immediately after unit mole ratio was reached. This means the addition of excess ionene bromide had not affected the compositions of the final complex to any appreciable extent. Therefore, the possibility of excess ionene bromide having taken a part in the formation of the greyish complex is justifiably ruled out.

The formation of a secondary complex may be accomplished in a large variety of ways. The most obvious and efficient way, however, is for the two primary complexes to interlock in the "six-nine" ("69") position. During the interlocking process, the "long tail" of cations on one primary complex will react with the sulfonate groups on the unreacted side of the NaPVS polyion that belongs to another primary complex. The proposed interlocking mechanism of the formation of a secondary complex is conveniently illustrated by the reaction of two

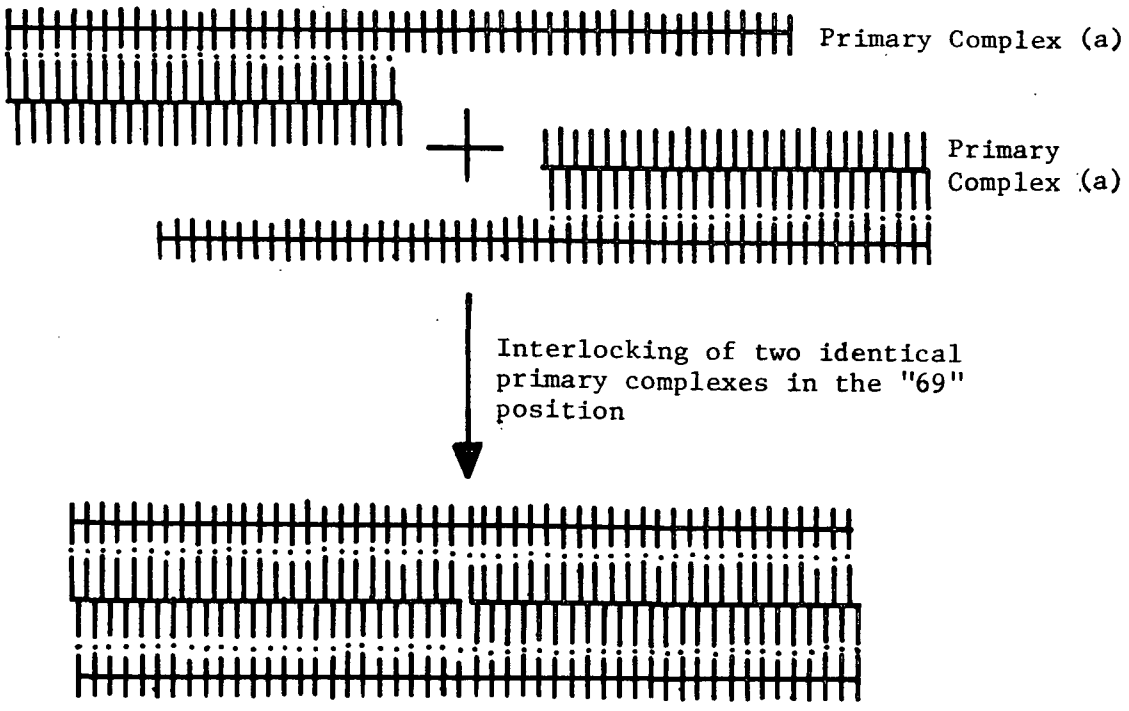
identical primary complexes of 3,3-ionene and NaPVS in Fig. 41. Since the interlocking process involves the coulombic interaction of two identical primary complexes, the total number of ionic groups in a secondary complex (hereafter called the duplex) is given by the expression: NTOT = 2* N. The interaction of the "long tails" and the sulfonate groups on the other side of the NaPVS molecules on the primary complex brings about an increase in the total number of reacted groups and the total number of reacted groups is now NRX. Thus, NRX = 4* NTOTP. The reaction completeness of the duplex is then expressed by:

$$P_D = 100* 4* NTOTP/NTOT \quad (9a)$$

$$= 2* P_p \quad (9b)$$

The predicted completeness of the reactions in the duplexes is tabulated in Table IX. The results show that by interlocking two primary complexes of 3,3-ionene and NaPVS, the reaction completeness has become 100%. The perfection of this reaction is undoubtedly brought about by the equality of ionic spacings of the two interacting polyelectrolytes. Thus, the suggested structure of the duplex in Fig. 41 could very well be the structure of the final greyish complex for this particular type of reaction. On the contrary, even though the completeness of the reactions between NaPVS and the other ionene bromides is doubled by the formation of the duplex, it is still considerably lower than its experimentally determined value. In order to attain a completeness value close to the experimental value, these duplexes must have undergone further reactions.

The proposed structure of a typical duplex from the interlocking of two primary complexes of NaPVS and an ionene bromide with a larger ionic spacing is shown in Fig. 42. The diagram shows that this duplex consists of (a) two regions of completely reacted cationic groups called the "dead portion," (b) a rib cage region of leftover unreacted sulfonate groups, and (c) two "arms"



(b) Duplex, completeness = 100%

Figure 41. Proposed Mechanism for the Formation of a Stoichiometric Duplex from Two Primary Complexes of NaPVS and 3,3-Ionene Bromide with Equal Degree of Polymerization

TABLE IX

PREDICTED REACTION OF COMPLETENESS FOR SECONDARY COMPLEXES AT UNIT IONIC MOLE RATIO

Reaction	P_D, %
3BND5	100.0
4CND5	78.6
5BND5	62.0
6DND5	57.2

of unreacted cationic groups. Thus, any further neutralization of electrical charges in the duplex must be due to the coulombic interaction of the cationic groups in the "arms" and the leftover anionic groups in the rib cage region. Perhaps, the "arms" are unable to bend backwards and react with the sulfonate groups in the same duplex. Therefore, a further reduction of electrical charges would have to be brought about by interactions among the duplexes.

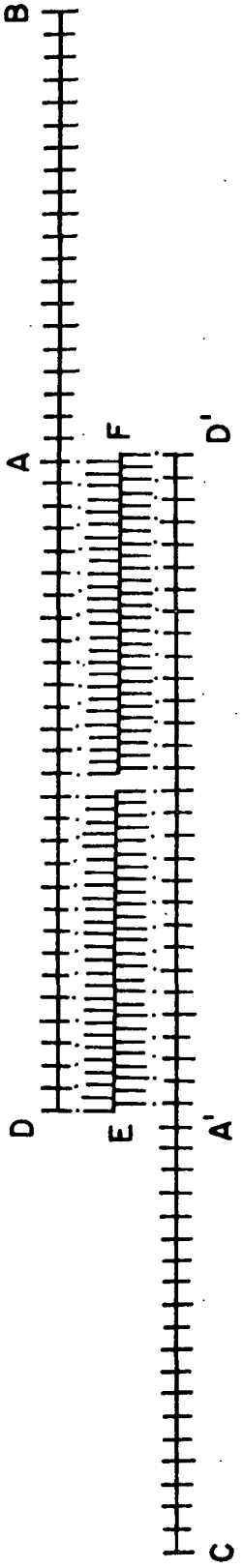


Figure 42. Scale Diagram of the Proposed Duplex From the Interlocking of Two Primary Complexes of NaPVS and 6,6-Ionene Bromide With Equal Degree of Polymerization

It is conceivable that some sort of an ordered reaction among the duplexes will eventually lead to the final greyish complex with a high degree of completeness. The most obvious of such a reaction is one of stacking these duplexes in such a way that the "arm" of one duplex will react with the sulfonate groups on one side of the rib cage of another. Meanwhile, the "arm" of the latter duplex will react with the sulfonate groups on one side of the rib cage of the former. In order to present a clearer picture of such an interaction, the diagram of the proposed duplex in Fig. 42 is simplified considerably to a schematic drawing as shown in Fig. 43. The orderly stacking of these duplexes into a final massive complex bears a striking resemblance to the construction of a structure by fitting together building blocks. Therefore, it would be appropriate to rename the duplexes "building blocks." The stacking of these building blocks is illustrated in Fig 44.

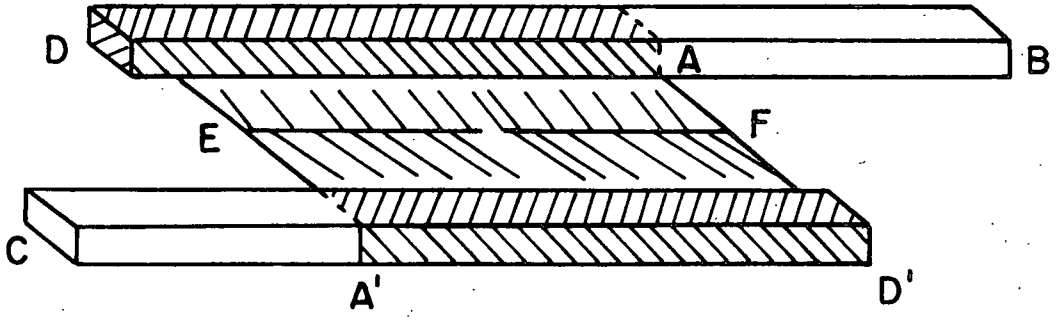


Figure 43. Dramatic Representation of the Proposed Duplex (Building Block) from the Complexation of NaPVS and Ionene Bromide with Similar Degree of Polymerization

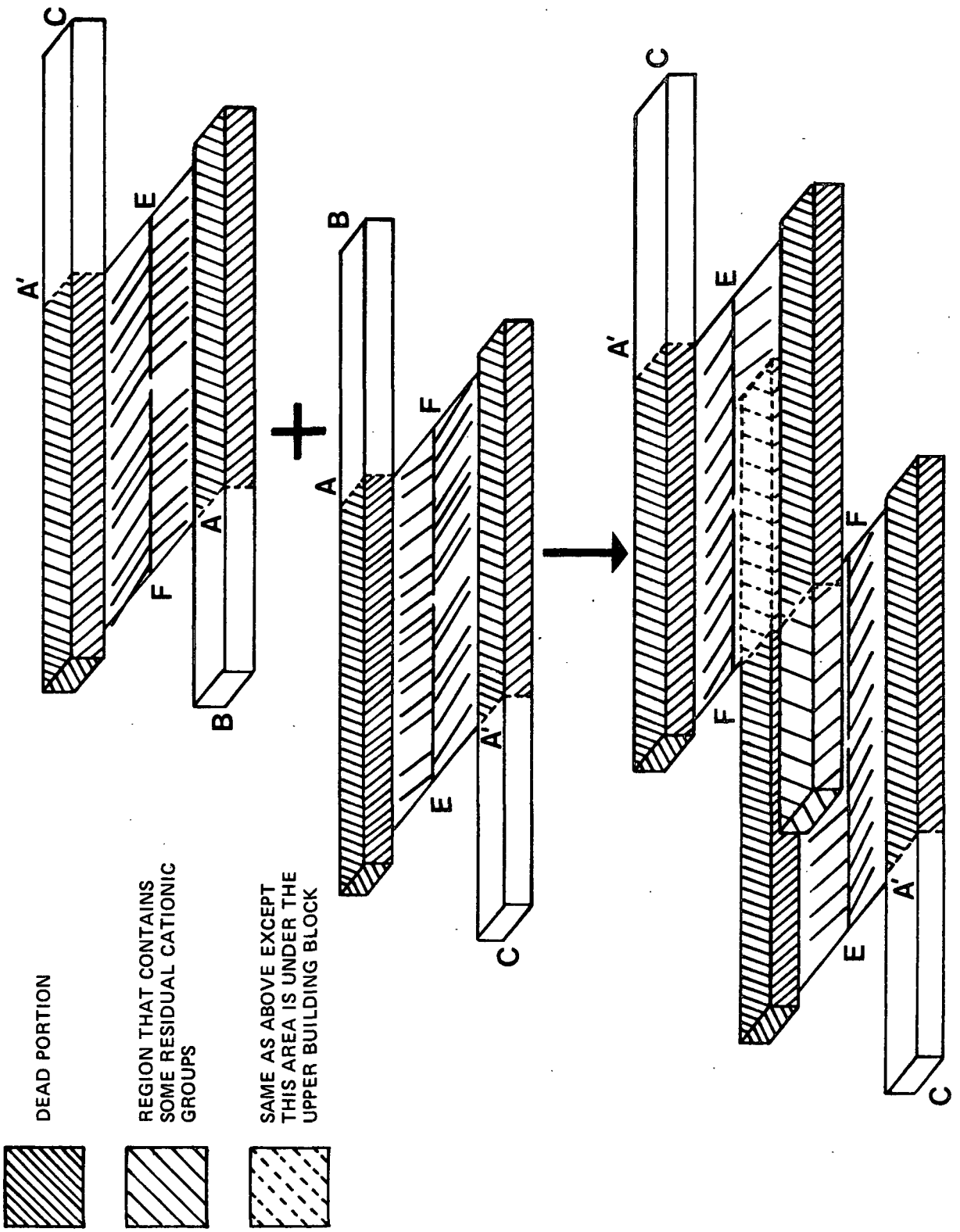


Figure 44. The Stacking of Building Blocks

In the formation of the building block, two molecules of NaPVS were arranged "head to tail." Therefore, the length of the rib cage region, EF, is given by the equation:

$$EF = DPN - 1$$

The number of unreacted sulfonate groups on either side of the rib cage, NCAGE, is given by:

$$NCAGE = 2* [0.5* DPN - ((0.5* DPN - 1)/R' + 1)], \quad (10)$$

the factor 2 comes from the fact that the rib cage is made up of two molecules of NaPVS. The average spacing, R", between these unreacted sulfonate groups is expressed by the equation:

$$R" = (DPN - 1)/(NCAGE - 1) \quad (11)$$

In this particular model, the two "arms" of cationic groups are of equal length. Thus, AB = CA' = (DPI - 1)* R' = (DPN - 1). During the stacking process, the sulfonate groups in a length AB on the rib cage and an equal number of cationic groups on the "arm" will be neutralized. The number, NSRC, of these sulfonate groups is expressed by the equation:

$$NSRC = AB/R" + 1 \quad (12)$$

Equation (12) holds only if $AB \leq EF$ or $R' \leq 2.0$. Since two "arms" and two rib cages are involved in the stacking process, the total increase in the number of reacted ionic groups, NI, is given by the equation:

$$NI = 4* NSRC \quad (13a)$$

$$= \frac{4* [(DPI-1)*R' - (DPN-1)] *[2*[0.5*DPN - ((0.5*DPN-1)/R' + 1)] - 1]}{(DPN - 1)} + 4 \quad (13b)$$

With the above equations at hand, the completeness of polyelectrolyte interaction can be formulated. One could express the percentage of reacted

ionogenic groups, P, in terms of the NRX, NTOT, NI and NDUP, the number of building blocks that makes up the complex. The theoretical completeness equation is:

$$P = [NRX/NTOT + (NDUP - 1)* NI/(NTOT*NDUP)]* 100, \quad (14a)$$

$$= [NRX/NTOT + NI/NTOT *(1 - 1/NDUP)]* 100 \quad (14b)$$

If one lets A = NRX/NTOT, and B = NI/NTOT, then:

$$P = [A + B*(1 - 1/NDUP)]* 100 \quad (15)$$

The significance of Equation (15) is that the limiting value of P as the number of building blocks approaches infinity is equal to the sum of the parameters A and B. Based on the above equations, a computer program was written to calculate the values of A, B and P, for the interaction of polyelectrolytes with approximately equal degrees of polymerization. A listing of this program is given in Appendix VIII. The theoretical maxima and the experimentally calculated values of the completeness of the interactions of NaPVS and the selected ionene bromides are compared in Table X.

