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**INVESTIGATION OF POLYANION-POLYCATION INTERACTIONS
IN AN AQUEOUS SOLUTION BY CONDUCTOMETRY**

M. Sc. THESIS

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**SULU ÇÖZELTİLERDEKİ POLİANYON-POLİKATYON GİRİŞİMLERİNİN
KONDÜKTOMETRİK YÖNTEMLE İNCELENMESİ**

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CONTENTS

ACKNOWLEDGEMENT	ii
CONTENTS	iii
ABBREVIATIONS	v
SUMMARY	vi
ÖZET	vii
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. THEORETICAL PART	3
2.1. Polyelectrolytes	3
2.2. Polyphosphates as Polyelectrolytes	5
2.3. Polyelectrolyte Complexes	6
2.4. Applications of Polyelectrolyte Complexes	6
2.5. Zwitter Ion	7
2.6. The Conductance of Polyelectrolytes	9
CHAPTER 3. EXPERIMENTAL PART	12
3.1. Chemicals	12
3.2. Solutions	12
3.3. Apparatus	13
3.4. Experiments	13
3.4.1. Polymerization of 4-vinyl Pyridine	13
3.4.2. Molecular Weight Determination of Polyions	13
3.4.2.1. Molecular Weight Determination of Polyanion	14
3.4.2.2. Molecular Weight Determination of Polycation by Viscosimetry	19
3.4.3. Equivalent Weight Determination of Polyions	19
3.4.4. Conductometric Measurements	20
3.4.4.1. Conductometric Measurements for Polyelectrolyte Complex Stoichiometry	20

3.4.4.2. Conductometric Measurements For Zwitter Ion Interaction With Polyions	27
3.4.4.3. Conductometric Titration of PCOH With HPA	34
3.4.4.4. Potentiometric Titration of HPA with PCOH	35
3.4.5. Turbidimetric Measurements For Complex Stoichiometry	37
3.4.6. Supernatant Analysis	38
3.4.6.1. Wet Chemistry	38
3.4.6.2. Viscosity Measurements	40
3.4.7. Preparation of Polyelectrolyte Complex	40
3.4.8. Swelling Measurements	41
CHAPTER 4. RESULTS AND DISCUSSION	43
REFERENCES	47
CURRICULUM VITAE	49

ABBREVIATION

PVPy = Poly(4-vinyl pyridine)

PVPyCl = Poly(4-vinyl pyridinium chloride)

$(\text{NaPO}_3)_n$ = Poly sodium phosphate

PA = Polyanion

PC = Polycation

PEC = Polyelectrolyte complex

PABA = Paraamino benzoic acid

PABCl = Paraamino benzoil chloride

NaPABA = Sodium salt of paraamino benzoic acid

PCOH = Polycation base

HPA = Polyanion acid

SUMMARY

The interaction between oppositely charged polyelectrolytes both in solid state and in solution results in complexation reactions depending on the polyelectrolyte concentration. The oppositely charged polyelectrolytes react by means of strong electrostatic attraction and give off their associated counter ions. If the reaction medium contains additional salts such as NaCl, NaBr, the interpretation of the results may lead to understanding reactions between micro ions and polyelectrolyte complexes encountered in biological system as well as the structural characteristics of both neutral and synthetic polyelectrolyte chains.

Literature studies reveals that most of the studies concern of polyelectrolyte complexes which are formed by polyions of strong acids and bases or their salts. Little is known about the dilute solution interaction of polyelectrolytes which have relatively weak acid and base functions. In the present study, the reaction between poly(4-vinyl pyridinium chloride) cation (PC) and poly(sodium phosphate) (PA) anion in an aqueous solution in the presence and absence of NaBr, NaCl and paraamino benzoic acid salts (NaPABA, PABCl) were studied by conductometry, turbidimetry potentiometry, viscosimetry and swelling properties of PEC were examined in different solvent mixtures. In addition, the interaction between polyions and the salt form of paraamino benzoic acid which have internal acid and base functions (zwitter ion) and swelling properties of polyelectrolyte complex in different solvent mixture were investigated.

SULU ÇÖZELTİLERDEKİ POLİANYON - POLİKATYON GİRİŞİMLERİNİN KONDÜKTOMETRİK YÖNTEMLE İNCELENMESİ

ÖZET

Polimer zincirinde iyonik gruplar içeren ve elektrolit özellikleri taşıyan makromoleküllere "polielektrolit" denir. Polielektrolitler polar çözücülerde çözünürler. Katyonik ve anyonik polielektrolitlerin gerek katı durumda gerekse çözeltideki girişimleri "Polielektrolit kompleks" (PEC)'leri oluşturur. İki zıt yüklü sentetik polielektrolitin sulu çözeltideki girişimleri, polielektrolit konsantrasyonuna bağlı olarak iki tip reaksiyon verir.

1- İki zıt yüklü poliiyon yüksek konsantrasyonda karıştırılırsa polielektrolit kompleks jel meydana gelir. PEC'ler suda şişerek hidrojelleri oluştururlar. Hidrojeller reaksiyon koşulları ve başlangıç polielektrolitlerin özellikleri kontrol edilerek hazırlanır. Yüksek poliiyon konsantrasyonlarında oluşan jeller saydam olur.

2- İki zıt yüklü poliiyon nispeten düşük konsantrasyonda karıştırılırsa çökelti verir. Bu çökeltilere "poli tuz" denir. Poli tuzlar, çarpaz bağlı karışık (scrambled) veya poliiyonlardaki tüm iyonik grupların karşı karşıya geldiği düzenli (ordered, ladder) yapı gösterirler. Polituzlar bazen oluşum sürecinde ince film oluştururlar.

Polimerik yapılı asit, baz ve tuzların oluşturdukları kompleksler, PEC sınıfının en önemli bölümünü oluşturur. Bugüne kadar yapılan çalışmalarda genellikle kuvvetli asit, baz ve bunların tuzu olan poliiyonları içeren sistemler incelenmiş, orta derecede zayıf asidik ve bazik fonksiyonlara ait poliiyonların girişimlerine ait çok az sayıda çalışma yapılmıştır.

Orta derecede zayıf asidik ve bazik özelliklere sahip poliiyonların seyreltik sulu çözeltideki reaksiyonlarının incelenmesi doğal ve sentetik polimerlerin yapısal karakteristiklerinin öğrenilmesinden başka, biyolojik sistemlerdeki makromoleküller ile proteinlerin reaksiyon mekanizmalarının anlaşılmasına olanak verecektir. Bu çalışmada, polianyon olarak polisodyumfosfat seçilmesi, fosfatların canlı hayatındaki fonksiyonları ve fosfor içeren polimerik maddelerle kazanılan endüstriyel özellikler dikkate alınarak düşünülmüştür. PEC'ler başlangıç maddelerinden farklı özellikleri nedeniyle endüstride değişik ve önemli alanlarda kullanılırlar. Bu alanlar kısaca:

- a) Ultrafiltrasyon için membran yapımında
- b) İyon değiştirici olarak

- c) Plastik teknolojisinde, plastik tabakaların nem alışverişini arttırmada
- d) Enzim teknolojisinde ve polimer üretiminde
- e) PEC'ler elektrolit ile doyurulduğu zaman düşük direnç göstererek pilin iç direncini kontrol olanağı sağladıkları için pil endüstrisinde
- f) PEC'ler protein yapılarına benzerler. Hidrojel yapıdaki PEC'ler vücut proteinlerinin doğal özelliklerini bozmazlar. Vücut yapısında bulunan tanecikleri ve sıvıları ayırma özellikleri nedeniyle tıpta kullanılırlar.

PEC'lerin oluşum reaksiyonları genel olarak başlıca iletkenlik yöntemi olmak üzere viskozimetri, potansiyometri, türbidimetri, kalorimetri, kinetik sedimentasyon ve λ -ışınları difraksiyonu ile incelenmektedir. Ancak, PEC'leri oluşturan polielektrolitler ve çözeltileri ile ilgili kuramlar tam olarak gelişmemiştir.

DENEYSEL ÇALIŞMALAR

1- Kimyasal Maddeler ve Aletler:

Kullanılan tüm kimyasallar püranaliz Merck ürünü olarak seçilmiştir. Çözeltiler işlemlere göre gerekli konsantrasyonlarda hazırlanmıştır. Çalışmada polianyon olarak seçilen poli(sodyumfosfat) Merck tarafından üretilmiştir, polikasyon ise 4-vinil piridin'in (Merck) azot atmosferinde ve 70 C'de polimerizasyonu ile elde edilmiştir.

Çalışmada WTW kondüktometre ve pH metre, Hatch Radio türbidimetre, Oswald viskozimetre kullanılmıştır.

2- Poliiyonların Molekül Ağırlıkları Tayini:

Polianyon ve polikasyonun molekül ağırlıkları viskozimetrik yöntem kullanılarak tayin edilmiştir. Polianyonun polimerizasyon derecesi "Son grup" titrasyon yöntemi ile belirlenmiştir (Tablo 3-1).

3- Poliiyonların Ekivalent Ağırlıkları Tayini:

Polianyonun ekivalent ağırlığı alkalimetri, polikasyonun ekivalent ağırlığı ise arjantometrik yöntem kullanılarak tayin edilmiştir.

4- Polielektrolit Kompleks Stokiyometrisinin Kondüktometrik Yöntemle Tayini:

Polielektrolit kompleks stokiyometrisi için kondüktometrik yöntemle yapılan çalışmalarda iki tip ölçüm yapılmıştır.

1) Farklı mol oranlarında karıştırılan PK-PA çözeltilerinin ve PK ve PA'nın p-aminobenzoik asit tuzları ile farklı mol oranındaki karışımlarının

tuzsuz ortamda direkt iletkenlik ölçümü (Tablo 3-6, Şekil 17, 29, 30).

2) Poliiyonların birbirleriyle ve poliiyonların p-amino benzoik asitle girişim reaksiyonları için iletkenlik titrasyonu.

Titrasyon işlemleri;

a) PK ve PA'nın Tablo 3-5'de görülen çeşitli titrasyon kombinasyonu ile farklı titrant-çözelti konsantrasyonlarında, tuzsuz ve farklı konsantrasyonlarda NaCl ve NaBr tuzları içeren çözeltilerde yapılmıştır (Tablo 3-5, Şekil 5-16).

b) p-aminobenzoik asidin sodyum ve klorür tuzlarının polianyon ve polikasyon ile çeşitli kombinasyonlardaki titrasyonları, farklı titrant-çözelti konsantrasyonlarında, tuzsuz ve farklı konsantrasyonlarda NaCl, NaBr içeren çözeltilerde yapılmıştır (Tablo 3-7, Şekil 18-28).

5- Polielektrolit Kompleks Stokiyometrisinin Potansiyometrik Yöntemle Tayini:

Poli(sodyum fosfat), kuvvetli asit Amberlite IR-120, kolondan geçirilerek sodyum iyonları hidrojen iyonları ile poly(4-vinilpiridinyumklorür), kuvvetli bazik lonexchanger III kolondan geçirilerek klorür iyonları hidroksil iyonları ile değiştirildikten sonra elde edilen sırasıyla asit ve baz poliiyonların birbirleriyle tuzsuz ortamda potansiyometrik yöntemle titrasyonları yapılmıştır (Şekil 32).

6- Polielektrolit Kompleks Stokiyometrisinin Türbidimetrik Yöntemle Tayini:

Farklı mol oranlarında karıştırılan PK-PA çözeltilerinin bulanıklıkları türbidimetre ile ölçülmüştür. Aynı şekilde, p-aminobenzoikasidin sodyum tuzunun PK ile yapılan çeşitli mol oranlarındaki karışımlarının bulanıklıkları tayin edilmiştir (Şekil 33, 34).

7- Supernatant Analizi:

Polianyon ve polikasyon çözeltileri farklı mol oranlarında karıştırıldıktan sonra elde edilen PEC, santrifüjlenerek ayrılır. Supernatant çözeltisindeki polikasyondan gelen klorür iyonları arjentometrik, polianyonun içerdiği fosfor, ortofosfata hidrolizlendikten sonra fosfat iyonları halinde alkalimetrik titrasyonla tayin edilmiştir. Supernatantta bulunabilecek poliiyonlar ayrıca, referans kontrol çözeltileri kullanılarak viskozite yöntemi ile de tayin edilmiştir.

8- Şişme Deneyleri:

Polianyon ve polikasyonu ekimolar oranda karıştırılarak hazırlanan polielektrolit kompleks su ve asetonla yıkanıp vakum etüvünde kurutulduk-

tan sonra şişme deneyleri için kullanılmıştır PEC'ten alınan belirli miktar, belirli hacimde su, elektrolit, su-elektrolit-organik çözücü sistemlerinde 1-3 gün bekletilerek PEC'nin şişme oranı tayin edilmiştir (Tablo 3-12).

Ayrıca PEC tarafından tutulan farklı elektrolitler, elektrolit konsantrasyonunun fonksiyonu olarak belirlenmiştir (Tablo 3-13).

SONUÇLAR

PK-PA Reaksiyonu:

İletkenlik yöntemi ile yapılan çalışmalar PK ve PA'nın tuz içermeyen ortamda ekimolar oranda birleştiğini mikroiyonik tuzların (NaCl, NaBr) bulunduğu ortamda ve yüksek poliyon konsantrasyonlarında stokiyometrinin kaydığını göstermiştir. Türbidimetrik ölçümler ve supernatant analizleri sonuçların birbirini desteklediğini göstermiştir.

PK-NaPABA ve PA-PABCI Reaksiyonu

İletkenlik ve Türbidimetrik yöntemler tuzsuz ortamda PK - NaPABA ve PA-PABCI'nin ekimolar oranda birleştiğini, tuz içeren ortamlardaki reaksiyonlarda ise tüm stokiyometrilere 1:1 oranından saptığı bulunmuştur.

Şişme:

Şişme deneyleri, oluşan polielektrolit kompleksin 48 saatte maksimum şişmeye ulaştığını, en fazla şişmenin Aseton + Su, NaBr + Su, NaBr + Su + Aseton karışımında olduğunu ve % şişme oranının % 120 ile % 140 arasında değiştiğini göstermiştir.

Poliiyonların ve mikroiyonların bulunduğu sulu çözeltilerde, başlıca elektrostatik etkileşim sonucu, PEC oluşumu reaksiyonları gelişir. Oluşan PEC stokiyometrisi büyük ölçüde, girişim yapan poliiyonların toplam yük yoğunluklarının farkına bağlıdır. Poliiyonlar su gibi yüksek dielektrik sabitine sahip çözücülerde açık zincir yapısındadır. Poliiyon zincirleri üzerindeki asidik ve bazik fonksiyonlar birbirleriyle girişim yaparken poliiyonlardan uzaklaşan karşı iyonların poliiyonlar üzerinde bıraktığı elektrik yükleri reaksiyonun başlangıcında, poliiyonların yük yoğunluklarının yanında ihmal edilir.

Reaksiyon ilerledikçe karşı iyonların önemli ölçüde iyonlaşması ile poliiyon çevresinde artan yük yoğunluğu karşı iyonların daha sonraki iyonizasyonunu bastırır. Poliiyonların yaklaşmasını engeller ve poliiyonlar üzerindeki asidik ve bazik fonksiyonların etkileşimini yavaşlatır. Bu arada bir miktar aktif grup etkileşmeden, absorpsiyon veya adsorpsiyon mekanizması ile oluşan PEC ile birlikte kalabilir. Bu durumda, poliiyonlar asidik ve bazik fonksiyonlarının etkileşmesini sağlayabilmek için açık zincir yapısından sor-

mal (coiled) yapıya geçerler. Sonuç olarak poliyon zincir yapısındaki değişim, stokiyometriden koymaya neden olur. Ortamda hareketli iyonların dışında bulunabilecek yüksek konsantrasyondaki mikroiyonik tuzlar poliyonların sarmal yapısının sıkı bir şekilde gelişmesine katkıda bulunacaklarından stokiyometriden kayma doğal olarak gelişir.



CHAPTER 1- INTRODUCTION

Polyelectrolytes can interact with each other in an aqueous medium through coulombic forces to form polyelectrolyte complexes and give off their associated counter ions. Two types of complexation reactions result in depending on the polyelectrolyte concentration[1].

1- Heterogeneous network complexes that is, polyelectrolyte gels which contain different ratios of polycation and polyanion can be obtained[2].

2- Such an interaction gives a precipitate which may form thin films[1,3]. Polycomplex salts, or polycation and polyanion remain in the solution as aggregates without significant phase separation. Interpretation of the results for the interactions of polyions in the presence of additional salts such as NaCl and NaBr etc in aqueous solution, may lead to understand the reactions between microions and polyelectrolyte complexes encountered in biological system as well as the structural characteristics of both natural and synthetic polymer chains.

Studies done on the solution characteristics of polyelectrolyte complexes mainly deals with the polyions of strong acids and bases or their salts[3,4,5]. No investigation has been encountered for the PEC which have relatively weak acid and base functions in aqueous solutions.

In this study poly(4-vinyl pyridinium chloride) was used as polycation. Because vinyl pyridine is an important class of polymers exhibiting interesting properties due to the presence of the nitrogen atom in the pyridine ring. The weakly basic nitrogen atom makes possible a variety of reactions in vinyl pyridine polymers because of its unique characteristics in polymerization mechanism. Vinyl pyridine polymers are particularly important in applications as polyelectrolytes[6].

Polyelectrolyte properties of polyphosphate have been largely

studied and they have some advantages to organic polymers so that they are easily prepared to a degree of purity higher than organic polymers and their biological functions are important in living organism[7]. Therefore, poly-sodium phosphate has attracted the attention as polyanion in this study.

The feature of PEC stoichiometry in the presence of paraamino benzoic acid which has internal acid and base functions was suggested to enlarge the complex molecule in order to gain further properties in the PEC nature so that such approach may lead an interesting feature for swelling mechanism of PEC.

Swelling is the first step in the solubilizing of a macromolecule therefore, polyelectrolyte complexes might be dissolved in a ternary solvent mixture which contain water, a strongly ionized simple electrolyte and a polar organic solvent miscible with electrolyte solution. Moderate or even very low concentrations of specific polyelectrolytes can plasticize the polyelectrolyte complex. This plasticizing action of a polyelectrolyte may be manifested as softening and swelling of the polyelectrolyte complex. Alkali and specially alkali earth elements interact strongly with polyelectrolyte complexes with a site binding mechanism which reduces the strength of ionic crosslinks so that swelling occurs.

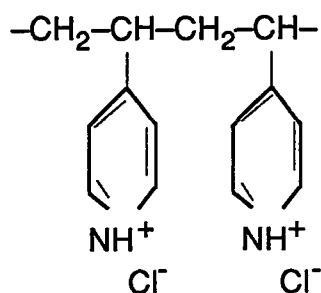
In the present study, a number of variables which affect the complex stoichiometry such as the types of released counter ions and added microionic salts, concentration of polyions, order of polyion addition, the stirring mode were undertaken to determine the interaction characteristics of polyions as well as the zwitter ion interaction with polyions and the swelling property of the polyelectrolyte complex formed in aqueous solution.

