STUDIES ON ION-EXCHANGE MEMBRANES AND FLOCCULANTS BASED ON POLY (STYRENE-CO-MALEIC ACID)

Thesis submitted to
the Cochin University of Science and Technology
in partial fulfilment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY

by

PHILIP K. C.

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022

DECEMBER 1993

CERTIFICATE

This is to certify that the thesis entitled "Studies on Ion-exchange Membranes and Flocculants Based on Poly(styrene-*co*-maleic acid)" is based on the authentic work done by Sri. Philip K. C. under my supervision and further that no part thereof has been presented before for the award of any other degree.

V. N. Sivasankara Pillai

(Supervising Teacher)

Kochi - 682 022
27th December, 1993.

PREFACE

The last three decades witnessed a phenomenal growth in the synthesis and application of a variety of speciality polymers. Their applications range from catalysis, dentistry, bio-transplants, micro encapsulation, soil modification and selective permeation of gases and solutes from solutions. Separation science is perhaps the single largest area in industry which has been enormously benefited from these materials. Their applications in separation range from the conventional ion-exchange to the state-of-the art asymmetric membranes used in targeted separations.

This thesis contains the results of my modest efforts to explore the properties of poly(styrene-*co*-maleic acid) of varying monomer ratio, cross-linked with hydrophilic, neutral, and ionic agents as membranes on one hand, and the linear polyelectrolyte and its hydroxamic acid derivative as flocculants to some typical metal hydroxides on the other hand.

Chapter I of the thesis is an overview of polymers as flocculants and membrane materials. Chapter II deals with the synthesis and characterization of the materials used in the study. Chapter III outlines the experimental methodology followed in the study of the poly(styrene-*co*-maleic acid) [PSMA] based ion-exchange membranes and a detailed discussion on the observations of the study. Chapter IV is an account of the flocculation of Fe(III), Cu(II) and U(VI) hydroxides using PSMA and its hydroxamic acid derivative [PSMH]. The last chapter briefly summarizes the conclusions drawn from the study.

The results obtained have been analyzed in the light of the structure of the materials. Efforts have also been made to suggest a plausible mechanism to explain the selective transport of materials.

Many of the specialized measuring gadgets required for the work were not readily available. During the course of this work, considerable inputs was spared to fabricate and standardize such devices. The details of such devices have been incorporated in the relevant sections of the thesis.

CONTENTS

CHAPTER III POLY(STYRENE-CO-MALEIC ACID) MEMBRANES

CHAPTER IV POLY(STYRENE-CO-MALEIC ACID) BASED FLOCCULANTS

CHAPTER V SUMMARY AND CONCLUSIONS

CHAPTER I

POLYELECTROLYTES - AN OVERVIEW

The introduction of synthetic polymers as reagents and as materials for the fabrication of separation media has revolutionized the scope of separation techniques in medicine, chemical analysis and industrial operations. Today tailor-made polymers are used as flocculants, protective colloids, demulsifiers in soluble form and as ion-exchangers,and active and passive media in a solid form for the selective transport of solutes.

This thesis deals with the synthesis and characterization of ion-exchange membranes and flocculants derived from poly(styrene-*co*-maleic acid). Accordingly the scope of this review confined to the relevent aspects of polymeric membranes and flocculants.

PART I

SYNTHETIC MEMBRANES IN SEPARATION PROCESSES

1.1 Introduction

A membrane may be defined as an imperfect barrier, or an interphase which restricts the transport of substances from one phase to another in a rather specific manner(1). There are two different types of membranes , namely biomembranes and synthetic membranes.

The first group which comprises of membranes occurring in living systems (biomembranes) acts as the functional boundaries between different spaces within the organism. There are several types of biomembranes which exist in living things, such as cell membranes, epithelial membranes, and membranes of intercellular organelles. These membranes are different in composition, structure and/or function. Although a lot of work has already been done on this subject, the facts and interrelationships among these three important properties are not understood thoroughly. Biomembranes not only act as a barriers between the living and the inanimate world, but also take up nutrients, eliminate waste, control environmental chemistry, regulate metabolism and act as transducers of chemicals, electricity, temperature and light into other energy forms(2).

The second group of membranes consists of a large variety of materials including natural and synthetic organic polymers, metals, ceramics, glass, carbon, or combinations of these materials with natural products like collagen, albumin etc.

Synthetic membrane may be homogeneous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, neutral or charged, or may have functional groups with specific binding or complexing abilities. Membrane thickness ranges from less than 100 μm to more than 1 cm. Electrical resistance may vary from thousands of megaohms to less than an ohm. Mass transport through a membrane can occur via diffusion of individual molecule or convection induced by a concentration, pressure, temperature or electrical gradient(3).

1.2 Structure of synthetic membranes

Synthetic membranes can be classified into five groups, namely (i) microporous membranes (ii) homogeneous membranes (iii) asymmetric membranes (iv) electrically charged barriers and (v) liquid films with selective barriers. A brief account of their important features are discussed below.

1.2.1 Microporous membranes

A microporous membrane has a very simple structure which closely resembles the conventional fiber filter as far as separation and mode of transport are concerned. Microporous membranes consist of a solid matrix containing holes or pores with diameters of 1 nm to 20 μm. Separation of chemical components is achieved strictly by a sieving mechanism determined by pore diameter and particle size. Microporous membranes can be made from materials such as ceramics, graphite, metals, metal oxides and polymers. Their structure may be symmetric i.e. pore diameter does not vary over the membrane cross section, or asymmetric i.e., pore diameter increases from one side of the membrane to the other by a factor of 10 to 1000. Microporous membranes are used in processes such as micro - and ultrafiltration or dialysis to separate compounds that differ markedly in size or molecular mass(4).

1.2.2 Homogeneous membranes

A homogeneous membrane is a dense film through which a mixture of molecules is transported by a pressure, concentration, or electrical potential gradient. Separation of the components of a mixture is directly related to their transport rates within the membrane phase, which in turn is determined mainly by their diffusivities and concentrations in the membrane matrix(5). An important property of homogeneous membranes is that chemical species of similar size, and hence similar diffusivity, can be separated efficiently when their concentrations differ significantly. Homogeneous membranes are prepared from polymers, metals, or metal alloys by film forming techniques. Because mass transport in homogeneous membranes occurs strictly by diffusion, their permeabilities are rather low. Homogeneous membranes are used mainly for compounds that have similar size but different chemical natures encountered in processes such as reverse osmosis and pervaporation(6).

1.2.3 Asymmetric membranes

Most of the membranes used in large-scale separation processes are rather sophisticated asymmetric structures in which the two basic properties required for any membrane i.e high mass transport rate for selected components and good mechanical strength, are physically separated. An asymmetric membrane consists of a very thin (0.1 to 1 μm) "skin" layer on a highly porous 100-200 μm thick structure. The skin on top of the asymmetric porous structure constitutes the actual selective membrane. The porous sublayer serves only as a support for the thin, fragile skin and has little effect on separation characteristics or on mass transfer rate. Asymmetric membranes are used primarily in pressure-driven processes such as reverse osmosis, ultrafiltration, or gas separation because these techniques can best utilize their high mass-transfer rates and good mechanical stability.

1.2.4 Electrically charged barriers

Electrically charged barriers, referred to as ion-exchange membranes, consist of highly swollen gels carrying fixed positive or negative charges. The properties and preparation of ion exchange membranes are closely related to ion-exchange resins. As with resins, many types are available with different organic polymer matrices or functional groups that determine the ion-exchange properties of the product(7). Although several inorganic ion-exchange materials exist, mainly based on zeolites and bentonites, they are much less important than organic polymers.

In cation exchange membranes negatively charged groups are fixed to the polymer matrix. In anion-exchange membranes positively charged groups are fixed to the polymer matrix. In cation-exchange membrane, the fixed anions are in electrical equilibrium with mobile cations in the polymer interstices. The mobile anions are almost completely excluded from the cation-exchange membrane because their electrical charge is identical to that of the fixed ions(8). As a result, a cation exchange membrane permits transfer of only cations. Analogously, anion-exchange membranes are premeable only to anions. The main applications of ion-exchange membranes are in electrodialysis electrolysis, batteries, fuel cells and more recently, in pervaporation.

1.2.5 Liquid membranes

Liquid membranes have become increasingly significant in the context of facilitated transport, which utilizes carriers to selectively transport components such as metal ions at a relatively high rate across the membrane interphase.

Generally, formation of a thin fluid film is not a problem. Difficulty is encountered, however, in maintaining and controlling this film and its properties during a mass separation process. Reinforcement is necessary to avoid breakup of the film. Two techniques are used for the preparation of liquid membranes. In the first method, the selective liquid barrier material is stabilized as a thin film by a surfactant in an emulsion. In the second technique a microporous polymer structure is filled with the liquid membrane phase. Both types of membranes are used for the selective removal of heavy metal ions and organic solvents from industrial waste streams (9,10). They have also been used in gas separations.

1.3 Preparation of ion-exchange membranes

Ion-exchange membranes consist of highly swollen gels carrying fixed positive or negative charges(11,12). The most important properties required for ion-exchange membranes are the following .

(i) High selectivity: An ion-exchange membrane should be highly permeable to counterions but impermeable to co-ions.

(ii) Low electrical resistance: The permeability of an ion-exchange membrane to counter ions under the driving force of an electrical potential gradient should be as high as possible. So as to minimize potential drop in the medium the ion-exchange membrane material should have only a low resistance.

(iii) Good mechanical stability: The membrane should be mechanically strong and should have a low degree of swelling or shrinking during the transition from dilute to concentrated ionic solutions. This permits the use of high pressure as driving force, e.g. in reverse osmosis.

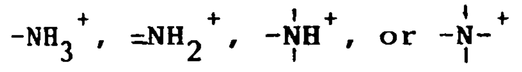
(iv) High chemical stability: The membrane should be stable over strongly acidic to alkaline media and in the presence of oxidizing agents.

The properties of ion-exchange membranes are determined by (i) the polymer matrix and (ii) the type and concentration of the fixed ionic moiety(1). The polymer matrix largely determines the mechanical, chemical and thermal stability of the membrane. It often consists of a hydrophobic polymer such as polystyrene, polyethylene or polysulfone. Although these polymers are insoluble in water and exhibit a low degree of swelling, they may become water soluble after the introduction of ionic moieties. The polymer matrix is frequently cross-linked. The degree of cross-linking decreases the degree of swelling, increases the chemical and thermal stability and electrical resistance. It also influences the permselectivity of the membrane(1).

The type and concentration of fixed ionic charge determine the permselectivity and electrical resistance of the membrane and also influence its mechanical properties. The degree of swelling is affected by the concentration of fixed charges. The following groups are commonly used as fixed charges in cation-exchange membranes,

$-SO_3^-$, $-COO^-$, $-PO_3^{-2}$, or $-ASO_3^{-2}$

In anion-exchange membranes, fixed charges may be



$-NH_3^+$, $=NH_2^+$, $-\underset{|}{\overset{|}{N}}H^+$, or $-\underset{|}{\overset{|}{N}}-^+$

The sulfonic acid group is completely dissociated over nearly the entire pH range, whereas the carboxylic acid group is virtually undisociated below pH 7. The quarternary ammonium group is completely dissociated at all pH values, whereas the primary and secondary amino groups are only weakly dissociated. Most commercial ion-exchange membranes are either homogeneous or heterogeneous. In homogeneous membranes the ion-exchange groups are homogeneously distributed throughout the polymer whereas in heterogeneous membranes the ion-exchange particles are dispersed in a neutral polymer matrix. In general, heterogeneous membranes have a relatively high electrical resistance, while homogeneous membranes have a more even distribution of fixed ions and often have a lower electrical resistance.

1.3.1 Homogeneous ion-exchange membranes

Homogeneous ion-exchange membranes can be prepared by three general procedures:

(i) polymerization of monomers

(ii) introduction of anionic or cationic moieties into a preformed film and

(iii) introduction of anionic or cationic moieties into a polymer, followed by film casting.

In polymerization of monomers, at least one monomer must contain a moiety that either is, or can be, made anionic or cationic. The first membranes of this type was prepared from the poly condensation of phenol and formaldehyde (7,11). Cation exchange membranes were made by the polymerization of styrene and divinyl benzene and subsequent sulfonation or amination (13,14,15).

In the second method of membrane preparation, anionic or cationic moieties are introduced into a preformed film. The membranes prepared by sulfochlorination and amination of polyethylene sheets have low electrical resistance, high permselectivity and excellent mechanical strength (16).

The third method of membrane preparation involves introduction of charge groups into a polymer chain, followed by preparation of membranes. Membranes are made by sulfonating polysulfone, followed by dissolving in DMF and casting around screens or other reinforcing materials to improve their strength (17).

Numerous methods are reported in the literature for the preparation of ion-exchange membranes with special properties for use in industrial separations, batteries, ion-selective electrodes, artificial organs or in chlor-alkali process(3). Significant effort has also been devoted to the development of ion-exchange membranes with low fouling tendencies(18,19).

1.3.2 Heterogeneous membranes

Heterogeneous membranes refer to structures composed of colloidal particles of ion-exchange materials embedded in an inert polymeric material. They are prepared by a variety of techniques. The ion-exchange particles can be pressed into a plastic film under pressure(20). Depending on the nature of the binder, this procedure may be facilitated by the application of heat. Alternatively, powdered thermoplastic film-forming resins can be initially mixed with the ion-exchange materials prior to calendering (21,22,23). Still another procedure involves evaporation followed by compression of a viscous solution of binder in which the ion-exchange particles are suspended(24). Both capacity and mechanical strength depend on the ratio of ion-exchange materials to binder.

1.3.3 Interpolymer membranes

Interpolymer membranes are formed by the evaporation of solutions containing two compatible polymers - as inert film former and a linear, ion-exchange polymer. It has some resemblance to heterogeneous membranes, and it shows homogeneity at the colloidal level.

1.3.4 Impregnation

One of the earliest procedures for the production of ion- exchange membranes by combining two or more separate materials was to utilize a porous substance as a binder and impregnate the interstices between elements of the binder network with ion- exchange material. Kressman prepared some of the earliest membranes of this type by impregnating filter paper and porous glass with ion-exchange resins (25). Juda and McRae prepared phenol-sulfonic acid-formaldehyde prepolymers and impregnated cloths of Saran, Vinyon, and glass (26). The extremely weak ion-exchange property of nitrocellulose membranes has been enhanced by impregnation with cation - and anion - exchange resins(27). The properties and functional behaviour of these membranes are comparable with membranes prepared by interpolymer method. The main disadvantages of these membranes are: (i) membrane resistance is poorly reproducible because of extreme sensitivity to slight variations in the ionogenic group, and concentration potentials deviate from linear relation with the number of charged groups at both low and high concentrations.

1.3.5 Graft copolymerization

Grafting of ionogenic materials onto neutral film substrates can be made use in the production of ion-exchange membranes. Since the grafted materials are covalently bonded to the film substrate, this method results in more stable structures than are produced by the impregnation technique. Vinyl monomers can be grafted on film substrates by chemical means by using peroxides(28), redox catalysts(29), high or low energy irradiation (30,31) or using plasma polymerization(32,33).

Considerable variation in the structure of the grafted membrane is possible. For a given amount of grafted material, the length of the grafted material can be controlled. Chain length decreases with increasing dose rate in the mutual- irradiation technique (monomer present during irradiation) and increases with increasing dose rate in the preirradiation technique (monomer added after irradiation) (34). Alternately, chain length can be decreased by increasing the concentration of initiator or by inclusion of chain transfer agents.

1.3.6 Mosaic membranes

Mosaic membranes are a type of inhomogeneous composite structure in which the various elements are placed in parallel rather than in series. Sollner et al (27,35,36,39) developed mosaic membranes which have a structure similar to a combination of two membrane concentration cells arranged in a short-circuited state without the presence of electrodes. A mosaic membrane consists of separate small domains of cation and anion exchangers.

1.3.7 Polyelectrolyte complexes

Polyelectrolyte complexes are materials formed by the interaction of soluble polyanions and polycations. The resultant polysalts can be neutral or posses an excess of cationic or anionic charge, and hence the system has considerable versatility. Dense or porous membranes are produced depending upon the extent of solvent loss prior to quenching in a nonsolvent gelation medium. Since polyelectrolyte complexes are formed by phase inversion process, their porosity and asymmetry in depth can be controlled by varying parameters such as casting solution composition, nature of desolvation environment, and duration of evaporation period(34,37,38). The products of reaction between strongly acidic and strongly basic polyanions and polycations have been utilized by Michaels and coworkers as the basis for a series of both neutral and charged ion-exchange membranes for almost the entire range of membrane separation processes and applications (40,41,42).

1.4 Fluxes and driving forces in membrane separation processes

Separation in membrane processes is the result of differences in the transport rates of chemical species through the membrane interphase. The transport rate is determined by the driving forces acting on the components and by their mobility and concentration within the membrane phase. The mobility is determined primarily by the molecular size of the component and the physical structure of the interphase material; the concentration of the solute in the interphase is determined primarily by the chemical compatibility of the permeating component and interphase material (5,43).

Three basic forms of mass transport are involved in membrane separation process.

1.4.1 Passive transport

This is the simplest form of mass transport in membrane separation process. Here the membrane acts as a physical barrier through which all components are transported under the driving force of a gradient in their chemical potential across the membrane interphase. Such gradients may be caused by hydrostatic pressure, concentration, temperature, or electrical potential differences between the two phases separated by the membrane (44).

1.4.2 Facilitated transport

In facilitated transport the driving force for the transport of the components is also the gradient in chemical potential. Transport of components is, however, facilitated by coupling to a specific carrier that is confined to the membrane phase. Facilitated transport is therefore a special form of passive transport, which is more selective and faster (45).