TABLE X

THE THEORETICAL AND EXPERIMENTAL COMPLETENESS OF POLYELECTROLYTE COMPLEXATION AT UNIT IONIC MOLE RATIO

Reaction	Ionene DP	NaPVS DP	NTOT	NRX	NI	A	B	P, % limiting	Completeness, % Experimental
3BND5	140	140	560	560	0	1.00	0.00	100.0	100.0
4CND5	135	140	550	433	35	0.79	0.06	85.4	89.4
5BND5	145	140	570	353	137	0.62	0.24	86.0	91.4
6DND5	135	140	550	315	182	0.57	0.33	90.1	92.0

The excellent agreement between the experimental completeness and the theoretical limiting completeness strongly suggests that the proposed reaction mechanisms and the proposed structure of the various complexes are valid for

the complexation between NaPVS and the ionene bromides with similar degrees of polymerization. A plot of the theoretical completeness against the number of building blocks revealed that the completeness value approaches the limiting completeness value asymptotically rather rapidly. In all of the three cases depicted in Fig. 45, the limiting values of completeness are being approached after fifty to a hundred building blocks were stacked. This may mean that the final greyish complex is made up of only a hundred or so duplexes or equivalently of about four to five hundred polyelectrolyte molecules. This observation is consistent with the fineness of the final precipitate.

It is interesting to note that Equation (15) also predicts a limiting P value of 100% for R' = 2. This is easy to understand because the ionic spacing of the unreacted sulfonate groups in the rib cage are doubled and are now separated at a distance equal to the ionic spacing of the ionene as a consequence of the coulombic interactions during the formation of the primary complex. Since the ionic spacing of the ionene is twice that of the NaPVS, the length of the ionene is four times that of the NaPVS and the "arm" of cations is just as long as the length of the rib cage. Therefore, during stacking, the reaction between the "arm" with the sulfonate groups on the rib cage would now be similar to the "zippering up" of two polyelectrolytes with equal ionic spacings. This prediction thus further strengthens the conclusion that ionic spacing is an important factor for the stoichiometry of polyelectrolyte interactions. One might predict that 7,7-ionene should have R' = 2 and P = 100%.

The calculation from the observed conductances of the completeness of polyelectrolyte interactions for Groups 4CND, 5BND and 6DND at other ionic mole ratios have revealed yet another interesting feature of the secondary complex. The results of the calculation showed that the completeness of reaction at mole ratios less than one is generally 3 to 4% higher than that of the reactions at

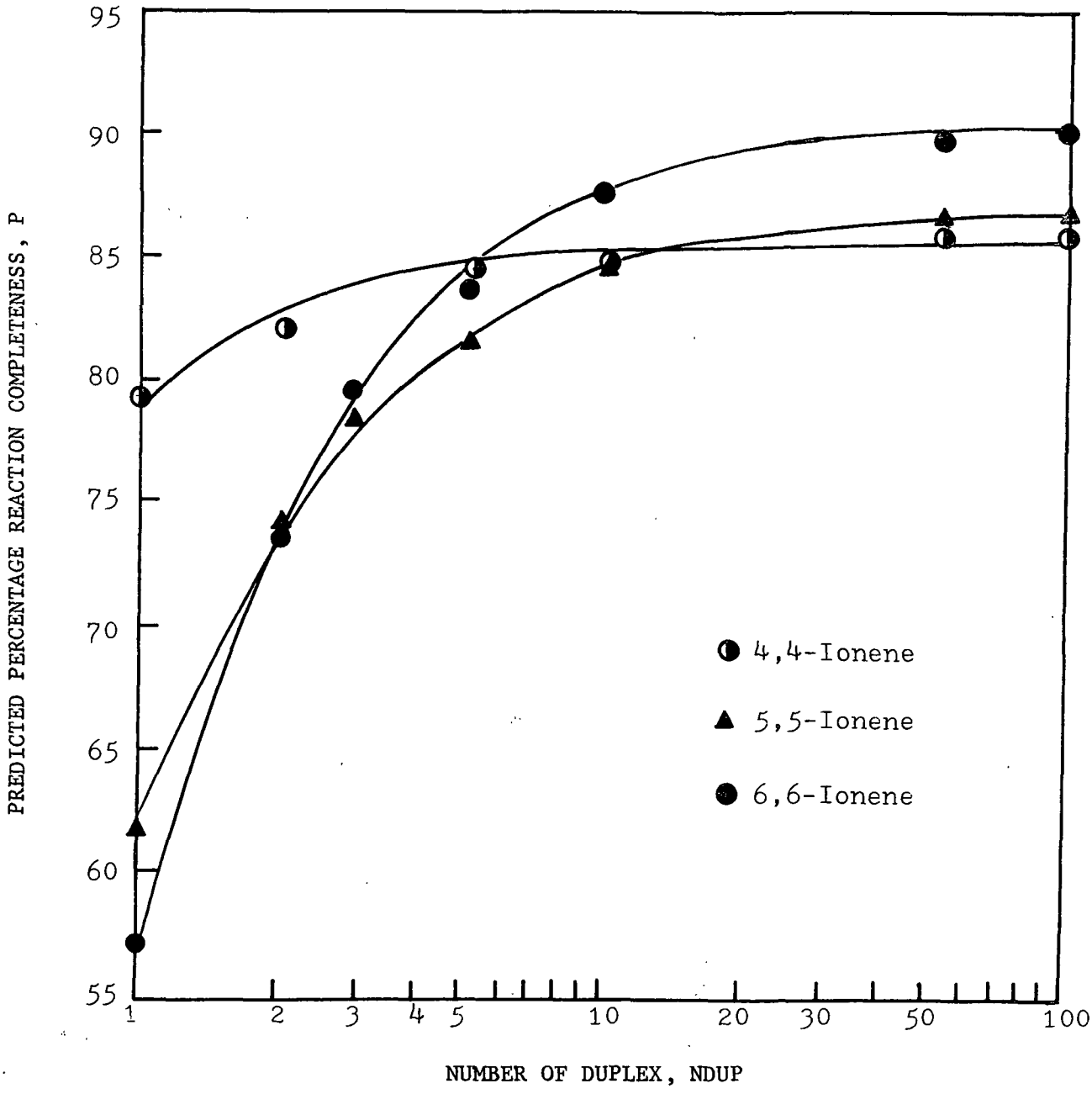


Figure 45. The Relation Between the Number of Building Blocks (Duplexes) and the Percentage of Reaction Completeness for the Complexation of NaPVS and Ionene Bromides with Similar DP

unit mole ratio. This strongly suggests that some of the excess NaPVS molecules had reacted with the accessible unreacted cationic groups on the stacked complex. On the contrary, there is hardly any improvement of reaction completeness beyond a mole ratio of one. This suggests that there are few unreacted anionic groups on the surface of the secondary complex. All of these anionic groups must have

been hidden or embedded inside the final stacked complex and have thus made themselves unavailable to the excess ionene bromide molecules. Therefore, this observation lends further support to the structure of the proposed stacked complex. In view of the stacked complex structure, the minute amount of viscous fluid coacervate in the reaction mixtures at mole ratios less than unity is probably due to the hydrated unreacted sulfonate groups of the excess NaPVS molecules that had reacted with the cationic groups on the surfaces of the secondary complex. But beyond a mole ratio of one, the viscous fluid coacervate must be attributed to the exposed, hydrated and unreacted cationic groups on the "arms" of the complex.

EFFECT OF DEGREE OF POLYMERIZATION

In an attempt to explain the formation of the dissolved complex in the nonstoichiometric reactions between the unfractionated polyelectrolytes, it was postulated earlier that the soluble complex was formed from the reaction between a low DP ionene and a high DP NaPVS. In order to test this hypothesis, the high molecular weight NaPVS fractions (DP = 160 and 180) were reacted with ionene fractions of relatively low molecular weight (DP = 30). The results of these complexation reactions are depicted in Fig. 46.

Contrary to what is expected, the results do not favor the hypothesis. No clear reaction mixture was obtained and the solutions were turbid. The turbid solutions, the fine precipitates and the fact that the specific conductance of the reaction mixtures being lower than that of the control solutions in the nonstoichiometric cases are indicative of the absence of the dissolved complex. These figures also reveal that 3,3-ionene bromide had again reacted stoichiometrically with NaPVS while the other ionenes had not. Excess ionene did not show any effect on the complexes or on the specific conductance of the supernatant solutions.

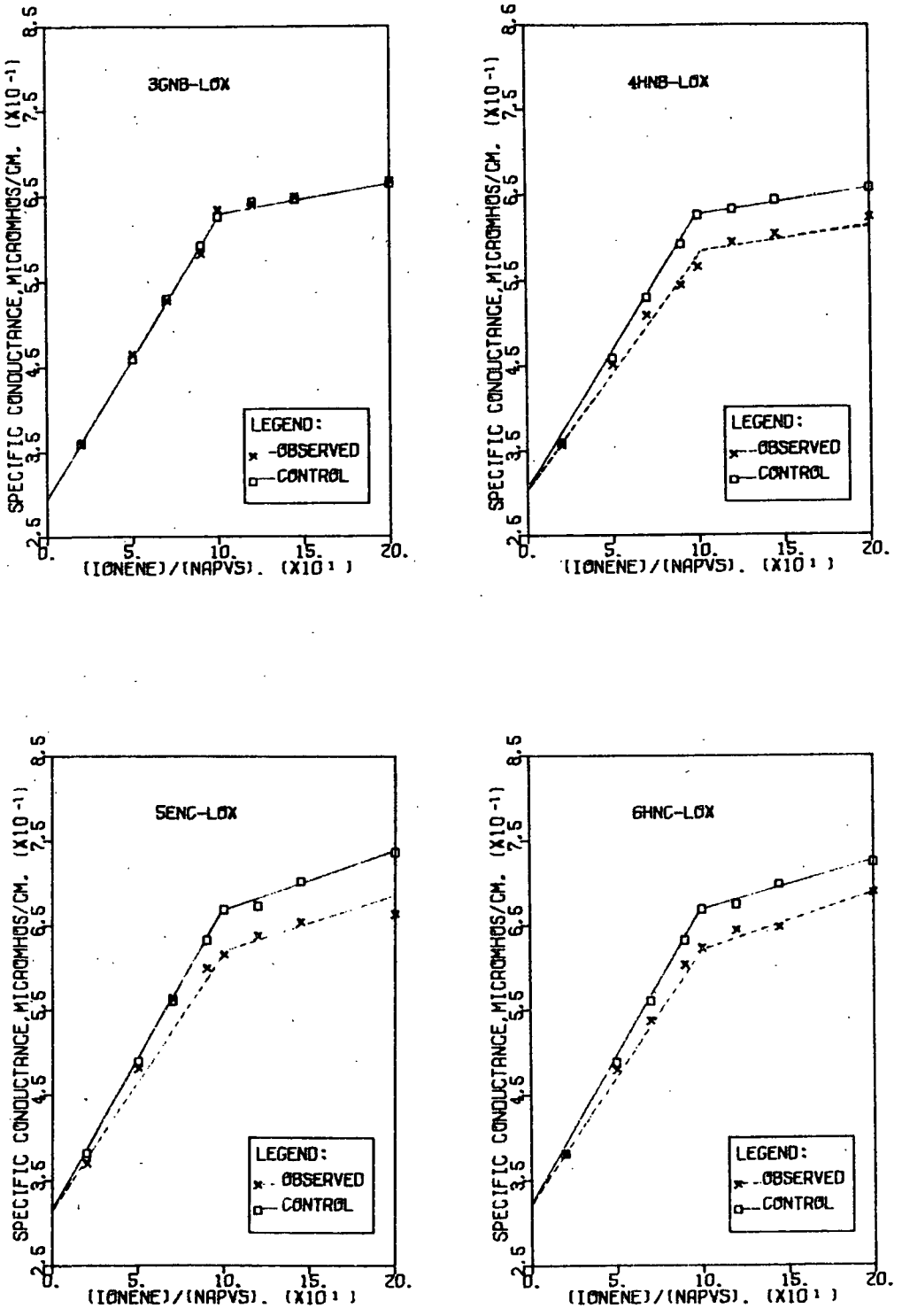


Figure 46. Specific Conductance Versus Ionic Mole Ratio of Reactions Between High DP NaPVS Fractions and Low DP Ionene Bromide Fractions

The reactions between a low molecular weight NaPVS fraction (DP = 30) and high molecular ionene fractions (DP = 140 and 160) showed similar results. These reactions are shown in Fig. 47.

At this point, it just seems reasonable to assume that an ionene with a DP of about 30 is not "low" enough to form a dissolved complex with a high DP NaPVS or vice versa.

In order to probe deeper into the hypothetical relation between the DP of the polyelectrolyte and the dissolved complex, an extremely low molecular weight 5,5-ionene bromide fraction (DP = 5) was reacted with a high molecular weight NaPVS fraction (DP = 180). Figure 48 shows that the reactions had been nonstoichiometric and that in all of the turbid reaction mixtures, a fine precipitate was obtained upon ultracentrifugation. Therefore, this experiment has demonstrated once and for all that the mechanism proposed for the formation of the dissolved complex is totally incorrect. Since a fine precipitate was obtained for all of these reactions regardless of molecular weights, the earlier statement that a fine precipitate was only formed from the reaction between high DP polyelectrolytes is obviously in part incorrect. In fact, these experiments have shown that a fine precipitate could be obtained as long as the completeness of reaction is high.

The completeness of reactions 3BNG-LON5 and 6BNG-LON5 as calculated from experimental data are 100 and 93%, respectively. The agreement with the predicted values given in Table X is excellent. The agreement between the calculated and predicted completeness for reaction 4BNG-LON5, however, was only fair with a difference of 8% between the calculated value of 93% and the theoretical value of 85.4%. Nevertheless, the mechanism of complex formation between a high DP ionene and a low DP NaPVS could be considered as quite similar to that proposed for the reaction of polyelectrolytes with equal DP but unequal ionic spacings.