CHAPTER 2- THEORETICAL PART

2.1. Polyelectrolytes:

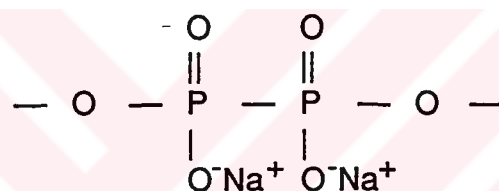
Polymers with ionizable groups along the chain, named polyelectrolytes and normally exhibit properties in solution which are quite different from those with nonionizable structures. Three major properties result in when polyelectrolytes are dissolved in aqueous solution. First, the mutual repulsion of the polyion and counter ions cause the expansion of the chain. The size of the polyelectrolyte random coil is a function of the concentration of polyion. Second, the ionization of the electrolyte groups leads a variety of unusual effect in the presence of small amounts of added salt. Finally, the ionic charges attached to the chains create regions of high local density, affecting the activity coefficients and properties of small ions in these localities.

Those properties depending on the size of the chain such as viscosity is strongly affected by chain expansion. The viscosity may even increase as polymer concentration decreases with the increase in the ionization of the polymer. When very high chain extensions are reached the effect reverses, but it does not disappear at infinite dilution. On the other hand, the addition of low molecular weight electrolyte to the aqueous solution increases the ionic strength of the solution outside the polymer coil relative to that inside and reduces the thickness of the bond layer of counterions around the chain[8]. If a polymer unit is positively charged, polyelectrolyte is called cationic polyelectrolyte (polycation). The associated counter-anions, the mobile ions belonging to the polyelectrolyte, may diffuse into the outer solution and they leave a residual net charge within the domain of the molecule. As a result of this net charge, the potential within the molecule is increased relative to the surroundings and further loss of anion is prevented. In this study, poly(4-vinyl pyridinium) is the cationic polyelectrolyte which is prepared by quarternizing poly(4-vinyl pyridine) with HCl.



The product is an analog of polystyrene with a substituent and positive charge at para position in each aromatic ring. It is a strong electrolyte by the fact that the quaternary ammonium ion claims the halogen ions only by electrostatic forces.

Polyelectrolyte which has negatively charged polymer unit is called anionic polyelectrolyte (polyanion). Poly(sodium phosphate) is an example of polyanion which is under this study.



At higher concentrations of the polyelectrolyte molecules overlap one another and a diluted regions which are not occupied by polymer molecules appear. The greater the dilution, the greater will be the volume of these regions compared with those occupied by polymer molecules and more of the mobile counter-ions will diffuse from the molecule into the intervening regions of pure solvent. Continued dilution removes more counter-ions from the domains of the molecules. As the net charge is increased on the molecules, further loss of counter-ions becomes more difficult so that extreme dilutions may be required before most of them are removed.

Polyelectrolyte solutions show large conductances. Conductance experiments give further information on the nature of polyelectrolytes in solution. Conductance of a polyelectrolyte increases when the dielectric constant of the medium is increased. Because the energy of removal of a mobile ion from the electrostatic field of the molecule decreases as the dielectric constant is increased and the number of "free" ions and the net charge on the polymeric ion should increase so that both contribute to in-

crease the conductance[9].

The characteristic phenomena of a polyelectrolyte solution are electrostatic dissociation and association. Debye-Hückel theory can not be valid for polyelectrolyte solution because of the high electrical charges of polyions. The theory of complete dissociation can only give distribution of dissociation degree in hypothetical dilute solution. For very rare polyelectrolytes in limited concentration range $I = 1/2 (C_1 \cdot Z^2)$ equation can be valid.

Theories on the solution behaviour of polyelectrolytes has been progressed yet. The latest theory valid to an extent is the theory of Poisson-Boltzman.

2.2. Polyphosphates as Polyelectrolytes:

Sodium phosphate polymerizes by condensation process when it is heated above 650°C and water soluble glasses are obtained. These products are known under various names such as Graham's Salt and poly(sodiumphosphate). For several reasons, the polyphosphates are ideally suited for a study of polyelectrolyte behavior. First, they are easily prepared to a degree of purity. Second, molecular weight distribution function has been determined both theoretically and experimentally. Third, viscosity behavior is uncomplicated because polyphosphate chains are unbranched[4,5]. In addition phosphorous element impart particular property to the synthetic polymer depending on phosphorous concentration. The structural differences of phosphorous containing polymer, e.g., whether phosphorous is linked to the main chain or to side chain or whether it is incorporated homogeneously or inhomogeneously exhibit important properties such as inflammability, increased water absorption, polarity and adhesion to glass, ceramic materials and metals etc. Graham's salts contain long chain phosphates and it is good precipitating agent. In general there are two types of precipitates formed with Graham's salt. One of them is viscous oils and jellies. It also precipitates with high molecular weight cations such as quaternary amines. Linear polyphosphates are stable in neutral or alkaline solutions at room temperature. The hydrolysis of polyphosphates are very slow so that the half life of P-O-P bond at 25°C is in the magnitude of years. They can not be converted to orthophosphate unless they are boiled with acid catalyst.

2.3. Polyelectrolyte Complexes (PEC):

Polyelectrolyte complexes can be prepared by mixing solutions of oppositely charged polyelectrolytes. The interaction of two polyelectrolytes depends on the characteristics of interacting groups. The position of interacting sites and the type of branching influence the formation and composition of PEC[10]. The product of interactions may precipitate as polysalts or when sufficiently concentrated solutions of strongly ionized polyelectrolytes are mixed, instead of a precipitate, thin continuous film is obtained at the interface between the two polyelectrolytes so that this film completely block further interpolymer reaction. The bond strength of a polyelectrolyte complex is in the second order because, these bonds can be hydrogen bond, ionic bond and bond of hydrophobic strength mainly. In dilute solution interactions, precipitate is occurred only in a narrow range of relative concentrations of ionic polyelectrolytes. At the maximum precipitation point polyelectrolytes are quantitatively reacted and no unreacted polyelectrolyte can be found in the supernatant liquid.

Pendent-pendent type PEC has a equimolar composition at any mixing ratio of polyanion and polycation and they are insoluble in water but, integral-pendent type PEC are soluble in water. Polyelectrolyte complexes are permeable to water and to small solute molecules. Permeability of solute molecules is selective. PEC might be dissolved in a ternary solvent consisting of water, a strongly ionized simple electrolyte and organic solvent miscible with the electrolyte solution[11].

2.4. Applications of PEC:

The major potential applications of polyelectrolyte complexes are in membranes, battery separators and in biomedical materials.

Membranes:

Ultrafiltration separates molecules in solution on the basis of size and shape. The high water permeability of PEC, with their controllable permselectivity to water-soluble solutes has led to their development as practical ultrafiltration membranes.

Battery Separators:

The use of PEC as battery separators is based on the following properties:

- a) Low resistivity when saturated with electrolytes
- b) Controllable permeability

Medical Field:

In many ways polyelectrolyte complexes have properties similar to protein structures. These include their ionic charge characteristics, controllable permeabilities to water and to solutes found in body fluids. PEC membranes show promise in dialytic-type artificial kidney. A new type of artificial kidney based on ultrafiltration of blood rather than dialysis employs PEC membranes. PEC are also being evaluated and promoted for use as materials for body repair such as coating and components of hearts valves, artificial hearts, for tissue repair. The optical clarity of these hydrogels, combined with the properties has prompted their use in contact lenses.

Miscellaneous Fields:

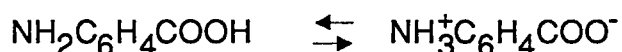
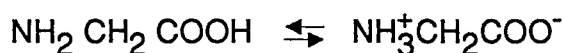
The sensitivity of conductive properties of polyelectrolyte complexes to moisture content and ion content suggests their use as detectors of moisture and detectors of specific ions. PEC are suitable for enzyme technology.

2.5. Zwitter Ion:

A substance that can behave both as an acid or a base when dissolved in a suitable solvent is called amphiprotic. If either its acidic or its basic character predominates sufficiently, titration of the species with a strong base or a strong acid may be feasible.

The simple amino acids represent an important class of amphiprotic compounds which owe their acid-base properties to the presence of both a weakly acid and a weakly basic functional group. In an aqueous solution of a typical amino acid such as glycine and paraaminobenzoic acid the following

equilibria exist,



All amino acids have at least two dissociation constants, one for the carboxyl group and one for the amino group. In addition several aminoacids have an ionizable side chains with a third dissociation constant, such as Glutamine, Asparagine.

The pH of a solution and dissociation of an ionizable group in solution are related by the Henderson-Hasselbalch equation.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

This equation can be used to determine the fraction of ionizable groups found in each of the possible ionization states in solution at a known pH. At $\text{pH} = \text{pK}_a$ half of the ionizable groups are dissociated. The pK_a 's of the ionizable groups of amino acids are affected by neighboring chemical groups on the molecule[13].

The amino acid species bearing a positive and a negative charge is called a Zwitter ion. The Zwitter ion of an amino acid has no tendency to migrate in an electric field. On the other hand, the singly charged anionic or the

cationic species is attracted to the positive and the negative electrodes respectively. No net migration of the amino acid occurs in an electric field when the pH of the solvent is such that the concentration of the anionic and the cationic forms are identical. The pH at which no net migration occurs is called the isoelectric point. The isoelectric point is related to the dissociation constants for the species. Dissociation constant for paraamino benzoic acid is given with the following equation,

$$\frac{[\text{H}_3\text{O}^+][\text{NH}_2\text{C}_6\text{H}_4\text{COO}^-]}{[\text{NH}_3^+\text{C}_6\text{H}_4\text{COO}^-]} = K_a \quad \frac{[\text{OH}^-][\text{NH}_3^+\text{C}_6\text{H}_4\text{COOH}]}{[\text{NH}_3^+\text{C}_6\text{H}_4\text{COO}^-]} = K_b$$

At the isoelectric point, cationic form concentration is equal to anionic form concentration of the given aminoacid thus,

$$\frac{K_a}{K_b} = \frac{[\text{H}_3\text{O}^+]}{[\text{OH}^-]} \quad \text{and} \quad [\text{H}_3\text{O}^+] = \sqrt{\frac{K_a \cdot K_w}{K_b}}$$

2.6. The Conductance of Electrolytes

By studying electrical conductance much useful information can be obtained about electrolytes. This is measured in terms of the electrolytic conductivity of the solution. Electrolytic conductivity is defined as the conductance between the opposite faces of a 1 m^3 . Since conductance is the reciprocal of resistance, the units are Sm^{-1} ($\text{S} = \Omega^{-1}$).

Measurement of electrolytic conductance is based on the wheatstone bridge principle. The resistance of a portion of a solution which is bounded by electrodes is measured. Usually platinum-platinum electrodes are used in conductivity measurements.

The conductivity is not the most convenient quantity to use for the study of electrolytic conduction. Because it measures the passage of current across a 1 m^3 of solution and it will vary with the number of ions present in that volume with the concentration of the solution. It is more useful to define molar conductivity which is equal to the conductivity divided by the concentration of the electrolyte. If the concentration of the solution is mol.m^{-3} then

the molar conductivity Ω is $\text{Sm}^2 \text{mol}^{-1}$. The value of Ω is equivalent to the conductance across a 1 m path, caused by all the ions in a volume of solution containing 1 mol of the electrolyte. Molar conductivity varies with concentration. For a weak electrolyte the value of Ω falls very rapidly with increasing concentration. A strong electrolyte shows a small drop in Ω as the concentration increases. If Ω is plotted against \sqrt{C} , it gives a straight line and from extrapolation to zero concentration the limiting molar conductivity (Ω_0) is obtained.

The current passing through an electrolyte is made up of two parts

- a) The current carried by the cations
- b) The current carried by the anions

The total conductance is the sum of the conductances of the two types of ion.

$$\Omega_0 = \Omega_+ + \Omega_-$$

Ω_+ and Ω_- are the ionic conductivities of the cation and anion respectively [14,15,16].

The conductance or specific and equivalent conductivity are the directly accessible properties that reflect the electric transport of the micro ions which have low molecular mass but these quantities do not truly reveal the transport of polyions and counter ions released from the polyions through the solution. In fact, no completely satisfactory theory for the conductivity of polyelectrolyte solutions is available. Many difficulties arise because of the asymmetry between the large, highly charged macroions and the small point like counter ions and coions with one of a few elementary charges only as well as the influence of the flexibility of polyelectrolyte chains. However the known treatment of conductivity and related phenomena in polyelectrolyte solution are in conflict apparently, conductivity is one of the valid methods in the study of polyelectrolyte solutions. The following empirical equation represents the equivalent conductivity of a polyelectrolyte solution.

$$\Omega = f' (\Omega_c^\circ + \bar{\Omega}_p)$$

Ω_c° , equivalent conductance of counterion at infinite dilute solution.

$\bar{\Omega}_p$, equivalent conductance of polyion.

f' , a correction factor related to the effective degree of ionization of the polyion, taking into account of association of condensation.

In fact, this empirical equation has been given a theoretical justification based on rodlike-condensation model (un-valid for the spherical and cylindrical polyions) so that f' represents the fraction of free counterions and it is derived from the self-diffusion coefficient for counterions and also from the thermodynamic arguments.



CHAPTER 3- EXPERIMENTAL PART

3.1. Chemicals

4-vinyl pyridine (Merck) was purified by vacuum distillation. Benzoin peroxide (Merck), sodium stearat, acetone (Merck) methyl alcohol (Merck), ether (Merck) were used in the polymerization process of polycation. Commercially available poly sodium phosphate (Merck) was utilized as polyanion. For the standardization of polyanion and polycation, silver nitrate (Merck), potassium chromate, sodium hydroxide (Merck), hydrochloric acid (Merck) were used. Ion exchanger III (Merck) (Strong base) and Amberlite IR 120 (Merck) (Strong acid) were used as ion exchange resins in the necessary reactions.

3.2. Solutions:

All solutions were freshly prepared for a weak period.

-10^{-2} M PVPyCl

0.170 g of PVPy is dissolved in 1 M, 1 ml of HCl and then diluted to 100 ml with distilled water (Stock solution pH; 2.7).

-10^{-1} M $(\text{NaPO}_3)_n$

1.02 g of $(\text{NaPO}_3)_n$ is dissolved in 100 ml of distilled water (Stock solution pH, 4,36).

-10^{-3} M PABCI

0,014 g of PABA is dissolved in 0,1 M, 1 ml of HCl, then diluted to 100 ml with distilled water (Stock solution pH, 3.05).

10^{-1} M NaPABA

1.37 g of PABA is dissolved in 1 M, 10 ml of NaOH, then diluted to 100 ml with distilled water (Stock solution pH 5.12).

3.3. Apparatus:

The following instruments were used in measurements.

Conductometer, WTW

pH meter, WTW

Turbidimeter, Hatch, Radiometer

Viscosimeter, Ostwald

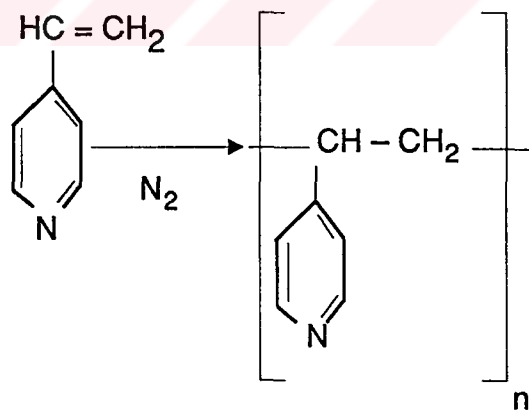
Atomic Absorption Spektrometer (Beckman 1272)

IR Spectrophotometer Perkin Elmer

3.4. Experiments:

3.4.1. Polimerization of 4-vinyl pyridine[17]:

In polymerization process 4-vinyl pyridine was purified by vacuum distillation. Under nitrogen atmosphere, 4-vinyl pyridine was polymerized using benzoyl peroxide as an initiator at 70°C.



3.4.2. Molecular Weight Determination of Polyions:

Molecular weight of polyions were determined viscosimetry. In addition, molecular weight of polyanion was also calculated from the polymeriza

zation degree which was determined by end group titration.

3.4.2.1. Molecular Weight Determination of PA[18]:

1- End Group Titration

0,5 g of polysodium phosphate was dissolved in 100 ml of water and pH was lowered to about 3 using HCl (1 M) and then titrated potentiometrically with standart NaOH (0,05 M) solution until the pH value of 4,5 and the procedure was continued beyond the second end point at about pH, 9 and the number of milli equivalents of base, A ml, consumed between two end points were determined. The curve is given in the following.