1.4.3 Active transport

In active transport components are transported against a gradient in chemical potential . The energy for transport is provided by a chemical reaction within the membrane phase. Active transport is usually coupled with a carrier mechanism in the membrane interphase and is found mainly in the membranes of living cells(46).

Transport processes are conventionally described by equations that relate the flux to the corresponding driving force in the form of linear relations(8). Fick's law describes the relation between the flux of individual components and a concentration gradient. Ohm's law describes the relation between electrical carrier and electrical potential gradient and Hagen-Poscuille's law describes the relation between a volume or momentum flux and a hydrostatic pressure gradient. In membrane processes, driving forces and fluxes are interdependent. Thus a concentration gradient across a membrane may result not only in a flux of materials but, under certain conditions can also cause building up of hydrostatic pressure and electrical potential difference. Similarly a gradient in one driving force can cause the formation of other driving forces and this may augment to a considerable change in the flux of the components.

Coupling of the kinetics of individual components may also occur resulting in a flux of other components. Osmotic transfer of water and ions will affect the permeabilities, membrane potential and transport number of ions under consideration (23,47,48,49).

PART II

POLYMERIC FLOCCULANTS

1.5 Introduction

The process of flocculation is the aggregation of small masses, usually in liquid media, into larger masses called flocs. Although the definition is generally applicable, various other definitions or refinements, especially when used in conjunction with the term coagulation are found in the literature. Throughout this thesis La Mer and Healy's(46) distinction between flocculation (aggregation of colloidal particles by polymers or polyelectrolytes) and coagulation (aggregation of colloidal particles by low molecular weight electrolytes) is followed.

Flocculants are used to optimize the separation of solid phase present as a suspension in a liquid phase. These suspensions usually contain organic or inorganic particles, which are finely divided and are distributed in water as a dispersion medium. With smaller particles the suspension is more stable, and the tendency for the particles to agglomerate and sediment is less. However, the addition of a flocculant causes aggregation of the suspended particles into larger particles and thereby increases the rate of sedimentation. The sludge so formed can be filtered rapidly or centrifuged, facilitating efficient separation.

The ability of synthetic polymers to increase the sedimentation rate of suspensions was first reported in 1939(49). The industrial application of flocculation was initiated by the introduction of synthetic water soluble polymers by Cyannamid Company in the 1950s in Canada. At the same time flocculants produced by BASF were used successfully for the clarification of wash water in German collieries (50,51). Dow Chemicals followed suit by introducing their flocculants into the United States' market. Since then polymeric flocculants have steadily gained importance and are now used worldwide in many branches of industrial separations and water treatment .

1.6 Classification of flocculants

1.6.1 Inorganic flocculants

Schulze (52,53) showed that certain colloids became unstable and coagulated on addition of electrolytes. The multivalent ions were very effective for negatively charged particles. The Schulze-Hardy rule states that the coagulation effect is determined by the valency of the ion with opposite charge to that of the solution. The most important inorganic coagulants currently in commercial use are listed in Table 1.1.

1.6.2 Natural polymeric flocculants

The natural flocculants are mainly derived from polysaccharides, proteins or functionalized derivatives of these two polymers. Starch is a nonionic polymer of glucose and is obtained principally from corn. Molecular weight depends upon the source and processing methods. Although some nonionic starch is used, most starch floculants are cationic. Derivatization with

Table 1.1. Inorganic floculants

Type	Formula	Comments
Alum	$Al_2(SO_4)_3.14H_2O$	Used as a (17 wt% Al_2O_3) or 50 wt% solution (8.5 wt% Al_2O_3
Poly(aluminium chloride)	$Al(OH)_{1.4}(SO_4)_{0.125}Cl_{1.25}$	Obtained by partially hydrolyzing $AlCl_3$;used as solution (10 wt% Al_2O_3).
Sodium aluminate	$NaAlO_2$	Used as powder
Iron (III) chloride	$FeCl_3$	Used as powder or solution
Iron (III) sulphate	$Fe_2(SO_4)_3$	Used as granulate
Iron (III) sulphate chloride	$FeClSO_4$	Obtained by the oxidation of $FeSO_4$ with chlorine, used as solution.
Iron (II) sulfate	$FeSO_4.7H_2O$	Used as crystalline powder.
Sodium silicate (actvated silica)	Na_2SiO_3	Used as solution.

diethylaminoethyl chloride or 2,3-epoxypropyltrimethylammonium chloride provides positive amine centers(54,55,56). Anionic starch is usually prepared by causticization with alkali(57). One unique commercial application, however, is the selective flocculation in a low grade iron ore pulp (58,59).

Guar gum is a water soluble high molecular weight polysaccharide. It is non-ionic and, hence, effective over a wide range of pH and ionic strengths(60). A disadvantage of guar gum is its relatively rapid biological decomposition in aqueous solutions.

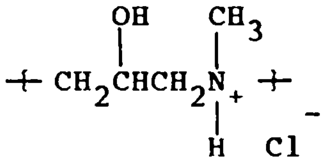
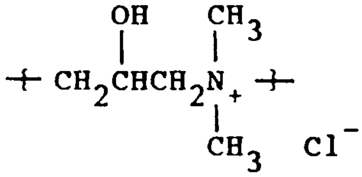
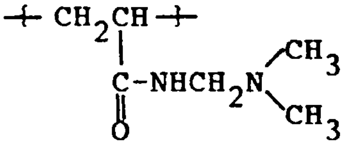
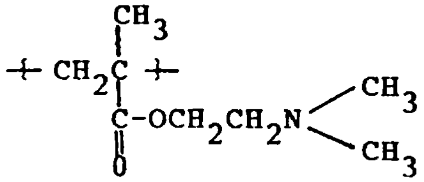
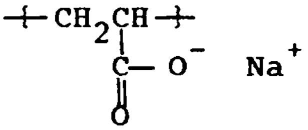
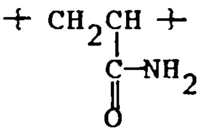
Animal glue or gelatin is derived from fibrous collagen, the major protein of skin, bones and connective tissues(61). The polypeptide chains contain a variety of aminoacids, with high content of glycine, proline, and hydroxyproline. Animal glue is used as a flocculant in mineral processing(62). Edible gelatin is used for the clarification of wine, beer, vinegar and nonalcoholic beverages(63).

Sodium alginate, another polysaccharide based flocculant, is produced from brown algae by alkaline extraction(64). The acid, either is a mixture of linear homopolymers or a copolymer of uronic acids.

Chitosan is a water-soluble cationic polysaccharide, made from chitin, by partial deacetylation with alkali. Chitin is derived from crustacean shells. Activity as a flocculant has been demonstrated (65).

In addition to these, a number of other natural product based flocculants are available. These include sodium carboxymethyl cellulose, tannins(66) and xanthans.

Table 1.2. Some commercially important synthetic polymeric flocculants.

Polymer	Empirical formula	Charge
Poly(ethyleneamine)	$-\!\!\!+ CH_2CH_2NH +\!\!\!-$	Cationic
Poly(2-hydroxypropyl-1-N-methylammonium chloride)	 $-\!\!\!+ CH_2CH(OH)CH_2N^{+}H(CH_3) +\!\!\!-\ Cl^-$	Cationic
Poly(2-hydroxypropyl-N,N-dimethylammonium chloride)	 $-\!\!\!+ CH_2CH(OH)CH_2N^{+}(CH_3)_2 +\!\!\!-\ Cl^-$	Cationic
Poly[N-(dimethylaminomethyl)-acrylamide]	 $-\!\!\!+ CH_2CH(C(=O)NHCH_2N(CH_3)_2) +\!\!\!-$	Cationic
Poly(N,N-dimethylaminoethyl methacrylate)	 $-\!\!\!+ CH_2C(CH_3)(C(=O)OCH_2CH_2N(CH_3)_2) +\!\!\!-$	Cationic
Poly(sodium acrylate)	 $-\!\!\!+ CH_2CH(C(=O)O^-) +\!\!\!-\ Na^+$	Anionic
Poly(sodium styrenesulfonate)	$-\!\!\!+ CH_2CH(C_6H_5SO_3^-\ Na^+) +\!\!\!-$	Anionic
Polyacrylamide	 $-\!\!\!+ CH_2CH(C(=O)NH_2) +\!\!\!-$	Nonionic
Poly(ethylene oxide)	$-\!\!\!+ CH_2CH_2O +\!\!\!-$	Nonionic

1.6.3 Synthetic polymeric flocculants

These are water-soluble polymers which can be classified into nonionic polymers, and ionic polymers (polyelectrolytes). The latter can be further subdivided into anionic, cationic and amphoteric depending on their charge characteristics. Examples of flocculants of the different groups are given in Table 1.2.

(a) Nonionic polymers

Unique polymerization characteristics of acrylamide allow production of very high molecular weight polymers of nonionic character(23). Polyacrylamide-based polymers play a dominant role in the flocculation market and it is the most extensively studied polymeric system (67,68). One feature that has been the subject of many basic investigations is the stability of dilute aqueous solutions on aging (69,70,71). The polymerization causes some degree of hydrolysis of the $-CONH_2$ group to -COOH, but with careful control, the polymer may contain 1% or less carboxyl. If the percentage of carboxyl is about 1% or less, the polyacrylamide is said to be nonionic, if it is higher, the polymer is referred to as an anionic polymer. Acrylamide may be converted to other ionic polymers which act as flocculants by methods described by Schiller and Suen(72). Sulfomethylation with formaldehyde and bisulphite yields an anionic polymer; Hofmann degradation or the Mannich reaction yields cationic polymers. All these polymers are being used successfully in several commercial applications.

Flocculant grade ethylene oxide polymers have much higher molecular weights ($>3x10^6$) (73). These polymers are made by special catalytic process, probably using alkaline earth carbonates, oxides, and amides (74,75,76). The primary utility of PEO appears to be in mining flotation process(77).

Poly(vinyl pyrrolidone) is produced by the addition polymerization of N-vinylpyrrolidone and is used in a variety of applications like calrification of beverages and other food products (78,79).

Poly(vinyl alcohol) is produced by the hydrolysis of poly(vinyl acetate). Molecular weight is rather low (3×10^5) for a nonionic flocculant, and it does not appear to have established a commercial position as a flocculant. On the other hand, it has been used in a number of fundamental studies on flocculation since it is easy to achieve a balance between hydrophobicity and hydrophilicity by controlling the extent of hydrolysis of the parent poly(vinyl acetate)(79,80).

(b) Polyampholytes

Polyelectrolytes having both anionic and cationic sites on the same chain are called amphoteric polyelectrolytes or polyampholytes. At the present time, polyampholytes find little commercial utility(81). It may be noted that the net charge on polymers of this type is strongly dependent upon the pH of the medium, since only quarternary ammonium salts have charges which are independent of pH. Copolymers containing 2-aminoethyl methacrylate and methacrylic acid have been reported effective in treating ionic substrates at or below the isoelectric point of the polyampholyte(82). Polymers which are amphoteric by virtue of an incomplete cationization reaction on anionic polymers have been reported (81).

(c) Cationic flocculants

Most of the high-molecular weight cationic flocculants available today are made by free-radical copolymerization of acrylamide with minor amounts (10 mol % or less) of the cationic monomer. The ratio of acrylamide to the cationic monomer is dictated by the economics of application and activity; for most of the applications in water treatment, 10 mol % is sufficient (37).

Although a number of polysulfonium and polyphosphonium compounds have been reported (83,84), quadrivalent nitrogen is the charged site in all commercial cationic flocculants at the present time. Cationicity derives from the quadrivalent nitrogen, either via protonation of primary, secondary, or tertiary amines, or via generation of quarternary nitrogen groupings. Cationicity of the quarternary nitrogen is independent of pH, although the other parts of the polymer molecule may exhibit sensitivity to pH, such as hydrolysis of ester linkage. Cationicity is dependent on protonation, which, in turn, is a function of pH. The step-growth polymers of polyfunctional amines and alkyl dihalides or bifunctional alkyl epoxides and alkyl epoxide derivatives are of relatively low molecular weight ($<10^5$) but have a high level of cationicity. Typically a poly(ethyleneamine) is produced by the reaction of ammonia, or low molecular weight alkylene polyamine, with ethylene dichloride in the presence of a base (85-89). Completely linear poly(ethyleneamine) is also known(90) but is not available commercially.

Poly(ethyleneimine) (PEI) is a material produced commercially from ethyleneimine in an aqueous medium by ring-opening polymerization using ethylene dichloride as initiator(91). PEI is highly branched, with primary, secondary and tertiary amine groupings. Its major use is in the manufacture of paper. Since a series of products with relatively well-defined molecular weights (10^3 to 10^5) have been available, PEI has been used in a number of model investigations on flocculation (92).

Cationic polyamine quarternaries are prepared either by quarternization of poly(alkylene polyamines) and poly(hydroxy alkylene polyamines) with alkyl halides or sulphates (93), or by step-growth polymerization of dialkylamines, tetralkyl amines, or their derivaties (94), with suitable bifunctional alkylating agents, and with or without small amounts of polyfunctional primary amines for molecular weight enhancement(95). Polyamines produced from ammonia and ethylene dichloride, quarternized with methyl chloride, and polyquarternaries produced directly from dimethylamine and 1-chloro-2,3-epoxypropane are of primary commercial significance. The fact that polyquarternaries are relatively insensitive to pH, broadens the spectrum of possible applications.

A diverse group of amino-aldehyde step-growth condensation products are included in the cationic cyanamide derivatives. Amino building blocks such as dicyandiamide(96), melamine (97,98), urea (99,100) and guanidine (101) can be derived from cyanamide as basic raw material. Formaldehyde is used for aldehyde (102). The products obtained are water dispersible and may be modified with multifunctional amines and amino alcohols .

The vinyl polymer conversion products are versatile commercially important synthetic organic flocculants. The homopolymer of acrylamide reacts with formaldehyde and a suitable amine (dimethylamine) via the Mannich reaction to form a polytertiary amine (103-106).

As a polycyclic amidine, poly(2-vinylimidazoline) has a structure unique for a flocculating agent with very high cationicity and medium or high molecular weight. It is produced from poly(acrylonitrile) by sulphur-catalyzed condensation with ethylenediamine (108). Poly(diallyldimethyl ammonium chloride) is a linear polymer synthesized from a 50-70% aqueous solution of diallyldimethylammonium chloride by free-radical copolymerization initiated with peroxide catalysts (109,110). The polymers are in the low to medium molecular weight range ($<10^6$), chlorine resistant, and insensitive to pH variations.

Other flocculants have also been synthesized from a number of cationic monomers, such as 2-vinylpyridine, 5-vinyl-2-picoline and 4-vinylbenzyltryimethylammonium chloride, but they have little commercial application (111,112).

(d) Anionic flocculants

The sulfonic acid group is an inherently stronger acid than the carboxyl group. Polymers with sulphonic acid moieties, therefore, retain their anionic charge in media of low pH. The sodium salt of poly(styrenesulfonic acid) is the best known economically available flocculant of this type. It can be derived from sodium styrene sulfonate by free radical polymerization(86) or form polystyrene by post sulfonation(113). Very high molecular weight products have been investigated as flocculants for the so-called red muds in the Bayer process for bauxite, to demonstrate the effect of molecular weight on that substrate(114). Copolymers of styrene sulfonate with acrylamide also have been patented as flocculants(115).

Poly(ethylene sulfonic acid) polymers, including copolymers with acrylamide, have been reported to be flocculants(116). 2-Acrylamide-2-methylpropane sulfonic acid is a monomer used in the preparation of both high molecular weight anionic flocculants, by homopolymerization or copolymerization with acrylamide or sodium acrylate (117,118,119) and low molecular weight deposit control agents, primarily as copolymers with acrylic acid (120,121). Sulfonic acid containing acrylates such as 2-sulfoethylmethacrylate and 3-sulfopropylacrylate have been used to prepare polyelectrolytes for water treatment (122,123).

Anionic polyelectrolytes containing phosphorous are among the most recent developments in the field of separation science. Many of the polymeric phosphonic acids reported were prepared using similar chemistry to that used for the preparation of phosphonic acids, by the Mannich reaction of an amine with formaldehyde and phosphorous acid (124,125,126).

Carboxyl-containing anionic polyelectrolytes is by far the most important class of anionics, both in the high and low molecular weight range. High molecular weight carboxyl containing anionic polyelectrolytes are used as flocculants in water and waste water treatment and in mineral processing (127,128).

The most common low molecular weight carboxyl containing polymers used as flocculants are polyacrylic (129,130,131) and polymethacrylic acids or their salts. Other carboxyl containing polymeric flocculants are acrylonitrile copolymers (132) copolymers of acrylic acid and 2-hydroxypropyl acrylate (133) and hydrolyzed homo and copolymers of maleic anhydride.

1.7 Maleic acid polymers in separation science

Although copolymerization of maleic anhydride has long been commercially important, homopolymerization was considered impossible for many years. There have been many reported techniques for homopolymerization since 1961 (134), including the use of peroxide in aromatic solvents(135), electrochemical polymerization (136), and gamma or UV irradiation (137). Poly(maleic acid) is now an article of commerce in textile sizers, levelling agents in dye baths and cleaning agents for metals.Table 1.3 lists comonomers and reported reactivity ratios in the copolymerization of maleic anhydride(111).