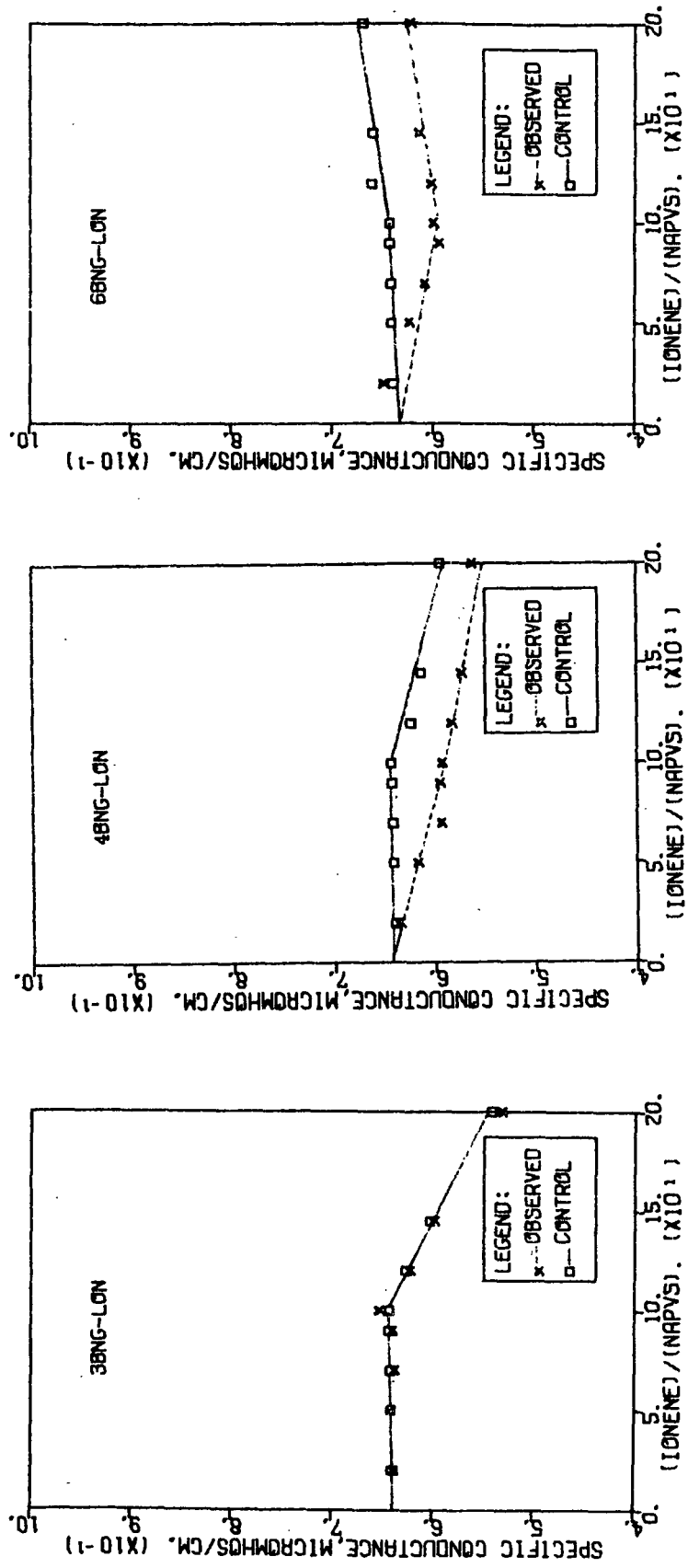


Figure 47. Specific Conductance Versus Ionic Mole Ratio of Reactions Between a Low DP NaPVS Fraction and High DP Ionene Bromide Fractions

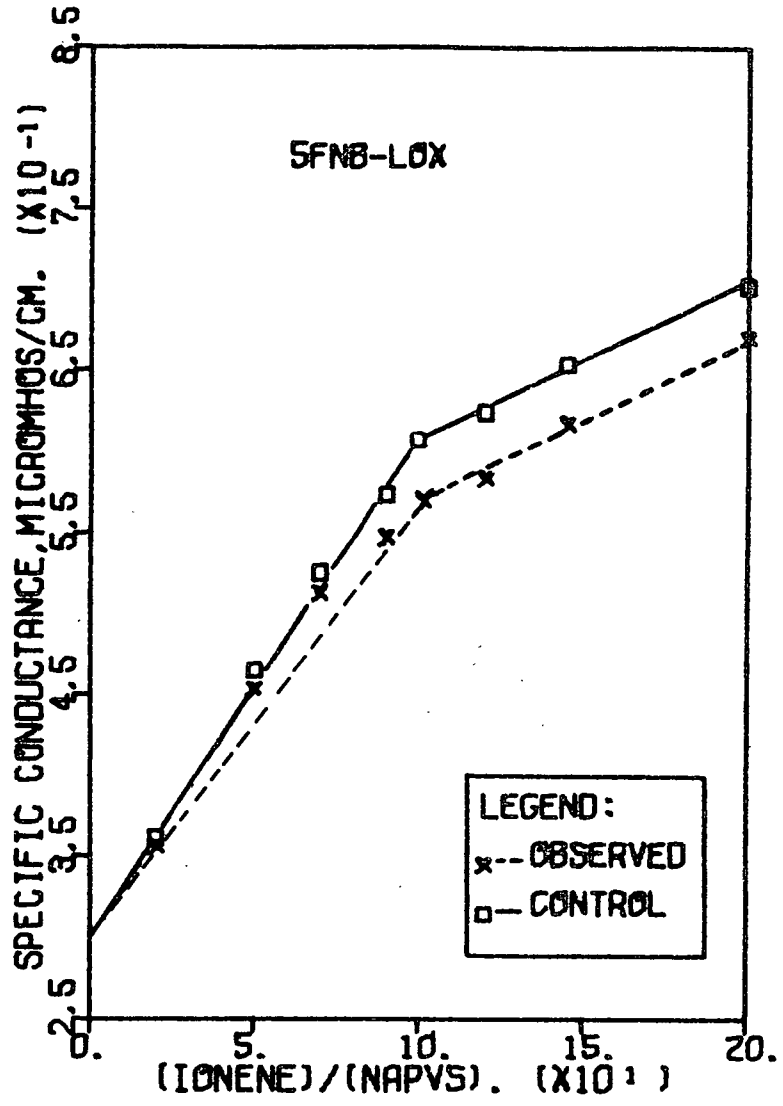


Figure 48. Specific Conductance Versus Ionic Mole Ratio of Reactions Between a High DP NaPVS Fraction and a Very Low DP 5,5-Ionene Bromide Fraction

In Set 4 of the complexation experiments, a high DP NaPVS was reacted with the low DP ionene bromides. Since the ionenes are oligomers in this set of reactions, the mechanisms for the formation of polyion complexes between polyelectrolytes with equal DP cannot be applied directly to the present case. Nevertheless, due to the similarity of the two systems, the previously proposed mechanisms can be easily modified to serve the purpose of explaining the completeness of the reactions in Set 4. As a consequence, such modifications have led to yet another mechanism which is depicted diagrammatically in Fig. 49 and is discussed in the following paragraphs.

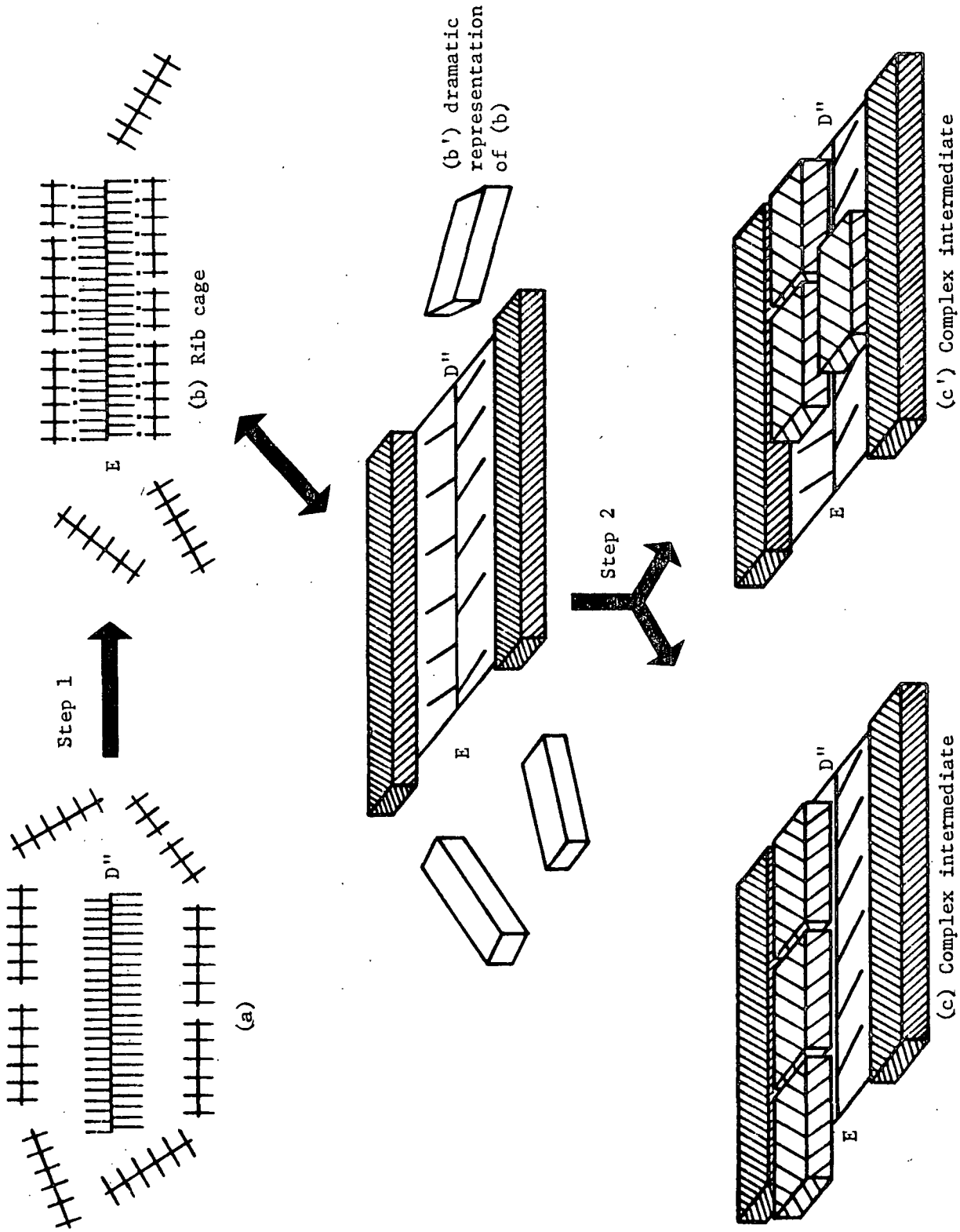


Figure 49. Proposed Mechanism for the Formation of Complex Intermediates for the Reaction of a High DP Sodium Poly(vinyl sulfonate) and a Low DP Ionene Bromide

In the experimental section, it was pointed out that during the mixing of polyelectrolytes the number of monomoles or simply the ionic groups of one polyelectrolyte was kept approximately equal to that of the other. In order to satisfy this preset condition, a certain number of molecules of an ionene fraction with a combined number of cationic groups equivalent to the number of sulfonate groups in one molecule of NaPVS would have to be delivered per molecule of the NaPVS. That is to say, during a reaction, in any isolated corner, one molecule of NaPVS will react with a definite number of ionene molecules. As Fig. 49a depicts, the NaPVS is swarmed by ionene oligomers.

To ensure clarity in the explanation to follow, the complexation process is broken down into three successive steps. The first two steps are shown in Fig. 49 and the third step is illustrated in Fig. 50. The first step (Step 1) is the reaction of the sulfonate groups with the ionene polyions to form a rib cage structure (Fig. 49b) similar to the one discussed earlier (Fig. 42). The length of the rib cage is simply equal to the length of the NaPVS polyion, ED". Since both sides of the NaPVS polyion are attacked, the combined length of all the ionene polyions that have reacted with the sulfonate groups is equivalent to twice the length of ED", or simply: DPN - 2. The number of cationic groups, RPG, in this length is also equal to the number of anionic groups that have reacted in this step of the complexation. Thus,

$$RPG = (DPN - 2)/R' + 1 \qquad (16)$$

Similarly, the number of unreacted anionic groups, NUNRX, at this stage of the complexation process is equal to the number of unreacted cationic groups, and NUNRX = DPN - RPG. NUNRX is distributed evenly among the reacted anionic groups on both sides of the rib cage. Therefore, the ionic spacing of the unreacted sulfonate groups, NEGSPA (qualitatively it is equivalent to R") is given by:

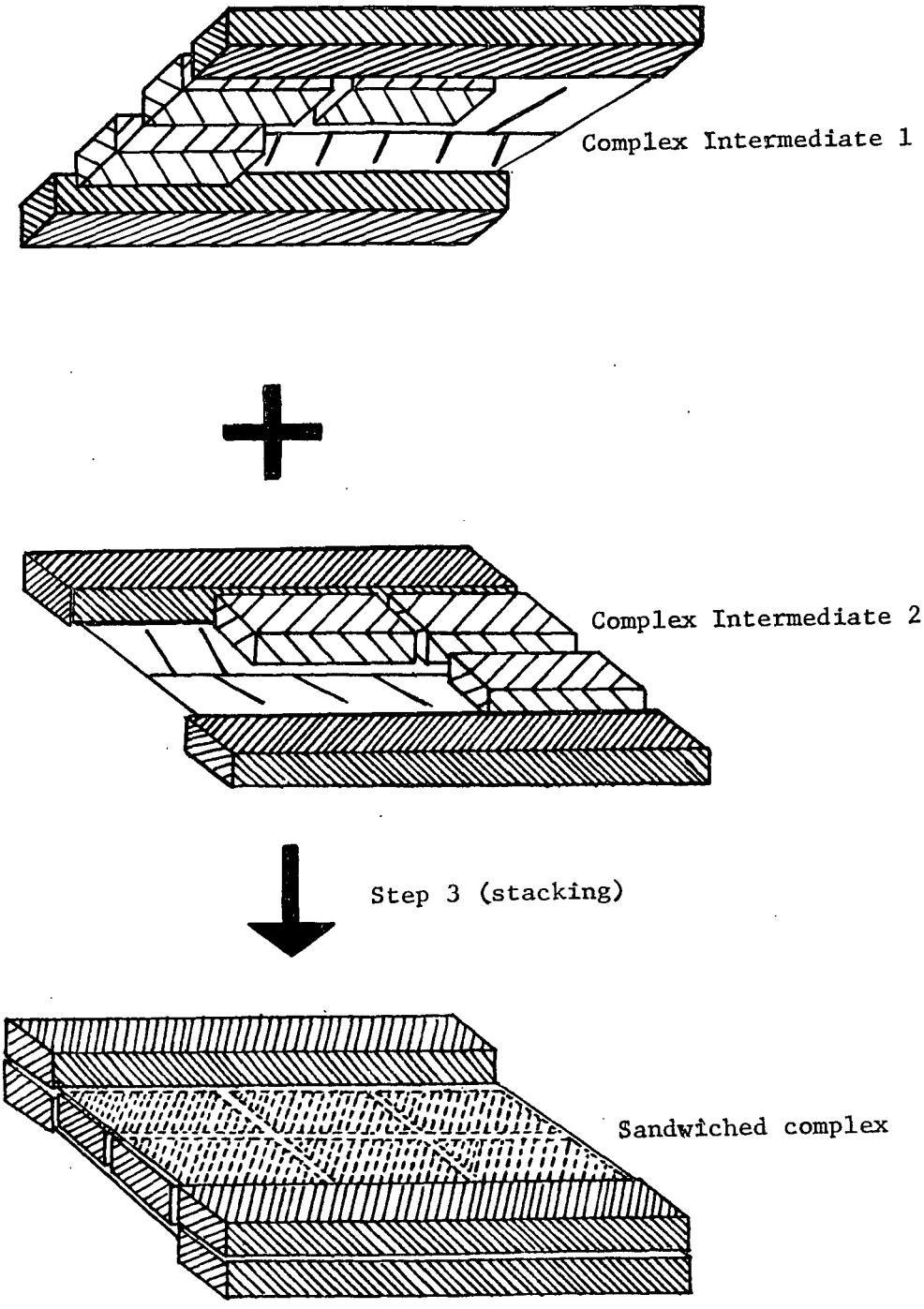


Figure 50. Schematic Drawing of Step 3 of the Mechanism for the Reaction of a High DP NaPVS and a Low DP Ionene