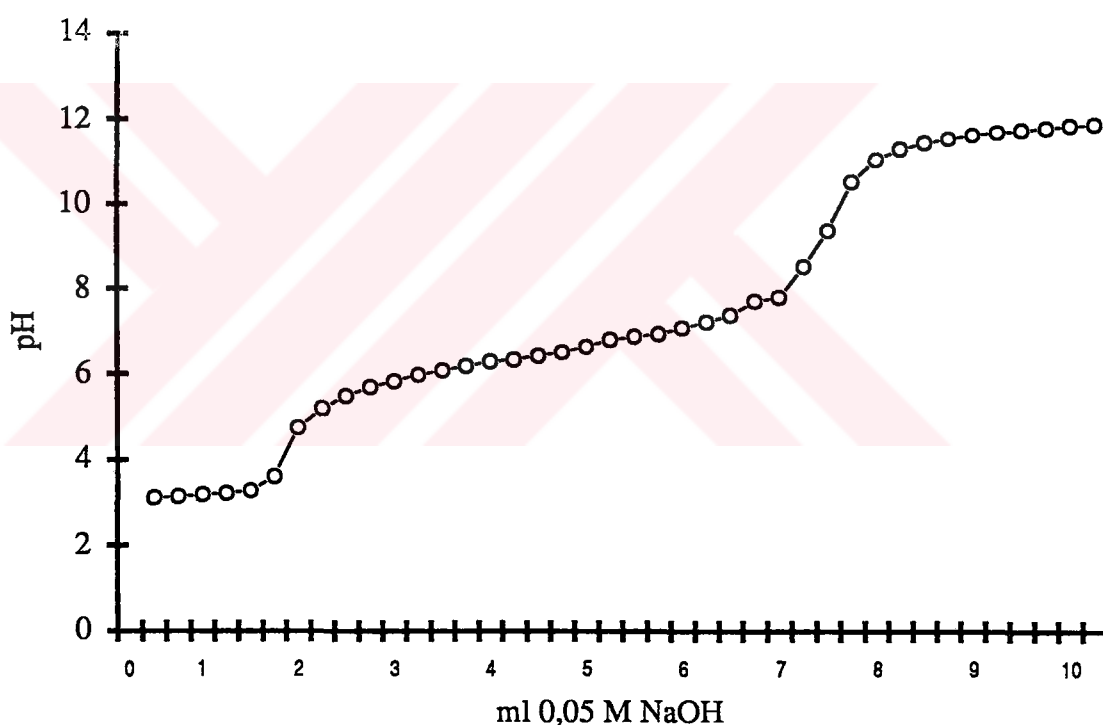


Figure 3.1. End Group Titration Curve of $(\text{NaPO}_3)_n$

The total phosphorus amount of the phosphate was determined in another poly sodium phosphate sample of the same weight after a complete hydrolysis procedure. The complete reversion of the polyphosphate to the orthophosphate form can be achieved by gently boiling the sample in a HNO_3 (1 M) solution for three hours under reflux then, pH was lowered to

about 3 and the solution was titrated with standart NaOH solution until the beyond of second end point near pH value of 9 then, A_h , milli equivalent of base consumption was obtained. The curve is as follows,

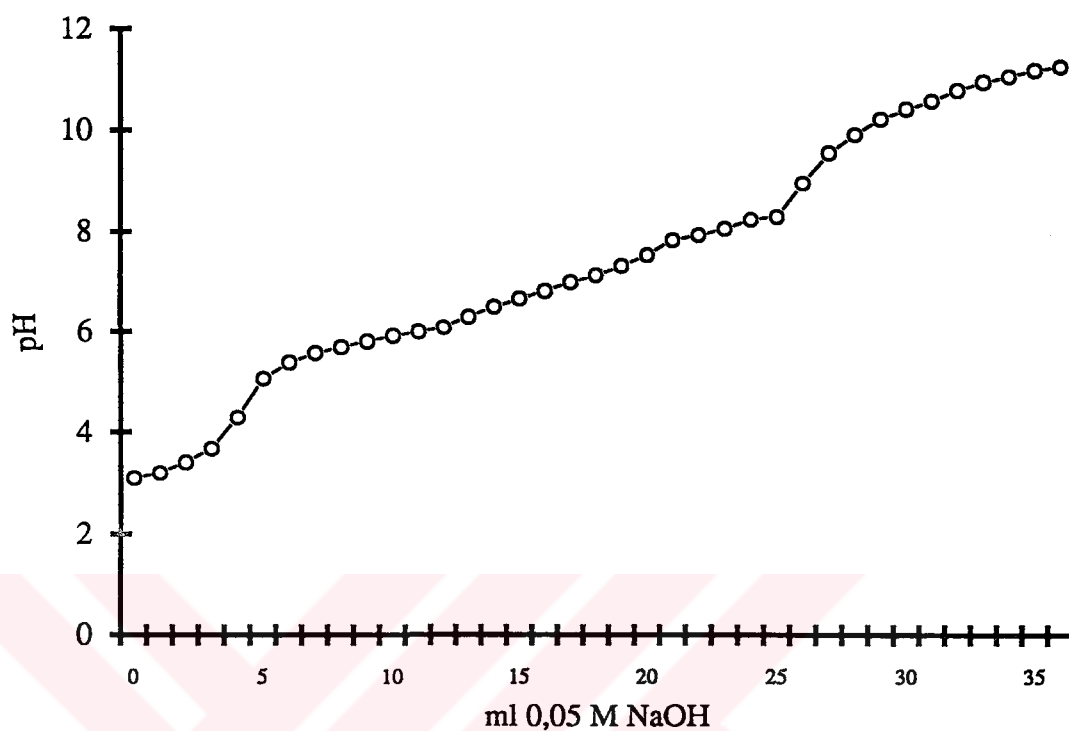


Figure 3.2. Titration curve of $(\text{NaPO}_3)_n$ After Hydrolysis

Finally P_2O_5 % (End Group) and P_2O_5 (Total) were calculated.

$$\text{P}_2\text{O}_5 \%_{\text{End Group}} = (A/A_h) \times 100$$

$$\frac{\text{P}_2\text{O}_5 (\text{Total})}{\text{P}_2\text{O}_5 (\text{End})} = \frac{n}{2} \quad (2 \text{ indicates two end groups})$$

Table 3-1. The Results of End Group Titration

Titration Procedure	ml of Base Added	P ₂ O ₅ %	Relative Precision ppt
For End Group	1,39	5,60	2,0
For Total Phosphorus	24,80	70,4	6,0
$\bar{n} = 25,14$ Molecular Weight: 2564,28			

Determination of moisture content:

A weighed amount of sample was dried at 110°C in furnace until a constant weight then, moisture % was calculated.

$$\text{Moisture \%} = \frac{\text{Loss of weight}}{\text{Sample weight}} \times 100$$

Determination of composition water

The dried sample was kept in oven at $440 \pm 10^\circ\text{C}$ upto a constant weight then, composition water % was calculated.

$$\text{Composition water \%} = \frac{\text{Loss of weight}}{\text{Sample weight}} \times 100$$

Determination of P₂O₅ content

A weighed amount of dried sample was dissolved in water and P₂O₅ was determined by ammonium molybdate method after the hydrolysis reaction then P₂O₅ % was calculated. All the results are shown in table 3-2.

Table 3-2. The Results of The Average Chain Length Determination of $(\text{NaPO}_3)_n$

Na ₂ O %	P ₂ O ₅ %	Moisture %	Composition Water %	Relative Precision ppt
29,21	69,58	0,20	1,01	5,0-20,0
n = 26,49 Molecular Weight: 2701,91				

2- Viscosimetry

Solution viscosity is basically a measure of the size of polymer molecules and it is empirically related to molecular weight of polymers. Thus, viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymer.

Dilute solution viscosity is usually measured in capillary viscometer of the Ostwald or Ubbelohde type and concentration, c , is expressed in grams per deciliter (g/dl, g/100 ml). Measurements of solution viscosity are usually made by comparing the efflux time, t , required for a specific volume of polymer solution to flow through a capillary tube with the corresponding efflux time, t_0 , for the solvent. From t_0 and the solute concentration the following equations are derived.

$$\text{Relative viscosity } \eta_r = t/t_0$$

$$\text{Specific viscosity } \eta_{sp} = \frac{t - t_0}{t_0} = \eta_r - 1$$

$$\text{Reduced viscosity } \eta_{red} = \eta_{sp}/c$$

$$\text{Intrinsic viscosity } [\eta] = (\eta_{sp}/c)_{c=0}$$

The molecular weights of linear polyions were calculated from the intrinsic viscosity of the solution by the following equation:

$$[\eta] = K.M^a$$

a, K = Constants depending on the temperature, solvent and polymer characteristics

M = Molecular weight

Procedure: Ostwald type of viscometer was used for the viscosity measurements of poly (sodium phosphate) in NaBr. The results are given in the table 3-3 and in Figure 3.

Table 3-3. Viscosity of Poly (sodium phosphate) ($a=0,50$ $K=49,4 \cdot 10^{-5}$ in NaBr)

Solute Concentration C (g/ml)	t (min)	η_r (t/t_0)	η_{sp}	η_{sp}/c
0,36	3,181	1,013	0,013	0,042
0,42	3,193	1,017	0,017	0,040
0,50	3,200	1,019	0,019	0,038
The Calculated Molecular Weight: 7500				

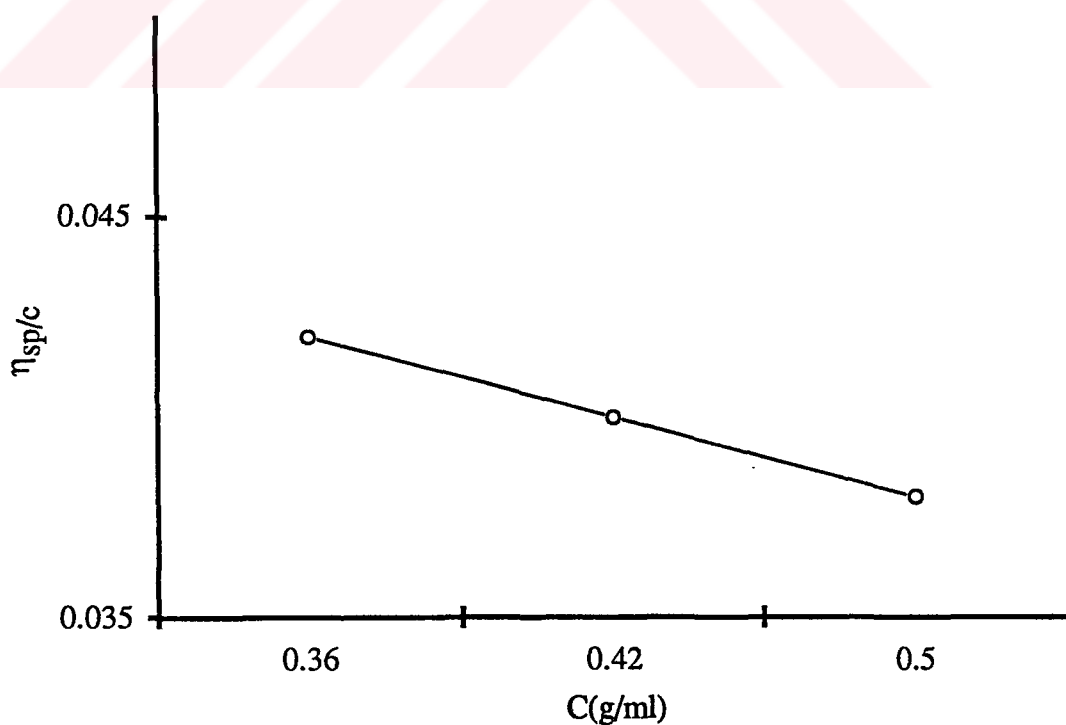


Figure 3.3. Viscosity Curve of Poly (Sodium phosphate) in NaBr.

3.4.2.2. Molecular Weight Determination of Polycation By Viscosimetry:

Ostwald type of viscometer was used for the viscosity measurements of poly(4-vinyl pyridinium chloride) in ethyl alcohol solution. The results are given in Table 3-4 and Figure 4.

Table 3-4. Viscosity of Poly (4-vinyl pyridine) ($a=0,52$ K= $1,51 \cdot 10^{-3}$ in ethyl alcohol)

Solute Concentration C (g/ml)	t(min)	η_r	η_{sp}	η_{sp}/c
0,25	11,87	1,335	0,335	0,670
0,33	12,22	1,242	0,242	0,730
0,50	13,12	1,207	0,207	0,830
The Calculated Molecular Weight: 278000				

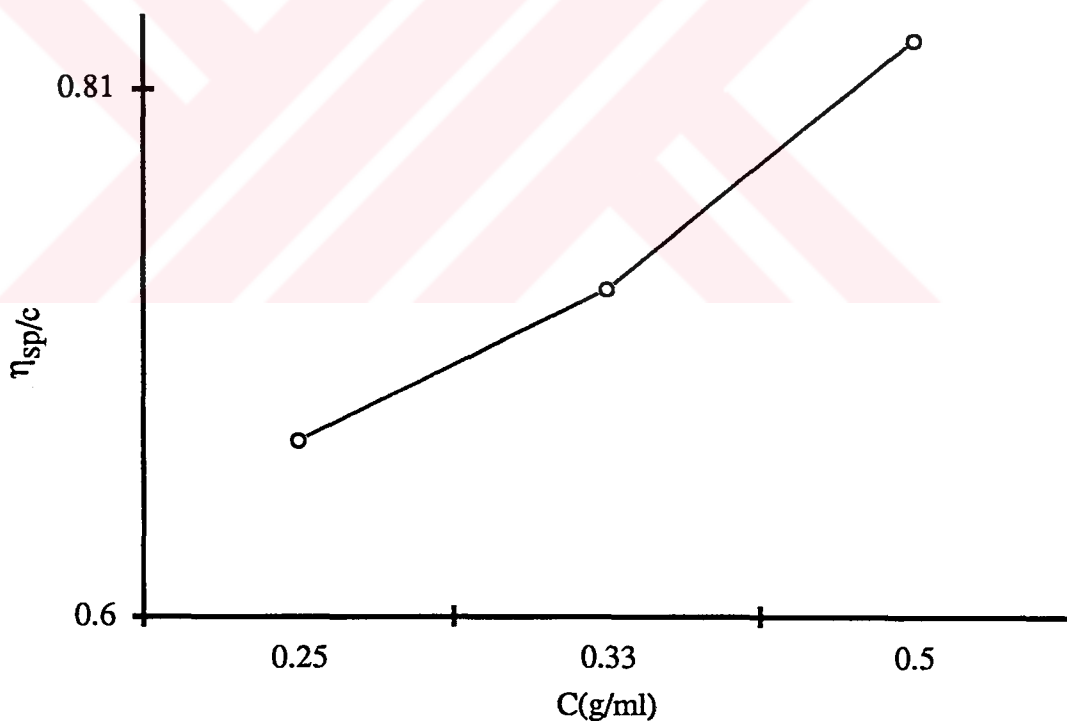


Figure 3.4. Viscosity Curve of Poly (4-vinyl pyridine) in Ethyl Alcohol

3.4.3. Equivalent Weight Determination of Polyions:

The ionic equivalent weights of polycation and polyanion were determined by argentometry and alkalimetry respectively and were found 170 g

for polycation with relative precision of 8 ppt and 102 g for polyanion with the relative precision of 2 ppt.

3.4.4. Conductometric Measurements:

Main features of PEC stoichiometry and PABA salt interaction with PA and PC in different experimental parameters were determined by conductometric measurements. Several runs were carried out to check the reproducibility of all the titrations.

3.4.4.1. Conductometric Measurements For Polyelectrolyte Complex Stoichiometry:

Two sets of conductometric measurements were carried out as in the following.

a) For the complex stoichiometry the conductometric titrations of PA with PC and also the reverse titrations were carried out for different polyions concentration in salt free and in NaBr, NaCl solutions with different concentrations to see the microions affect on the complex formation. The titration curves are shown in figures 5-16.

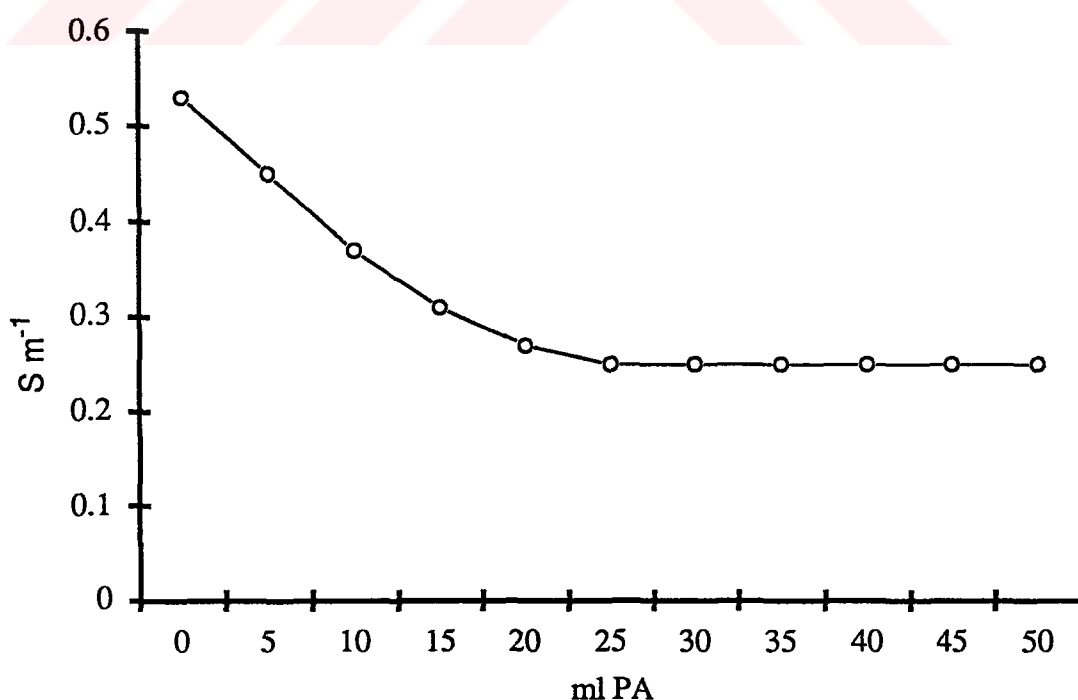


Figure 3.5. Conductometric Titration of 25 ml 4.10^{-3} M PC with 4.10^{-3} M PA, Salt Free Solution

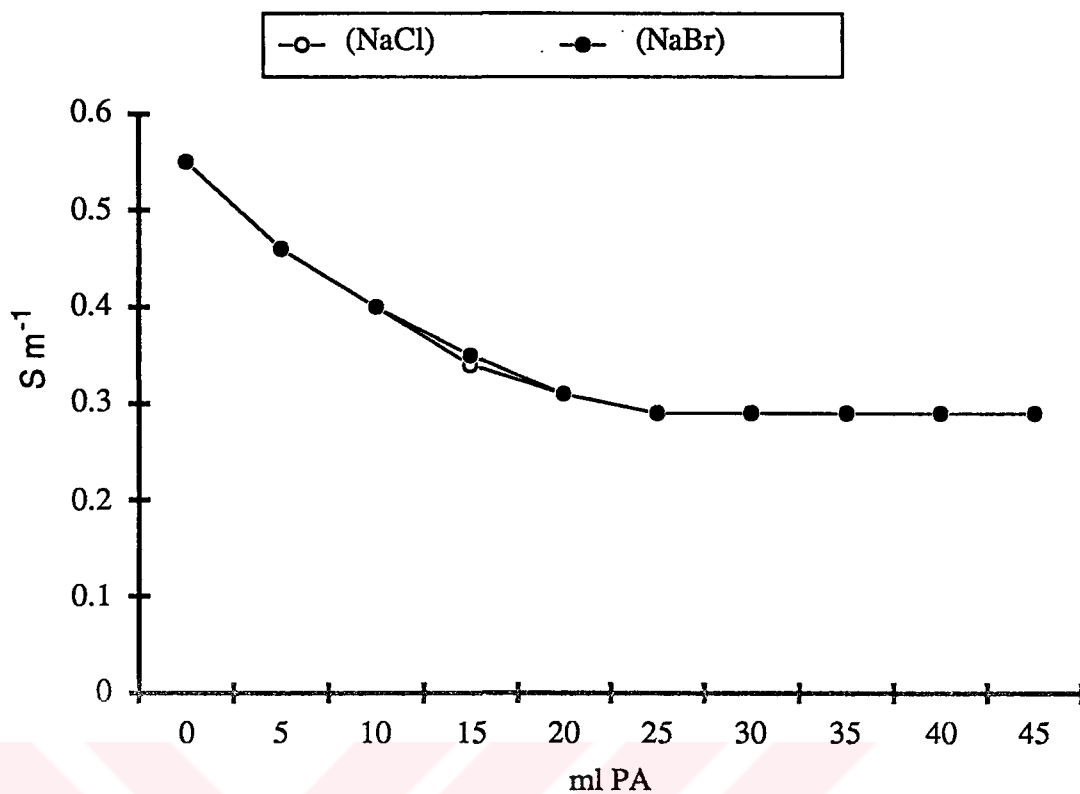


Figure 3.6. Conductometric Titration of 25 ml 4.10^{-3} M PC with 4.10^{-3} M PA, in 1.10^{-3} M Salt Solution