The comonomers M_2 can be classified into two groups in accordance with their polarity. Electropositive monomers, such as acrylic esters and vinylidene chloride have high reactivity ratios and show little tendency to copolymerize with maleic anhydride. By contrast, electronegative monomers, such as styrene or vinyl esters or ethers, have reactivity ratios close to zero(138). In these cases each monomer greatly prefers to react with the opposite unit in the growing radical chain, so that alternating copolymers are produced (139).

Cocea et al in their studies on the reactivity of carbonyl groups of poly (styrene-*co*-maleic acid) prepared a number of derivatives (140). The carboxylic acid and the hydroxamic acid derivative formed tridimensional, coloured complexes with salts of

Table 1.3 Reactivity ratios of maleic anhydride.

M_1	M_2	Temperature (°C)	r_1	r_2
Maleic anhydride	Acrylamide	50	0	0.75
	Acrilonitrile	60	0	6
	Allyl acetate	38.5	0.03	0.008
	Allyl glycidyl ether	60	0.002	0.001
	Butyl vinyl ether	50	0.045	0
	Dodecyl vinyl ether	50	0.046	0
	Isopropenyl acetate	75	0.002	0.032
	Methyl arylate	60	0	2.5
		75	0.02	2.8
	Methyl methacrylate	30	0	4.6
		60	0.03	3.5
		75	0.02	6.7
	α-Methyl styrene	60	0.08	0.038
	Styrene	50	0.015	0.04
		50	0	0.097
		50	0	0.019
		60	1.0	0.02
		80	0	0.042
	Vinyl acetate	75	0.003	0.072
	Vinyl chloride	75	0.088	0.3
	Vinyl N, N-diethyl carbonate	80	0	0.035
	Vniylidene chloride	60	0	9
	N-Vinyl succinimide	90	0.15	0.03

heavy metals. Treatment with dilute HCl removed the metal, and the colour disappeared. Thus they predicted that these polymers can be used as ion-exchange resin for Fe (III), Cu (II), Cd (II) and U (VI) which can be regenerated with HCl. Earlier to this, in 1961 Nakanishi and Hisayana (141) prepared ion-exchange resin by grafting maleic anhydride on a copolymer of styrene and divinylbenzene using aluminium chloride. The ammonium salt of copolymers with methyl or ethyl methacrylate were being used as wash solutions in the processing of photographic films (142).

Copolymers of styrene, ethyl acrylate, maleic anhydride, and divinylbenzene (67:21:10:2), were produced in a casting mold with benzoyl peroxide at 72-75 $^{\circ}$C. The resulting sheet was heated in 17% aqueous sodium hydroxide at 90-100 $^{\circ}$C until swelling ceased. The pliable transparent sheet was utilized as an ion-permselective membrane in cells for the electrolysis of brine (143).

A mixture of acrylamide, maleic anhydride, urea (foaming agent), and water (50:30:10:10) was melted to a uniform solution and on X-ray irradiation, formed tan, opalescent resin. Heating at 170 C expanded the resin to a rigid crosslinked foam, which can be used as ion exchange resin or filter (144).

Water-soluble copolymers of acrylamide, methacrylic acid and maleic anhydride were obtained as white granular solids by a water-in-oil dispersion process (145). There were reports on these polymers as effective flocculating agents for paper-pulp slurries and retention aids for the deposition of fillers in papers (146).

Maleic anhydride was grafted on poly(butadiene) and ammonolysis gave a water-soluble amide-ammonium salt, which can be incroporated into water-based coating baths. On curing it formed hard, flexible films. Epoxides or their hydrolyzed products were obtained by treatment with peroxyformic acid or peroxyacetic acid (147). Copolymers of maleic anhydride with isobutylene (148) and 1-octadecene (149) have been used in water treatment. These polymers appear to function in applications where poly(acrylic acid) or hydrolyzed poly(acrylamide)s are ineffective. It appears that the combination of the hydrophilic carboxylic group with hydrophobic groups lead to unique activity for many depositing species. This hydrophilic-hydrophobic combination has become of interest in the area of flocculation. Another deposit control agent used in water treatment is the low molecular weight hydrolyzed sulfonated styrene-maleic anhydride copolymers (150-152).

Quarternized polyimide-amines were prepared from styrene- maleic anhydride copolymer, using 3-(dimethylamino) propylamine. These cationic polymers were found useful in flocculating aqueous suspensions of inorganic particles (153,154). Amphoteric flocculants have been prepared by reaction of maleic anhydride copolymers with ammonia, followed by Hofmann degradation of the product (155).

Uragami et al prepared ion exchange membranes from poly(isobutylene-*co*-maleic anhydride) cross-linked with poly(vinyl alcohol) and studied the mechanism of active transport of alkali metal ions, ammonium ion, aniline and amino acids (156-162). Fukuda et al studied the metal ion permeation using poly(maleic anhydride-*alt*-2-methyl-2-propen-1-ol) and poly(acrylonitrile) (163). Selective transport of alkali metal ions was studied using poly(styrene-*co*-maleic acid) cross-linked with tetraethylene glycol (164).

The degree of purification of wastewater was increased by treating with a polymer based on maleic acid and acrylamide (165). Imide group was introduced onto polymer containing maleic acid and was used as flocculant in paper industry (166). Amphoteric polyelectrolytes were prepared by introducing amide group intro styrene-maleic acid copolymer (167) and the dependence of flocculation of SiO2 on pH was studied (168).

Kandori et al (169) studied the dispersion stability of needle like and octahedral iron (III) oxides of magnetic or nonmagnetic particles in 2-butanone using poly(vinyl acetate-vinyl chloride-maleic acid). The sedimentation of dispersions, the adsorption of copolymer dispersants on the particles and zeta potentials were measured. Polymeric flocculant compositions with improved salt resistance containing 5-95% maleic acid-styrene copolymer monoalkyl ester, N,N-dialkylamino-propylene ammonium salts 5-95% and N,N-dialkylaminopropylene monoamide of maleic acid and styrene copolymer prepared and applied on a number of suspensions (170).

Maclaw and Alicja reported water insoluble membranes produced from PVA cross-linked with maleic acid and fumaric acid (171,172). Ion exchange membranes were prepared from a copolymer of maleic anhydride and vinyl acetate partially cross-linked with bifunctional cross-linking agents (173). Eiichi and Junji prepared amphoteric polyelectrolyte membranes from hydrolyzed N-vinylsuccinimide-maleic anhydride copolymer and studied the selective permeability for inorganic salts and organic compounds (174). The membrane showed permeability towards anions, cations and neutral species.

Dhandhukia et al prepared ion-exchange resins from maleic anhydride, styrene and DVB (175). Hydrolyzed resins showed high affinity for divalent metal ions. The selectivity of these resins were improved by incorporating hydroxamic acid and N-phenyl hydroxamic acid (176,177).

The flocculating ability of acrylamide-maleic acid copolymers with varying monomer ratio was studied by Asanov et al (178) using bentonite suspensions. The effect of pH on flocculation ability was examined by sedimentation studies (179). A condensation-coupling reaction between hydroxyl groups of PVA and anhydride group of methyl methacrylate-maleic anhydride copolymer to produce graft terpolymer. This on treatment with ethanolamine to give polymer containing N-ethylmaleic oxide units (180). Dieter et al removed coal fines from wastewater by flocculation with 0.5-4 mg/L flocculant prepared by reacting maleic anhydride-olefin copolymers with diamine having primary and tertiary amino group (181).

The kinetics of transport of alkali metal ions against their concentration gradient across poly-(isobutylene-*alt*-maleic acid) and poly(styrenesulfonic acid) membranes has also been reported (182).

REFERENCES

1. R. E. Kesting, Synthetic Polymeric Membranes, A Structural Perspective, 1985, Wiley-Interscience, New York.
2. E. Piskin in Polymeric Biomaterials, ed. E. Piskin, A. S.Hoffman, 1986, Martinus Nijhoff Publishers, Dordrecht, The Netherlands.
3. H. Strathmann, in Ullman's Encyclopedia of Industrial Chemistry, ed. B. Elvers, S. Hawkins, G. Schulz, 1990, A16, VCH, FRG.
4. A. S. Michaels, in Progress in Separation and Purification, ed. E. S. Perry, 1968, 1, Interscience, New York.
5. J. Crank, G. S. Park, Diffusion in Polymers, 1968, Academic Press, New York.
6. R. E. Kesting, Synthetic Polymeric Membranes, 1971, Mc Graw-Hill, Inc., New York.
7. F. Helfferich, Ion-Exchange, 1962. McGraw-Hill, London.
8. N. Lakshminarayanaiah, Transport Phenomena in Membranes, Academic Press, 1969, New York.
9. N. N. Li, Al.Ch.E.J., 1971, 17, 459.
10. S. G. Kimura, S. L. Matson, in Recent Developments in Separation Sceince, ed. N.N. Li, 1979, 5, CRC Press, Boca Raton, Florida.
11. D. S. Flett, Ion Exchange Membranes, 1983. Ellis Horwood Chichester, UK.
12. R. Kunin, Ion-Exchange Resins, 1958, Wiley-Interscience, New York.
13. W. Juda, W. A. McRac, US Pat., 1953, 2636851.
14. K. Ogeni, C. Kanda, JP., 1958, 1897.

15. T. Sata et al, US. Pat., 1972, 3647086.

16. F. de Korosy , Y. Schorr, US. Pat.,1963, 891562.

17. P. Zschocke, D. Quellmalz, J. Memb. Sci.,1985, 22, 325.

18. A. E. Allegrezza, E. C. Bellantoni, Proc.Int.Conf.Memb., 1990, Chicago, 426.

19. L. K. Silva et al., Proc.Int.Conf.Memb., 1990, Chicago, 1143.

20. G. Bodamer, US. Pats.,1954, 2681319, 2681320.

21. H. Patnode, M. Wyllie, US. Pat., 1952, 2614976.

22. M. R. J. Wyllie, H. Patnode, J. Phys. Chem., 1950, 54, 204.

23. M. R. J. Wyllie, S. Kannan, J. Phys. Chem., 1954, 58, 73.

24. D. Woermann, K. Bonhoeffer , F. Helfferich, Z. Physik. Chem., 1956, 8, 265.

25. T. Kressman, Nature, 1950, 165, 568.

26. W. Juda, W. Mc Rac, U.S. Pats., 1953, 2636851, 2636852.

27. R. Neihof, J. Phys. Chem., 1954, 58, 916.

28. G. Smets, J. Roevers, W. Van Humbck, J. Appl. Polymer Sci., 1961, 5, 149.

29. G. Mino, S. Kaizerman, E. Ramussen, J. Polymer Sci., 1959, 38, 393.

30. A. Myers et al., J. Appl. Polymer Sci., 1960, 4, 159.

31. W. K. W. Chen, US. Pat., 1966, 3247133.

32. Z. Ogumi, Y. Uchimoto, K. Yasuda, Z. Takehara, Chemistry Letters, 1990, 953.

33. Z. Ogumi, Y. Uchimoto, M. Tsujikawa, Z. Takehara, Chemistry Letters, 1990, 513.

34. R. Kesting, V. Stannet, Makromol. Chem., 1963, 65, 247.

35. K. Sollner, Biochem. Z., 1932, 244, 370.

36. K. Sollner, R. Neihof, Arch. Biochem. Biophys., 1951, 33, 166.

37. W. Grot, Chem.Ing.Tech., 1975, 47, 617.

38 A. Eisenberg, H. L. Yeager, ACS Symp.Ser., 1982, 180,

39. H. Gregor, K. Sollner, J. Phys. Chem., 1946, 50, 88.

40. A. Michaels, Ind. Eng. Chem., 1965, 57, 32.

41. A. Michaels, R. Miecka, J. Phys. Chem., 1961, 65, 1765.

42. A. Michaels, H. Bixler, R. Hausslein, S. Fleming, OSW Res. Develop. Rept., 1965, December, 149.

43. U. Morten, Desalination by Reverse Osmosis, 1966, MIT Press, Cambridge, Mass.

44. K. S. Spiegler, A. D. K. Laird, Principles of Desalination, 1980, Academic Press, New York.

45. J. S. Schultz, J. D. Goddard, S. R. Suchdes, AlChE. J., 1974, 20, 417.

46. A. Katchaslky, R. Spangler, Q. Rev. Biophys., 1968, 1, 127.

47. M. D. Dumy, A. Lindheimer, C. Gavach, J.Membrane Sci., 1991, 57, 57.

48. W. F. Graydon, R. J. Stewart, J. Phys. Chem., 1955, 59, 86.

49. R. Wycisk, W. M. Trochimezuk, J. Memb. Sci., 1992, 65, 141.

50. F. Drexler, Gluckauf, 1956, 92, 1023.

51. B. Franke, Gluckauf, 1956, 92, 1028.

52. H. Schulze, J. Prakt. Chem., 1882, 25, 431.

53. H. Schulze, J. Prakt. Chem., 1883, 27, 320.

54. C. C. Caldwell, O. B. Wurgburg, US Pat., 1957, 2813093.

55. C. H. Hullinger, N. H. Ui, US Pat., 1961, 2970140.

56. D. A. Jones, G. F. Fanta, R. C. Burr, US Pat., 1972, 3669915.

57. S. D. Faust, J. V. Hunter, Principles and Applications of Water Chemistry, 1967, John Wiley and Sons, Inc., New York.

58. D. W. Frommer, A. F. Colombo, US Pat., 1966, 3292780.

59. J. W. Villar, G. A. Dawe, Min. Cong. J., 1975, 61, 40.

60. A. M. Goldsfein, E. N. Alter, in Industrial Gums, eds., R. L. Whistler, J. N. BeMiller, Acadamic Press, Inc., New York,

1959.

61. N. M. Bikales, Encyclopedia of Polymer Science and Technology VII, 1967, John Wiley and Sons, Inc., New York.
62. P. D. Word, C. A. Ward, A. Courts, Science and Technology of Gelatin, 1977, Academic Press, London.
63. Gelatin, Gelatin Manufacturers Institute of America Inc., 1973, New York.
64. A. Standen, Encyclopedia of Chemical Technology, 1968, 17, Wiley-Interscience, New York.
65. R. A. A. Muzarelli, Chitin, 1977, Porgamom Press, New York.
66. O. Berger, Br. Pat., 1973, 1310491.
67. Chemistry of Acrylamide, American Cyanamid Company, 1969, Wayne, NJ.
68. N. M. Bikales, Water Soluble Polymers, 1973, Plenum Press, New York.
69. W. M. Kulicke, J. Klein, Die Angew. Makromol. Chem., 1977. 69, 169.
70. K. L. Gardner, W.R. Murphy, T. G. Geehan, J. Appl. Polym. Sci., 1978, 22, 88.
71. W. P. Shyluk, F. S. Stow Jr., J. Appl. Polym. Sci., 1969, 13, 1073.
72. A. M. Schiller, T. J. Suen, Ind. Eng. Chem., 1956, 48, 2132.
73. Union Carbide Product Bulletin, 1973, F-44029 A, Union Carbide Corporation, New York.
74. F. N. Hill, F. E. Bailey Jr., J. T. Fitzpatrik, Ind. Eng. Chem., 1958, 50, 5.
75. F. E. Bailey, F. N. Hill, US Pat., 1961, 2987489.
76. F. E. Bailey, F. N. Hill, US Pat., 1966, 3271328.
77. N. M. Bikales, Encyclopedia of Polymer Science and Technology,

VI, 1967, Interscience, New York.