$$NEGSPA = ED''/(0.5* NUNRX - 1) \quad (17)$$

In the second step, the unreacted sulfonate groups in the rib cage will react with the remaining ionene oligomers in one of two fashions. The ionene polyions will either attack one side of the rib cage exclusively or attack both sides of the rib cage simultaneously. Which ever fashion it may be, the number of sulfonate groups that will react in this stage, RIBSUL, is governed by the combined length of the remaining ionene molecules. Since there were equal numbers of cationic and anionic groups, the entire combined length of these ionene molecules at the beginning of Step 1, ELEN, is equal to (DPN - 1)* R'. In Step 1, however, a length equal to DPN - 2 was used up. Therefore, the residual combined length (which is equal to the sum of the lengths of the leftover oligomers in Fig. 49b), RELEN, that is available for reaction in Step 2 is given by:

$$RELEN = (DPN - 1)* R' - (DPN - 2) \quad (18)$$

Hence,

$$RIBSUL = (RELEN/NEGSPA) + 1 \quad (19)$$

The completeness of the reaction up to the end of Step 2, P_p', is expressed by:

$$\begin{aligned} P_p' &= 2* (RPG + RIBSUL)* 100/(DPN* 2) \\ &= ((RPG + RIBSUL)/DPN)* 100 \\ &= 100/DPN* \left\{ \left(\frac{DPN-2}{R'} + 1 \right) + \frac{(DPN - 1)* R' - (DPN - 2)}{0.5* DPN - 1} + 1 \right\} \end{aligned} \quad (20)$$

A computer program was written to calculate the predicted completeness of these reactions according to Equation (20). A listing of the program is given in Appendix IX (Part A). The theoretical completeness values as predicted by P_p' are tabulated in Table XI.

TABLE XI

THEORETICAL COMPLETENESS OF COMPLEX INTERMEDIATE OF COMPLEXATION BETWEEN LOW DP IONENE AND HIGH DP NaPVS AT UNIT MOLE RATIO

Reaction	Ionene DP	NaPVS DP	P_p', % Predicted
3GNB-LOX5	35	180	100
4HNB-LOX5	33	180	84
5ENC-LOX5	30	160	85
6HNC-LOX5	20	160	91

The agreement between the predicted and the experimental completeness for 3,3-ionene bromide and NaPVS is excellent. In fact, since their ionic spacings are equal, in their reaction, the final complex is formed in Step 1 of the proposed mechanism and no further reaction into Step 2 is possible because there are no surplus 3,3-ionene molecules available. As for the other reactions, the predicted values are quite a few percentage points lower than the experimental values. Especially in the case of the reactions between NaPVS and 4,4- and 5,5-ionenes, the differences are as much as 8 and 9%. This indicates that their complexes formed in Step 2 of the proposed mechanism are only intermediates to the final complex. Figures 49c and 49c' illustrate that the complex intermediates contain both unreacted cationic and anionic groups. The unreacted anionic groups are in the rib cage region of the intermediate while the unreacted cationic groups are on the ionene oligomers which have partially reacted with some of the sulfonate groups in the rib cage region in Step 2. Therefore, it is conceivable that these complex intermediates will further react by coulombic interactions to give the final complex. The most illustrative explanation to this further interaction is the stacking of two identical complex intermediates (Step 3) as shown in Fig. 50.

In Step 3, the unreacted cationic groups in one complex intermediate will seek to react with the unreacted sulfonate groups in the other and vice versa. Such interactions bring about an increase in the number of interactions among the ionogenic groups, TOTIMP, and the product is a sandwiched complex with a higher reaction completeness. In order to formulate an expression for the reaction completeness of the sandwiched complex, information on the following quantities are essential. The number of cationic groups in the length RELEN, RELENI, is given by: RELENI = RELEN/R' + 1. Since a number of these cationic groups have taken part in the interaction with an equal number of sulfonate groups (RIBSUL) in Step 2 of the proposed mechanism, the number of surplus cationic groups, S2PLUS, in the complex intermediate that is available for Step 3 interaction is given by the difference between RELENI and RIBSUL. The new ionic spacing of the surplus cationic groups in the length RELEN, PLUSPA, is thus:

$$\text{PLUSPA} = \text{RELEN}/(\text{S2PLUS} - 1) \tag{21}$$

If RELEN is shorter than the length of the rib cage region (ED"), TOTIMP would simply be dependent upon the length RELEN. This is because in this case there is ample room in the rib cage region for "fitting in" of the unreacted cationic groups in the combined length RELEN. When R' < 1.5, PLUSPA is less than NEGSPA, then:

$$\text{TOTIMP} = 4^{*}\ (\text{RELEN}/\text{NEGSPA} + 1) \tag{22a}$$

$$= 4^{*}\ \text{RIBSUL} \tag{22b}$$

This is because under this condition all of the sulfonate groups in a combined length of the rib cage equivalent to RELEN will be reacted. The factor 4 accounts for the two complex intermediates and the two species of ionogenic groups.

For an ionene with an R' value greater than 1.5, the length RELEN is longer than the rib cage region. Under this condition, the equivalent length of sulfonate groups in the rib cage region that is available for interaction

in Step 3, SULENG, is restricted. In other words, as RELEN gets larger, SULENG becomes smaller. The quantity SULENG can be expressed as a function of RELEN and the length of the rib cage region by the equations:

$$SULENG = 2^* ED'' - RELEN \quad (23a)$$

$$= (DPN - 2) - RELEN \quad (23b)$$

For $R' > 1.5$, PLUSPA is greater than NEGSPA. All of the surplus cations in a length of the oligomers equivalent to SULENG will be reacted. Thus,

$$TOTIMP = 4^* (SULENG/PLUSPA + 1) \quad (24)$$

The percentage reaction completeness of the sandwiched complex, PPDP, is expressed by the following equation:

$$PPDP = 100^* (2^*(2^*RPG + RIBSUL) + TOTIMP)/(4^* DPN), \quad (25)$$

where the first term of the numerator accounts for the number of ionogenic groups reacted in Steps 1 and 2 of the proposed mechanism for two complex intermediates, and the denominator accounts for all of the ionogenic groups in the sandwiched complex. Depending on the condition, the term TOTIMP in the numerator is substituted appropriately by one of the two expressions [Equations (22b) and (24)] discussed above.

A computer program was written to calculate PPDP according to Equation (25); a listing of which is given in Appendix IX (Part B). The theoretical and experimental completeness for the reactions of a high DP NaPVS and low DP ionene fractions are tabulated in Table XII.

The excellent agreement between the predicted and the experimental reaction completeness indicates that the proposed 3-step mechanism is highly feasible for the reactions of high DP NaPVS and low DP ionenes whose ionic spacings are larger than that of the NaPVS.

TABLE XII

THE THEORETICAL AND EXPERIMENTAL COMPLETENESS OF COMPLEXATION BETWEEN LOW DP IONENE AND HIGH DP NaPVS AT UNIT MOLE RATIO

Reaction	Ionene DP	NaPVS DP	PPDP, % Predicted	Completeness, % Experimental
4HNB-LOX5	33	180	91.4	92.0 ± 0.4
5ENC-LOX5	30	160	95.0	93.7 ± 0.6
6HNC-LOX5	20	160	94.0	95.0 ± 0.2

EFFECT OF POLYDISPERSITY

Although the conductance of long-chain polyelectrolytes is independent of the chain length of the polyion, a chain length dependency should be observed at relatively low degrees of polymerization. This behavior may be interpreted as reflecting the superposition of two effects. First, the ratio of the charge of the polyion to its frictional coefficient tends to increase with increasing chain length. Second, counterion binding increases as the polyion chain increases in length. When the equivalent conductivity of the selected polyelectrolyte fractions are examined closely (Fig. 51), one can see immediately that the equivalent conductivity increases rapidly as the degree of polymerization decreases. This phenomenon is consistent with Schindewolf's conclusion from his study on various sodium poly(phosphate) molecular weight fractions (64). Based on this observation, a plausible mechanism for the formation of the dissolved complex is proposed.

Let us consider a hypothetical system in which a high molecular weight NaPVS fraction (DP = 140) is to react with a mixture of a medium low molecular weight (DP = 30) fraction and an extremely low molecular weight (DP = 5) fraction of the 5,5-ionene bromide in the ratio of 1:22.

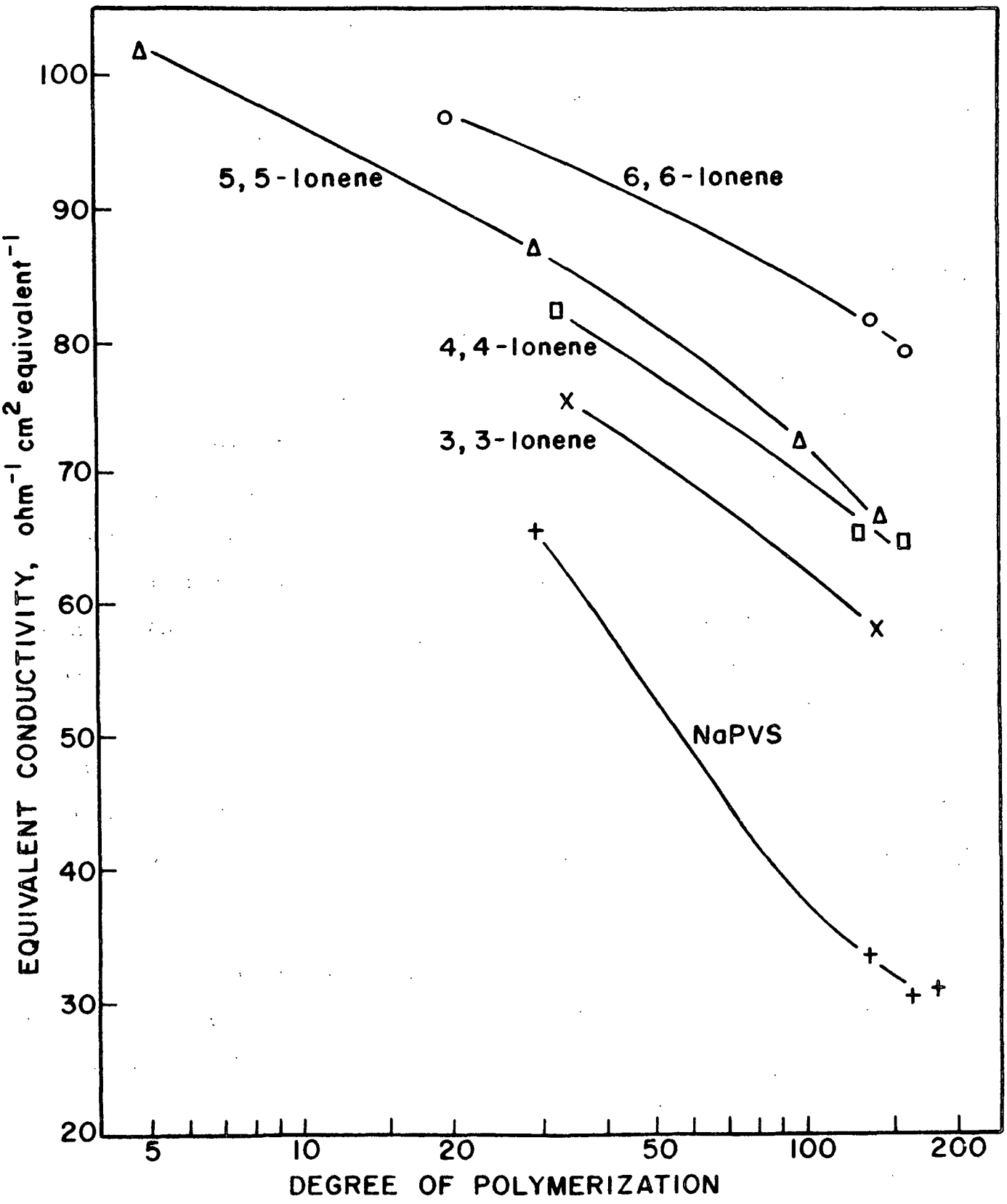
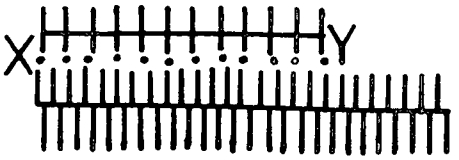


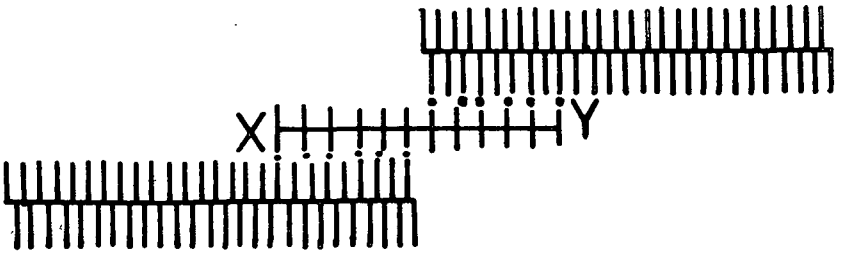
Figure 51. Equivalent Conductivity of Polyelectrolyte Fractions as a Function of the Degree of Polymerization

The equivalent conductivity of the 5,5-ionene Fraction E (DP = 30) is 85 mho cm^2/equivalent and that of the 5,5-ionene Fraction F (DP = 5) is 102 mho cm^2/equivalent. The big difference in the equivalent conductivity indicates that the shorter polyion chain has a higher degree of dissociation than the longer chain. This also means that the electrostatic potential of the shorter polyion is higher. The shorter polyion should also diffuse faster. As a consequence, the shorter polyion should be more reactive than the longer polyion. Therefore, during the complexation reaction, the longer ionene chains may remain unreacted until all of the shorter chains have reacted since they have a lower electrostatic potential than the shorter chains. The reaction and the structure of the complex from the interaction between the 5-mers and the NaPVS should be quite similar to those depicted in Fig. 49 and 50. When this interaction is completed, if no excess NaPVS is available, the longer chains will have to react with any available unreacted sulfonate groups that are left in or on the primary complex formed by the NaPVS and the shorter ionene chains. However, if an excess of NaPVS is added to the reaction mixture immediately beyond the completion of the interaction between the 5-mers and the NaPVS, each of the medium length ionene chains may react with only one long NaPVS chain (Fig. 52a). On the other hand, it may also "bridge" with two or more molecules of NaPVS since the concentration of the NaPVS is (Fig. 52b) now in excess. In fact, the "bridging" of molecules may be more probable since no excess NaPVS was found by electrophoresis in a previous experiment. Which ever case it may be, the large amount of unreacted hydrophilic sulfonate groups on such a complex is causing it to remain dissolved. With reference to Fig. 52, all of the cationic groups in the dissolved complex have reacted. However, the completeness of the reaction of the ammonium ions is brought about at the expense of some of the sulfonate groups of the excess NaPVS molecules which are now a part of the dissolved complex. Thus, in spite of the stoichiometric amount of sodium bromide

in the reaction mixture, intuitively, the specific conductance of the supernatant solution should still be lower than that of the control solution.