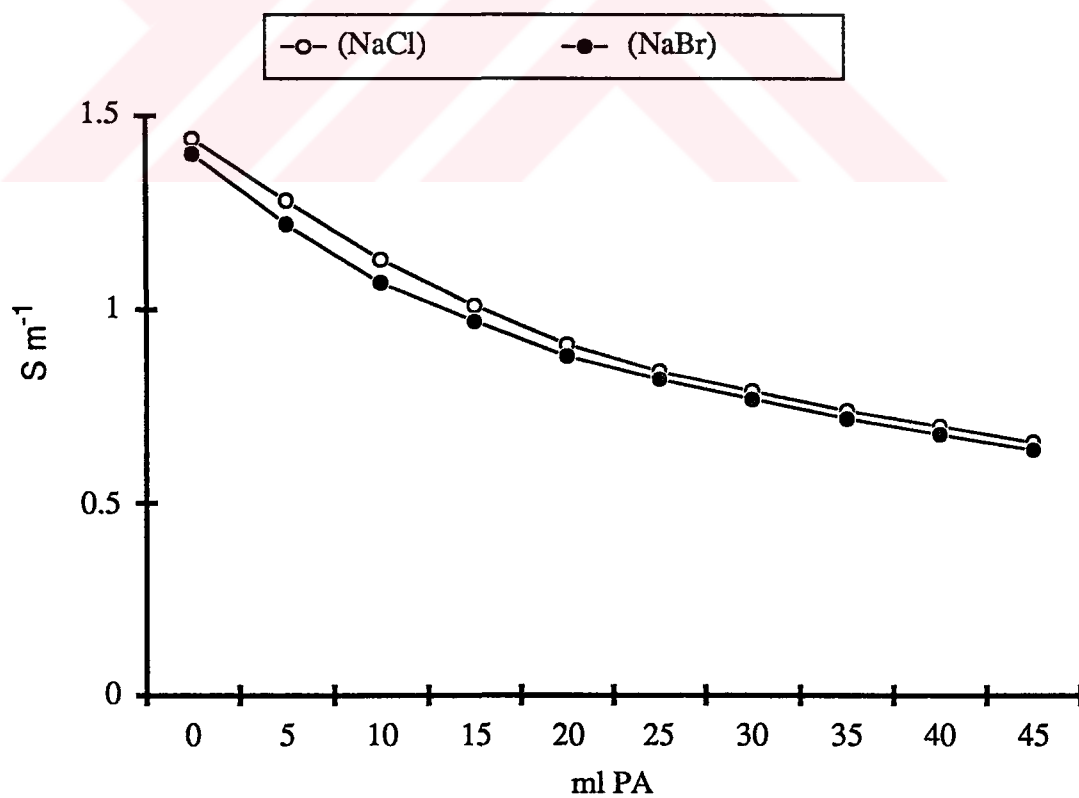


Figure 3.7. Conductometric Titration of 25 ml 4.10^{-3} M PC with 4.10^{-3} M PA, in 1.10^{-2} M Salt Solution

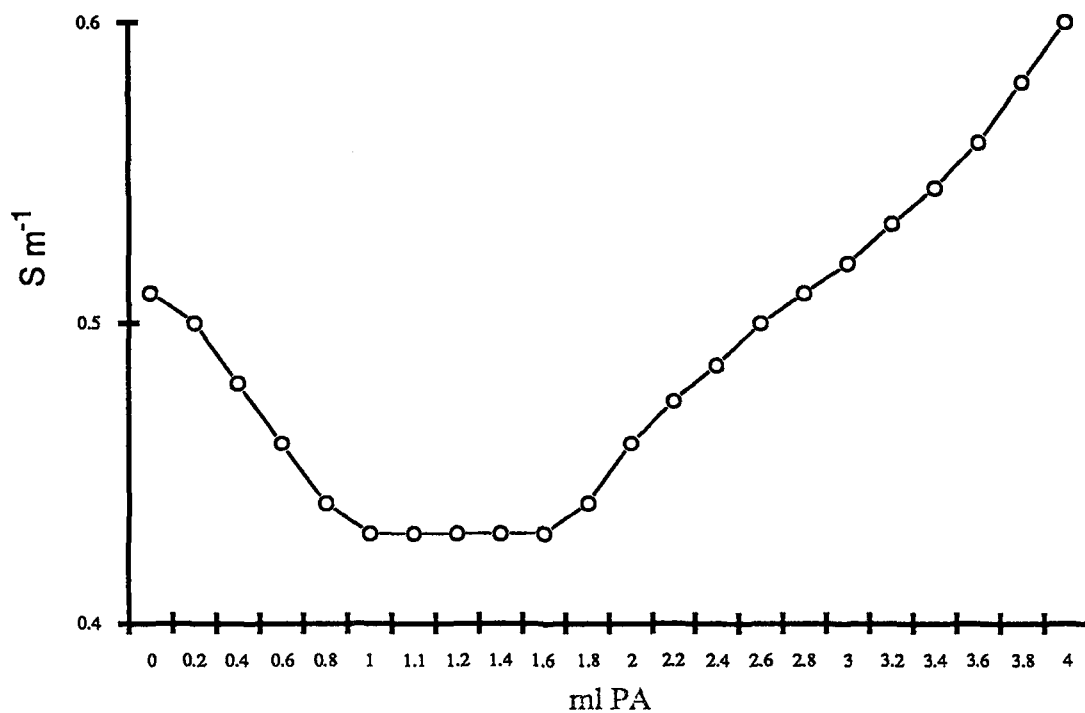


Figure 3.8. Conductometric Titration of 25 ml 4.10^{-3} M PC with $9.8,10^{-2}$ M PA, Salt Free Solution

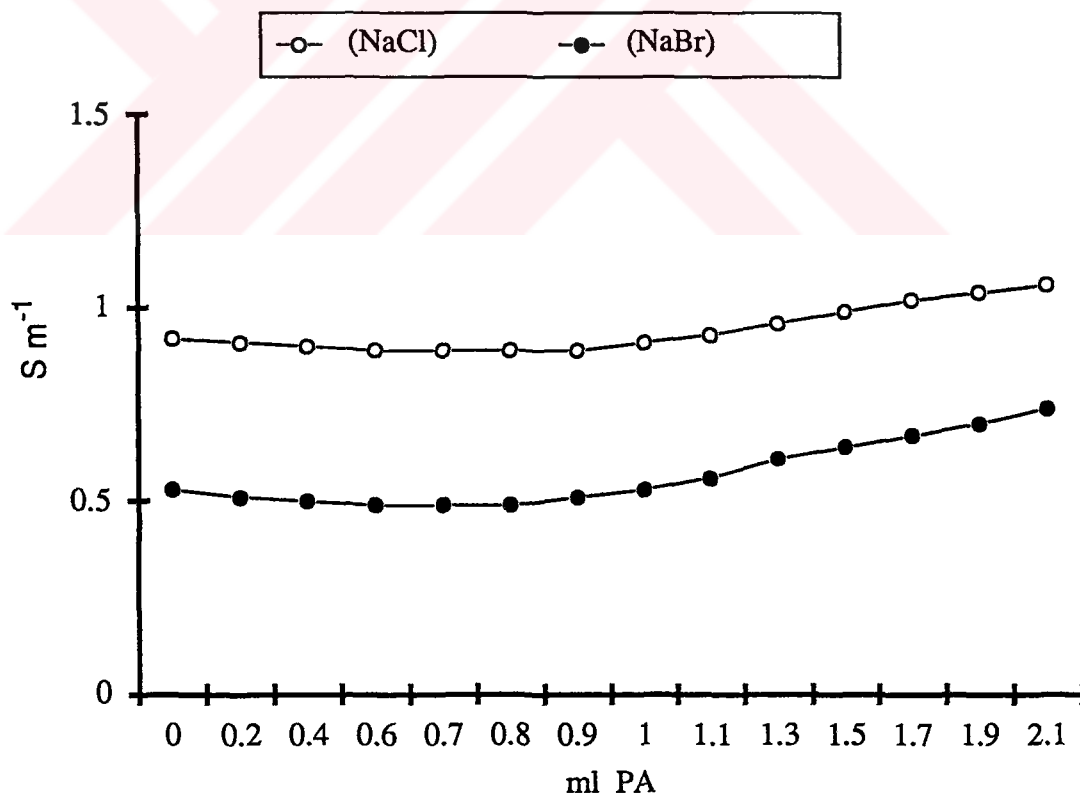


Figure 3.9. Conductometric Titration of 25 ml 4.10^{-3} M PC with $9.8,10^{-2}$ M PA, in 1.10^{-3} M Salt Solution

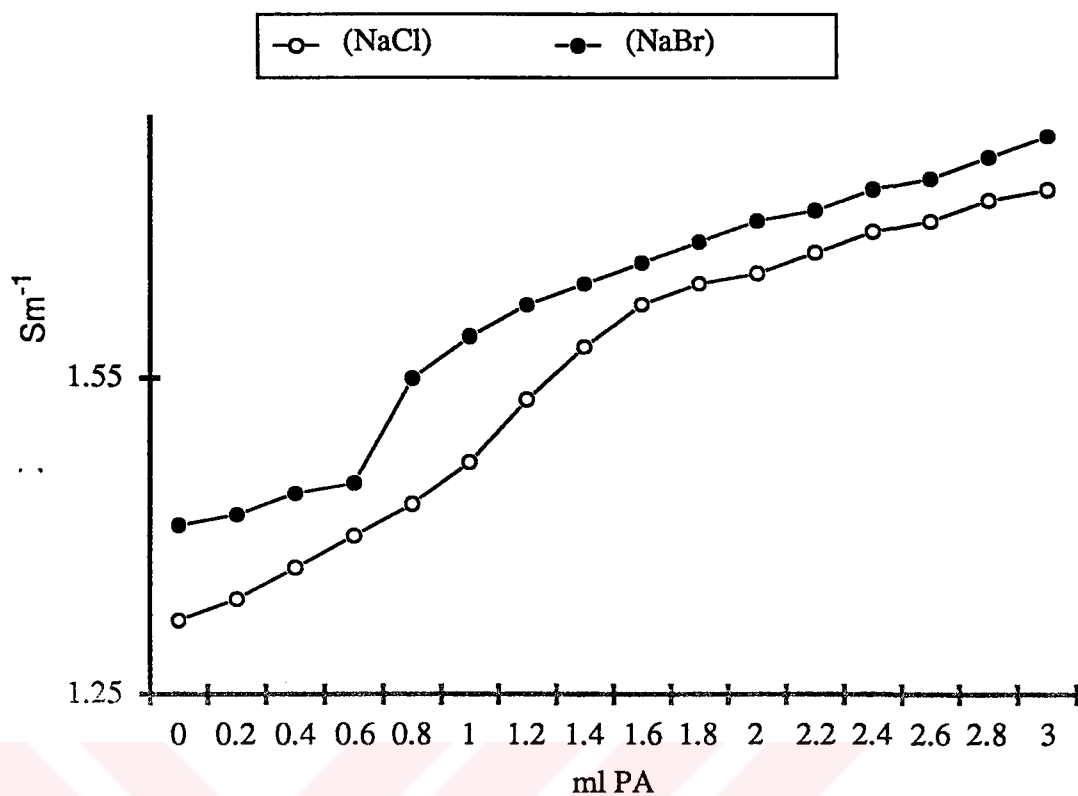


Figure 3.10. Conductometric Titration of 25 ml $4 \cdot 10^{-3}$ M PC with $9.8 \cdot 10^{-2}$ M PA in $1 \cdot 10^{-2}$ M Salt Solution

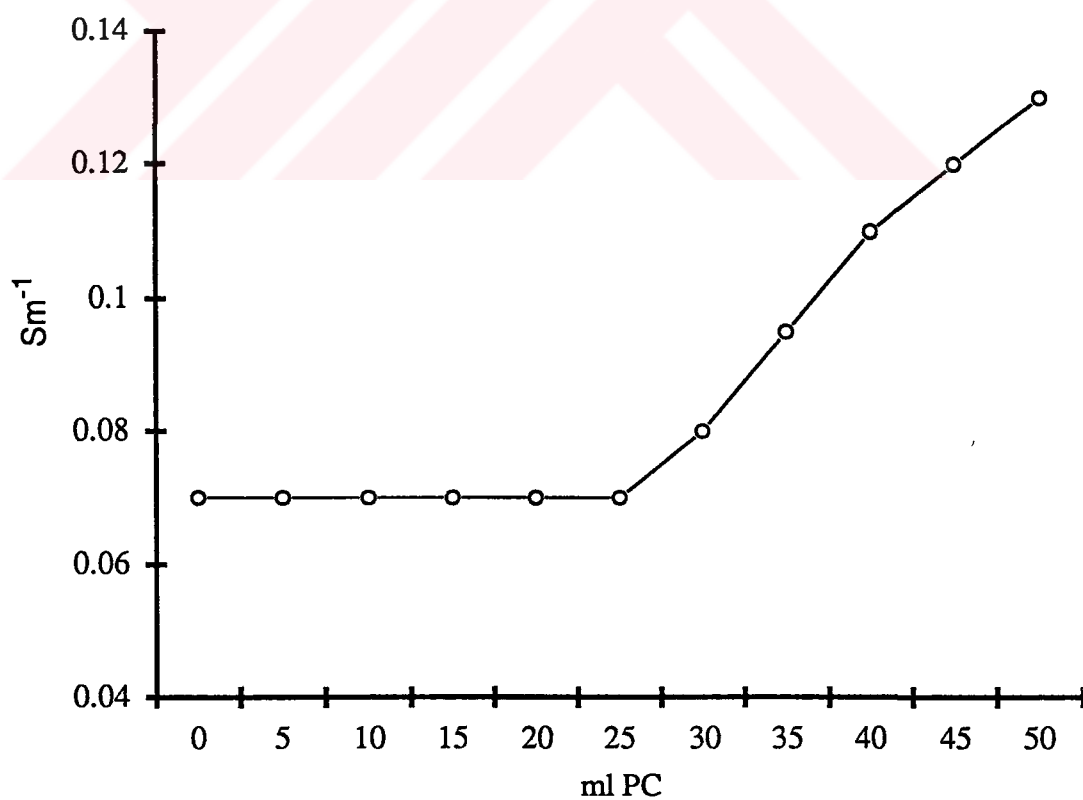


Figure 3.11. Conductometric Titration of 25 ml $1 \cdot 10^{-3}$ M PA with $1 \cdot 10^{-3}$ M PC in Salt Solution

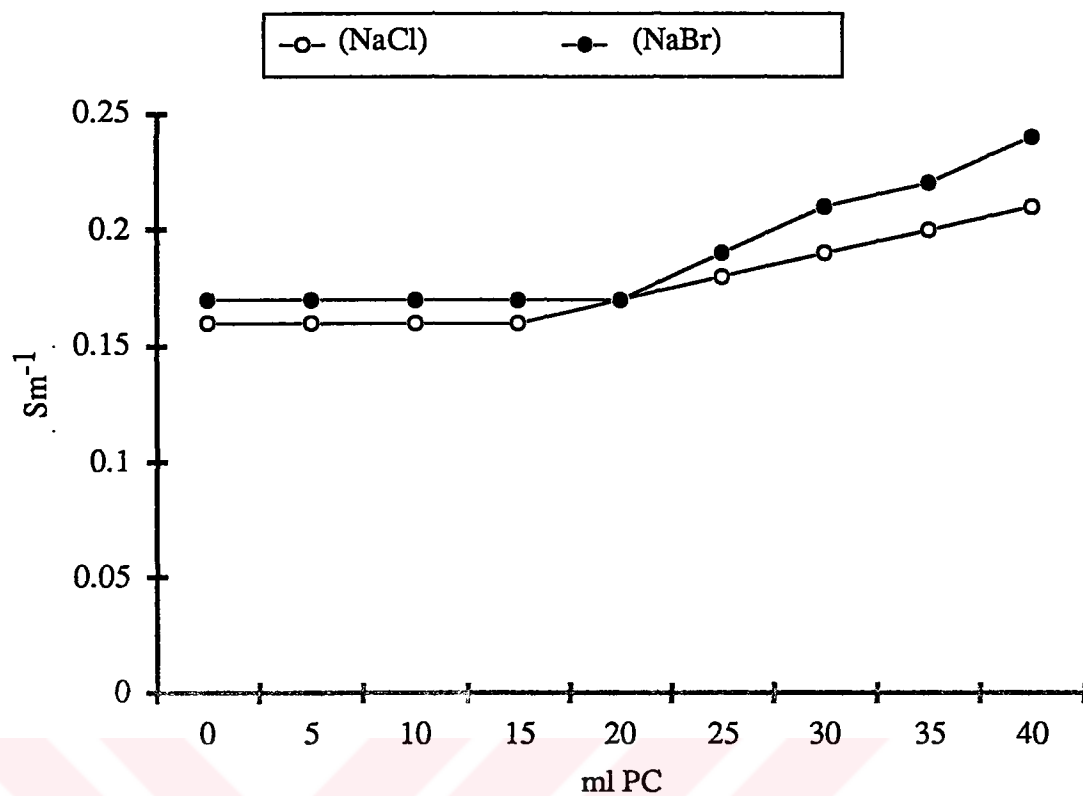


Figure 3.12. Conductometric Titration of 25 ml 1.10^{-3} M PA with 1.10^{-3} M PC in 1.10^{-3} M Salt Solution

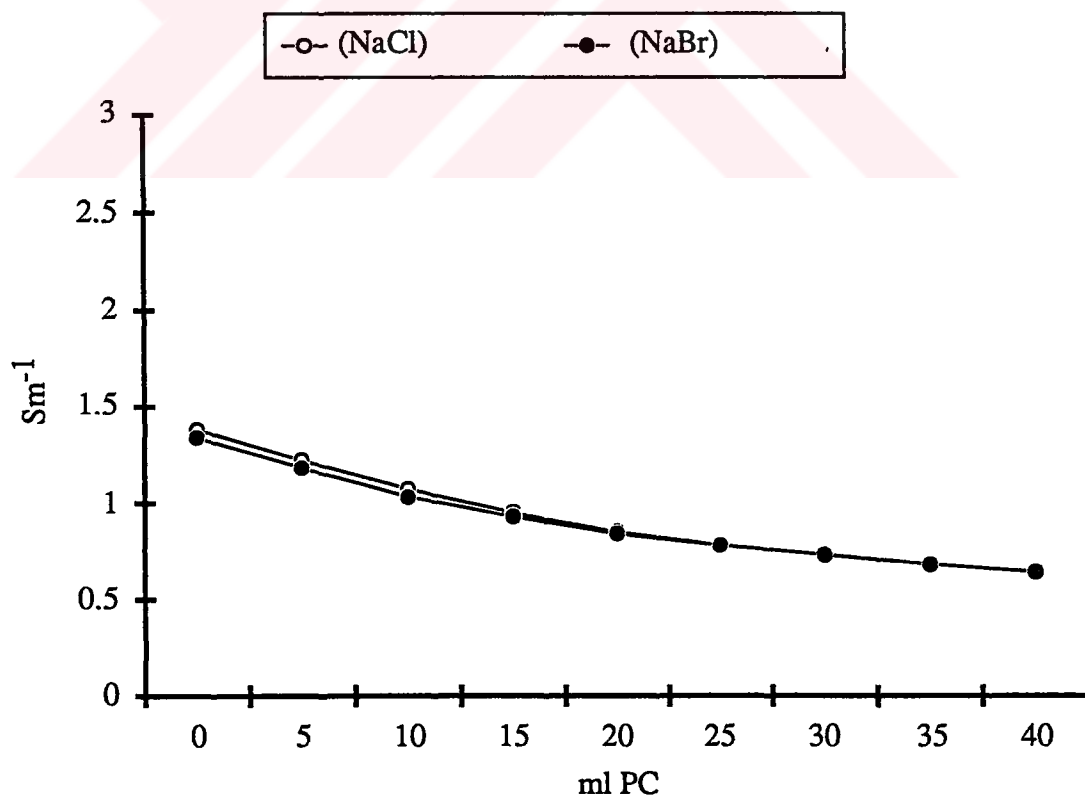


Figure 3.13. Conductometric Titration of 25 ml 1.10^{-3} M PA with 1.10^{-3} M PC in 1.10^{-2} M Salt Solution