78. N. M. Bikales, Encyclopedia of Polymer Science and Technology, XIV, 1974.

79. G. J. Fleer, L. R. Koopal, J. Lyklema, Kolloid Z., 1972, 250, 689.

80. G. J. Fleer, J. Lyklema, J. Colloid Interface Sci., 1974, 46, 1; 1976, 55, 228.

81. W. L. K. Schwoyer, Polyelectrolyte for Water and Wastewater Treatment, 1981, CRC Press, Inc., Florida.

82. D. A. Kangas, W. R. Neuendorf, US Pat., 1976, 3947396.

83. F. E. Bailey, E. M. La Combe, J. Macromol. Sci. Chem., 1970, A4, 1293.

84. M. F. Hoover, J. Macromol. Sci. Chem., 1970, A4, 1327.

85. D. W. Jayne, Jr., N. M. Day, S. E. Erickson, Br. Pat., 1936, 454723.

86. D. W. Jayne Jr., N. M. Day, S. E. Erickson, US Pat., 1944, 232201.

87. D. G. Garms, US Pat., 1966, 3275588.

88. K. G. Philips, Fr. Pat., 1966, 1449204.

89. N. M. Bikales, Encyclopedia of Polymer Science and Technology, X, 1969, John Wiley and Sons, Inc., New York.

90. T. Saegusa, H. Idoda, H. Fujii, Polym. J., 1972, 3, 35.

91. O. C. Dermer, G. E. Hem, Ethyleneimine and Other Aziridines, 1969, Academic Press, Inc., New York.

92. M. Ku, J. Colloid Interface Sci., 1976, 56, 596.

93. H. P. Panzer, R. Rubinowitz, US Pat., 1973, 3725312.

94. H. P. Panzer, K. W. Dixon, US Pat., 1973, 3738445.

95. D. E. Nagy, US Pat., 1971, 3567659.

96. J. Hasek et al, Listy Cukrov, 1977, 93, 104.

97. H. P. Wohnsiedler, W. M. Thomas, US Pat., 1944, 2345543.

98. A. Renner, US Pat., 1973, 3716483.

99. R. Schwarz, T. Hennig, Belg. Pat., 1956, 549049.

100. R. Schwarz, T. Hennig, Ger. Offen, 1967, 1243646.

101. J. J. Odum, T. P. Shumaker, P. R. Bloomquist, US Pat., 1969, 3484887.

102. R. W. Auten, Tappi, Sepec, Tech. Assoc. Publ., 1948, 31, 468.

103. A. M. Schiller, T. J. Suen, Ind. Eng. Chem., 1956, 48, 21312.

104. T. J. Suen, A. M. Schiller, US Pat., 1965, 3171805.

105. R. L. Wisner, US Pat., 1970, 3539535.

106. C. J. McDonald, R. H. Beaver, Macromolecules, 1979, 12, 203.

108. M. J. Hurwitz, H. Aschkenasy, US Pat., 1968, 3406139.

109. G. B. Butler, US Pat., 1966, 3288770.

110. J. E. Boothe, H. G. Flock, M. J. Hoover, J. Macromol. Sci. Chem., 1970, A4, 1419.

111. R. H. Yocum, E. B. Nyquist, Functional Monomers, II, 1974, Marcel Dekker, Inc., New York.

112. M. C. Clarke, Br. Polym. J., 1990, 22, 47.

113. T. E. Durocher, US. Pat., 1967, 3336271.

114. W. E. Walles, J. Colloid Interface Sci., 1971, 37, 364.

115. G. D. Jones, US. Pat., 1959, 2909508.

116. D. J. Monagle, US. Pat., 1971, 3617572.

117. D. L. Murfin, L. E. Miller, US, Pat., 1969, 3478091.

118. L. E. Miller, D. L. Murfin, US. Pat., 1970, 3506707.

119. D. I. Hoke, US Pat., 1972, 3692673.

120. L. J. Persinski, P. H. Raltson, Gorden Jr., US Pat., 1975, 3898037.

121. K. R. Lange, R. H. Schicsser, R. G. Tonkyn, R. T. Dean, US. Pat., 1975, 3898037.

122. A. S. Teot, US, Pat., 1973, 3770390.

123. D. J. Pye, US Pat., 1968, 3399725.

124. P. M. Quinilan, US Pat., 1978, 4080375.

125. P. M. Quinilan, US Pat., 1977, 4035412.

126. P. M. Quinilan, US Pat., 1977, 4051110.

127. J. P. Friend, J. A. Kitchener, Chem. Eng.Sci., 1973, 28, 1071

128. Y. A. Attia, D. W. Fuerstenau, Recent Development in Separation Science IV, CREC, Florida.

129. G. L. Greenfield, US. Pat., 1974, 3787488.

130. G. L. Greenfield, US. Pat., 1975, 3904522.

131. H. L. Rice, A. Cizek, M. O. Thaemër, US. Pat. 1972, 3665035.

132. L. E. Dannals, US. Pat., 1972, 3646099.

133. J. T. Godlewski, J. J. Schuck, B. L. Libutti, US. Pat., 1977, 4029577.

134. J.L. Lang, W. A. Parelich, H. D. Clarey, J. Polym. Sci., 1961, 55, 531.

135. C. J. Lancelot, J. H. Blumberge ,D. G. Mackellar, Brit.Pat., 1974,1349769.

136. C. C. Cochrane, US Pat., 1969, 3427233.

137. J. L. Lang, W. A. Parelich, US. Pat., 1965, 3186972.

138. Y. Shahab, A. Mohamed, A. Khettab, A. Siddiq, Eur. Polym., 1991, 27, 227.

139. J. M. G. Cowie, Alternating Copolymers, 1985, Plenum Press, New York.

140. E. Cocca, M. Grigorous, M. Tantoreann, CA, 1966, 64, 19800.

141. S. Nakanishi, H. Hisayana, JP., 1961, 17839.

142. E. H. Land, E. R. Blant, H.C. Hans, US. Pat., 1958, 2830900 .

143. P. E. Hoch, P. Robitschek, US. Pat., 1961, 2978402.

144. Sekismi Kogaku Kagyo Kabushiki Kerisha, Br.Pat., 1965,

994725.

145. A. M. Stephenson, US. Pat., 1966, 3256141.

146. M. J. Jursich, G. T. Randich, US. Pat., 1969, 3450680.

147. G. B. M. Dickakian, US. Pat., 1970, 3 511816.

148. Food and Drug Administration, 21 CPR 176-180, 1977.

149. Anon, Gulf PA-18, Chem. Eng. News, 1977, 38.

150. A. C. Perricene, H. F. Young, 1973, US. Pat., 3730900.

151. L. J. Perinski, F. D. Martin, S. L. Adams, US. Pat., 1976, 3952805.

152. D. H. Cuisia, C. H. Hwa, US. Pat., 1977, 4048066.

153. R. J. Pratt, R. K. Diefenbach, US. Pat., 1970, 3507787.

154. R. J. Pratt, R. J. Conboy, 1970, US. Pat., 1970, 3520 892.

155. R. M. Summers, US. Pat., 1961, 2 967175.

156. T. Uragami, S. Watanabe, R. Nakamura, F. Yoshida, M. Sugihara, J. Appl. Polym. Sci., 1983,28, 1613.

157. T. Uragami, S. Watanabe, R. Nakamura, M. Sugihara Polym. Bull., 1982, 7, 71.

158. T. Wada, T. Uragami, M. Sugihara, Polym. Bull., 1985, 14, 219.

159. T. Uragami, S. Watanabe, M. Sugihara, Angew. Makromol. Chem., 1982, 107, 209.

160. T. Uragami, S. Watanabe, M. Sugihara, J. Polym. Sci. Polym. Chem. Ed., 1982, 20, 1193.

161. T. Uragami, S. Watanabe, M. Sugihara Makromol. Chem. Rapid Commun., 1982, 3, 141.

162. T. Uragami, K. Moriyama, M. Yamamoto, M. Sugihara, Makromol. Chem., 1987, 187, 583 .

163. K. Fukuda, S. Suzuc, S. Kakinchi, Chem. Soc. Jpn., 1983, 880 .

164. S. Iwabuchi, T. Nakahira, H. Ando, H. Kawaguchi, M. Murakoshi K. Kojima, Polym. Commun., 1989, 30, 58.

165. T. Abullaev, M. A. Khakimova, A. Asnnov, USSR Pat., 1981, 842041 .

166. Ger. Offen. DE., 1982, 3024325.

167. G. Irena, Z. Danuta, Pol. PL., 1981, 110037.

168. M. A. Umarava, A. M. Karimova, M. A. Askarov, Uzb. Khim. Zh., 1981,6, 37.

169. K. Kanderi, A. Kitahara, K. Kon-no, Bull. Chem. Soc. Jpn., 1983, 56, 1581.

170. V. N. Bilichenko, Yu. G. Tarasonko, I. A. Uskov, L. V. Gofman, USSR, SU, 1983, 992540.

171. W. Waclaw, V. Alicja, Polimery, 1983, 28, 153.

172. W. Waclaw , V. Alicja, Polimery, 1984, 29, 114.

173. Agony of Industrial Science and Technology, JP., 1982, 57192463 .

174. K. Eiichi, P. Junji, Kocoshu Kyete Daigaku Nippon Kogaku Senii Kenkyusho, 1981, 38, 103.

175. M. K. Dhandukia, V. K. Indusekhar, K. P. Govindan , Indian J. Tech., 1982, 20, 203.

176. R. Mendez, V. N. S. Pillai, Analyst, 1990, 115, 213.

177. R. Mendez, V. N. S. Pillai, Talanta, 1990, 37, 591.

178. A. Asanov, V. V. Zinoveva, K. S. Akhmedov Dokl., Akad. Nauk., USSR, 1985, 2, 31.

179. A. Asanov, U.V. Sinoveva, K.S. Akhemedov Dokl. Akad. Nauk., USSR, 1985, 2, 38.

180. C. W. Yen, C.H. Min, J. Appl. Polym. Sci., 1988, 36, 1979.

181. S. Dieter et al, Ger (EoA) DD., 1990, 282, 444.

182. T. Uragami, T. Tamura, Makromolekulure Chemie- Macromolecular Chemistry and Physics, 1993, 194, 1027.

CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF POLYELECTROLYTES

ABSTRACT

Poly(styrene-*co*-maleic acid) (PSMA) with varying acid content were prepared by free radical polymerization. Hydroxamic acid derivative (PSMH) was prepared by the acid chloride route. The polyelectrolytes were characterized by infrared spectroscopy, acid content and viscosity average molecular weight. The effect of pH and added electrolytes on the viscosity of the polymer solutions are discussed.

2.1 INTRODUCTION

Water soluble high molecular weight polyelectrolytes have been attracting increasing attention because of their industrial application. Preeminent among these is their ability to flocculate suspended solids(1). Other important applications are in petroleum recovery, drag reduction, and as components of water based finishes developed in response to environmental constraints(2). Polyelectrolytes in solution exhibit properties which are quite different from those of non-ionizable polymers. It is well established that the main factors contributing to the effectiveness of such polymers are molecular flexibility, high molecular weight and high solubility. In non-ionizing solvents, they behave in the normal fashion whereas in aqueous solutions, they are ionized and exhibit significantly different properties(3). An important difference lies in the manner in which the reduced viscosity depends on concentration. The reduced viscosity of uncharged polymers increase linearly with increasing polymer concentration, whereas in the case of polyelectrolytes, the reduced viscosity increases with decreasing concentration.

2.2 EXPERIMENTAL

2.2.1 Synthesis of poly(styrene-co-maleic acid) (PSMA)

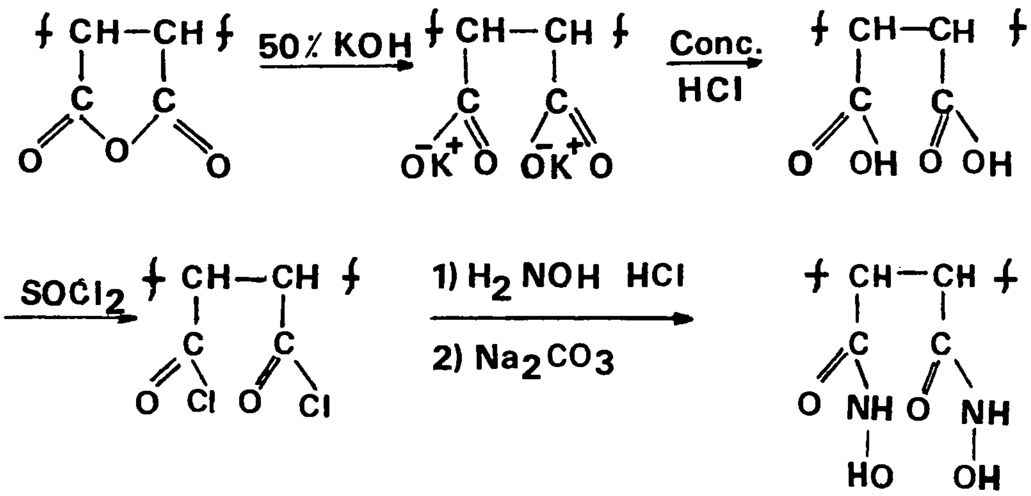
Poly(styrene-*co*-maleic anhydride) (PSMA) was prepared by a modification of the method of Shahab et al(4).

Maleic anhydride was purified by vacuum distillation. Stabilizers were removed from styrene by extracting with aqueous

OH solution (1%). The monomers were taken in different mole tios, and mixed with benzoyl peroxide (0.05 wt %) in clohexanone. The mixture was refluxed on a boiling water bath r 4 h. The polymer was precipitated by adding methanol, iltered and washed with methanol. The polymer was purified by peated precipitation and dried in vacuum at 80^{o}C.

The copolymers were hydrolysed by refluxing with excess 10 M NaOH for 10 h . The free acid polymers (PSMA) were recipitated with concentrated hydrochloric acid. The product was ashed with water, dried in vacuum at 80^{o}C for 10 h.

.2.2 Preparation of hydroxamic acid (PSMH)



SCHEME OF CONVERSION OF COPOLYMER TO HYDROXAMIC ACID

Hydroxamic acid derivative (PSMH) of the polymer was prepared by acid chloride route (5). The dry acid sample with highest maleic acid content was refluxed with excess of thionyl chloride on a boiling water bath for 3 h, with intermittent stirring. The excess of thionyl chloride was distilled off under reduced pressure.

To 1 g of acid chloride was added 2.1 g of sodium carbonate, 1.4 g of hydroxylammonium chloride, 10 ml of diethyl ether and 2.5 ml of water. The mixture was stirred for 3 h, the product was filtered off, washed with methanol, and dried in vacuum at 80°C for 8 h.

2.2.3 Polymer characterization

The polymers were characterized by infrared spectroscopy, carboxylic content, molecular weight and dilute solution viscosity.

(a) Determination of carboxylic acid content

The carboxylic acid content of PSMA samples as well as that of the PSMH sample was determined.

About 500 mg of dry sample was accurately weighed and equilibrated with 40 ml 0.5 M NaOH solution for 6 h. The filtrate was titrated against hydrochloric acid. The free carboxylic acid content was calculated using equation 2.1.

where

V_1 = titre for NaOH (ml)

V_2 = titre for sample + NaOH (ml)

N = normality of HCl

W = weight of sample taken (g)

(b) Viscosity measurements

Viscosity average molecular weight was estimated by the solution viscosity method using an Ubbelhode viscometer(6). THF was used as solvent and molecular weight was calculated using the Mark-Houwink equation (2.2).

$$[\eta] = 3.98 \times 10^{-4}\, \bar{M}v^{0.596} \quad (2.2)$$

where

$[\eta]$ = intrinsic viscosity

$\bar{M}v$ = viscosity average molecular weight

Dilute solution viscosity measurements were carried in aqueous medium at different concentrations in the temperature range 30 to 50°C. Effect of monomer content, pH, and added electrolytes on the rheological characteristics of the polymer was evaluated.

2.3 RESULTS AND DISCUSSIONS

Viscosity average molecular weight and acid content of polymer samples prepared are given in Table 2.1.

2.3.1 Infrared spectra

The infrared spectral data of PSMAn,PSMA and PSMH are given in Table 2.2.

IR peaks at 1856 and 1779 cm^{-1} for cyclic anhydride found in PSMAn are absent in PSMA and PSMH. Peaks at 3400 and 1400 cm^{-1} due to the presence of -COOH groups are present in PSMA and PSMH. Additional peaks at 1654, 1562, 1250 and 1085 cm^{-1} due to the presence of -CONHOH confirms the conversion of anhydride into hydroxamic acid(7).

2.3.2 Dilute solution viscosity measurements

Reduced viscosity (η_{red}) of polymer solutions was calculated using the following equation (8).

$$\eta_{red} = \frac{t-t_0}{Ct_0} \quad dlg^{-1} \qquad (2.3)$$

where

C = polymer concentration (gdl^{-1})

t = efflux time of polymer solution (s)

t_0 = efflux time of solvent(s)

The viscosities of dilute polyelectrolyte solutions measured in salt-free water or at very low salt concentration have led to the following empirical relationship (9).

$$\eta_{red} = D + A(1+BC^{0.5})^{-1} \qquad (2.4)$$

Table 2.1 Characteristics of the polymer samples used in the study.

Polymer	Functional group	Viscosity average molecular weight x 10^{-6}	Acid content (meq/g)
F_1	-COOH	2.4	7.8
F_2	-COOH	3.1	5.6
F_3	-COOH	2.1	3.2
F_4	-CONHOH	2.4	
	-COOH		3.6

Table 2.2 IR spectral band assignment for the polymer samples.

Band frequency (cm^{-1})			Assignment of relevant bands
PSMAn	PSMA	PSMH	
	3400	3400	OH,COOH (bound water)
1856			Cyclic anhydride (strain)
1779			Cyclic anhydride (strain)
		1654	C = O (Hydroxamic acid) (stretching)
		1562	N-H (bending)
1495	1495	1495	C-C (Ar)
	1400	1400	C =O (stretching) [COOH] OH (bending) [COOH]
		1259	C-N (stretching)
		1085	N-O

where D, A and B are constants for polyelectrolytes.

According to this expression, the reduced viscosity should increase when the polyelectrolyte concentration decreases. Consequently, it is not possible to obtain the intrinsic viscosity of the polyelectrolyte [η] from the limit of reduced viscosity at infinite dilution, The main difference between a polyelectrolyte and a non-ionic polymer lies in the behavior of their reduced viscosity. The reduced viscosity of the uncharged polymer increases linearly with increasing polymer concentration, whereas in the case of polyelectrolytes, the reduced viscosity increases with decreasing concentration.

The viscosity measurements have been carried out for different concentrations of PSMA and PSMH solutions in water , at various temperatures. Figures 2.1 to 2.4 shows the dependence of reduced viscosity of polymer concentration. It is evident that the reduced viscosity increases considerably with dilution. This tendency gradually decreases with decreasing acid content. In the case of PSMH, reduced viscosity decreases on dilution. The upswing is assumed to be due the electrostatic repulsion between like charges on polymer molecule. Consequently the chain undergoes a stretching. This tendency becomes less pronounced as the -COOH content of the polymer decreases. This may be due to the reduced electrostatic repulsion of the polar groups and hence less effective stretching of the polymer chain. The PSMH which shows linear decrease in reduced viscosity with dilution and resembles non-ionic polymer in this respect.