(a)



(b)

Figure 52. Proposed Structures of Dissolved Complex from the Interaction of Medium Low DP Ionene with an Excess of High DP NaPVS of Unequal Ionic Spacing

In the study of counterions distribution in polyelectrolytic solutions, Imai and Onishi (65) suggested that a rodlike polyion cannot sustain a charge density exceeding a critical value. This concept has been elaborated by Manning (66,67). His theory leads to a maximum charge density corresponding to one ionic charge per 8 A of the polyion. Therefore, if a higher charge density is produced by closely spaced ionized groups counterions will "condense" on the polyion. On the contrary, an increase in spacing between neighboring charges will surely lead to a reduction in counterion binding. In the proposed dissolved complexes, the ionic spacing of those unreacted sulfonate groups among the reacted ones (Region XY on Fig. 52) is wider as a consequence of ionic bonding with the ionene molecule. In view of Imai and Onishi's conclusion,

there should be a drastic reduction of counterion binding among these unreacted sulfonate groups. Nagasawa, et al. (68) estimated that about 70% of the counterions of a 100% neutralized poly(acrylic acid)are condensed on its polyion even in very dilute solutions. This accounts for the intrinsically low conductivity of polyelectrolyte solutions. Eisenberg (69) had shown that the conductance of a polyelectrolyte is an inverse function of its degree of neutralization. Thus, an increase in conductivity accompanies the reduction of counterion binding and the anomalously higher conductivity of the supernatant solutions is proposed to be attributed to this effect.

In order to substantiate this hypothesis, the hypothetical system considered above was actually carried out in the experiment 5EFND-LOX. The results of this experiment are depicted in Fig. 53. The reaction mixtures that were obtained before a mole ratio of unity were slightly turbid and some fine precipitate was obtained upon centrifugation. Unlike the experiments with the unfractionated polyelectrolytes, no viscous fluid coacervate was obtained. This indicates that the primary complex formed by the 5-mer and the NaPVS has a Hp much less than Hp_c. The structure of this primary complex should be somewhat similar to the complex intermediate depicted in Fig. 49. This happens when the ratio of 5-mer to 30-mer is high. However, if this ratio is low, the primary complex is likely to assume a viscous fluid form due to the larger amount of unreacted sulfonate groups. The anomalously high specific conductance of these reaction mixtures is indicative of the presence of the dissolved complex.

At mole ratio equal to unity, however, a very turbid mixture with a fine precipitate was obtained. The specific conductance of this mixture was now lower than that of its control solution, confirming that when no more NaPVS is available the longer chain would have to react with the "accessible" unreacted charges on the primary complex that is formed from the NaPVS and the shorter

ionene chains alone. Addition of salt to the supernatant solution did not change its clarity, confirming that the dissolved complex was absent.

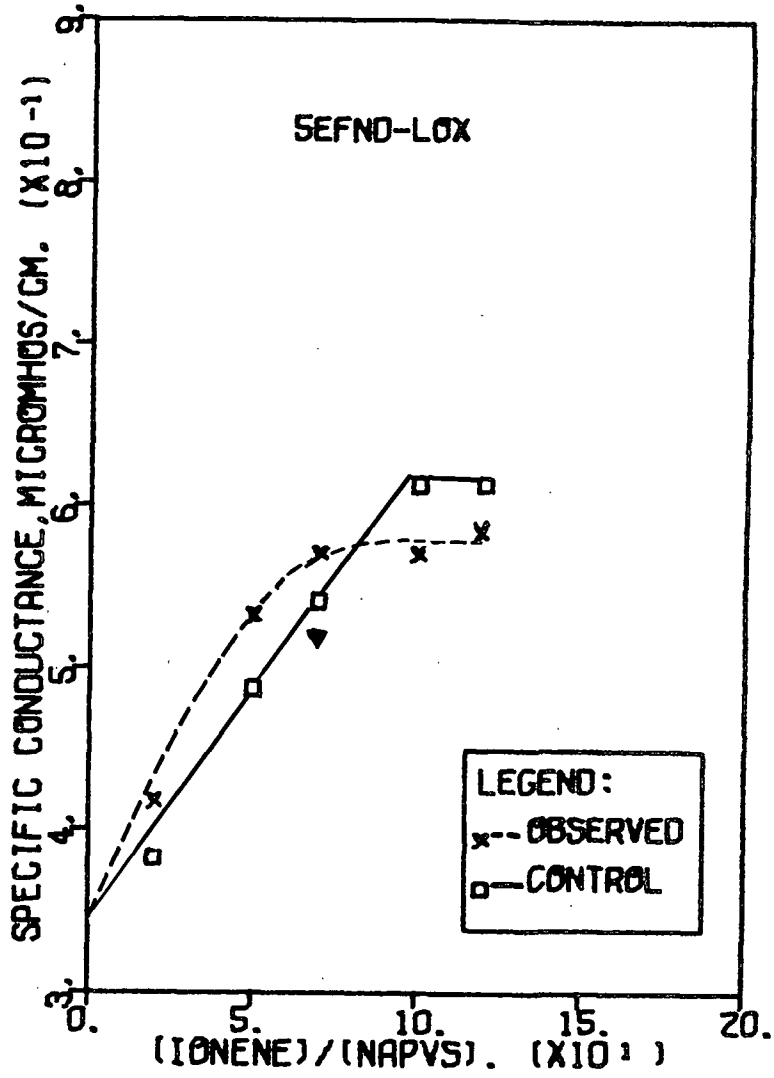


Figure 53. Specific Conductance Versus Ionic Mole Ratio of Reactions Between a High DP NaPVS Fraction and a Mixture of Two Low DP 5,5-Ionene Fractions

One more experiment was necessary to show that the medium DP ionene chains had indeed remained unreacted until all of the shorter chains had reacted. In proving this effect, the reaction at a mole ratio equal to 0.7 in the above experiment (5EFND-LOX3) was repeated with a slight modification in the procedures. Instead of continuously adding the excess NaPVS after the molar stoichiometric amount of NaPVS had been added, the reaction mixture was allowed to sit for one and one-half hours before continuing the addition.

Contrary to its counterpart obtained with the standard procedures, this reaction mixture was very turbid and a larger amount of fine precipitate was separated upon ultracentrifugation. No dissolved complex was obtained and the specific conductance of the supernatant solution (52 μmhos cm^{-1}, represented by the inverted black triangle in Fig. 53) was lower than that of its control solution (55 μmhos cm^{-1}).

At this point, it is clear that the anomalous conductivity phenomenon is directly caused by kinetic factors. The anomalously high conductivity is due to the released "bound" counterions and to the dissolved complex. Thus, it is concluded that kinetics plays a very important role in the reaction between a long-chain polyion and a mixture of low molecular weight polycation fractions, or vice versa. However, this kinetic effect should vanish in cases where the interacting species are of such molecular weights that their equivalent conductivities are independent (or less dependent) of the degree of polymerization as evidenced by the results of the group of reactions 3N-UDM. It should also be pointed out that even if a dissolved complex had formed in the reactions 3N-UDM, due to the equality of ionic spacings, the dissolved complex would not contain any unreacted groups in the Region XY in Fig. 52. Thus, there would be no widening of spacing between the unreacted sulfonate groups (which are in this case nonexistent) and there would be no reduction of counterion binding in this region. Such a dissolved complex will be unable to show any anomalous conductivity effect and the specific conductance of the supernatant solution is expected to be lower than that of its control solution for the reason mentioned earlier in this section.

CONCLUSIONS

The effects of ionic spacing, degree of polymerization and polydispersity on the stoichiometry of polyelectrolytic reactions have been investigated and explained by classical coulombic interaction and mathematical models. It was found that the equality of ionic spacings between the interacting polyelectrolytes is essential for a stoichiometric reaction. The mathematical models proposed for these reactions are in excellent agreement with experimental results. They depict all of the reactions as being highly ordered such that the maximum possible degree of ionic interaction can be achieved.

It was found that the degree of polymerization (DP) does not affect the stoichiometry of the reactions between polyelectrolytes with equal ionic spacings. On the contrary, when a low DP ionene and a high DP NaPVS are reacted, the completeness of the reaction is somewhat higher than that of the reactions between polyelectrolytes with equal DP or that of the reactions between a high DP ionene and a low DP NaPVS. This effect is chiefly due to the stereochemistry of the selected polyelectrolytes, which allows the low DP ionene molecules to react more efficiently with the high DP NaPVS to achieve a higher degree of reaction completeness.

Polydispersity does not seem to have any effect on polyelectrolyte reactions if the average molecular weights of the interacting species are high. However, if the average molecular weights are extremely low, the reactions are governed by a kinetic effect resulting from the difference in the electrostatic potentials of the various low molecular weight polyelectrolyte fractions.

ACKNOWLEDGMENTS

The author wishes to acknowledge the advice and suggestions of his Thesis Advisory Committee: Dr. R. A. Stratton (Chairman), Dr. D. B. Easty and Professor (Emeritus) E. E. Dickey. The author is also indebted to Mr. J. C. Carlson for the determination of polyelectrolyte molecular weights on the ultracentrifuge, to Mr. A. Webb for helpful assistance in the fractionation of polyelectrolytes by gel permeation chromatography and to Messrs. Sweeney, Beyer, Sommers, Schabo and Mrs. J. Gonnering of the Photography and Duplicating Departments for their speedy services and cooperation.

The author also gratefully recognizes the constant encouragement, sacrifice and understanding shown by his wife, Nancy, and his two loving children. Their contributions were immeasurable.

Finally, and most importantly, special gratitude is extended to the author's most generous parents for their spiritual and financial support throughout the entire course of his pursuit of higher education abroad.

GLOSSARY OF SYMBOLS

A = NRX/NTOT

a = mass of dibromoalkane, gram

AB = length of the "arm" of cationic groups in the duplex, arbitrary units

B = NI/NTOT

b = mass of tetramethylalkane-diamine, gram

C = titer of silver nitrate, mole/liter

c = concentration of pure sodium bromide solution, mole/liter

C_o = concentration of unknown bromide containing solution, mole/liter

CA' = length of the "arm" of cationic groups in the duplex, arbitary units (see AB)

C_x = concentration of polyelectrolyte in fringes at distance x from the axis of rotation

d = molar concentration of tetramethylalkane-diamine and dibromoalkane, mole/liter

DP = degree of polymerization

DPI = degree of polymerization of ionene or the number of ionogenic groups in a molecule of ionene

DPN = degree of polymerization of sodium poly(vinyl sulfonate) or the number of ionogenic groups in a molecule of sodium poly(vinyl sulfonate)

E = measured electrode potential of the unknown solution, volts

E_j = junction potential, volts

E_o = standard electrode potential, volts

ED" = length of a sodium poly(vinyl sulfonate) molecule, arbitrary units

EF = length of rib cage region of the duplex, arbitary units

ELEN = length of a molecule of ionene bromide, arbitrary units

F = Faraday constant

G = acceleration due to gravity

G_x = corrected specific conductance of a solution, μmho cm^{-1}

Hp = ratio of unreacted ionogenic groups to the hydrophobic portion of a complex

Hp_c = critical Hp

L = conductance of a solution, μmhos

$M(w)_{app}$ = apparent weight average molecular weight of a polyelectrolyte (sedimentation equilibrium at finite concentration)

N = total number of ionogenic groups in a primary complex from the reaction of polyelectrolytes with equal DP

n = number of moles of tetramethylalkane-diamine and dibromoalkane

NaPVS = sodium poly(vinyl sulfonate)

NCAGE = the number of unreacted sulfonate groups on either side of the rib cage region of the duplex from the reaction of polyelectrolytes with equal DP

NDUP = number of duplexes

NEGSPA = ionic spacing of unreacted sulfonate groups in the rib cage region of the complex intermediate from the reaction of a high DP NaPVS and low DP ionene bromide; qualitatively NEGSPA is equivalent to R", arbitrary units

NI = the number of ionogenic groups reacted from the stacking of the two duplexes

NMR = nuclear magnetic resonance

NPCRX = the number of cationic groups (or anionic groups) that has taken part in the formation of the primary complex from the reaction of polyelectrolytes with equal DP

NTOT = the total number of ionogenic groups in a duplex

NTOTP = the number of ionogenic groups reacted in the formation of a primary complex from the reaction of polyelectrolytes with equal DP

NRX = the total number of reacted ionogenic groups in the duplex

NSRC = the number of sulfonate groups on one side of the rib cage region of the duplex that have reacted as a result of stacking

NUNRX = the number of unreacted sulfonate groups in the rib cage region of the complex intermediate formed by the reaction of a high DP NaPVS and a low DP ionene bromide

P = theoretical percentage completeness of reactions between polyelectrolytes with equal DP

P_1 = concentration of ionene bromide solution, mole/liter

P_2 = concentration of NaPVS solution, mole/liter

P_D = theoretical percentage completeness of reaction of the duplex

P_p = theoretical percentage completeness of reaction of the primary complex formed from the reaction of polyelectrolytes with equal DP

P'_p = theoretical percentage reaction completeness of the complex intermediate formed from the reaction of a high DP NaPVS and a low DP ionene bromide

PPDP = theoretical percentage reaction completeness of the sandwiched complex

PLUSPA = average ionic spacing of unreacted cationic groups in the rib cage region of the complex intermediate, arbitrary units

R = universal gas constant

R' = ratio of ionic spacing of ionene to that of NaPVS

R" = average ionic spacing of unreacted sulfonate groups in rib cage region of the duplex, arbitrary units

RELEN = combined length of remaining ionene oligomers after Step 1 of the reaction between a high DP NaPVS and a low DP ionene bromide, arbitrary units

RELENI = number of cationic groups in the length RELEN

RIBSUL = the number of sulfonate groups (or cationic groups) that have reacted in Step 2 of the reaction between a high DP NaPVS and a low DP ionene bromide