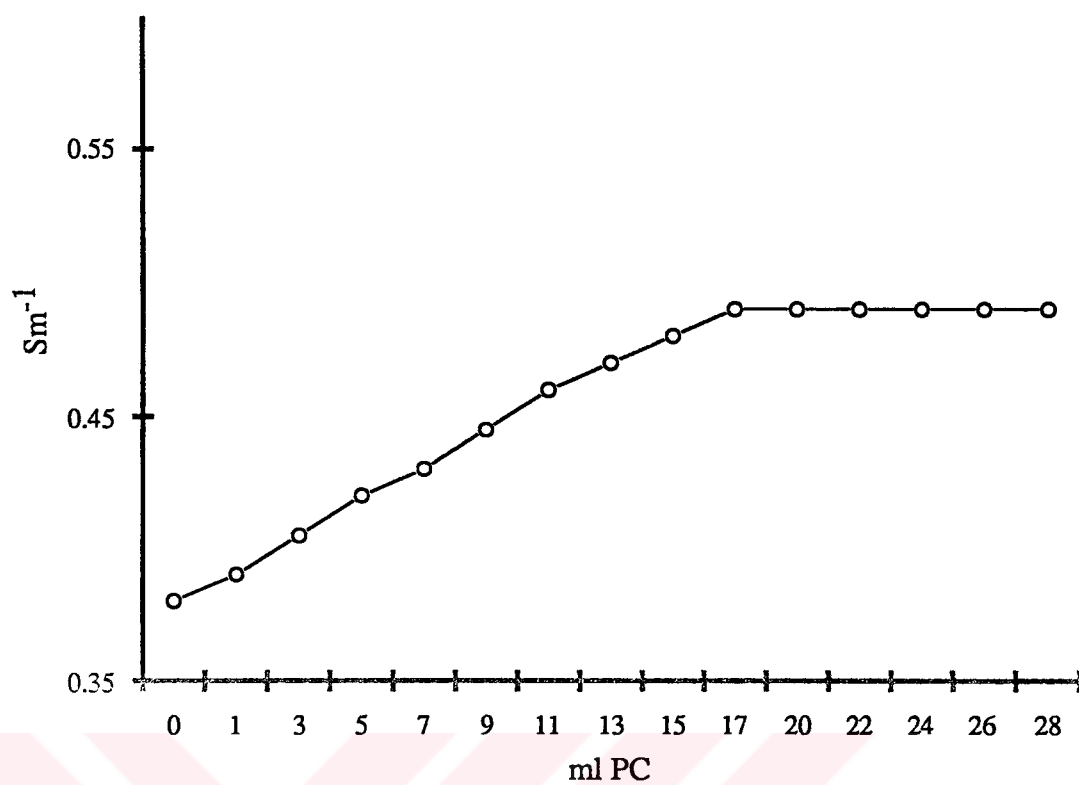


Figure 3.14. Conductometric Titration of 25 ml $7.7 \cdot 10^{-3}$ M PA with $7.7 \cdot 10^{-3}$ M PC, Salt Free Solution.

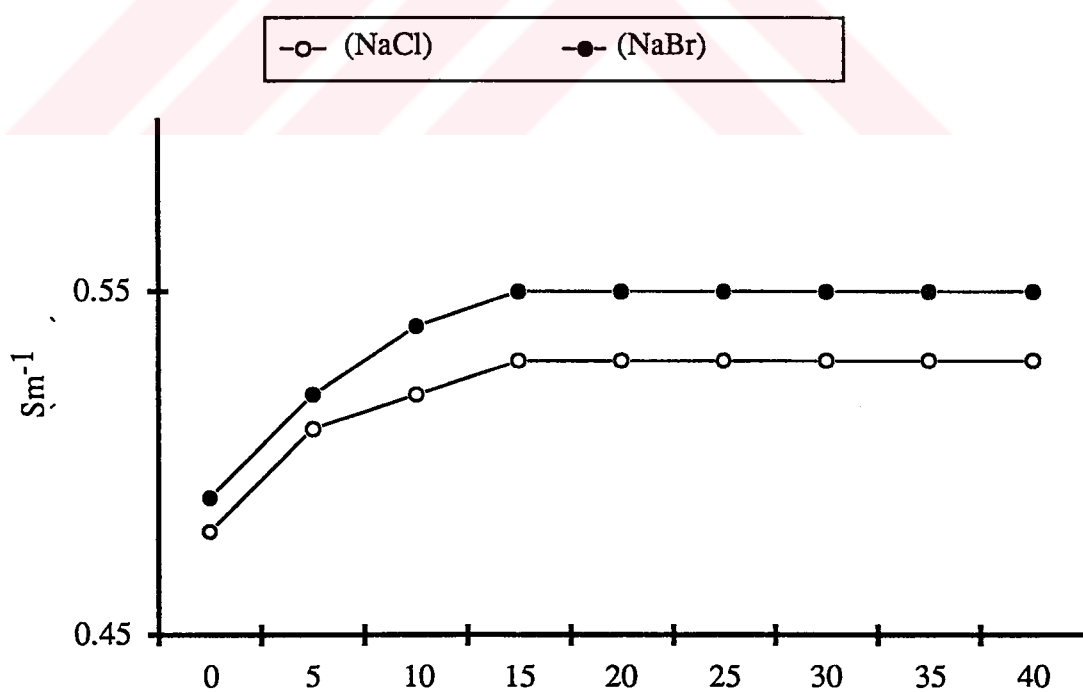


Figure 3.15. Conductometric Titration of 25 ml $7.7 \cdot 10^{-3}$ M PA with $7.7 \cdot 10^{-3}$ M PC in $1 \cdot 10^{-3}$ M Salt Solution

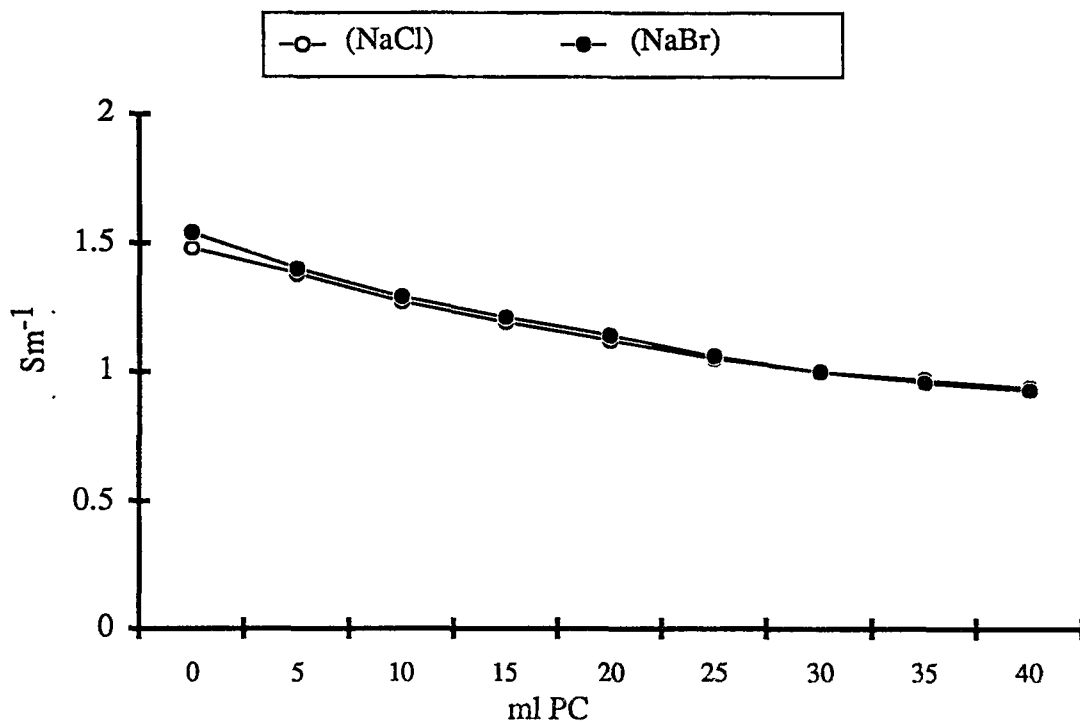


Figure 3.16. Conductometric Titration of 25 ml $7.7 \cdot 10^{-3}$ M PA with $7.7 \cdot 10^{-3}$ M PC in $1 \cdot 10^{-2}$ M Salt Solution

b) The direct conductances of PC and PA mixtures in different unit mole ratios were measured in salt free solutions. The titration curve is shown in figure 17.

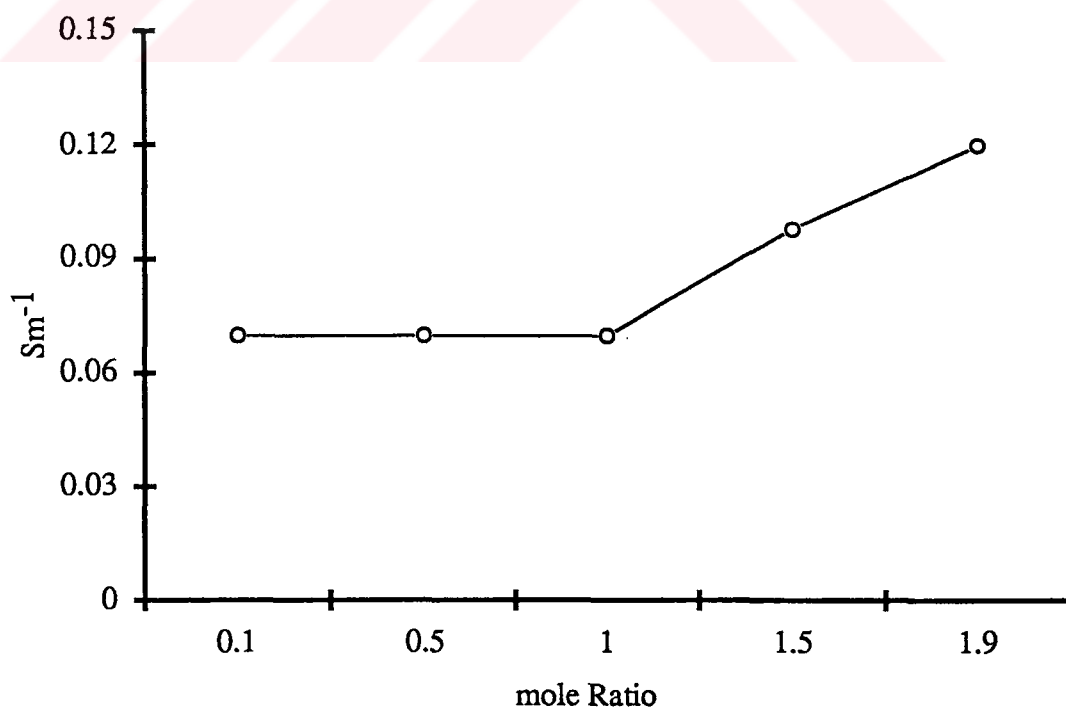


Figure 3.17. The Conductance of $1 \cdot 10^{-3}$ M PC and $1 \cdot 10^{-3}$ M PA Mixture, Salt Free Solution.

3.4.4.2. Conductometric Measurements For Zwitter Ion Interaction With Polyions:

Two sets of conductometric measurements were carried out as in the following.

a) Conductometric titration of PABA salts and polyions

Poly (4-vinyl pyridinium chloride) was titrated with para amino benzoic acid sodium salt in salt free and in salt solutions. The reverse titration was also done with different concentration. The titration curves are shown in Figure 18-23.

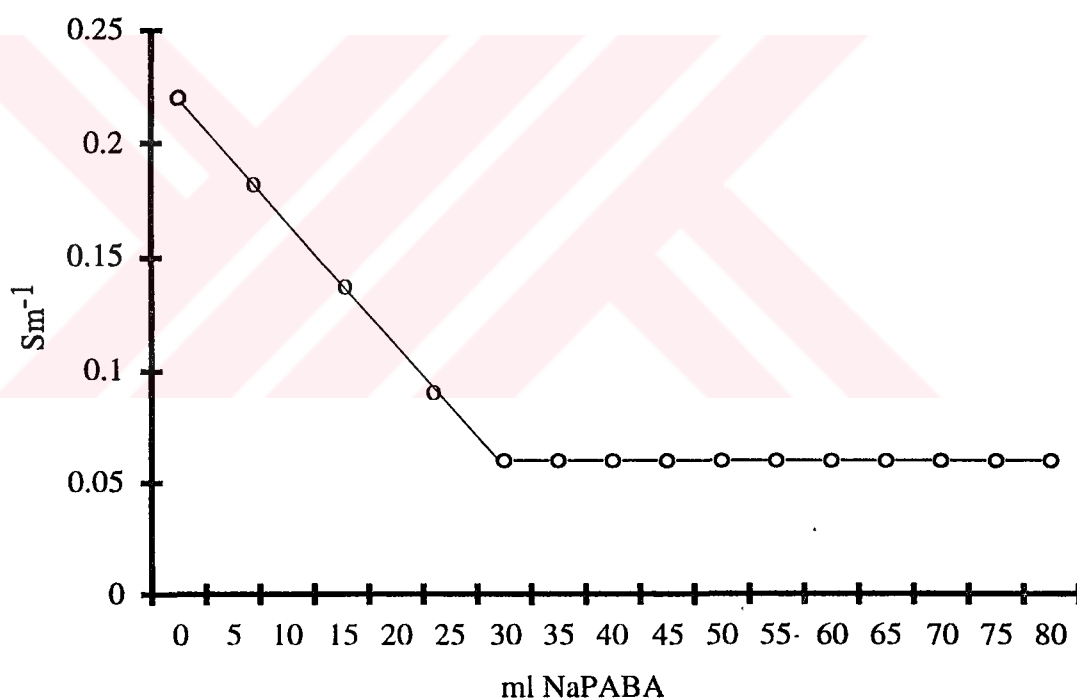


Figure 3.18. Conductometric Titration of 25 ml 1.10^{-3} M NaPABA with 1.10^{-3} M PC, Salt Free Solution

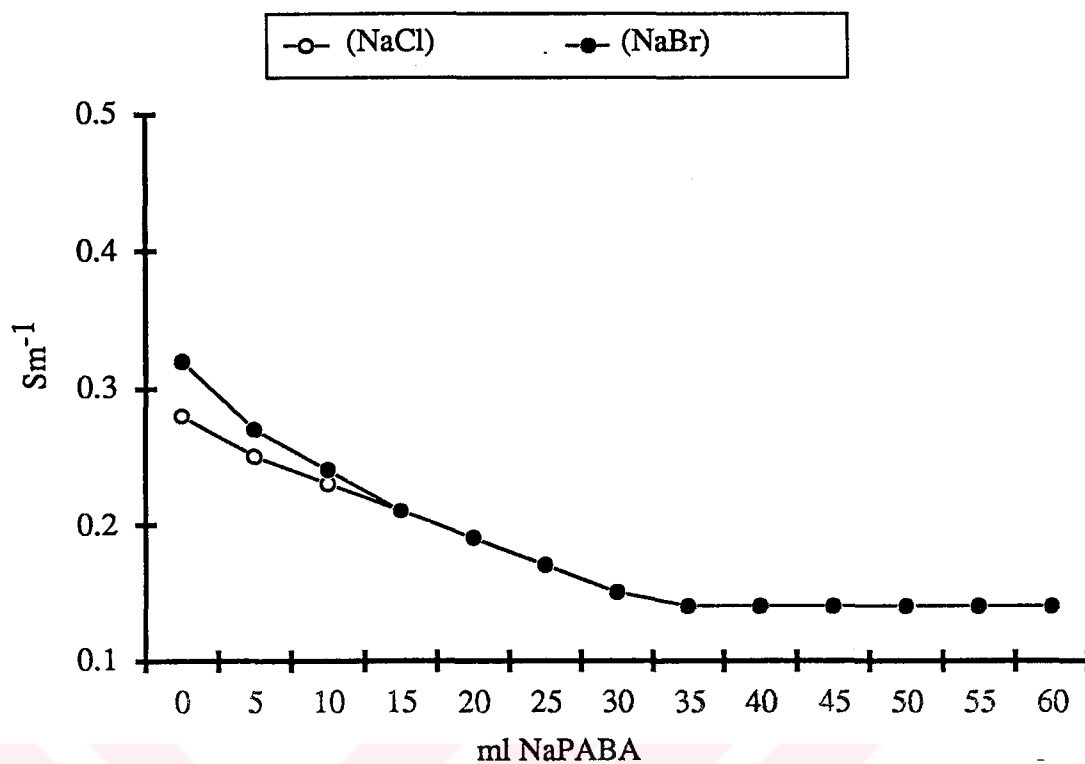


Figure 3.19. Conductometric Titration of 25 ml 1.10^{-3} M PC with 1.10^{-3} M NaPABA in 1.10^{-3} M Salt Free Solution

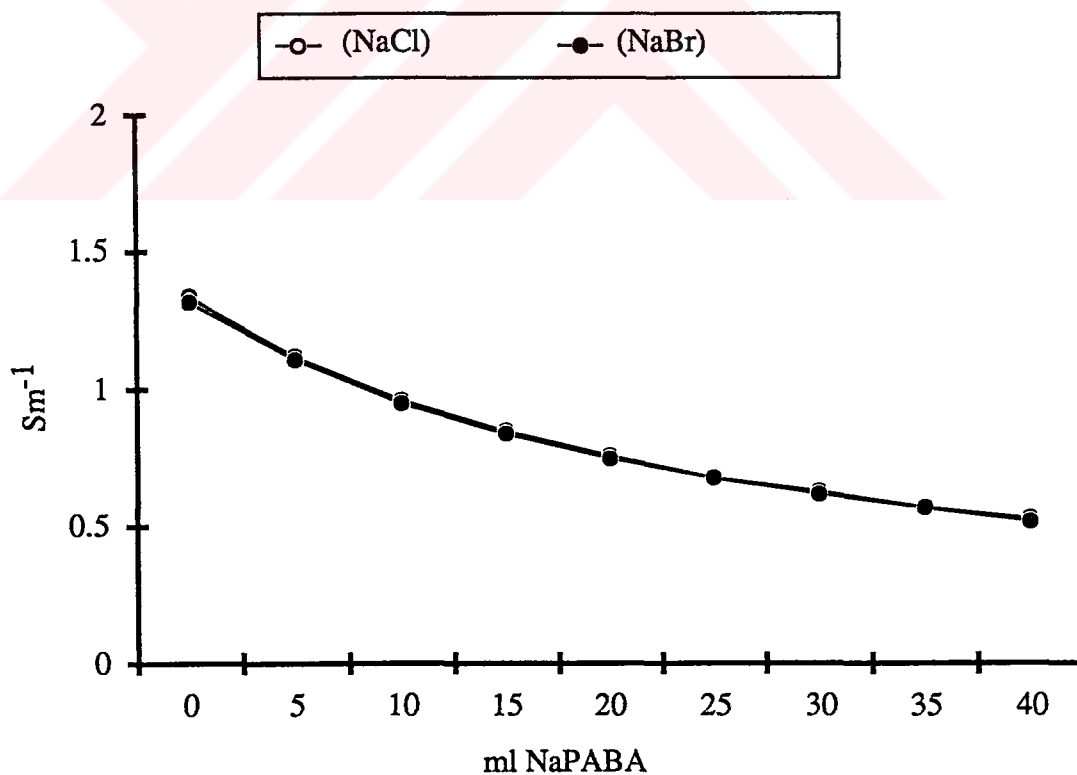


Figure 3.20. Conductometric Titration of 25 ml 1.10^{-3} M PC with 1.10^{-3} M NaPABA in 1.10^{-2} M Salt Free Solution