The dependence of pH on reduced viscosity is illustrated in figure 2.5. The reduced viscosity increases considerably with pH. The effect decreases with decreasing charge content of the

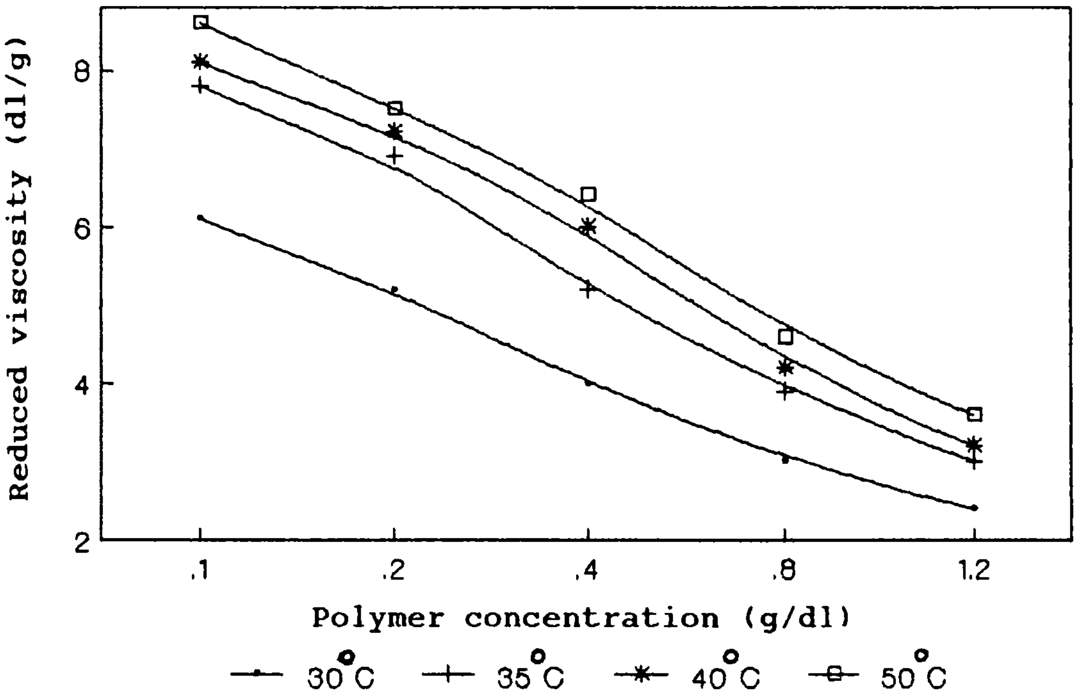


Figure 2.1 Effect of polymer concentration on the reduced viscosity of F_1 at different temperatures.

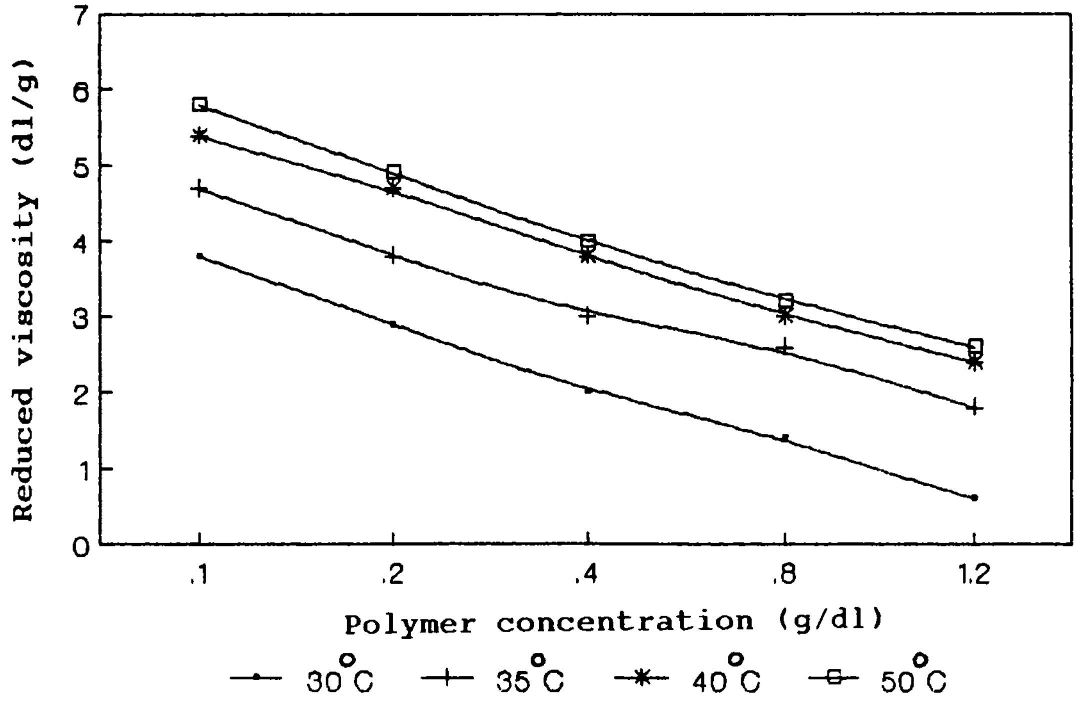


Figure 2.2 Effect of polymer concentration on the reduced viscosity of F_2 at different temperatures.

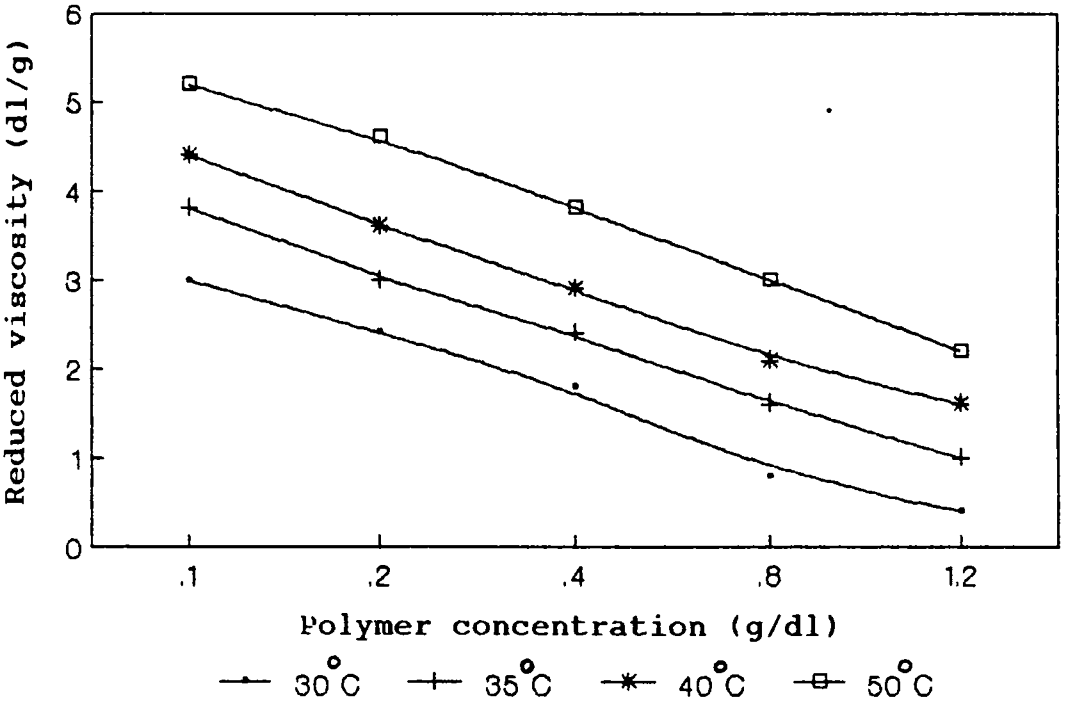


Figure 2.3 Effect of polymer concentration on the reduced viscosity of F_3 at different temperatures.

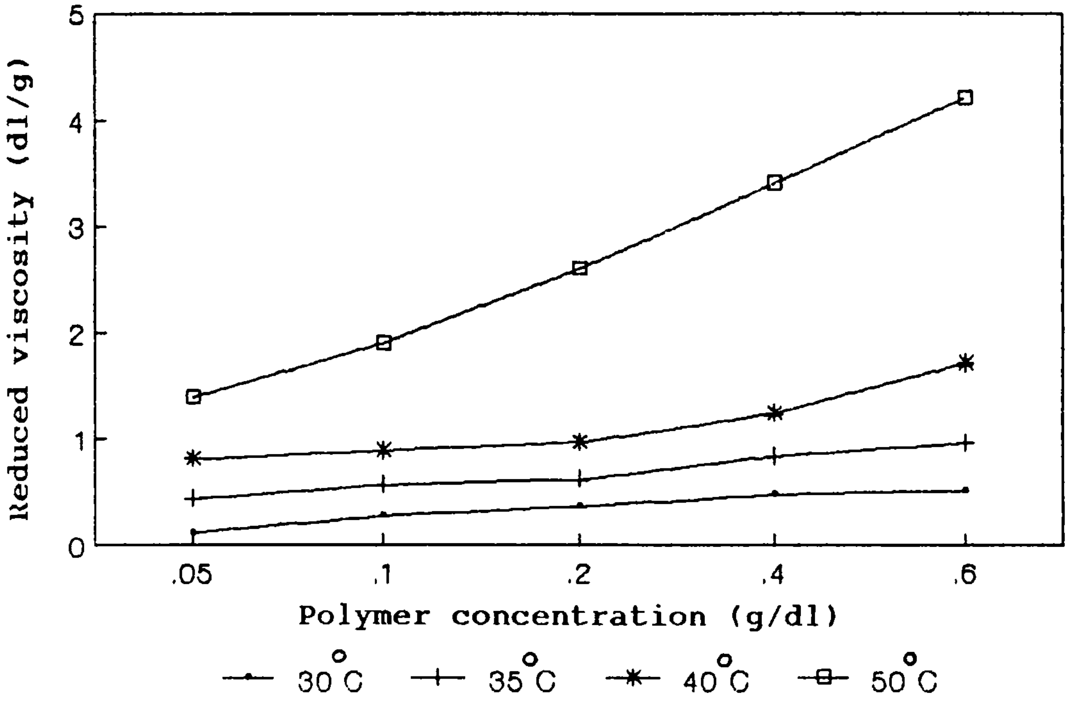
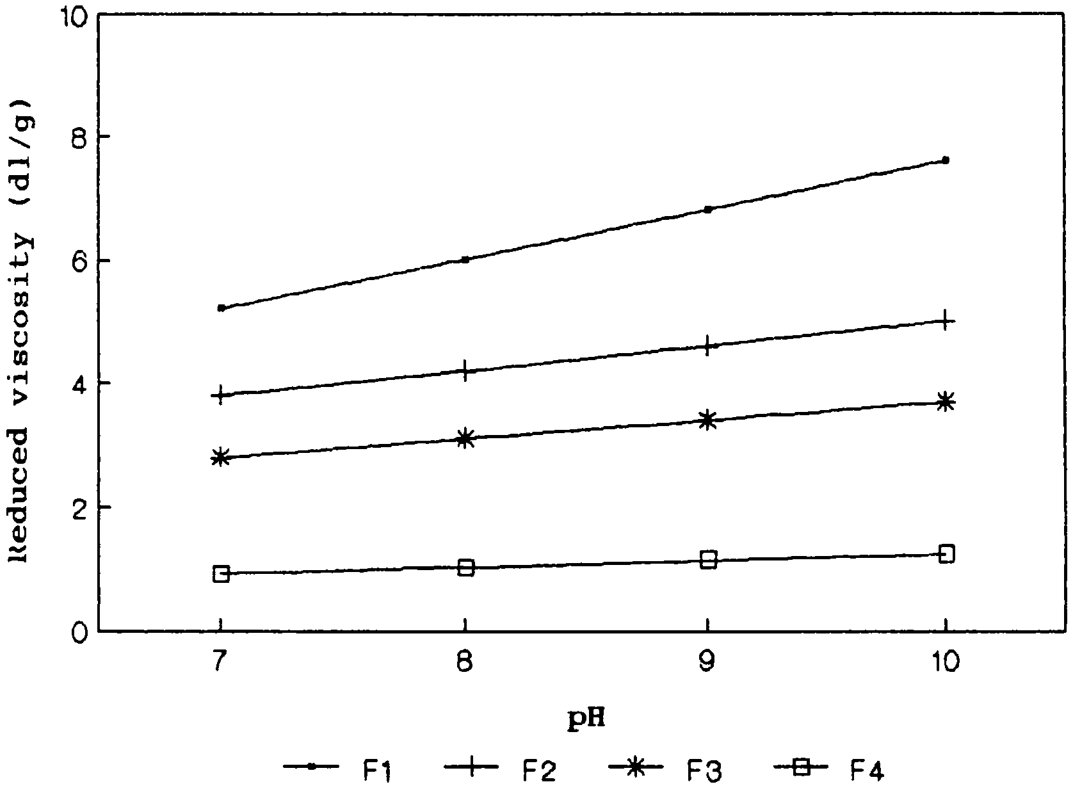


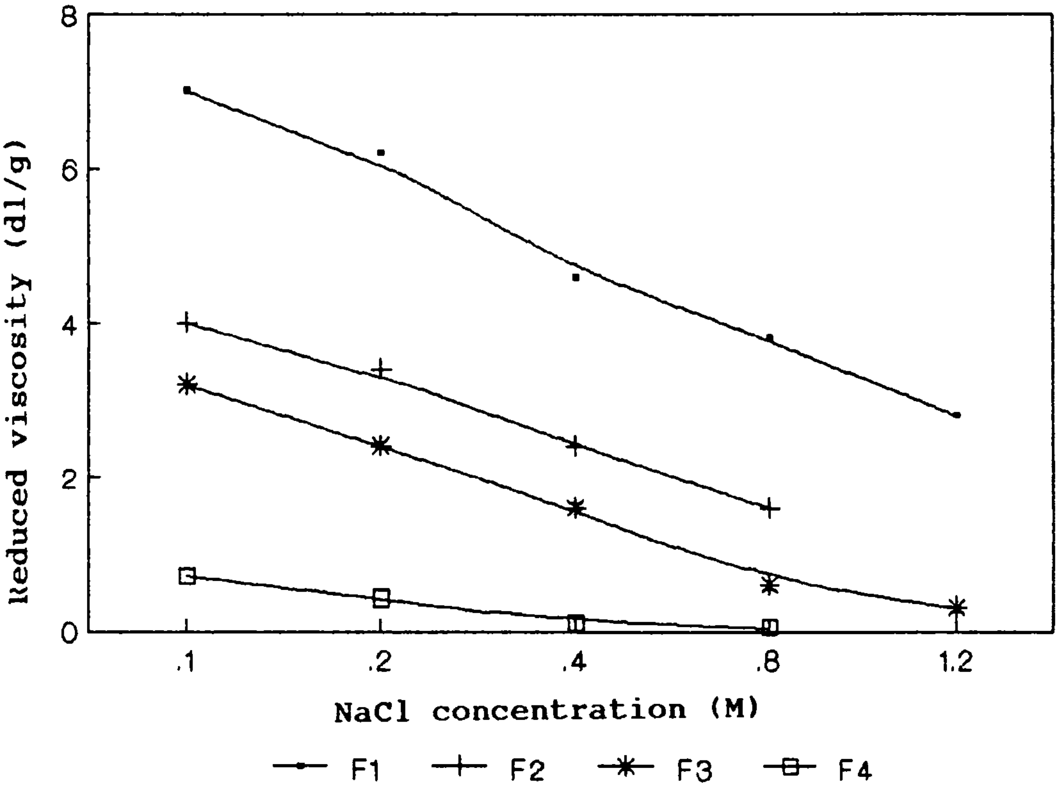
Figure 2.4 Effect of polymer concentration on the reduced viscosity of F_4 at different temperatures.



2.5 Effect of pH on the reduced viscosity of the polymer samples at 30°C.

polymer. This may be due the dissociation of -COOH groups at higher pH. Ionization leads to change in polymer rheology by uncoiling the chain due to the electrostatic repulsion of ionized groups.

At high ionic strengths, the charged groups on the polymer are shielded and the polymer will coil up. A decrease in reduced viscosity of polyelectrolytes is observed as the salt concentration is increased. Figure 2.6 shows the influence of sodium chloride, while 2.7 shows the influence of calcium chloride on the polymer's reduced viscosity. As expected, polyvalent ions such as calcium have a much greater impact on the solution viscosity. It is also observed that the effect decreases with decreasing acid content on the polymer. Figure 2.8 shows the the effect of added NaCl on the viscosity of the PSMA (7.8 meq/g). It is seen that reduced viscosity increases sharply with decreasing polymer concentration in salt free solutions. By adding a salt like $CaCl_2$ reduced viscosity decreases with dilution. This may be explained on the basis of the screening of ionic charges along the polymer chain by counterions.