RPG = number of cationic groups (or anionic groups) that have reacted in Step 1 of the reaction between a high DP NaPVS and a low DP ionene bromide

S = 2.303 RT/F

S' = concentration of sodium bromide stock solution, mole/liter

S2PLUS = number of cationic groups in the complex intermediate that is available for reaction Step 3 in the interaction of a high DP NaPVS and a low DP ionene bromide

SULENG = combined length of sulfonate groups in the rib cage region of the complex intermediate that is available for reaction in Step 3 in the interaction of a high DP NaPVS and a low DP ionene bromide, arbitrary units

T = temperature, °K

t = temperature, °C

TOTIMP = number of reacted ionogenic groups in Step 3 of the reaction between a high DP NaPVS and a low DP ionene bromide

V' = volume of titrant (silver nitrate) added, mL

V_o = volume of unknown bromide containing solution, mL

$\bar{v}$ = specific volume of polyelectrolyte solution, cc/g

$\bar{v}_1^o$ = specific volume of solvent, cc/g

$\bar{v}_2$ = partial specific volume of polyelectrolyte, cc/g

$\bar{v}_2^*$ = apparent partial specific volume of polyelectrolyte, cc/g

W = time, hours

w_2 = weight fraction of polyelectrolyte

x = radial distant from the axis of rotation, cm

α = α-carbon atom in dibromoalkane and tetramethyldiaminoalkane

γ = activity coefficient of silver ions

δ = parts per million, ppm

κ = specific conductance of a solution, μmho cm^{-1}

ρ = density of a solution or solvent, g/cc

θ = conductivity cell constant, cm^{-1}

Θ = theta-solvent for polyelectrolyte

Ω = angular velocity, rpm

ω = number of methylene groups separating two neighboring quaternary groups in an ionene bromide molecule

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APPENDIX I

PROGRAM FOR STANDARDIZATION OF NaPVS SOLUTIONS

```
C A PROGRAM TO PLOT THE LINEAR REGRESSION CALIBRATION CURVE FOR THE
C SODIUM-ION ELECTRODE FOR THE DIRECT POTENTIOMETRIC DETERMINATION
C OF THE CONCENTRATION OF NA-POLY(VINYLSULFONATE) SOLUTIONS.
C EMF IS THE ELECTRODE POTENTIAL OF THE STANDARD NA-SOLUTIONS
C SAMEMF IS THE ELECTRODE POTENTIAL OF THE UNKNOWN NAPVS SOLUTION OR AN
C UNKNOWN SODIUM SOLUTION.
C ANA IS THE SODIUM CONCENTRATION OF THE STANDARDS
C ALOGNA IS THE LOG(10) OF ANA.
C ITITLE IS THE CAPTION FOR THE GRAPH, 52-ALPHANUMERIC CHARACTERS.
C ITLX AND ITLY ARE THE TITLES ON THE X- AND Y- AXES, RESPECTIVELY.
C E AND C ARE PARAMETERS USED IN THE PLOTTING OF THE REGRESSION LINE
C THROUGH THE DATA POINTS
C TITLE IS THE TITLE FOR THE TABLE OF DATA PREPARED BY THE PRINT-OUT.
C NAPVS IS THE CONCENTRATION OF SODIUM-POLY(VINYLSULFONATE) IN MOLES/L.
      DIMENSION EMF(100),ANA(100),ALOGNA(100),ITITLE(20),ITLX(20)
      DIMENSION ITLY(20), E(100), C(100), TITLE(20)
      REAL NAPVS
 9001 READ(5,1) TITLE
    1 FORMAT(20A4)
      READ(5,2) ITITLE
    2 FORMAT(20A4)
C N IS THE NUMBER OF (ANA,EMF) DATA SET.
C J IS THE NUMBER OF SAMEMF.
C
      READ(5,3) N,J
    3 FORMAT(2I3)
      READ(5,4) (ANA(I),EMF(I), I=1,N)
    4 FORMAT(2F10.4)
      DO 5 I=1,N
    5 ALOGNA(I)=ALOG10(ANA(I))
      SX=0.
      SY=0.
      SXY=0.
      SX2=0.
      SY2=0.
      DO 6 I=1,N
      SX=SX+ALOGNA(I)
      SY=SY+EMF(I)
      SXY=SXY+ALOGNA(I)*EMF(I)
      SX2=SX2+ALOGNA(I)**2
    6 SY2=SY2+EMF(I)**2
      AN=N
      SLOPE=(AN*SXY-SX*SY)/(AN*SX2-SX**2)
      AINCPT=(SY-SLOPE*SX)/AN
      R=(SXY-SX*SY/AN)/SQRT((SX2-(SX**2)/AN)*(SY2-(SY**2)/AN))
      WRITE(6,7)
    7 FORMAT(1H1,31X,'CALIBRATION DATA OF SODIUM ION ELECTRODE FOR THE'/
     *1H ,32X,'STANDARDIZATION OF SODIUM-POLY(VINYLSULFONATE)'/1H ,34X,
     *'FOR THE COMPLEXATION WITH IONENE-BROMIDES')
      WRITE(6,1000) TITLE
 1000 FORMAT(1H ,41X,20A4)
      WRITE(6,8)
    8 FORMAT(1H ,31X,'SODIUM STANDARD(PPM)',6X,'ELECTRODE POTENTIAL(MV)'
     *//)
      WRITE(6,9) (ANA(I),EMF(I), I=1,N)
    9 FORMAT(1H ,37X,F7.3,20X,F7.2)
      WRITE(6,10)SLOPE,AINCPT, R
```

APPENDIX I (continued)

```
10 FORMAT(//1H ,'THE EQUATION OF THE REGRESSION LINE IS E=',F8.3,'LOG
  *(C)+',F8.3/1H ,'THE CORRELATION COEFFICIENT=',F9.7//)
   K=1
11 READ(5,12)SAMEMF
12 FORMAT(F10.2)
   W=2.303*(SAMEMF-AINCPT)/SLOPE
   Z=EXP(W)
   NAPVS=Z/23000.
   WRITE(6,13) SAMEMF, NAPVS
13 FORMAT(1H ,'WHEN SAMPLE EMF=',F7.2,' THE CONCENTRATION OF THE SODI
  *UM-POLY(VINYLSULFONATE) SOLUTION IS',1PE12.5,' MOLES/LITER'//)
   K=K+1
   IF(K-J) 11,11,14
14 CALL ITLZ
   CALL DPT(1,4)
   CALL PLOT(0.,-11.,-2)
   CALL PLOT(2.,2.,-3)
   CALL PLOT(0.,8.,3)
   CALL PLOT(6.,8.,2)
   CALL PLOT(6.,0.,1)
   CALL INITS(ITLX,1,226,214,196,201,228,212,64,195,214,213,195,197,
  *213,227,217,193,227,201,214,213,77,215,215,212,93)
   CALL INITS(ITLY,1,197,211,197,195,227,217,214,196,197,64,215,214,
  *227,197,213,227,201,193,211,77,212,229,93,64,64,64,226,195,193,
  *211,197,122)
   CALL SCALOG(ANA,6.,N,1)
   EMF(N+1)=-160.
   EMF(N+2)=20.
   E(92)=-160.
   E(93)=20.
   C(92)=ANA(N+1)
   C(93)=ANA(N+2)
   SODIUM=10.
   DO 15 I=1,91
   C(I)=SODIUM
   E(I)=ALOG10(C(I))*SLOPE+AINCPT
15 SODIUM=SODIUM+1.
   CALL AXLOG(0.,0.,ITLX,-25,6.,0.,ANA(N+1),ANA(N+2))
   CALL SYMBOL(0.0,-.75,.14,ITITLE,0.,52)
   CALL AXIS(0.,0.,ITLY,32,8.,90.,-160.,20.)
   CALL LILOG(ANA,2,EMF,1,N,1,-1,4)
   CALL LILOG(C,2,E,1,91,1,0,0)
   CALL FINAL
   GO TO 9001
   END
```

APPENDIX II

PROGRAM FOR DETERMINATION OF END POINT OF POTENTIOMETRIC TITRATION BY GRAN'S METHOD

```
C A PROGRAM TO DETERMINE THE END POINT OF THE ARGENTOMETRIC TITRATION
C OF IONENE-BROMIDE SOLUTION AND SODIUM BROMIDE SOLUTION FOR THE COM-
C PLEXATION WITH NAPVS.
C THIS PROGRAM ALSO DETERMINES THE EQUATION OF THE STRAIGHT LINE OF THE
C RAPIDLY RISING POINTS BEYOND THE END POINT. THE TITRATION CURVES ARE
C PLOTTED IF A FLAG OF 1 IN COLUMN 1 OF CARD 4 IS DETECTED.
C THE CURVES WILL NOT BE PLOTTED IF A BLANK IS IN COLUMN 1 OF CARD 4.
C VTITR IS THE VOLUME OF TITRANT IN MLS.
C X AND Y ARE THE RECTANGULAR CO-ORDINATES FOR PLOTTING. X REPRESNTS
C THE VOLUME OF TITRANT AND Y REPRESENTS THE VALUE OF THE GRAN FUNCTION.
C E IS THE EMF IN MILLIVOLTS.
C B1 AND BO ARE THE SLOPE AND THE INTERCEPT OF THE REGRESSION LINE.
C R IS THE CORRELATION COEFFICIENT OF THE REGRESSION LINE.
C VOL IS THE VOLUME OF TITRATE IN MLS.
C TICONC IS THE CONCENTRATION OF TITRANT(AGNO3) IN MOLES/L.
C N IS THE NUMBER OF DATA CARDS PER TITRATION.
C VOLDIL IS THE VOLUME OF DILUTION WATER ADDED IN MILLILITERS.
      DIMENSION VTITR(100),X(103),Y(103),TITLE(20),E(100)
      DIMENSION B1(100),BO(100),R(100),ITLX(20),ITLY(20),ITITLE(20)
 9001 READ(5,1) TITLE
C TITLE IS THE TITLE OF THE DATA TABLE
      READ(5,1)ITITLE
C ITITLE IS THE CAPTION OF THE GRAPH
    1 FORMAT(20A4)
      READ(5,8000) VOLDIL
 8000 FORMAT(F10.4)
      READ(5,9003) IPLOT
 9003 FORMAT(I1)
      READ(5,2) VOL,TICONC,BLANK,N
    2 FORMAT(3F10.5,I3)
      READ(5,3) (VTITR(I),E(I),I=1,N)
    3 FORMAT(2F10.2)
      WRITE(6,4)
    4 FORMAT(////1H1,26X,'THE POTENTIOMETRIC TITRATION PERTAINING TO THE
     * STANDARDIZATION OF ')
      WRITE(6,7)TITLE
    7 FORMAT(1H ,26X,20A4)
      WRITE(6,8)
    8 FORMAT(1H ,27X,'VOLUME OF TITRANT(ML)',2X,
     *'ELECTRODE POTENTIAL(MV)', 7X,'GRAN (ML)'//)
C TO CALCULATE THE GRAN FUNCTION FROM THE GIVEN DATA.
      DO 6 I=1,N
      TOTVOL=VOL+VTITR(I)+VOLDIL
      X(I)=VTITR(I)
      EXPO=-0.038968*E(I)
      GRAN=TOTVOL*EXP(EXPO)
      Y(I)=GRAN
      WRITE(6,5) VTITR(I),E(I),GRAN
    5 FORMAT(1H ,34X,F6.2,18X,F7.2,14X,1PE12.5)
    6 CONTINUE
C STARTING FROM THE LAST DATA POINT, INITIALLY TAKE 3 POINTS IN DESCEND-
C ING ORDER AND CALCULATE THE CORRELATION COEFFICIENT, SLOPE AND INTER-
C CEPT FOR THIS THREE-POINT LINE.
      SX=X(N)+X(N-1)+X(N-2)
      SY=Y(N)+Y(N-1)+Y(N-2)
      SXY=X(N)*Y(N)+X(N-1)*Y(N-1)+X(N-2)*Y(N-2)
      SX2=X(N)**2+X(N-1)**2+X(N-2)**2
      SY2=Y(N)**2+Y(N-1)**2+Y(N-2)**2
```

APPENDIX II (continued)

```
      B1(3)=(3.0*SXY-SX*SY)/(3.0*SX2-SX**2)
      BO(3)=(SY-B1(3)*SX)/3.0
      R(3)=(SXY-SX*SY/3.)/SQRT((SX2-(SX**2)/3.)*(SY2-(SY**2)/3.0))
C THEN, TAKE ANOTHER POINT WHICH IS 1 PLACE LOWER IN ORDER THAN THE LAST
C ONE AND CALCULATE THE SLOPE, INTERCEPT AND CORRELATION COEFFICIENT FOR
C THIS FOUR-POINT LINE.
      J=N-3
      K=4
   20 AK=K
      SX=SX+X(J)
      SY=SY+Y(J)
      SXY=SXY+X(J)*Y(J)
      SX2=SX2+X(J)**2
      SY2=SY2+Y(J)**2
      B1(K)=(AK*SXY-SX*SY)/(AK*SX2-SX**2)
      BO(K)=(SY-B1(K)*SX)/AK
      R(K)=(SXY-SX*SY/AK)/SQRT((SX2-(SX**2)/AK)*(SY2-(SY**2)/AK))
C COMPARE THE CORRELATION COEFFICIENTS OF THE PREVIOUS LINE AND OF THE
C PRESENT LINE.
      IF(ABS(R(K)-R(3))-0.001) 10,10,30
C IF DIFFERENCE IN R IS LESS THAN PRESCRIBED VALUE, PICK UP ANOTHER POINT
C AND DO IT OVER AGAIN.
   10 R(3)=R(K)
      K=K+1
      J=J-1
      IF(J) 30,30,20
C IF DIFFERENCE IS GREATER THAN PRESCRIBED VALUE, REPORT THE PARAMETERS
C FOR THE PREVIOUS LINE. ALSO, CALCULATE THE INTERCEPT OF THIS LINE WITH
C THE X OR VOLUME OF TITRANT AXIS. THEN, CALCULATE THE CONCENTRATION OF
C THE UNKNOWN SOLUTION.
   30 M=K-1
      ENDPT=ABS(BO(M)/B1(M))-BLANK
      IF(ENDPT)32,32,33
   32 CONCBR=0.
      GO TO 34
   33 CONCBR=ENDPT*TICONC/VOL
   34 WRITE(6,31) VOL,TICONC,M,B1(M),BO(M),R(M),ENDPT,CONCBR
   31 FORMAT(///1H ,25X,'VOLUME OF TITRATE=',F6.2,' ML'/26X,
     *'CONCENTRATION OF TITRANT=',F8.6,' MOLES/L'/26X,
     *'NUMBER OF POINTS THAT FIT THE REGRESSION LINE=',I3/26X,
     *'THE EQUATION OF THE REGRESSION LINE IS  Y= ',1PE12.5,1X,'X+ ',
     *1PE12.5/26X,'THE CORRELATION COEFFICIENT IS ',1PE12.5/26X,
     *'THE EQUIVALENCE POINT=',1PE12.5,' ML'/26X,
     *'THE CONCENTRATION OF THE SOLUTION IS',1PE12.5,' MOLES/L')
      IF(IPLOT) 9002,9004,9002
C ENTER PLOT MODE.
 9002 CALL ITLZ
      CALL DPT(1,4)
      CALL PLOT(0.,-11.,-2)
      CALL PLOT(2.,2.,-3)
      CALL PLOT(0.,6.,3)
      CALL PLOT(9.,6.,2)
      CALL PLOT(9.,0.,1)
      CALL INITS(ITLX, 1, 229,214,211,228,212,197,64,214,198,64,226,201,
     *211,229,197,217,64,213,201,227,217,193,227,197,64,193,196,196,197,
     *196,107,212,211,75)
      CALL INITS(ITLY,1,127,199,217,193,213,127,107,212,211,75,64,64,
     *64,226,195,193,211,197,122)
      CALL SCALE(Y,6.,N,1)
      X(N+1)=0.
```