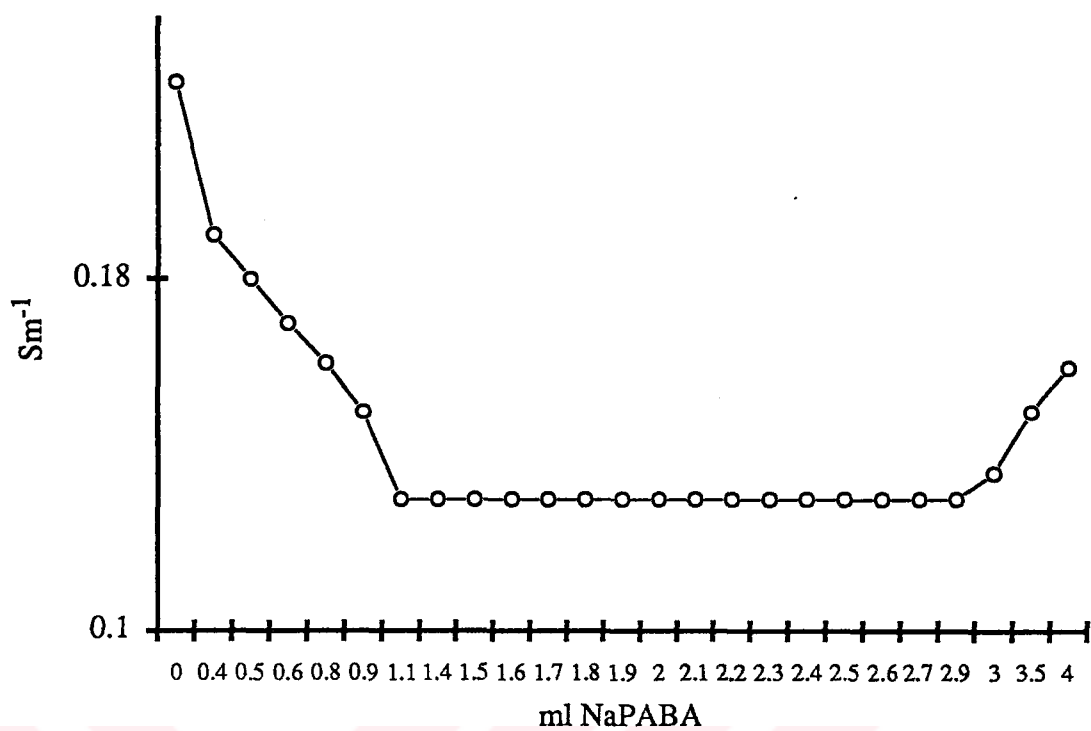


Figure 3.21. Conductometric Titration of 25 ml 1.10^{-3} M PC with 1.10^{-2} M NaPABA, Salt Free Solution

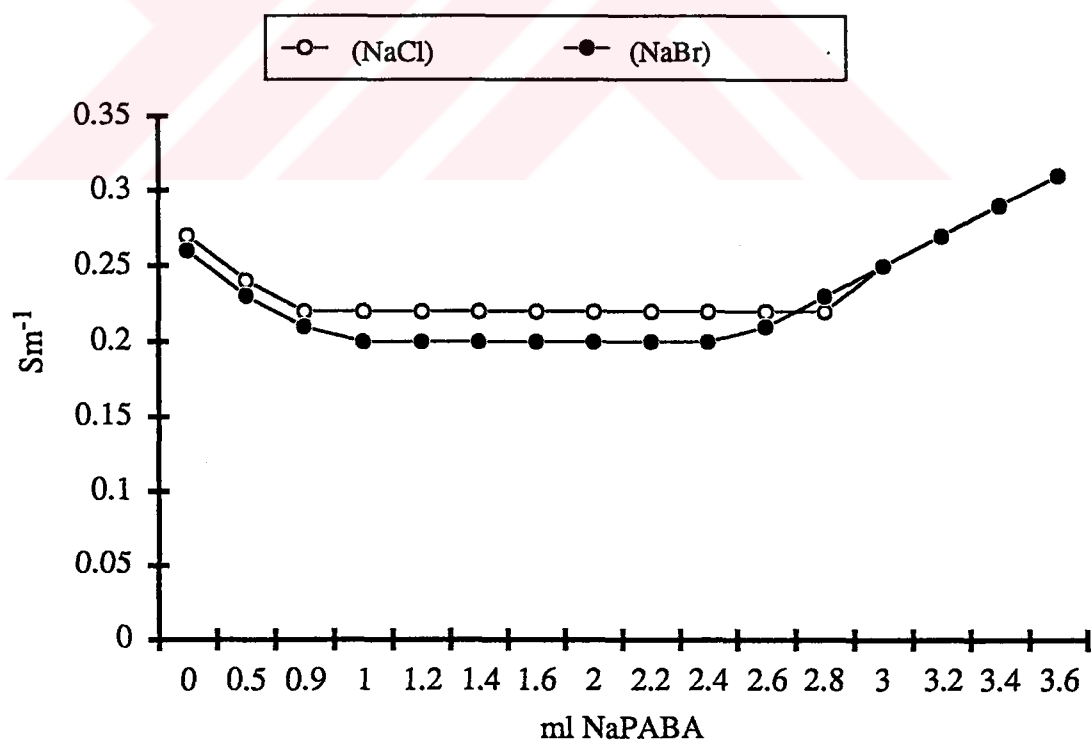


Figure 3.22. Conductometric Titration of 25 ml 1.10^{-3} M PC with 1.10^{-2} M NaPABA in Salt Solution

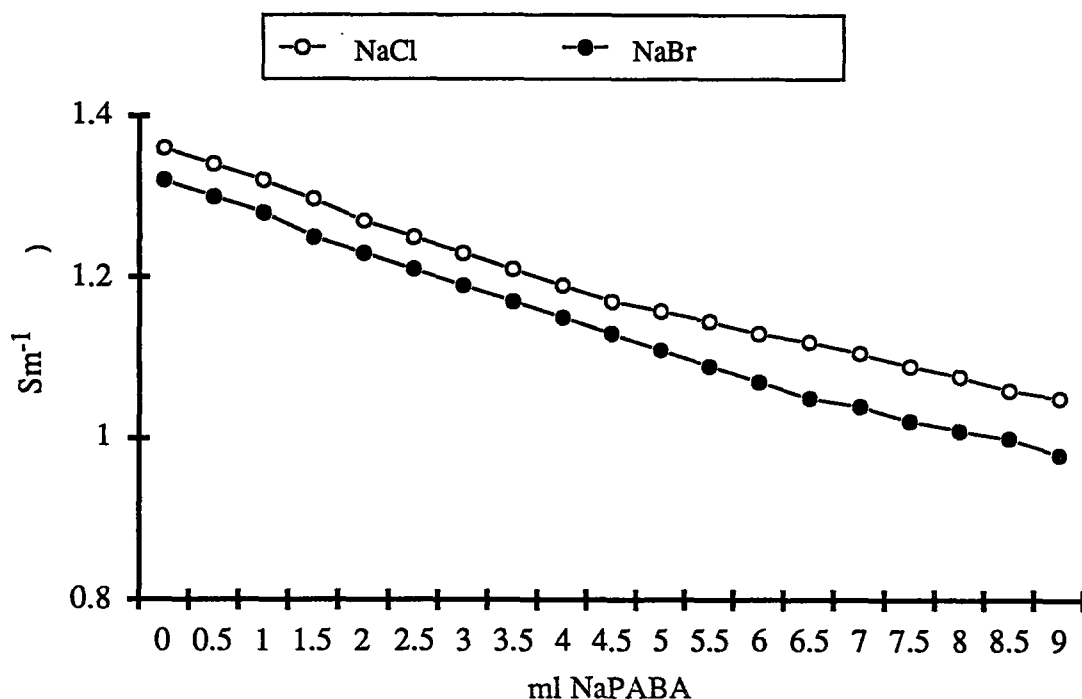


Figure 3.23. Conductometric Titration of 25 ml $1.10^{-3}M$ PC with $1.10^{-2}M$ NaPABA in $1.10^{-2}M$ Salt Solution

Poly (sodium phosphate) was titrated paraaminobenzoil chloride in salt free and in salt solutions. The results are shown in figures 24-28.

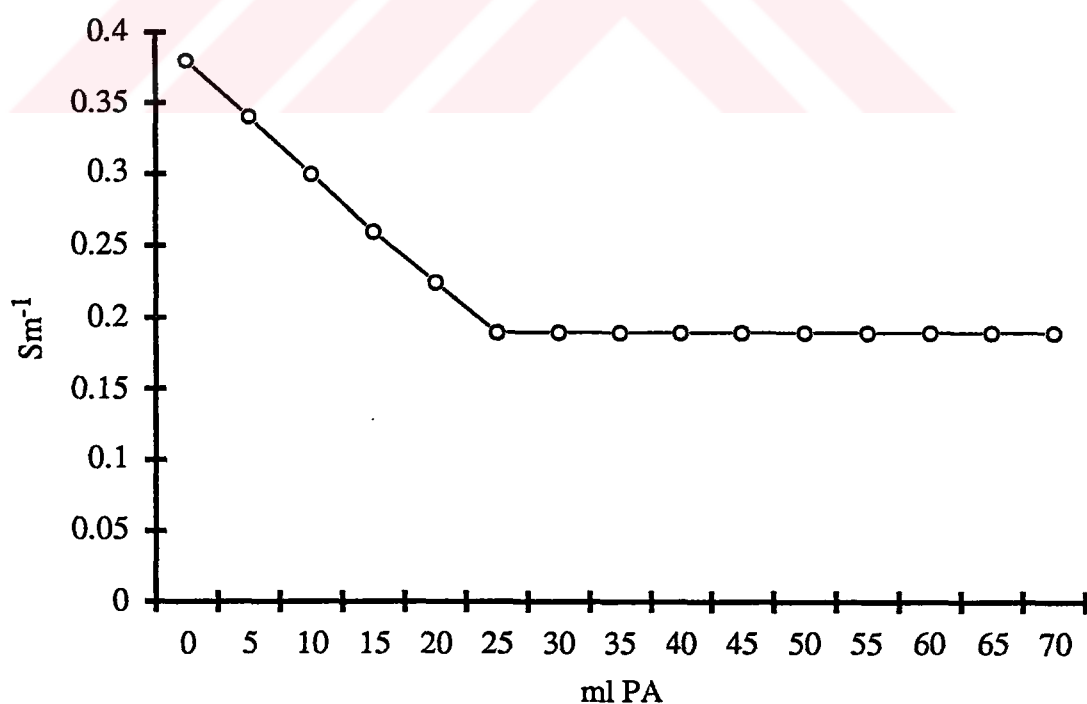


Figure 3.24. Conductometric Titration of 25 ml $1.10^{-3}M$ PABCl with $1. 10^{-3}M$ PA, Salt Free Solution

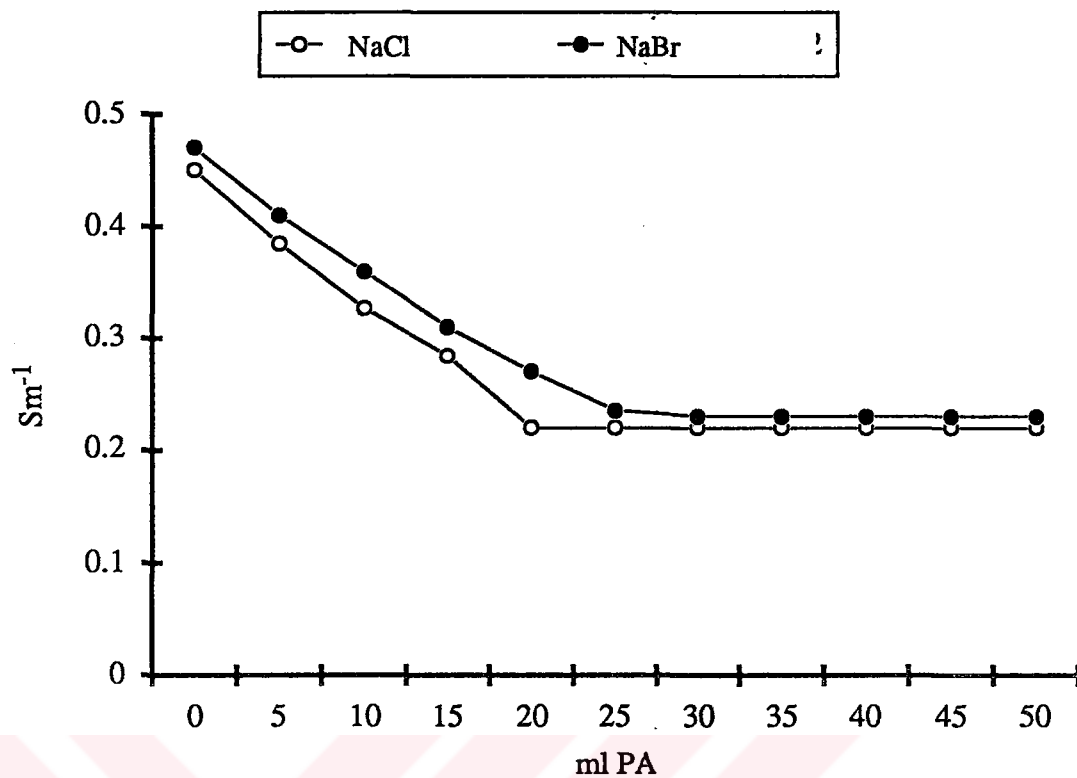


Figure 3.25. Conductometric Titration of 25 ml 1.10^{-3}M PABCI with 1.10^{-3}M PA, in 1.10^{-3}M Salt Solution

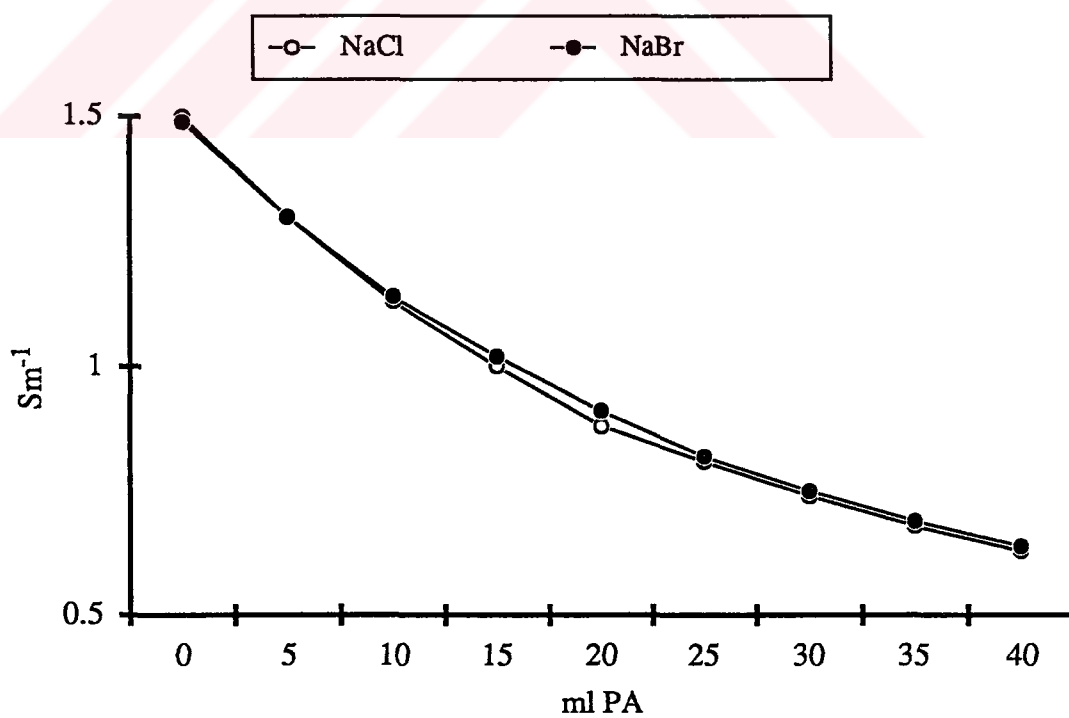


Figure 3.26. Conductometric Titration of 25 ml 1.10^{-3}M PABCI with 1.10^{-3}M PA, in 1.10^{-2}M Salt Solution

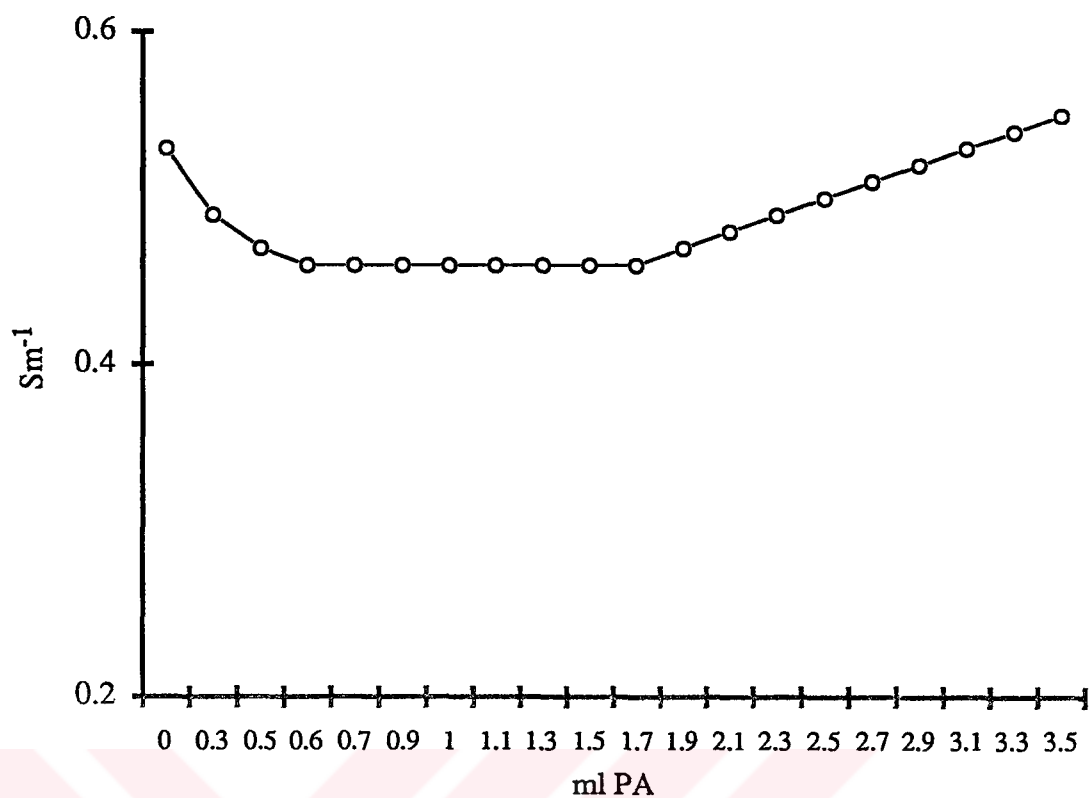


Figure 3.27. Conductometric Titration of 25 ml 1.10^{-3} M PABCI with 5.10^{-2} M PA, Salt Free Solution