2.6 Effect of NaCl concentration on the reduced viscosity at 30°C.

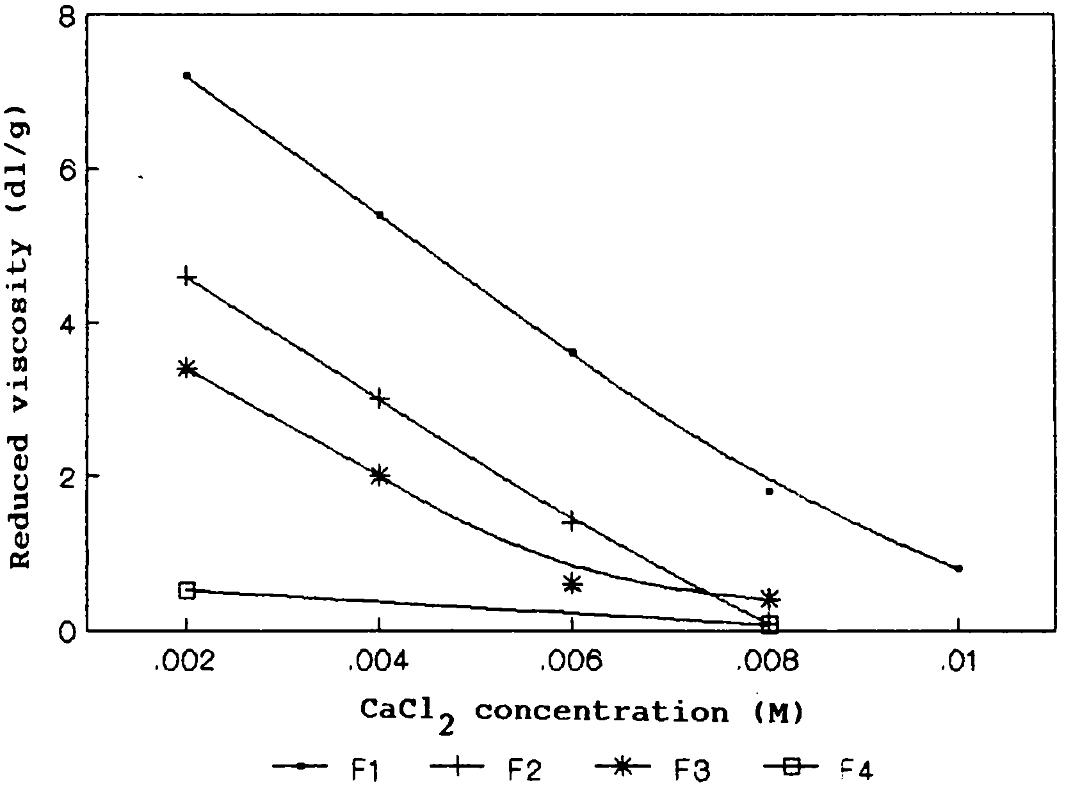
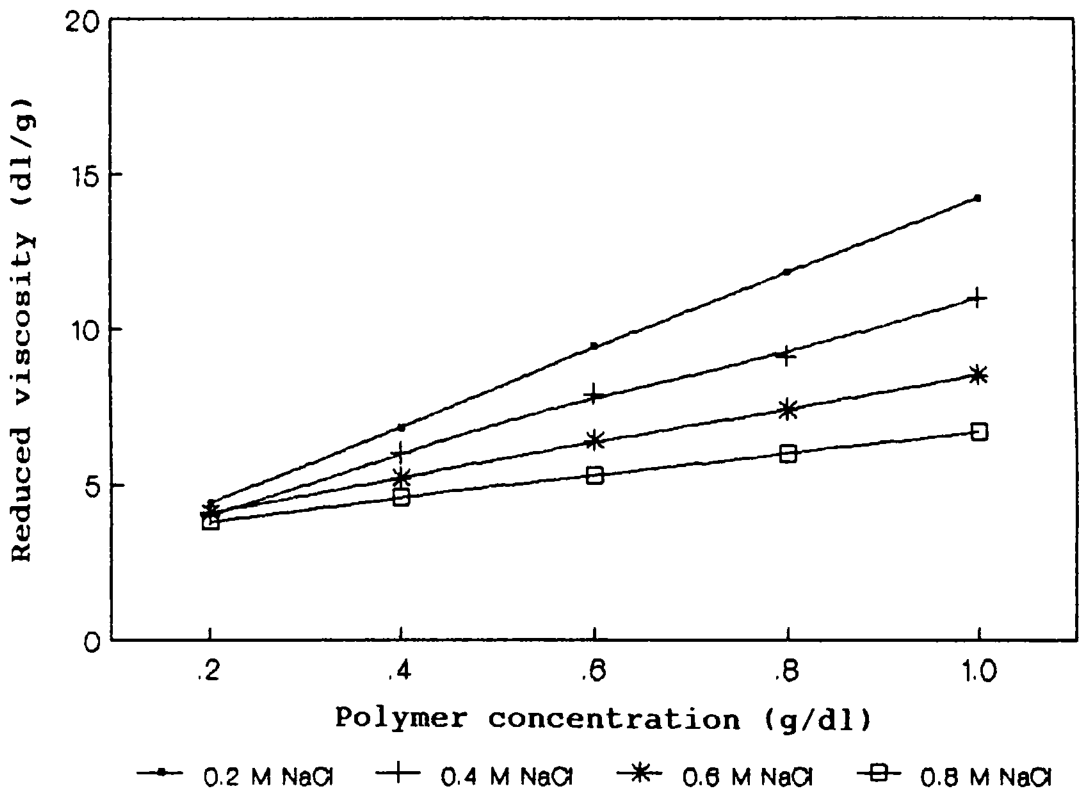


Figure 2.7 Effect of $CaCl_2$ concentration on reduced viscosity at 30°C.



gure 2.8 Effect of polymer dosage on reduced viscosity of F_1 at different concentrations of NaCl.

REFERENCES

1. W. L. K. Schwoyer, Polyelectrolytes for Water and Wastewater Treatment, 1981, CRC Press, Inc., US.
2. N. M. Bikales, Polymer Science and Technology: Water Soluble Polymers, 1973, Plenum, London.
3. M. J. Parets, R. Garcia, V. Soria, A. Campos, Eur. Polymer J., 1990, 26, 767.
4. V. Shahab, A. Mohamed, A. Khettab, A. Siddiq, Eur. Polym. J., 1991, 27, 227.
5. R. Mendez, V. N. S. Pillai, Talanta, 1990, 37, 591.
6. C. D. Chow, J. Appl. Polym. Sci., 1976, 20, 1619.
7. R. M. Silverstein, G. C. Bassler, T. C. Morril, 1981, John Wiley and Sons, New York.
8. J. F. Rabek, Experimental Methods in Polymer Chemistry, 1980, John Wiley and Sons, New York.
9. R. M. Fuoss, G. I. Cathers, J. Polym. 1949, 4, 97.

CHAPTER - III

POLY(STYRENE-CO-MALEIC ACID) MEMBRANES

ABSTRACT

Ion-exchange membranes were prepared by cross-linking PSMA with Al^{+3} ions, ethylenediamine, and poly(vinyl alcohol). Different membranes were obtained by varying monomer concentration and preparation conditions. The membranes were characterized by measuring thickness, water content, mechanical strength, electrical resistance, membrane potential and permeability coefficients of different solutes. The ion-exchange capacity varied from 2 to 6 meq/g for different membranes. Membrane resistance decreases with increasing pH owing to the dissociation of -COOH groups. Burst strength, was measured as a function of exchange capacity. Transport number and permselectivity values were evaluated from the membrane potential data. Membrane potential studies reveal that these membranes are highly permselective towards cations. The permselectivity values decrease with increasing solute concentration. The effect of pH on permselectivity was also evaluated. All the membranes show good permeability to NaOH, KCl and Na_2SO_4 and low permeability to urea and creatinine. Due to the difference in anion mobility and size, the permeability coefficients of alkali metal salts are higher than that of neutral solutes. Mean transport rate, transport fraction and selectivity were obtained from active and selective transport of Na^+ and K^+ through the membranes. The membranes also show selectivity to K^+ over Na^+.

3.1 INTRODUCTION

Membranes constitute a relatively recent addition to the materials available for separation process. Improvements in the structural and engineering properties of membranes have greatly enhanced their attractive economics and applicability. They have already captured the attention of several areas such as pharmaceutical, medical and food industries, biotechnology, water purification and demineralization. Although membranes and membrane processes were first introduced as an analytical tool in chemical and biochemical laboratories, they were very rapidly transformed to industrial products with significant technical and commercial impact(1). Today, membranes are used on a large scale to produce potable water from the sea, to clean industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular solutions in the food and drug industries, to remove urea and toxins from the blood stream, and to release drugs at a controlled rate.

Membrane process offers significant advantages over conventional separation techniques like distillation, precipitation, crystallization, extraction, adsorption and ion-exchange. The process is modest in energy requirements, in most cases more economical and simpler, more efficient and faster. They do not produce wastes. Separation is performed by physical means at ambient temperature without damaging or chemically altering the constituents. This is important in food and drug industries, as well as in the downstream processing of bioproducts where temperature-sensitive substances are often handled. The technique is equally suited for large scale continuous operations as well as batchwise treatment of very small quantities.

Separation process using ion-exchange membranes constitutes an important class. Electro-dialysis is by far the most important industrial membrane separation process. Here an electrical potential gradient acts as driving force. Others include electrolysis for the production of chlorine and caustic soda, electrodialysis with bipolar membranes for the production of acids and bases from the corresponding salts or a combination of conventional electrodialysis with regular ion exchange techniques to produce ultrapure water. Other areas where ion-exchange membranes find application include batteries, fuel cells, controlled release devices, artificial kidneys and sensors(2,3).

Preparing ion-exchange membranes with adequate operational characteristics like exchange capacity, ion selectivity, electrical conductivity and mechanical strength is a difficult task. Homogeneous membranes have good electrical properties but in general have only poor mechanical strength. An improvement in electrical properties will often adversely affect their stability (4). The insolubility and mutual incompatibility of the component polymers is the main constraint in the preparation of interpolymer mebranes. Impregnation produces membranes showing irreproducible results. Ionically cross-linked polyelectrolytes are used in dialysis and reverse osmosis, and in general these membranes have high electrical resistance(5). A survey of the literature has shown that the development of ion-exchange membranes with advantageous properties depends not only on the selection of polymeric matrix and fixed ionic groups but also on the cross-linking agent and the reinforcing material (6).

Preparation and characterization of ion-exchange membranes produced from poly(styrene-*co*-maleic acid) (PSMA) is described in this chapter. Membranes were prepared by cross-linking PSMA with, Al^{+3} ions, ethylene diamine (EDA) and poly(vinyl alcohol) (PVA). Membranes were characterized by different physico- chemical techniques.

3.2 EXPERIMENTAL

3.2.1 Membrane preparation

Poly(styrene-*co*-maleic acid) (PSMA) with 1:1 monomer ratio prepared by free radical polymerization described in the section 2.2.1 was used for the membrane preparation. Membranes with different cross-linking agents under different conditions were prepared by a dry technique(7).

(a) PSMA - Al membranes

A solution of $AlCl_3.6H2O$ in DMF (4-10 Wt.% with respect to PSMA) was added to 5 ml of a 10% solution of PSMA in DMF. The mixture was stirred for 6 h. The solution was cast on a petridish and heated in an oven at 60 to 90 °C. The plate was cooled to room temperature and then immersed in distilled water overnight. The film was removed and stored in distilled water at room temperature.

(b) PSMA-EDA membranes

A solution of ethylene diamine in DMF (0.5-5 Wt.% with respect to PSMA) was added to PSMA solution in DMF with stirring. After all the insolubles disappeared, the solution was cast on a petridish and heated to 60°C for 4 h. The remaining procedure was the same as that for the preparation of PSMA-Al membranes.

(c) PSMA-PVA membranes

To a DMF solution containing PSMAn and PVA (10-50 Wt.% with respect to PSMAn) triethylamine (10 mg) was added as a catalyst. The mixture was cast on a petridish and membranes were obtained by the procedure outlined in 3.2.1 (a).

3.2.2 Membrane characterization

(a) Pretreatment and equilibration

The counterions associated with the fixed ions in an ion- exchange membrane are changed to selected ionic species by allowing it to come to equilibrium in a solution containing a high concentration of ions of the desired kind.. The reference ionic form of the membrane is designated by this counter ion.

Membranes were converted to Na^+ form by equilibrating with excess of NaOH solution (1 M) for 72 h. The completion of exchange was indicated by a steady residual concentration of alkali. Membranes in H^+ form were prepared by dipping the Na^+ form in HCl acid (1 M) for 24 h. The equilibrated membrane samples were washed with a copious amount of distilled water and kept in distilled water at room temperature.

(b) Thickness

The thickness of the membrane was determined using a micrometer after clasping it between two glass plates. The thickness of the two plates was separately determined in the same way.

(c) Determination of pinholes : The dye solution method

The method permits the detection of small apertures by forcing a solution of food grade dye through the membrane under firm hand wiping pressure into an absorbent white paper (8). The membrane samples were placed on a white absorbent paper. Erythrosein B solution (2.0 g/l) was repeatedly applied on the sample with a sponge. The absence of pinholes was confirmed by the non-appearance of dye spots on the paper.

(d) Water retention capacity

The water retention capacity was determined experimentally by blotting excess water from the surface of a wet membrane sample and weighing before and after drying for 16 h in vacuum oven at 60° C. Water retention capacity was calculated using the following equation (8).

$$\text{Water retention capacity (\%)} = \frac{(W-D)\,100}{W} \qquad (3.1)$$

W = weight of wet sample

D = weight of dry sample

(e) Ion-exchange capacity

Exchange capacity of a membrane is expressed as milliequivalents of exchangeable ions per gram of wet sample. The exchange capacity was found out by equilibrating a weighed sample with NaOH solution and estimating the amount of Na^+ exchanged by titration with standard HCl. Exchange capacity was calculated using the equation (3.2):

$$\text{Ion exchange capacity (meq/g)} = \frac{(C_o - C)V}{W} \qquad (3.2)$$

where Co and C are the NaOH concentration in the blank and in the membrane equilibrated solution, respectively. V(ml) is the volume of 1M NaOH solution consumed by the membrane and W(g) is the weight of dry membrane sample.

(f) Burst strength

Burst strength is expressed as the hydrostatic pressure required to produce rupture on an ion-exchange membrane that has an exposed circular test area 30.5 mm in diameter (8). Burst strength is a measure of the ability of the membrane to resist pressure difference which may occur in applications . The apparatus used to measure burst strength is a clamp cell fabricated according to ASTM standards(8) in Figure 3.1.

Figure 3.1 shows the schematic diagram of the clamp cell for testing burst strength. The upper clamping surface consists of stainless steel ring having a circular opening 30.48 ± 0.02 mm in diameter. The surface that is in contact with the membrane during testing has a continuous spiral 60-degree V-groove, 2.5 mm deep and 0.8 mm pitch. The lower clamping surface has a thickness of 3.25 mm and an opening 33.07 ±0.08 mm in diameter. The surface has a series of concentric 60 - degree V-grooves, 0.3 mm deep, 0.8 mm apart, the centre of the first groove being 3.2 mm from the edge of the opening. The thickness of the plate at the opening is 0.64 mm. The lower edge which is in contact with a rubber diaphragm has 6.4 mm radius.

The membrane sample was clamped around the periphery over a gum rubber diaphragm. Hydrostatic pressure on the diaphragm was increased by increasing the height of the water level at a uniform rate until the membrane material ruptured. The maximum pressure indicated by the water height was recorded as the burst strength.

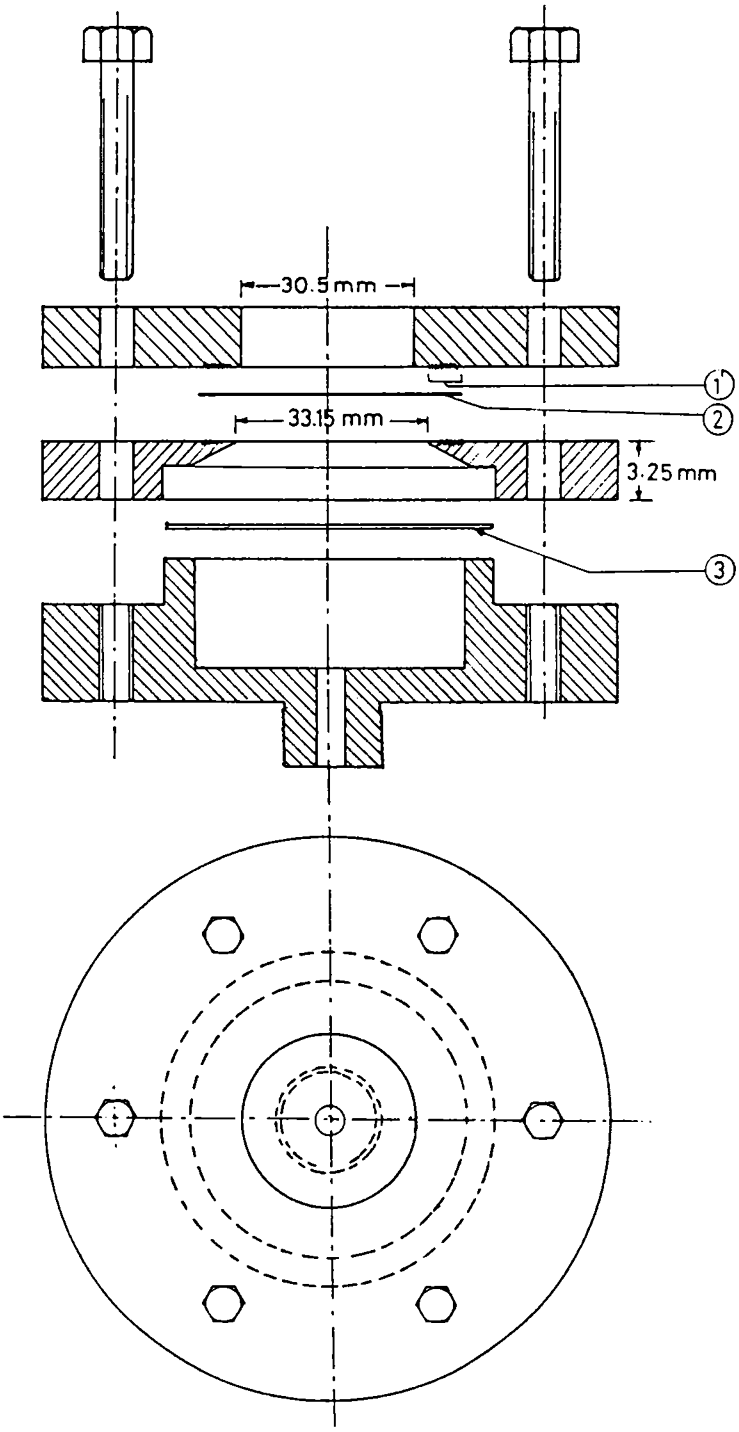


Figure 3.1 Burst strength apparatus
1. V - grooves 2. Membrane 3. Rubber diaphragm

(g) Membrane resistance

Electrical resistance is a measure of the ability of membrane material to carry electric current under an electrical potential which may be applied in electrodialysis and electrolysis. It is expressed as ohm cm^2, which is the electrical resistance of 1 cm^2 of membrane material(8).