APPENDIX II (continued)

```
      X(N+2)=1.0
      CALL AXIS(0.,0.,ITLX,-34, 9.,0.,X(N+1),X(N+2))
      CALL SYMBOL(0.0,-.75,0.14,ITITLE,0.,80)
      CALL AXIS(0.,0.,ITLY,+19,6.,90.,Y(N+1),Y(N+2))
      CALL LINE(X,Y,N,1,-1,1)
      CALL FINAL
 9004 GO TO 9C01
      END
```

APPENDIX III

PROGRAM TO CALCULATE THE TIMES OF DELIVERY OF POLYELECTROLYTE SOLUTIONS IN COMPLEXATION REACTIONS AND OF SOLUTIONS REQUIRED FOR PREPARING THE CONTROL SOLUTIONS

```
C CALTNA IS THE CALIBRATION TIME FOR SODIUM-POLY(VINYLSULFONATE).(ML/M)
C CALTX IS THE CALIBRATION TIME FOR THE IONENE BROMIDE.(ML/M)
C NAPVS IS THE CONCENTRATION OF SODIUM-POLY(VINYLSULFONATE).(MOLES/L)
C IONENE IS THE CONCENTRATION OF THE IONENE BROMIDE.(MOLES/L)
C NABR IS THE CONCENTRATION OF THE STANDARD NABR SOLUTION.(MOLES/L)
C VOLX IS THE VOLUME OF IONENE BROMIDE USED. (ML)
C VOLNA IS THE VOLUME OF SODIUM-POLY(VINYLSULFONATE).(ML)
C VOLCON IS THE VOLUME OF THE CONTROL SOLUTION.(ML)
C TOTVOL IS THE SUM OF VOLX AND VOLNA.(ML)
C MRATIO IS THE MOLE-RATIO OF IONENE TO NAPVS
C NAFORM IS THE MILLIMOLES OF SODIUM BROMIDE FORMED IN THE REACTION
C NALEFT IS THE MILLIMOLES OF EXCESS NAPVS
C XLEFT IS THE MILLIMOLES OF EXCESS IONENE
C XRD IS THE VOLUME OF IONENE REQUIRED FOR THE CONTROL SOLUTION(ML)
C PVSRD IS THE VOLUME OF NAPVS REQUIRED FOR THE CONTROL SOLUTION(ML)
C NABRRD IS THE VOLUME OF STANDARD NABR REQUIRED FOR THE CONTROL(ML)
C
      DOUBLE PRECISION A(10)
      REAL CALTNA,CALTX,NAPVS,IONENE,NABR,VOLX,VOLNA,TOTVOL,X,Y,MRATIO
      REAL TIMENA,TIMEX,NAFORM,NALEFT,XLEFT,XRD,PVSRD,VOLCON,NABRRD
 9001 READ(5,1) CALTNA,CALTX,IONENE,NAPVS,NABR,VOLCON
    1 FORMAT(6F10.5)
      READ(5,29) N
   29 FORMAT(I5)
      DO 10 I=1,N
      READ(5,30) A
   30 FORMAT(10A8)
      READ(5,2) VOLX,VOLNA
    2 FORMAT(2F10.2)
      WRITE(6,3)
    3 FORMAT(1H1,24X,'THE DATA PERTAINING TO THE TIMES OF DELIVERY OF PO
     *LYELECTROLYTES '/25X,' AND THE MAKE-UP OF THE CORRESPONDING CONTRO
     *L SOLUTION FOR THE')
      WRITE(6,4)A
    4 FORMAT(1H ,24X,10A8///)
      TOTVOL=VOLX+VOLNA
      X=VOLX*IONENE
      Y=VOLNA*NAPVS
      MRATIO=X/Y
C TO CALCULATE THE TIME OF DELIVERY OF NAPVS
      CALL MINSEC(VOLNA,CALTNA,MINS,ISECS)
C TO CALCULATE THE TIME OF DELIVERY OF IONENE
      CALL MINSEC(VOLX,CALTX,MINX,ISECX)
      IF(MRATIO-1.) 5,6,7
    5 NAFORM=X
      NALEFT=Y-X
      XLEFT=0.
      XRD=0.
      MINXC=0
      ISECXC=0
      PVSRD=(NALEFT/TOTVOL)*VOLCON/NAPVS
      CALL MINSEC(PVSRD,CALTNA,MINSC,ISECSC)
      GO TO 8
    6 NAFORM=X
      NALEFT=0.
      PVSRD=0.
      MINSC=0
      ISECSC=0
```

APPENDIX III (continued)

```
      XLEFT=0.
      XRD=0.
      MINXC=0
      ISECXC=0
      GO TO 8
    7 NAFORM=Y
      NALEFT=0.
      PVSRD=0.
      MINSC=0
      ISECSC=0
      XLEFT=X-Y
      XRD=(XLEFT/TOTVOL)*VOLCON/IONENE
      CALL MINSEC(XRD,CALTNA,MINXC,ISECXC)
    8 NABRRD=(NAFORM/TOTVOL)*VOLCON/NABR
      CALL MINSEC(NABRRD,CALTX,MINBR,ISECBR)
      WRITE(6,9) IONENE,NAPVS,CALTX,CALTNA,VOLX,VOLNA,TOTVOL,MRATIO,
     *MINX,ISECX,MINS,ISECS,NAFORM,NABR,VOLCON,NABRRD,MINBR,ISECBR,
     *NALEFT,PVSRD,MINSC,ISECSC,XLEFT,XRD,MINXC,ISECXC
   10 CONTINUE
    9 FORMAT(25X,'CONCENTRATION OF IONENE=',F7.5,' MOLES/LITER'/25X,'CON
     *CENTRATION OF NAPVS=',F7.5,' MOLES/LITER'/25X,'CALIBRATION TIME FO
     *R IONENE=',F6.3,' ML/MINUTE'/25X,'CALIBRATION TIME FOR NAPVS=',
     *F6.3,' ML/MINUTE'/25X,'VOLUME OF IONENE=',F6.2,' ML'/25X,'VOLUME O
     *F NAPVS=',F6.2,' ML'/25X,'TOTAL VOLUME OF REACTION MIXTURE=',F6.2,
     *' ML'/25X,'MOLE-RATIO OF IONENE TO NAPVS=',F5.2/25X,'TIME OF DELIV
     *ERY OF IONENE =',I3,'MIN',I3,'SEC'/25X,'TIME OF DELIVERY OF NAPVS
     *=',I3,'MIN',I3,'SEC'/25X,'INFORMATION FOR THE MAKE-UP OF THE CONTR
     *OL SOLUTION'/25X,'NABR FORMED IN THE REACTION=',F8.5,
     *' MILLIMOLES'/25X,'CONCENTRATION OF STOCK NABR=',F7.5,' MOLES/LITE
     *R'/25X,'VOLUME OF CONTROL SOLUTION=',F6.2,' ML'/25X,'VOLUME OF STO
     *CK NABR REQUIRED FOR THE CONTROL SOLUTION=',F7.3,' ML'/25X,'USING
     *THE IONENE PUMP,THE TIME OF DELIVERY OF NABR=',I3,'MIN',I3,'SEC'/
     *25X,'NAPVS LEFT UNREACTED=',F9.6,' MILLIMOLES'/25X,'VOLUME OF NAPV
     *S REQUIRED FOR THE CONTROL=',F8.3,' ML'/25X,'USING THE NAPVS PUMP,
     *TIME OF DELIVERY OF NAPVS=',I3,'MIN',I3,'SEC'/25X,'IONENE LEFT UNR
     *EACTED=',F9.6,' MILLIMOLES'/25X,'VOLUME OF IONENE REQUIRED FOR CON
     *TROL=',F8.3,' ML'/25X,'USING NAPVS PUMP,TIME OF DELIVERY OF IONENE
     * FOR CONTROL SOLUTION=',I3,'MIN',I3,'SEC'///)
      GO TO 9001
      END


      SUBROUTINE MINSEC(VOL, CALT, MIN, ISEC)
      TDECM=VOL/CALT
      TMIN=AINT(TDECM)
      MIN= TMIN
      SEC=(TDECM-TMIN)*60.
      ISEC=SEC
      RETURN
      END
```

APPENDIX IV

PROGRAM FOR CALCULATION OF AVERAGE CORRECTED SPECIFIC CONDUCTANCE

```
C A PROGRAM TO CALCULATE THE SPECIFIC CONDUCTIVITIES OF DILUTE AQUEOUS
C SOLUTIONS USING THE REVERSE MODE OF THE GENERAL RADIO COMPANY TYPE
C 1603-A Z-Y BRIDGE
C ALL FREQUENCIES ARE EXPRESSED IN KILOHERTZ
C NEGATIVE RB MEANS CAPACITIVE SUSCEPTANCE(+BX)
C POSITIVE RB MEANS INDUCTIVE SUSCEPTANCE(-BX)
C GF, GI, C AND CONH2O ARE EXPRESSED IN MICROMHO
C SPECIFIC CONDUCTANCE IS EXPRESSED IN MICROMHO/CM
C THE CONDUCTIVITY CELL CONSTANT=1.0144
C
      DIMENSION AVECON(100),STDDEV(100),A(20)
      REAL M,N
      READ(5,303) ISET,IFLAG
303   FORMAT(2I2)
      IF(ISET-1) 404,404,403
  403 DO 308 J=1,ISET
  404 READ(5,309)IK
      IF(IK-1) 300,300,405
  309 FORMAT(I2)
  405 DO 304 K=1,IK
  300 READ(5,301) A
  301 FORMAT(20A4)
      READ(5,20) N,CONH2O
   20 FORMAT(F5.0,F6.2)
      SC=0.
      SC2=0.
      IF(IFLAG) 112,112,111
  111 WRITE(6,49)
   49 FORMAT(1H1,////35X,'SPECIFIC CONDUCTIVITY DATA PERTAINING TO THE S
     1YSTEM OF'/)
      WRITE(6,302) A
  302 FORMAT(28X,20A4///)
  102 WRITE(6,50)
   50 FORMAT(28X, '  F1    FO     F     RB     GI     GF      GA     CONH2O
     1 C       SPCON '/)
  112 L=N
      DO 305 JJ=1,L
   11 READ(5,1)F1, FO, GF, GI, RB
    1 FORMAT(2F5.2, 3F10.3)
      IF(ABS(RB)-500.0) 2,2,3
    2 M=8.667E-10*(ABS(RB)**3)-1.51E-6*(ABS(RB)**2)+9.623E-4*ABS(RB)
     1-1.2E-2
      GO TO 4
    3 M=-2.5417E-9*(ABS(RB)**3)+4.675E-6*(ABS(RB)**2)-2.9646E-3*ABS(RB)+
     10.83125
    4 F=F1**2/FO
      IF(RB-0.) 5,6,7
    5 IF(FO-10.) 8,9,8
    8 GA=1.1*M*F
      GO TO 10
    9 GA=2.5*M*F
      GO TO 10
    6 GA=0.
      GO TO 10
    7 GA=2.4*M*F
   10 C=GI-GF-GA-CONH2O
      SPCON =1.0144*C
      IF(IFLAG)113,113,100
```

APPENDIX IV (continued)

```
100 WRITE(6,101) F1,FO,F, RB,GI, GF,GA,CONH2O, C, SPCON
101 FORMAT(28X, 3F5.1,F7.1,F5.0,F6.1,F8.4,1X,F6.2,2X,F7.2,2X,F7.2)
113 SC=SC+SPCON
305 SC2=SC2+SPCON**2
200 AVE=SC/N
    AVECON(K)=AVE
    VAR=(SC2-(SC**2)/N)/(N-1.)
    IF(VAR) 401,401,400
401 STDDEV(K)=0.
    IF(IFLAG)115,115,114
114 WRITE(6,402) AVE,VAR
402 FORMAT(//30X,'AVERAGE SPECIFIC CONDUCTIVITY= ',F6.2,' MICROMHO/CM'
   */30X,'VARIANCE= ',F11.7/30X,'STANDARD DEVIATION= ERROR DUE TO NEGA
   *TIVE OR ZERO VARIANCE.'///)
115 CONTINUE
    GO TO 304
400 SDEV=SQRT(VAR)
    STDDEV(K)=SDEV
    IF(IFLAG)304,304,116
116 WRITE(6,201)AVE, VAR, SDEV
201 FORMAT(//30X,'AVERAGE SPECIFIC CONDUCTIVITY= ',F6.2,' MICROMHO/CM
   *'/30X,'VARIANCE= ',F6.2/30X,'STANDARD DEVIATION= ',F6.2///)
304 CONTINUE
    IF(IK-1) 406,406,407
407 WRITE(6,306)
306 FORMAT('1',////38X,'AVERAGE CONDUCTIVITY',10X,
   *'STANDARD DEVIATION'//)
308 WRITE(6,307) (AVECON(II),STDDEV(II),II=1,K)
307 FORMAT(' ',45X,F6.2,23X,F6.2)
406 CALL EXIT
    END
```