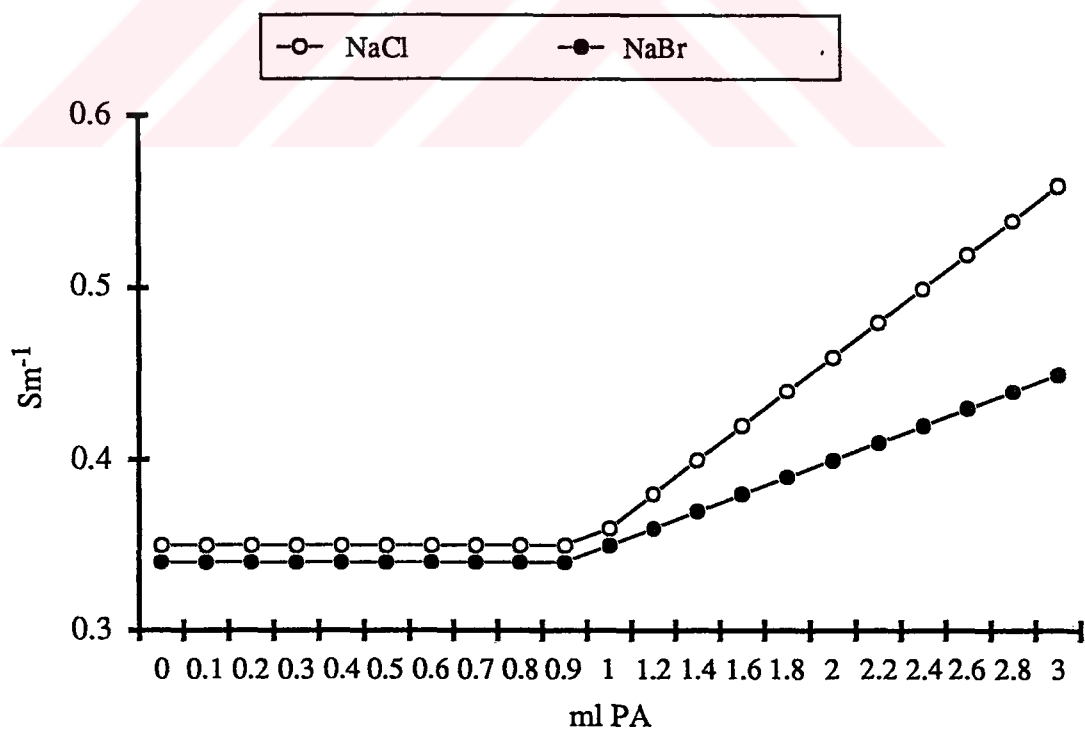


Figure 3.28. Conductometric Titration of 25 ml 1.10^{-3} M PABCI with 5.10^{-2} M PA in 1.10^{-3} M Salt Solution

b) The direct conductances of paraamino benzoic acid salts and polyanion and polycation mixtures which contain PA-PABCI and NaPABA-PC in different unit mole ratio were measured in salt free solutions. The results are shown in figure 29-30.

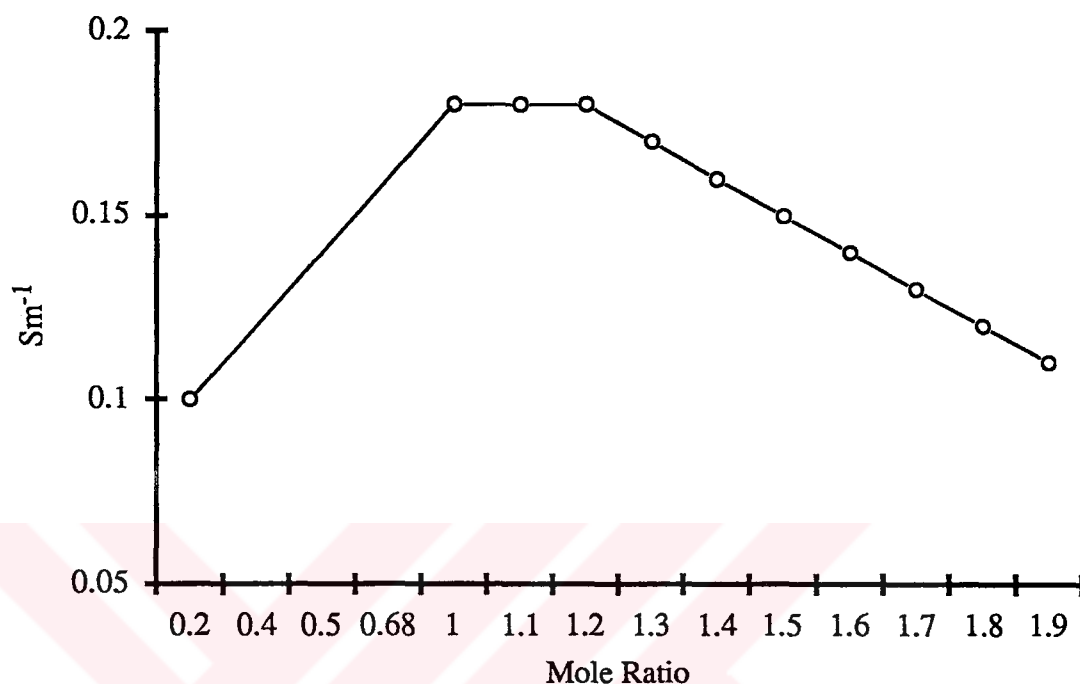


Figure 3.29. The Conductance of 1.10^{-3}M PABCI with 1.10^{-3}M PA Mixture In Salt Free Solution

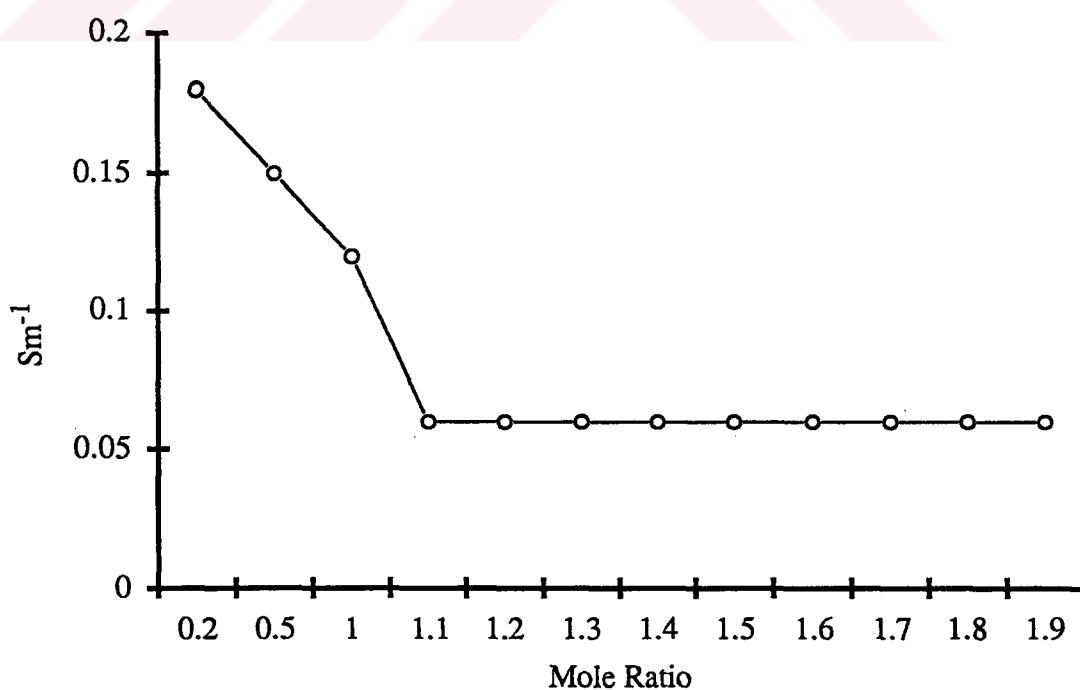


Figure 3.30. The Conductance of 1.10^{-3}M NaPABA with 1.10^{-3}M PC Mixture In Salt Free Solution

3.4.4.3. Conductometric Titration of PCOH with HPA

In order to see the pH changes during the PEC formation and the interaction between the acid form of polyanion and the base form of polycation were prepared by ion exchange procedure.

The conversion of $(\text{NaPO}_3)_n$ to $(\text{HPO}_3)_n$ was completed on an Ion Exchanger Amberlite IR-120 (strong acid) and Ion Exchanger III (strong base) column was used for obtaining PVPyOH form of polycation.

Preparation of the ion exchange column:

1,5 g of the cation and anion exchange resins were covered with water and let to stand for overnight. After pouring off the water HCl (3M) was added to it, shaken well and filtered. Acid treatment was repeated three times, it was washed with large portions of water by shaking. After decantation of water, cation and anion exchangers were let to stand for 3 hours in 1M NaOH and 0,5 M NaOH respectively then, was washed with water several times. The activated resin was transferred into the column with dilute HCl solution. The column has 50 cm length and 1 cm in diameter, two thirds of the column was occupied with resin and 1-1,5 ml of water remained above the resin. Same glass wool was placed above the resin column to avoid any disturbance. The excess of acid or alkali were removed by distilled water. The flow rate of polyions through the column was adjusted as 2 ml per minute. The concentration of PCOH form obtained from the anion exchange column was determined with standart acid titration was found to be $1,8 \times 10^{-3} \text{M}$. The concentration of HPA form of polyanion was determined with standart base titration and found to be $1,5 \times 10^{-2} \text{M}$.

20 ml of $1,8 \times 10^{-3} \text{M}$ of PCOH was titrated with $1,5 \times 10^{-2} \text{M}$ of HPA. The titration curve is shown in the following.

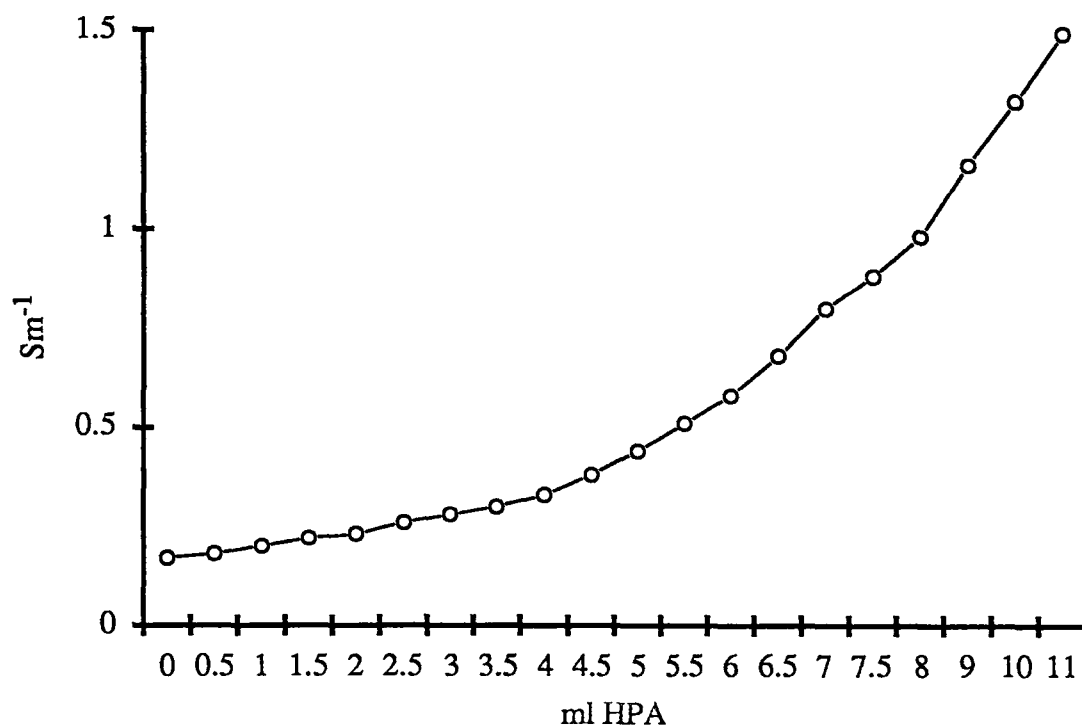


Figure 3.31. The Conductometric Titration of 20 ml $1.8 \cdot 10^{-3} \text{M}$ PCOH with $1.5 \cdot 10^{-2} \text{M}$ HPA

3.4.4.4. Potentiometric Titration Of HPA With PCOH

10 ml of $2 \cdot 10^{-4} \text{M}$ HPA salt free solution was titrated with $1.8 \cdot 10^{-3} \text{M}$ of PCOH solution. The titration curve is shown in figure 32.

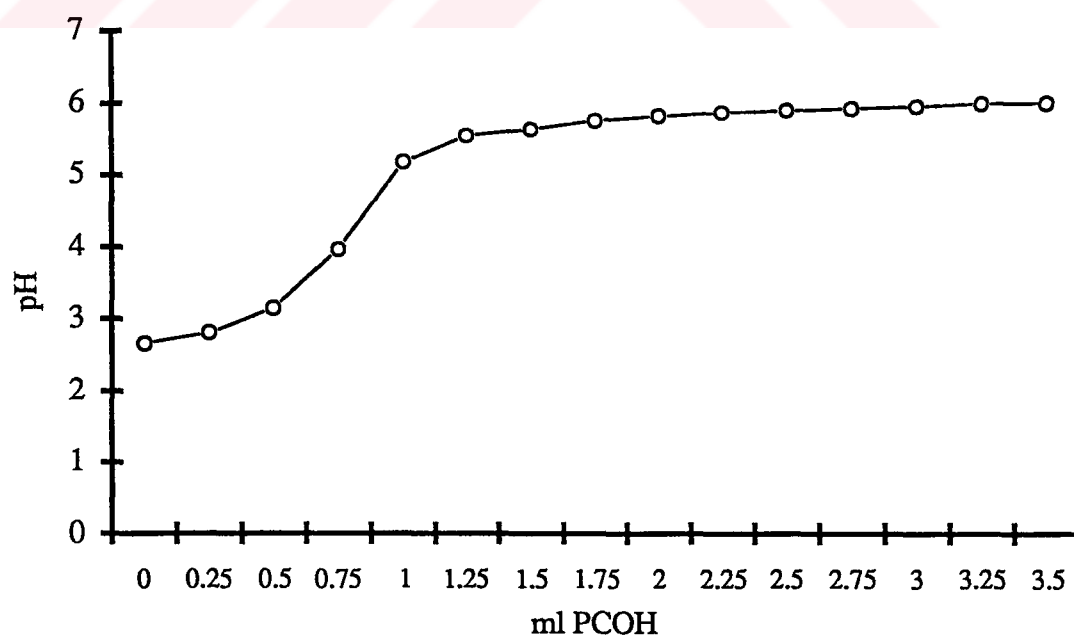


Figure 3.32. The Potentiometric Titration of 10 ml $2 \cdot 10^{-4} \text{M}$ HPA with $1.8 \cdot 10^{-3} \text{M}$ PCOH

Table 3-5. Results of Conductometric Titration Data

Titrant	Solution	Mol Ratio of PA to PC					Figure No
		Salt free Solution	Salt Solution				
			NaCl (1.10 ⁻³ M)	NaBr (1.10 ⁻³ M)	NaCl (1.10 ⁻² M)	NaBr (1.10 ⁻² M)	
PA (4.10 ⁻³ M)	PC (4.10 ⁻³ M)	0,8	0,72	0,76	Decreased curve	Decreased curve	5,6,7
PA (9,8.10 ⁻² M)	PC (4.10 ⁻³ M)	0,93-1,6	0,50-0,78	0,49-0,78	1,6	1,08	8,9,10
PC (1.10 ⁻³ M)	PA (1.10 ⁻³ M)	1,00	0,80	0,80	Decreased curve	Decreased curve	11,12,13
PC (7.7.10 ⁻³ M)	PA (7.7.10 ⁻³ M)	1,40	2,27	2,27	Decreased curve	Decreased curve	14,15,16

Table 3-6. The Result of Direct Conductometric Data

PA (1.10 ⁻³ M)	PC (1.10 ⁻³ M)	Stoichiometry	Figure No
25 ml	25 ml	1 : 1	17

Table 3-7. The Results of Polyions and PABA Salts Titration Curves

Titration	Solution	Mol Ratio of PA to PABCl and PC to NaPABA			Figure No
		Salt Free Solution	Salt Solution		
			NaCl(1.10 ⁻³ M)	NaBr(1.10 ⁻³ M)	
PA (1.10 ⁻³ M)	PABCl (1.10 ⁻³ M)	1	0,9	0,92	24
PA (5.10 ⁻² M)	PABCl (1.10 ⁻³ M)	1,2	1,5	1,6	27
PC (1.10 ⁻³ M)	NaPABA (1.10 ⁻³ M)	1,4 - 3,4	1,6	1,8	18
PC (1.10 ⁻² M)	NaPABA (1.10 ⁻³ M)	0,44 - 1,16	0,9 - 1,12	0,96	21

Table 3-8. The Conductometric and Potentiometric Data of HPA and PCOH Interaction

Titrant	Solution	Mol Ratio of HPA to PCOH and Stoichiometry		
		From Conductometric Data	From Potentiometric Data	Figure No
HPA (0,015 M)	PCOH ($1,8 \cdot 10^{-3}$ M)	1,38	-	31
PCOH ($1,8 \cdot 10^{-3}$ M)	HPA ($2 \cdot 10^{-4}$ M)	-	1,48	32

3.4.5. Turbidimetric Measurements For Complex Stoichiometry

The reflected light intensity of the turbid solutions of PC-PA and PC-NaPABA in different mole ratios were measurement in salt free solution. Results are shown in figures 33,34.