Membrane sample was clamped in a cell of the configuration shown in Figure 3.2.

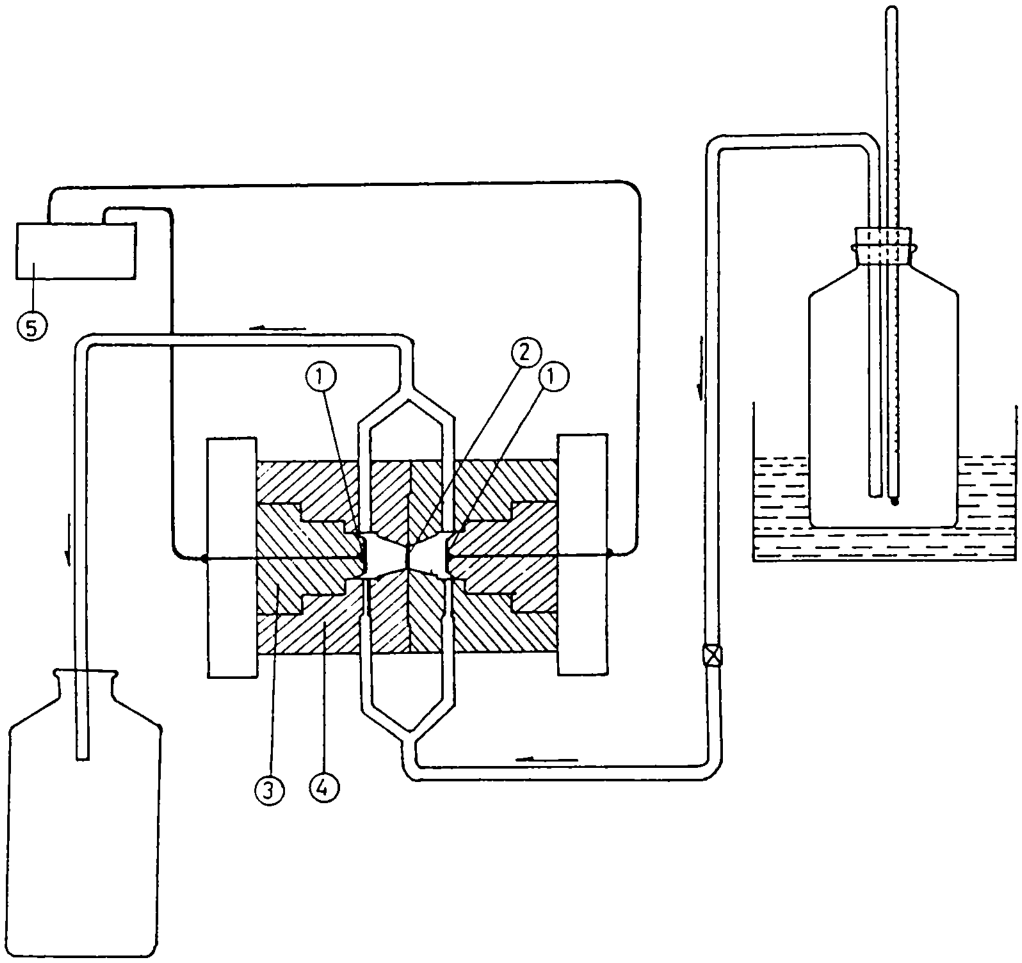
The cell was filled with 0.1N KCl whose pH was adjusted using HCl/KOH. After equilibration, the resistance of the membrane and electrolyte solution was measured using two gold electrodes. The resistance of the cell containing only electrolyte was measured separately. The difference between the two values multiplied by the area of one principal face of the sample exposed to the electrolyte solution gave the resistance of the sample per unit area.

The temperature was maintained at 25 ± 1 °C and the measurements were made using a conductivity meter operating at 1 k Hz. The measurement were replicated and average values are given.

(h) Membrane potential

An electrochemical cell, in which the membrane was placed between two electrolyte solutions was employed to measure the membrane potential (9). The potential was measured using two calomel electrodes equipped with luggin capillary.

$$NaCl_{(C_1M)} \;\vdots\; \text{Membrane} \;\vdots\; NaCl_{(C_2M)}$$



igure 3.2 Membrane resistance cell

1. Gold electrode 2. Membrane 3. Electrode holder

4. Cell body 5. Conductivity cell

All the measurements were made with the solutions at rest. The solutions on the two sides were renewed until further renewal did not cause any change in potential ($\pm$.0.02 mV) over a period of 1 h. In order to overcome the asymmetry of the membrane or the electrodes, all the potentials are reported as average of four measurements (10).

(i) Dialysis experiments

Transport experiments were performed in a two-compartment glass cell (Figure 3.3) thermostated at 30 $\pm$ 1 ^{o}C. The compartments were separated by the membrane. One of the compartments contained the aqueous solution of KCl, NaCl, Na_2SO_4, NaOH, urea or creatinine. An equal volume of distilled water was placed in the other compartment. The contents of the compartments were stirred magnetically using identical stirrers driven by the same motor. At specified intervals, aliquots were withdrawn from both the compartments and the concentration of sodium and potassium were determined by flame photometry. Concentrations of urea and creatinine were measured spectrophotometrically (11).

(j) Active and selective transport of Na+ and K+

For active transport studies of cations, KCl (10^{-2} M) was taken in the right side compartment and an equal volume of KOH (10^{-2} M) was taken in the left side compartment. For selective transport, solutions of 5 x 10^{-3} M with respect to both NaOH and KOH were placed in the left cell and the right cell contained a solution (5 x 10^{-3} M) with respect to both KCl and NaCl. pH of the R side solutions was adjusted using HCl.

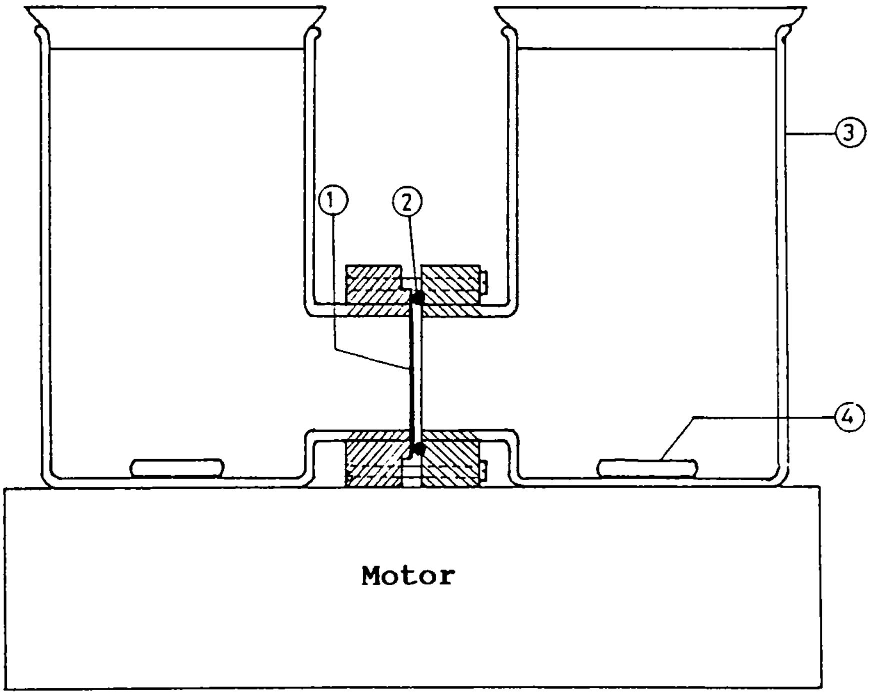


Figure 3.3 Transport cell

1. Membrane 2. Neoprene O' ring 3. Glass cell

4. Magnetic stirrer

3.3 RESULTS AND DISCUSSION

3.3.1 Membrane preparation

The preparation conditions and properties of membranes are summarized in Tables 3.1, 3.2 and 3.3.

In this study the amount of cross-linking agent was controlled so as to retain a considerable concentration of free ionogenic groups on the membranes. Different membranes were prepared by varying curing conditions. All the membranes were found to be colourless and transparent.

3.3.2 Membrane characterization

(a) Ion-exchange capacity and water content

Exchange capacity is a measure of the number of active ion exchange groups available in a membrane sample. Both ion-exchange capacity and water content decrease with increasing cross-linking content. This indicates a decrease in the availability of exchangeable groups in the membrane due to their binding with cross-linking agents.

(b) Membrane resistance

The variation of electrical resistance of the membrane with pH is illustrated in Figures 3.4 to 3.6.

The membrane resistance influenced by the degree of ionization of -COOH groups which, in turn, depends on the pKa of the ionizable groups and the pH of the medium. In acid medium the ionization of -COOH group is suppressed. As the pH is increased the -COOH groups dissociate progressively and this results in a decrease in the electrical resistance of the membranes. Of the three types of membranes, PSMA-Al membranes of higher aluminium

Table 3.1 Preparation conditions and properties of PSMA-AL membranes

Membrane	Aluminium content (wt%)	Drying temperature (^{o}C)	Time (h)	Exchange capacity (meq/g)	Water content (wt%)
A1	4.0	60	4	5.71	32.2
A2	6.0	60	4	4.83	31.4
A3	10.0	60	4	3.74	29.7
A4	4.0	70	4	5.41	28.6
A5	4.0	90	4	5.67	29.4
A6	4.0	60	8	5.01	29.6

Table 3.2 Preparation conditions and properties of PSMA-EDA membranes

Membrane	Ethylene diamene content (wt %)	Drying temperature (^{o}C)	Time (h)	Exchange capacity (meq/g)	Water content (wt %)
E1	0.5	60	4	4.01	40.2
E2	1.0	60	4	3.20	34.9
E3	2.0	60	4	2.60	28.7
E4	4.0	60	4	2.05	24.9
E5	5.0	60	4	1.78	25.0

Table 3.3 Preparation conditions and properties of PSMA-PVA membranes

Membrane	PVA content (wt %)	Drying temperature (^{o}C)	Time (h)	Exchange capacity (meq/g)	Water content (wt %)
P1	10	80	4	4.2	52.2
P2	20	80	4	3.8	46.5
P3	50	80	4	2.3	40.3
P4	10	70	4	4.1	48.8
P5	10	60	4	4.2	40.4
P6	10	60	6	3.8	45.6
P7	10	60	8	3.6	46.4

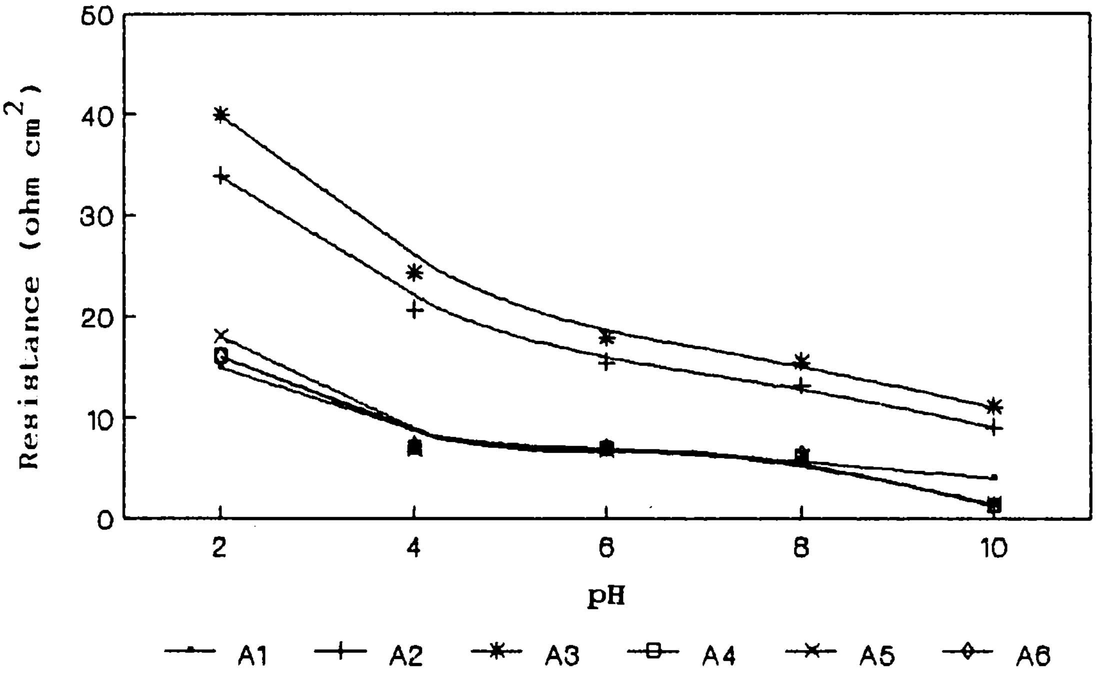


Figure 3.4 Resistance of PSMA-Al membranes as a function of pH.

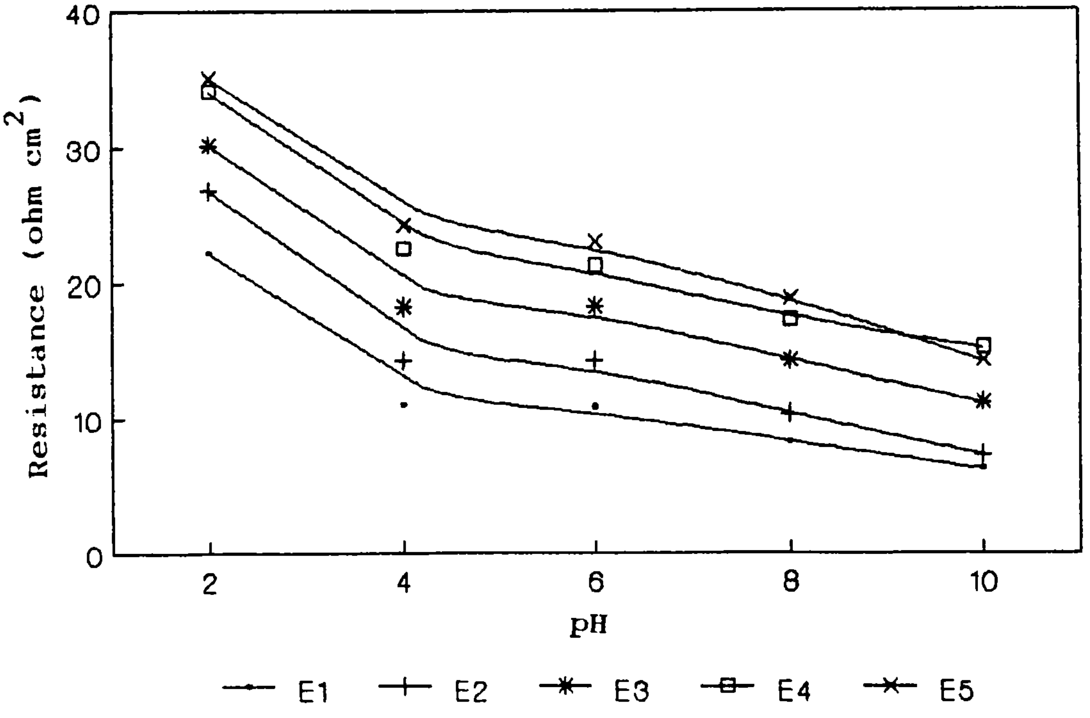


Figure 3.5 Resistance of PSMA-EDA membranes as a function of pH.