APPENDIX V

PROGRAM FOR PLOTTING SPECIFIC CONDUCTANCE DATA AGAINST IONIC MOLE RATIO

```
      DIMENSION X(203),Y(203),XC(203),YC(203),ITLX(20),ITLY(20)
      DIMENSION ITIL(20),ILEGD1(20),ILEGD2(20)
      DIMENSION ILEG(20)
C READ THE TITLE OF THE GRAPH
 9001 READ(5,9002) ITIL
 9002 FORMAT(20A4)
C READ THE NUMBER OF SETS OF DATA POINTS.
C ONE SET = ( X(I),Y(I) ) AND ( XC(I),YC(I) ).
C Y(I) AND YC(I) ARE THE SPECIFIC CONDUCTANCE OF THE REACTION MIXTURE
C AND OF THE CORRESPONDING CONTROL SOLUTION, RESPECTIVELY.
      READ(5,1) N
    1 FORMAT(I3)
C SINCE X(I)=XC(I)=MOLE-RATIO, THEREFORE , ONLY READ EITHER ONE ONCE
C AND SET X(I)=XC(I) LATER.
      READ(5,2) (X(I),Y(I),YC(I),I=1,N)
    2 FORMAT(3F10.3)
      DO 9003 I=1,N
 9003 XC(I)=X(I)
C INITIALIZE THE PLOTTING MODE.
      CALL ITLZ
      CALL DPT(1,4)
C DRAW A LINE ALONG Y-AXIS TO SEPARATE GRAPHS AND TO WET PEN.
      CALL PLOT(0.,-11.,-2)
C ESTABLISH THE ORIGIN.
      CALL PLOT(2.,2.,-3)
      CALL PLOT(0.,8.,3)
      CALL PLOT(7.,8.,2)
      CALL PLOT(7.,0.,1)
      CALL PLOT(5.2,2.1,3)
      CALL PLOT(5.2,1.0,2)
      CALL PLOT(6.8,1.0,1)
      CALL PLOT(6.8,2.1,1)
      CALL PLOT(5.2,2.1,1)
C STORE THE X- AND Y- AXES TITLES IN CORE.
      CALL INITS(ITLX,1,77,201,214,213,197,213,197,93,97,77,213,193,215,
     *229,226,93,75)
      CALL INITS(ITLY,1,226,215,197,195,201,198,201,195,64,195,214,213,
     *196,228,195,227,193,213,195,197,107,212,201,195,217,214,212,200,
     *214,226,97,195,212,75)
C DRAW THE X-AXIS AND WRITE THE TITLE. DO THE SAME FOR THE Y-AXIS.
      CALL AXIS(0.,0.,ITLX,-17, 7.,0.,0.,0.3)
      CALL AXIS(0.,0.,ITLY,+34, 8.,90.,30.,6.0)
C WRITE THE TITLE OF THE GRAPH PARALLEL TO THE X-AXIS
      CALL SYMBOL(-.13,-1.0,.14,ITIL,0.,62)
C STORE LEGENDS IN CORE.
      CALL INITS(ILEG,1,211,197,199,197,213,196,122)
C     CALL INITS(ITLX2,1,77,213,193,215,229,226,93,97,77,201,214,213,
      CALL INITS(ILEGD1,1,214,194,226,197,217,229,197,196)
      CALL INITS(ILEGD2,1,195,214,213,227,217,214,211)
C DRAW THE LEGENDS.
      CALL DRAW(5.5,1.5,0.,170,1.0,0.,0.28)
      CALL DRAW(5.5,1.2,0.,175,1.0,0.,0.28)
      CALL SYMBOL(5.8,1.5,.14,ILEGD1,0., 8)
      CALL SYMBOL(5.5,1.8,0.14,ILEG,0.,7)
      CALL SYMBOL(5.8,1.2,0.14,ILEGD2,0.,7)
C STORE MINIMUM AND INCREMENT VALUES IN MEMORY.
      X(N+1)=0.0
      X(N+2)=0.3
```

APPENDIX V (continued)

```
      Y(N+1)=30.
      Y(N+2)=6.0
      XC(N+1)=0.0
      XC(N+2)=0.3
      YC(N+1)=30.
      YC(N+2)=6.0
C PLOT THE POINTS.
      CALL LINE(X,Y,N,1,-1,1)
      CALL LINE(XC,YC,N,1,-1,3)
      CALL FINAL
      GO TO 9C01
      END
```

APPENDIX VI

HYDROPHOBIC INTERACTION

The hydrophobic interaction is a unique organizing force, based on repulsion by the solvent instead of attractive forces at the site of organization. It is responsible for many biological assemblies and a typical example is the spontaneous folding of proteins. Under suitable conditions, hydrophobic interaction also acts on synthetic organic molecules as well.

When an aliphatic hydrocarbon is introduced into an aqueous solution, a large positive deviation from Raoult's Law is observed. The dissolution of an organic molecule in water is exothermic. Therefore, the low solubility of organic compounds in water is a consequence of a large negative excess entropy of mixing. According to Frank and Evans (70), the negative enthalpy and negative entropy of mixing may be represented by a model in which an iceberg is stabilized in close proximity to the organic molecules. Therefore, the heat evolved may be considered as the latent heat given off in the freezing of the "icebergs." The freezing of icebergs results in regions of crystallinity which accompanies a loss in entropy. The tendency of hydrocarbons chains to aggregate in water reduces the number of water molecules surrounding them and leads to the "melting" of the "icebergs." This provides the driving force toward the aggregation of organic solutes in aqueous media.

APPENDIX VII

ESTIMATION OF COMPLETENESS OF POLYELECTROLYTE COMPLEXATIONS

The positive difference between the specific conductance of the control solution and of the supernatant solution (DELTAK) represents a deficit of sodium bromide in the supernatant solution. This deficit is attributed to the incomplete release of counterions due to the nonstoichiometry of complexation. In order to express DELTAK in terms of sodium bromide concentration, a relationship between sodium bromide solution and its specific conductance at various concentrations must be known (Fig. 54). Since the molar concentration of sodium bromide in the control solution (CBRCON) is known, the degree of ionic reaction in the complexation experiments (PERCEN) could be calculated. The computer program for the estimation of completeness of polyelectrolyte interaction is listed as follows. (April, 1967).

```
      DIMENSION TITLE(20)
9001  READ(5,1) TITLE
    1 FORMAT(20A4)
      WRITE(6,2) TITLE
    2 FORMAT('1',////,10X,20A4)
      READ(5,3) NMR
    3 FORMAT(I1)
      WRITE(6,4)
    4 FORMAT(' ',//,3X, 'MOLE-RATIO', 3X,'SPCON', 3X,'SPCONC', 3X,'NABR
     *IN CONTROL', 3X,'NABR DEFECIT', 3X,'0/0 IONIC GROUPS REACTED',//)
    7 DO 9CO0 I=1,NMR
    8 READ(5,5) XMR,SPCON,SPCONC,CBRCON
    5 FORMAT(4F10.0)
      DELTAK=SPCONC-SPCON
      CBRUNR=(DELTAK-1.21)/124171.26
    9 IF(XMR-1.)12,10,12
   10 CBRCON=(SPCONC-1.21)/124171.26
   12 PERCEN =100.-(CBRUNR/CBRCON)*100.0
      IF(CBRUNR)11,11,90CO
   11 PERCEN=100.
9000  WRITE(6,6) XMR,SPCON,SPCONC,CBRCON,CBRUNR,PERCEN
    6 FORMAT(' ', 5X,F4.2,6X, F5.2, 4X, F5.2, 6X,F9.6, 7X,F9.6,12X,F7.2)
      GO TO 9001
      END
```

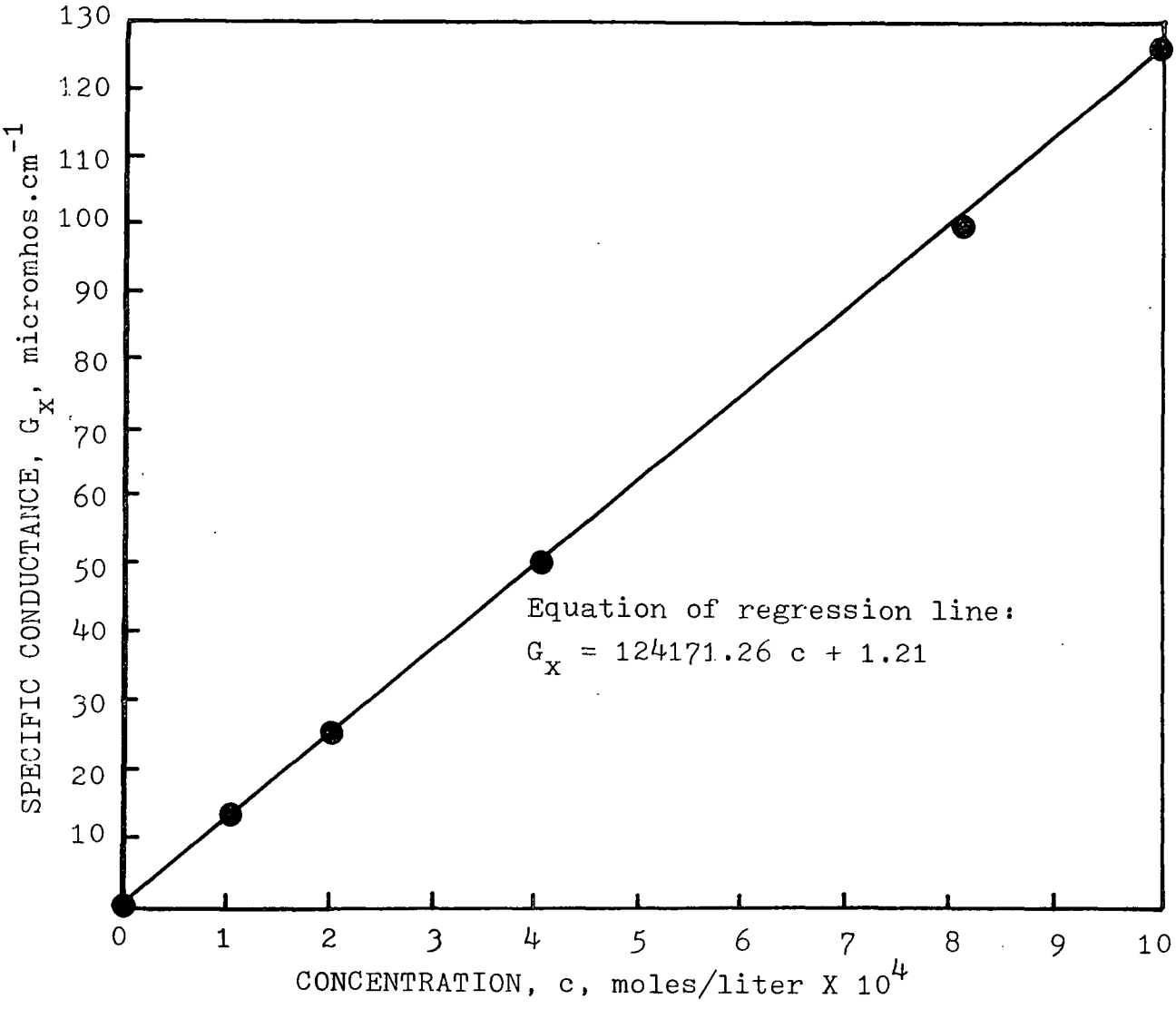

Figure 54. Specific Conductance Curve for Pure Aqueous Sodium Bromide Solutions at 25°C

APPENDIX VIII

PROGRAM FOR CALCULATION OF COMPLETENESS OF REACTION BETWEEN NaPVS AND IONENE BROMIDES WITH EQUAL DP

```
      REAL NI,NTOT,NRX
C     DPI IS THE DEGREE OF POLYMERIZATION OF IONENE
C     DPN IS THE DEGREE OF POLYMERIZATION OF NaPVS
.C    NRX IS THE NUMBER OF REACTED GROUPS IN THE DUPLEX
.C    NTOT IS THE NUMBER OF IONIC GROUPS IN A DUPLEX
.C    NI IS THE NUMBER OF IONIC GROUPS REACTED UPON STACKING OF 2 DUPLEX
.C    R IS THE IONIC SPACING RATIO OF IONENE TO NaPVS
.C    A IS THE FIRST PARAMETER IN THE THEORETICAL COMPLETENESS EQUATION
C     B IS THE SECOND PARAMETER IN THE THEORETICAL COMPLETENESS EQUATION
      WRITE(6,1)
    1 FORMAT(1H1, ////, 4X,'IONENE',4X,'D.P.',4X,'NaPVS D.P.',4X,
     *'NTOT',4X,'NRX',4X,'NI',6X,'A',5X,'B',//)
    4 READ(5,2) IONENE,DPI, DPN, R
    2 FORMAT(I1, 3F10.0)
      NTOT=2.*(DPN+DPI)
      NRX=8.*((0.5*DPN-1.0)/R+1.0)
      NI=(4./(DPN-1.))*((DPI-1.)*R-(DPN-1.))*(2.*(.5*DPN-((.5*DPN-1.)/R)
     *-1.)-1.)+4.
      A=NRX/NTOT
      B=NI/NTOT
      WRITE(6,3) IONENE,IONENE,DPI,DPN,NTOT,NRX,NI,A,B
    3 FORMAT(6X ,I1,',',I1,5X,F4.0,2(7X,F4.0),4X,F4.0,3X,F4.0,2X,F4.2,
     *3X,F4.2)
      GO TO 4
      END
```

APPENDIX IX

PROGRAMS FOR CALCULATION OF COMPLETENESS OF REACTION BETWEEN HIGH DP NaPVS AND LOW DP IONENES

PART A

```
      REAL NEGSPA
 9001 READ(5,1) IONENE, DPN,R
    1 FORMAT(I1,F3.0,F3.1)
      RPG=(DPN-2.)/R+1.
      TRG=2.*RPG
      UNEGP=DPN-RPG
      NEGSPA=(0.5*DPN-1.)/(0.5*UNEGP-1.)
      RIBCAG=2.*(((DPN-1.)*R-DPN+2.)/NEGSPA+1.)
      PERCEN=50./DPN*(TRG+RIBCAG)
      WRITE(6,2) IONENE,IONENE,DPN,PERCEN
    2 FORMAT(I1,',',I1,4X,F4.0,5X,F6.2)
      GO TO 9001
      END
```

PART B

```
      REAL NEGSPA
 9001 READ(5,1) IONENE,DPN,R
    1 FORMAT(I1,F3.0,F3.1)
      RPG=(DPN 2.)/R+1.
      TRG=2.*RPG
      UNEGP=DPN-RPG
      NEGSPA=(0.5*DPN-1.)/(0.5*UNEGP-1.)
      RIBCAG=2.*(((DPN-1.)*R-DPN+2.)/NEGSPA+1.)
      RELEN=(DPN-1.)*R-(DPN-2.)
      RELENI=RELEN/R+1.
      RIBSUL=(RELEN/NEGSPA)+1.
      S2PLUS=RELENI-RIBSUL
      PLUSPA=RELEN/(S2PLUS-1.)
      IF(RELEN-(0.5*DPN-1.)) 99,99,103
  103 SULENG=(DPN-2.)-RELEN
      IF(PLUSPA-NEGSPA) 104,104,105
  104 TOTIMP=4.*(SULENG/NEGSPA+1.)
      GO TO 102
  105 TOTIMP=4.*(SULENG/PLUSPA+1.)
      GO TO 102
   99 IF(PLUSPA-NEGSPA) 100,100,101
  100 TOTIMP=4.*RIBSUL
      GO TO 102
  101 TOTIMP=4.*(RELEN/PLUSPA +1.)
  102 PPDP=(2.*(TRG+RIBCAG)+TOTIMP)*25./DPN
      WRITE(6,2) IONENE,IONENE,DPN,RPG,TRG,UNEGP,NEGSPA,RIBCAG,RELEN,
     *RELENI,RIBSUL,S2PLUS,PLUSPA,TOTIMP,PPDP
    2 FORMAT(I1,',',I1,4X,13F8.2)
      GO TO 9001
      END
```