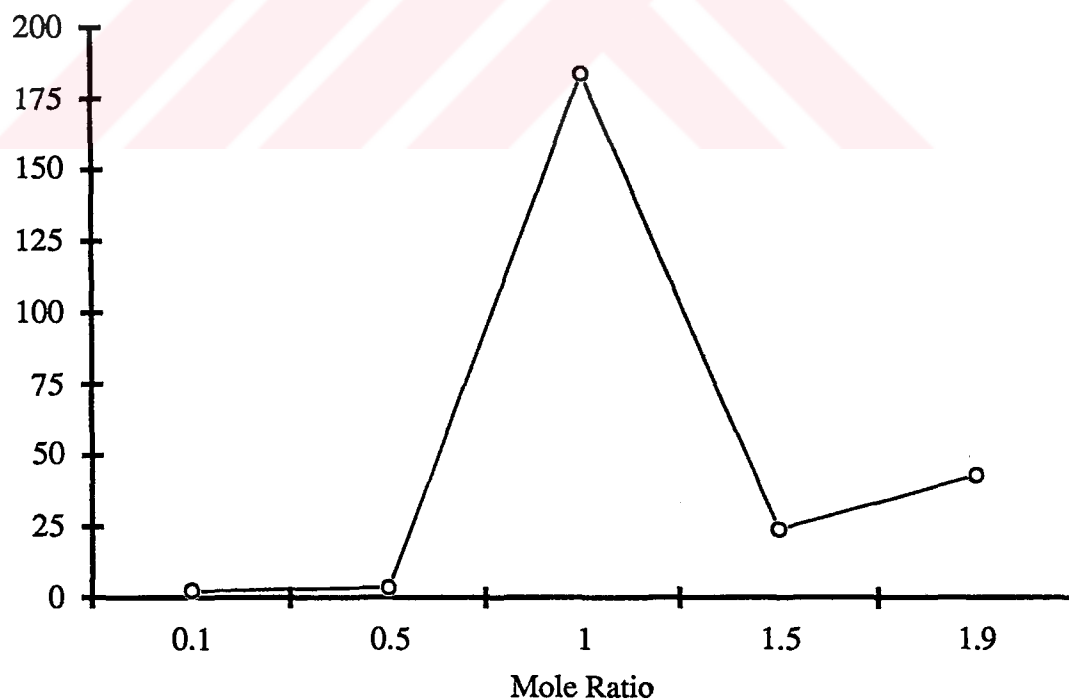


Figure 3.33. Turbidimetric Curve of $1 \cdot 10^{-3}$ M PC and $1 \cdot 10^{-3}$ M PA Mixture In Different Mole Ratio

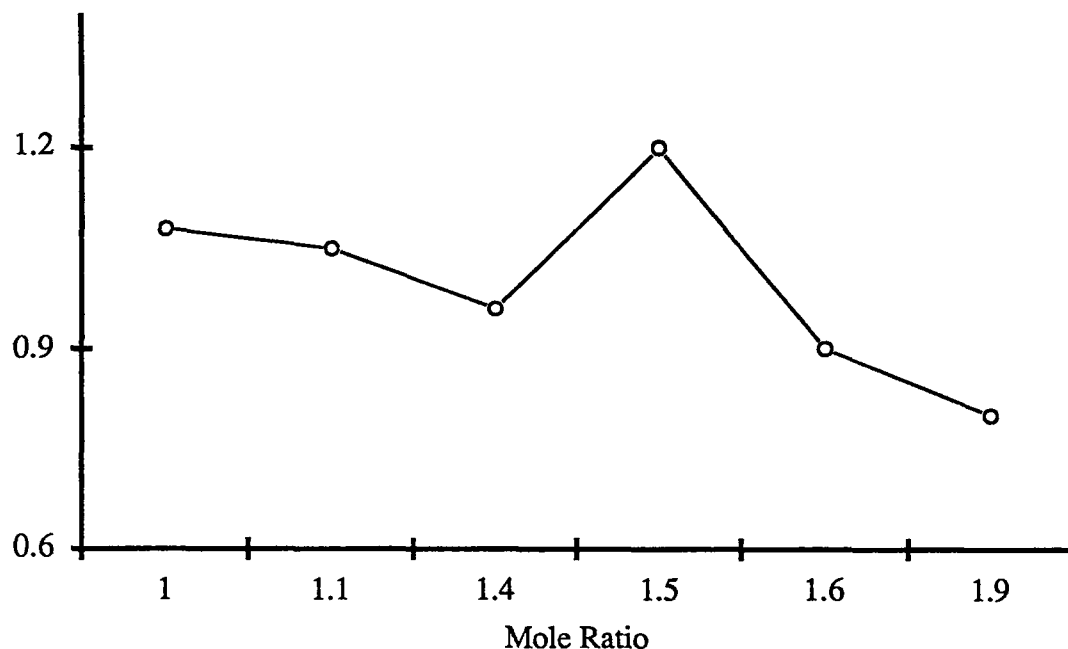


Figure 3.34. Turbidimetric Curve of 1.10^{-3}M NaPABA and 1.10^{-3}M PC Mixture In Different Mole Ratio

3.4.6. Supernatant Analysis

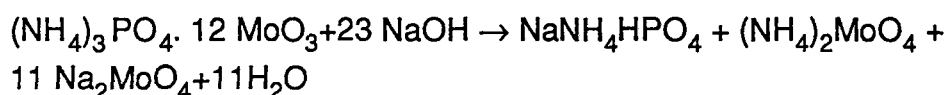
The supernatant liquids obtained after the removal of PEC precipitate from the solution which contained polyanion and polycation in different mole ratios were analysed by wet chemistry and viscosity method. Besides, control samples which contained polyanion and polycation alone but, as in the same concentration with the mixture of polyanion and polycation solutions in different mole ratios, were prepared and analysed with the same method.

3.4.6.1. Wet Chemistry

Polyanion and polycation solutions were mixed at different mole ratios in a certain volume. Each mixture was centrifuged to remove the precipitate then the chloride and the phosphorus content of aliquot solutions were determined by argentometry and alkalimetry respectively. Chloride content was also determined after phosphate removal.

Procedure For Phosphorus: 25 ml of aliquot from the supernatant solution was boiled with HNO_3 (1 M) solution for 3 hours under a reflux in order to hydrolyse the phosphorus in polymer chain to orthophosphate ions. After

this process ammonium molybdate solution was added into the orthophosphate solution slowly with continuous stirring. The precipitate was separated by filtration, washed with 25 ml of 1% KNO₃ solution two times and excess of 0.324 N NaOH solution was added until the yellow phosphomolybdate precipitate was dissolved. The excess of NaOH solution was neutralized by 0.324 N HNO₃ solution in the presence of phenolphthalein as an indicator then, the solution was titrated with NaOH solution. The same procedure was also applied to the control solutions which contained polyions individually. The reaction equation is given as follow:



Results are shown in Table 3-8.

Table 3-9. Supernatant Analysis

	Mol Ratio of PC and PC mixture	Supernatant Composition				Individual Control Sample			
		Chloride (g)	Relative Precision ppt	Phosphorus (g)	Relative Precision ppt	Chloride (g)	Relative Precision ppt	Phosphorus (g)	Relative Precision ppt
PC:PA	1:1	0.015	3.5	0.015	5	0.018	3.5	0.083	4
	1:2	0.014	4	0.030	6	0.018	4	0.166	5
	1:3	-		0.037	8	0.018	5	0.249	6
PA:PC	1:2	-		0.025		0.036		0.083	

Table 3-10. Chloride Content of The Supernatant After Phosphate Removal

	Mol Ratio of PA and PC mixture	Supernatant Composition Chloride (g)	Relative precision ppt
PC:PA	1:1	0.015	3.5
	1:2	0.014	4
	1:3	-	

3.4.6.2. Viscosity Measurements

A series of mixtures containing different amount of PC and PA were prepared as salt free solutions. An aliquot of each mixture were centrifuged to remove the precipitate and the viscosity of the supernatant liquid was measured at 25°C in an Ostwald capillary type viscometer with a flow time of 6 seconds for 2 ml H₂O. For each mixture a control sample was made up containing the ionic excess of the more concentrated polyelectrolyte plus the amount of NaCl which would be released from the precipitate upon complete ionic interaction between the polyions. The viscosities of these solutions were measured for comparison with the supernatant viscosities. The results are given in Table 3-10.

Table 3-11. Viscosity Measurements of Supernatant Composition

Mixture	Mixture Composition meq/50 ml		Ionic Excess		NaCl concent. of supernatant Liquid	η_{sp} of supernatant Liquid	η_{sp} of control sample
	PVPyCl	(NaPO ₃) _n	PVPyCl	(NaPO ₃) _n			
1	0.425	0.128	0.213	-	0.025	2.18	3.34
2	0.340	0.128	0.128	-	0.025	1.08	1.40
3	0.255	0.153	-	-	0.030	0.03	0.06
4	0.213	0.204	-	0.077	0.025	0.46	0.49
5	0.213	0.255	-	0.128	0.025	0.49	0.53

3.4.7. Preparation of Polyelectrolyte Complex

The polyanion solution (1.275 g/25 ml) was slowly dropped into the polycation solution (2.125 g/25 ml) and mixing was continued for 30 minutes. The precipitate was separated by means of a centrifuge (5000 r.p.m), and was dried under vacuum after being washed several times with water and acetone. IR spectra of PEC are shown in figure 35. For the comparison IR spectra of polyanion and polycation are given in Figure 35.

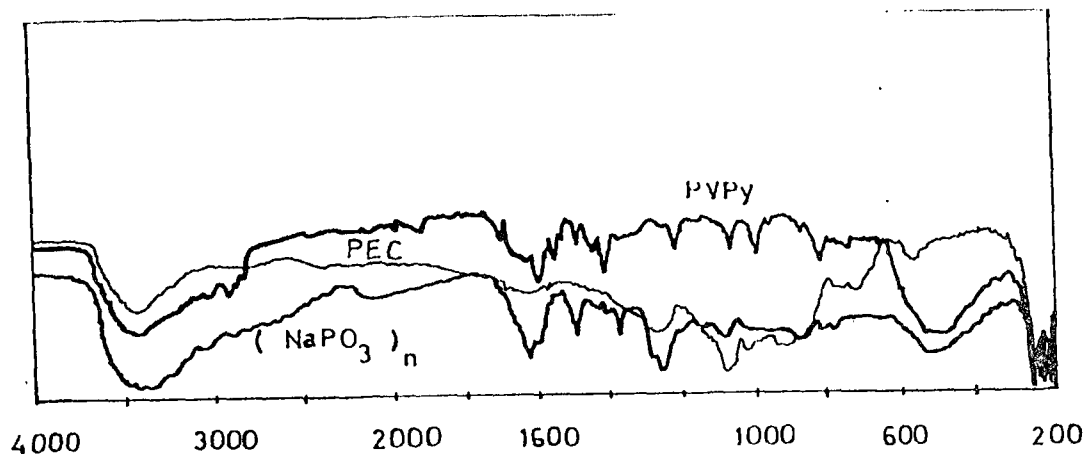


Figure 3.35. IR Spectra of PEC, PA and PC

3.4.8. Swelling Measurements

For swelling measurements 0.1 g of samples of dried PEC are equilibrated with approximately 10 ml volumes of various solvent mixtures which contain all components in equal volume. 5M of NaCl and NaBr were used in the mixture and let stand for 24, 48 and 72 hours at room temperature. Increase of the polyelectrolyte complex volume was determined at the end of different hours period. Results are shown in table.

Table 3-12. Swelling Measurements of PEC in Different Solvent

Mixtures	24 hours		48 hours		72 hours		Swelling Ratio %			Density of PEC g/ml)
	Volume increase (ml)	Mass (g)	Volume Increase (ml)	Mass (g)	Volume Increase (ml)	Mass (g)	24 hours	48 hours	72 hours	
Water	0.21	0.14	0.18	0.12	0.18	0.12	40	20	20	0.68
NaBr	0.15	0.10	0.21	0.14	0.21	0.14	-	40	40	0.68
NaBr+Water	0.21	0.14	0.35	0.24	0.35	0.24	40	140	140	0.68
Aceton+Water	0.21	0.14	0.32	0.22	0.32	0.22	40	120	120	0.68
NaBr+Acetone + Water	0.15	0.10	0.35	0.24	0.35	0.24	-	140	140	0.68
NaCl	0.15	0.10	0.18	0.12	0.18	0.12	-	20	20	0.68
NaCl+Water	0.15	0.10	0.21	0.14	0.21	0.14	-	40	40	0.68
NaCl+Water + Acetone	0.15	0.10	0.26	0.18	0.26	0.18	-	80	80	0.68

Chloride and Bromide content of the supernatant solution which result in 0.1 g PEC interaction with 10 ml of NaBr and NaCl solution in different concentrations for 48 hours were determined. Results are shown in Table 3-13.

Table 3-13. Supernatant Analysis of Swelling Measurements

Electrolyte Concentration (Mol/L)	Supernatant Composition		Sorbed Electrolyte %	
	Chloride (g)	Bromide (g)	Chloride (g)	Bromide (g)
0.2	0.035	0.042	2.5	18
1	0.151	0.008	15.17	52
3	0.462	0.959	6.67	20

CHAPTER 4- RESULTS AND DISCUSSION

Conductance and Turbidity Measurements:

The end point stoichiometry of PA and PC mixture in different mole ratios determined from the conductance and turbidity curves. Show that polyelectrolyte complex is formed with a unit molar ratio of PA to PC in dilute, salt free solution.

The conductance and turbidity data shows that the interaction of Na-PABA and PC give a unit mole ratio (Fig.30,34) as the stoichiometry of PA and PABCl reaction deviates from unity in salt free solution.

Conductometric titration

The end point stoichiometry of various titration modes of PA and PC which are derived with experimental parameters such as the order of polyion addition, polyions and added salts concentrations. Show that mole ratio of PA to PC changes between 1 and 1.6 for all polyion concentrations under examination. The extent of mole ratio from unity occurs in the solution which contain excess of polyanion. This result is reasonable since PA has low molecular weight compare to PC. The titration curve shown in Figure 8. Shows two intersection points. The distinct decrease of the titration curve indicates the PA binding to PC with the equivalent release of counter ions. Initially, the substantial ionization of counter ions in salt free solution cause an electrostatic suppression on the subsequent liberation of counter ions as the reaction proceeds. Therefore, a straight line appear after the first intersection point and the bound between PA and PC is completed at the second intersection point which corresponds to the 1:1.6 mole ratio of PC to PA. Stoichiometric excess of PA which is also 25 times more concentrated than PC can be explained with the low molecular weight of PA. 1.10^{-3}M of low molecular salt (NaCl, NaBr) addition to reaction medium give a pronounced deviation from the stoichiometry (Fig.9). The titration curve derived in the case of

1.10^{-2}M NaCl, NaBr addition to the system exhibits an increased curve with two probable intersection. The first increased part of the curve may be resulted in from the high concentration of PA which give substantial counter-ions during the PC binding then, the ionization of one of the polyions may occur and the conductance increases because of the high concentration of micro and counter-ions until second intersection point and finally, the low slope of the curve indicates that all micro and polyions remain together.

In general, the continuous decrease in titration curves which is obtained 1.10^{-2}M of NaCl and NaBr addition to reaction medium suggest that PA and PC are ionized due to the high concentration of NaCl and NaBr, no binding occur and the high charge densities on polyions can not be satisfied by microions.

The mole ratios of PA to PABCI and NaPABA to PC are found between 1 and 1.4 in all concentrations of interacted ions in salt free solution. The extent of unit mole ratio proceeds on the side of reactive polyion (titrant). It may be expected to have excess of the monomer (NaPABA) in the NaPABA-PC composition as a result of the occurrence of complex species which always contain excess of either ions taking part in complexation reactions. The titration curve shown in figure 28 give the result that in 1.10^{-3}M of NaCl solution, all interacted ions remain together up to the intersection point with a charge condensation phenomenon then, the conductance increased with free micro ions. In the case of 1.10^{-2}M of NaCl and NaBr addition to PA-PABCI and NaPABA-PC mixture, decreased curves are derived in general. This result also indicates that monomers are not bounded polyions. The curves (11,18,24) which give distinct decrease and a straight line beyond the intersection point show that a binding process between the interacted ions progress until the end point then, all ions remain together with a probable sorption or charge condensation mechanism.

The conductometric titration of the acid form of PA with the base form of PC show similar feature with dilute solution (1.10^{-3}M) interaction of the salt form PA and PC (Fig.11,12,13) in salt free and in salt solution. The PEC formed contain excess of PA that is the usual result of complexation reaction. The same result is also obtained from the potentiometric titration curve derived from the interaction of acid and base form of PA and PC (Fig.32).

Supernatant Analysis:

Specific viscosities of the supernatant are almost exactly equal to those of control samples made up to contain the ionic excess of more concentrated polyion plus NaCl equivalent to maximum possible counter ion release from the precipitated polyions.

The results of wet analysis carried out for phosphorus and chloride contents of supernatant liquid are given in Table 3-9. The supernatant composition indicates that nearly 18% of polyanion is left with polycation and the result is also verified with the chloride content of supernatant. Taking into consideration that wet chemistry is subject to a degree of uncertainty more than viscosity measurements so that the both viscosity and wet analysis data of the supernatant liquid can be considered as corroborated with conductometric data.

End Group titration of PA:

Potentiometric end group titration method which is carried out for the determination of polymerization degree hence the molecular weight of PA, do not give satisfactory result. This may be due to the uncertainty of hydrolysis procedure which is done in order to convert PA to orthophosphate.

Swelling Measurements:

Maximum degree of swelling is attained to an equilibrium in 48 hours period for different solvent systems except water alone and the PEC complex changes the appearance to rubbery state during the swelling. The highest percent of swelling volume is obtained in the solvent mixtures of NaBr + water, NaBr + water + acetone. The acetone conjunction with water in the ternary solvent system may cause the rearrangement of PEC structure into an expandable form. In addition the PEC may be composed of loosely ionic crosslinked so that it is slightly ionized from the crosslinked points due to the very high concentration of NaBr (5M) in the solvent mixture. Sorption mechanism is also probable in swelling. In fact sorption process might be effective in order to study the morphological structure of PEC in the swollen state.

The results of different electrolyte sorption by PEC show that sorption increases with increasing electrolyte concentration and NaBr is sorbed in higher percent than NaCl. This result also shows that the function of NaBr is more active than NaCl in the solvent systems which are used for the swelling measurements.

Conclusion:

It is concluded from the present study that results achieved from the conductometric and supernatant data reveals the stoichiometric composition of PEC irrespective of whether either polyion is present in excess. The excess polyion remain either dissolved in the aqueous phase or buried in the ionic cross link of PEC by probable sorption or charge condensation mechanism which arise from the coulombic interaction of all ions take part in the reaction depending on the difference between the total charge densities of PC and PA. Polyions are in extended conformation in the solvents which have high dielectric constant such as water. The coulombic entanglement which occur at the domain of the interacted sites during the release of counter ions can be neglected compare to the total charges of polyion chains at the beginning of the reaction. The excess charges which arise from the ionization of counter ions and also from the ionization of added salts suppress the subsequent liberation of counter ions so that efficient pairing of active sites on polyion chain slow down and a fraction of active sites might remain to be unreacted as the reaction proceeds. Thus, a change in the polyion chains, from an extended to a coiled conformation, occurs necessarily and this phenomena cause a deviation from the stoichiometry in salt free and in salt solutions. The experimental conditions such as the concentration of the reactive ions, the sequence of polyions addition and the mode of stirring affects the PEC stoichiometry. The result obtained in this work coincidence the theoretical approaches which are in progress yet. Swelling properties of the PEC complex formed give very promising future for the application in some field. In addition, the interaction between polyions and the derivatives of para amino benzoic acid give further thoughts for the analytical application of polyelectrolytes in the determination of proteins.

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