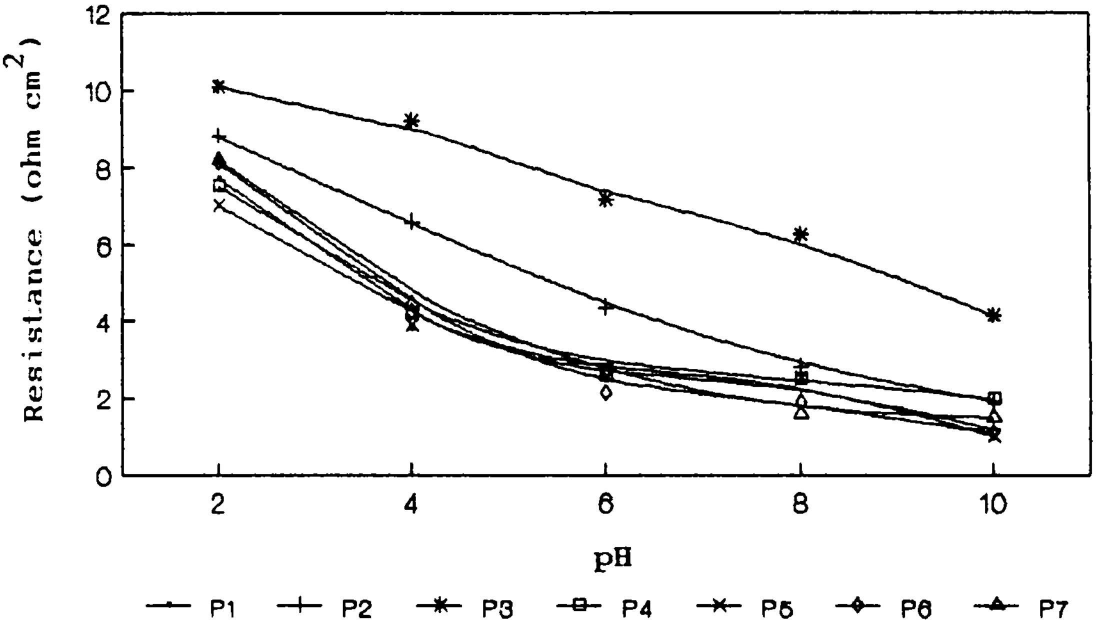
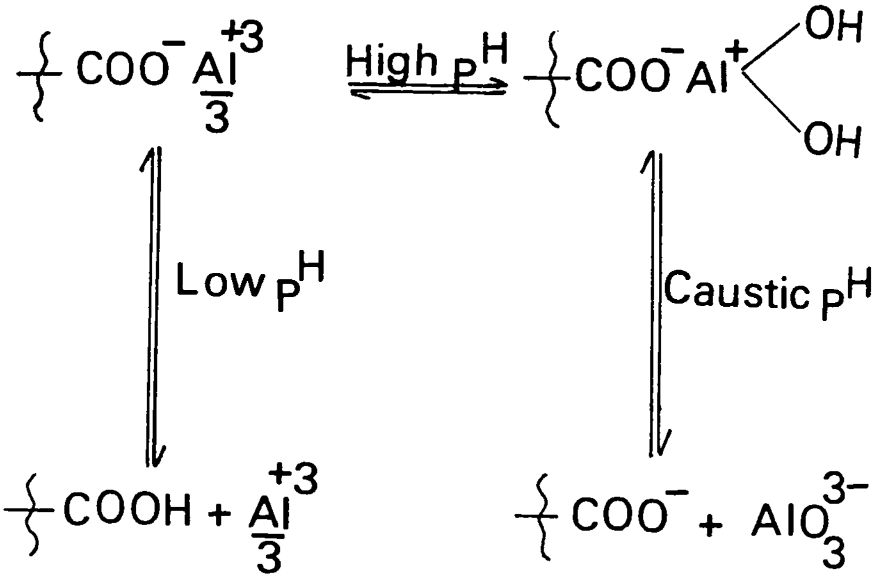
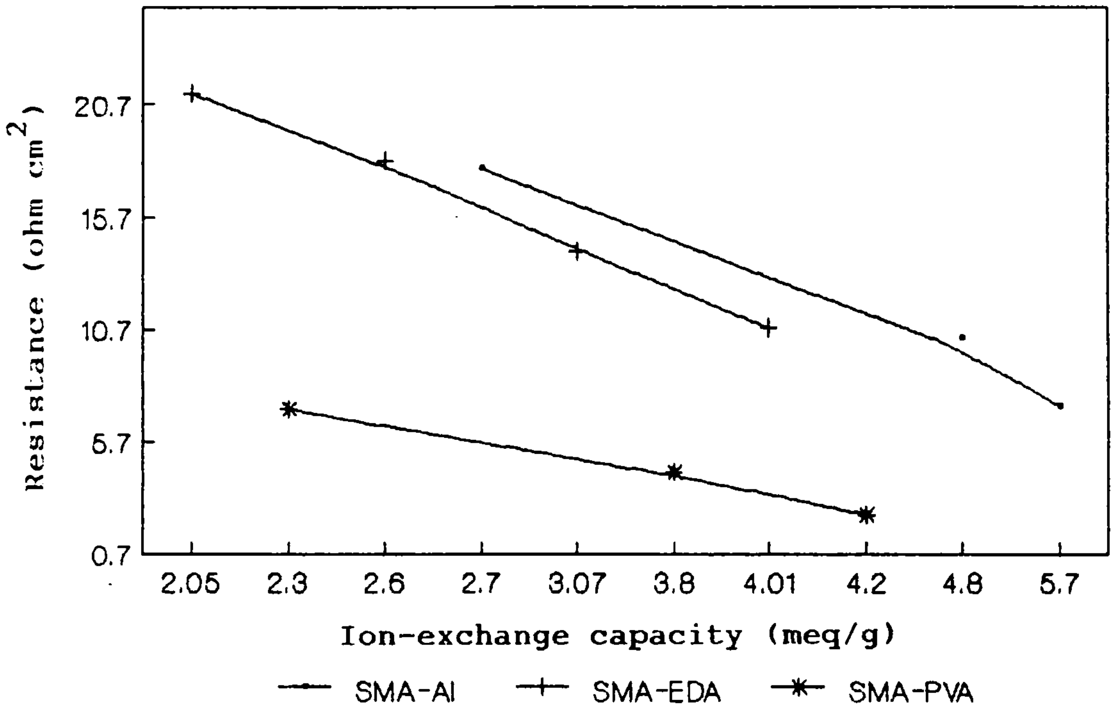


Figure 3.6 Resistance of PSMA-PVA membranes as a function of pH.

content show a higher resistance. This may be explained on the basis of the decreased affinity of aluminium carboxylate for water as indicated by their lower water content. This in turn leads to a resistance to the flow of ions through such a transit environment.

PSMA-PVA membranes show much lower resistance than the other two. PVA segments contain a number of free -OH groups which render the membranes with increased affinity for water molecules. Even with almost double the quantity of PVA incorporated into the PSMA matrix, the matrix has lower resistance and higher water retention than those of PSMA-Al and PSMA-EDA at same pH. In all the three cases membrane resistance increases with increasing concentration of cross-linking agent. For the same weight of cross-linking against the membrane resistance is in the order of EDA > Al3+> PVA. This may be explained on the basis of the variation in the hydrophilic character of the cross-linked membrane in terms of the residual form of the cross-linking moiety. EDA forms an amide. Al^{+3} ions associated with the polymer may exist as hydrolyzed species depending on pH.





igure 3.7 Membrane resistance as a function of ion-exchange capacity.

Thus the aluminium cross-linked membrane is stable only in a limited pH range. The pH dependent speciation leads to the formation of hydrophilic hydroxy species.

Figure 3.7 illustrates the relation between membrane resistance and exchange capacity. Ion exchange capacity and membrane resistance are compared at pH 6 where the membrane resistance vs pH plot shows a plateau indicating complete ionization of -COOH groups. The decrease in membrane resistance with exchange capacity is quite reasonable since the ionizable groups are responsible for both the properties. But in the case of membrane resistance, it depends not only on the concentration of ionogenic groups but also on the polymeric backbone. It follows that cross-linking content, swelling and pH of the medium will have a significant effect on membrane resistance.

(c) Membrane potential

When solutions of unequal concentrations of an electrolyte are separated by a membrane, an electrical potential develops across the membrane due to the tendency of the oppositely charged ions to move with different speeds. The magnitude of this membrane potential depends on the electrical characteristics of the membrane. Teorell, Meyer and Siever theory gives a reasonable explanation for membrane potential across an ion-exchange membrane (12). In the case of a cation exchange membrane, the membrane potential E is given by the following equation:

$$E = (1 - 2\bar{t}_+)\,\frac{RT}{F}\ln\frac{a_1}{a_2} \qquad (3.3)$$

Where $\bar{t}_+$ denotes the transport number of cation in the membrane phase and a_1 and a_2 are the activities of the electrolyte solutions separated by the membrane. In an ideal ion-exchange membrane co-ion transfer does not take place at all and a maximum value of the membrane potential is given by equation (3.4)

$$E_{max} = \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (3.4)$$

From equations (3.3) and (3.4) it follows that

$$\bar{t}_+ = 0.5(E / E_{max} + 1) \qquad (3.5)$$

Membrane potentials measured using PSMA membranes are given in Tables 3.4 to 3.6. Since the accuracy of potential measurements do not match with the accuracy with which 'a' has been measured, it is reasonable to use concentrations rather than activity in this context. Moreover, in the computation of t_+ values the ratio of the activities is taken. Hence the influence of activity coefficient on the accuracy of computed values becomes diminished. In order to clearly bring out the dependence of membrane potential on mean concentration, C1/C2 was kept fixed in all cases.

The relative ease with which counterions migrate through a charged membrane is expressed in terms of permselectivity, defined as (12)

$$Ps = \frac{\bar{t}_+ - t_+}{t_+ - (2t+-1)\bar{t}_+} \qquad (3.6)$$

where t_+ is the cation transport number in the solution phase.

E_{max} calculated using equation (3.4) and t_+ values used for calculations are shown in Table 3.7.

The variation in transport number and permselectivity values of the membranes with mean concentration of NaCl are given

Table 3.4 Membrane potential of PSMA-Al membranes at different mean concentrations of NaCl

C1 (M)	C2 (M)	Mean concentration (M)	Membrane potential (mV)					
			A1	A2	A3	A4	A5	A6
0.025	0.075	0.05	27.01	26.91	26.82	27.00	26.87	26.87
0.05	0.15	0.10	24.72	26.34	25.11	24.86	24.82	24.75
0.10	0.30	0.20	21.64	25.45	23.24	21.51	21.85	21.66
0.20	0.60	0.40	18.73	20.11	19.01	18.88	19.12	19.20

Table 3.5 Membrane potential of PSMA-EDA membranes at different mean concentrations of NaCl

C1 (M)	C2 (M)	Mean concentration (M)	Membrane potential (mV)				
			E1	E2	E3	E4	45
0.005	0.015	0.010	27.41	27.38	27.47	27.45	27.52
0.025	0.075	0.050	25.08	24.58	25.65	25.51	25.82
0.050	0.150	0.100	22.21	21.53	22.08	21.71	21.87
0.100	0.300	0.200	19.17	19.30	19.56	18.72	19.17
0.200	0.600	0.400	17.67	16.55	16.65	16.98	17.66

Table 3.6 Membrane potential of PSMA-PVA membranes at different mean concentrations of NaCl.

C1 (M)	C2 (M)	Mean concentration C	Membrane potential (mV)						
			P1	P2	P3	P4	P5	P6	P7
0.005	0.025	0.010	27.31	27.02	26.27	27.44	27.21	27.47	27.54
0.025	0.075	0.050	24.34	23.84	23.00	24.47	24.50	24.91	25.12
0.050	0.150	0.100	22.52	22.11	22.00	22.21	22.47	23.07	23.54
0.100	0.300	0.200	20.74	19.75	18.92	20.57	20.68	21.29	22.21
0.200	0.600	0.400	19.62	18.83	17.17	19.34	19.21	19.91	20.17

Table 3.7 E_{max} and t_+ values for NaCl at different mean concentrations

M	E_{max}	t_+
0.010	27.68	0.342
0.050	27.23	0.388
0.100	26.99	0.385
0.200	26.74	0.382
0.400	26.83	0.365

Table 3.8 Transport number of PSMA-Al membranes at different mean concentrations

Mean concentration (M)	Transport number ($\bar{t}_+$)					
	A1	A2	A3	A4	A5	A6
0.05	0.996	0.994	0.992	0.996	0.992	0.992
0.10	0.998	0.987	0.965	0.959	0.959	0.958
0.20	0.904	0.975	0.934	0.902	0.908	0.849
0.40	0.849	0.875	0.854	0.851	0.856	0.838

Table 3.9 Transport number of PSMA-EDA membranes at different mean concentrations

Mean concentration (M)	Transport number ($\bar{t}_+$)				
	E1	E2	E3	E4	E5
0.01	0.995	0.995	0.996	0.996	0.994
0.05	0.961	0.951	0.971	0.968	0.973
0.10	0.911	0.911	0.909	0.908	0.905
0.20	0.858	0.861	0.866	0.850	0.858
0.40	0.829	0.808	0.810	0.816	0.829

Table 3.10 Transport number of PSMA-PVA membranes at different mean concentrations

Mean concentration (M)	Transport number ($\bar{t}_+$)						
	P1	P2	P3	P4	P5	P6	P7
0.01	0.993	0.988	0.973	0.998	0.991	0.995	0.997
0.05	0.946	0.937	0.922	0.948	0.950	0.957	0.969
0.10	0.917	0.909	0.908	0.911	0.915	0.926	0.935
0.20	0.887	0.868	0.853	0.883	0.885	0.895	0.915
0.40	0.865	0.850	0.819	0.860	0.858	0.871	0.875

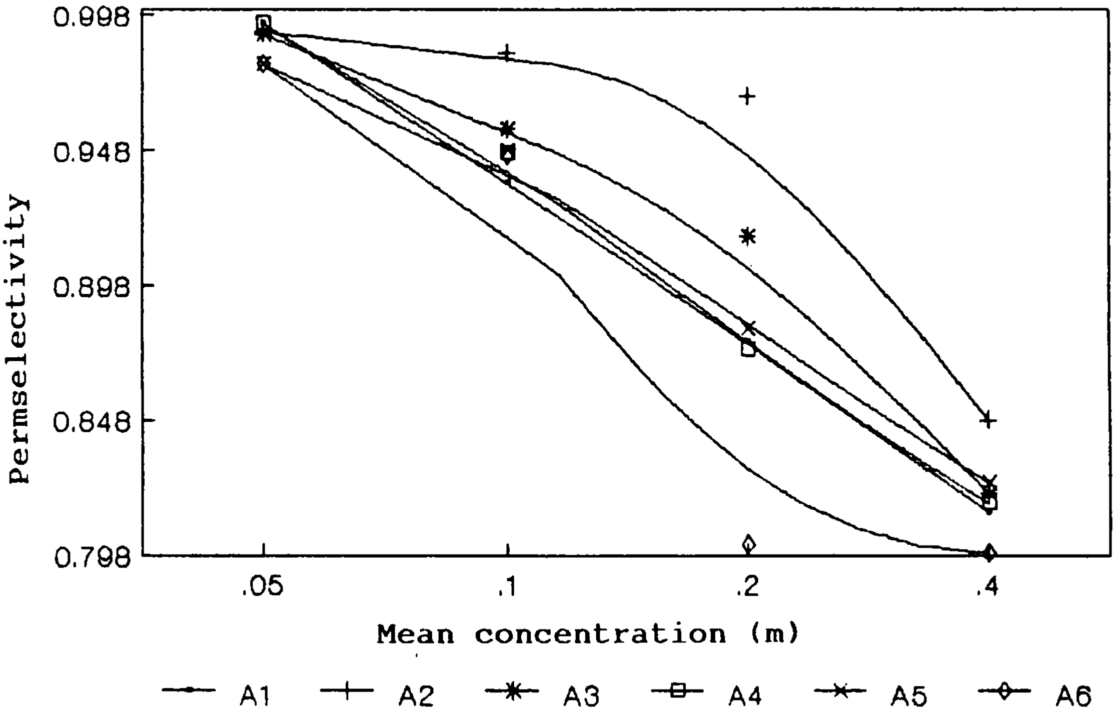


Figure 3.8 Permselectivity values of PSMA-Al membranes at different mean concentrations of NaCl.

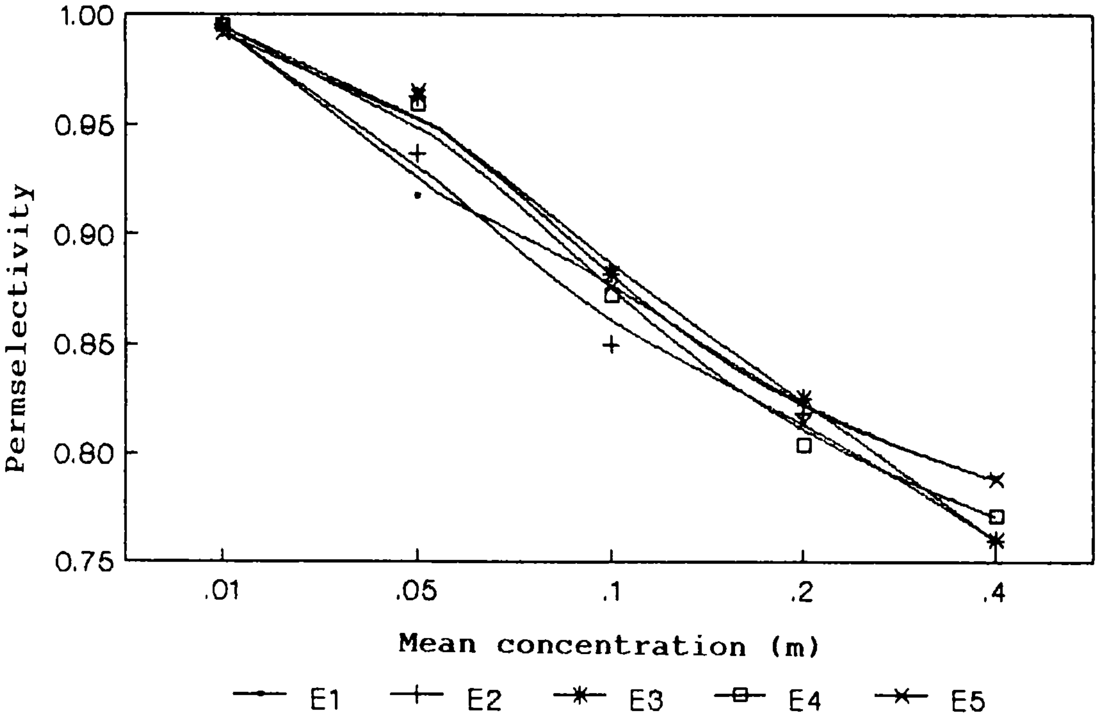


Figure 3.9 Permselectivity values of PSMA-EDA membranes at different mean concentrations of NaCl.

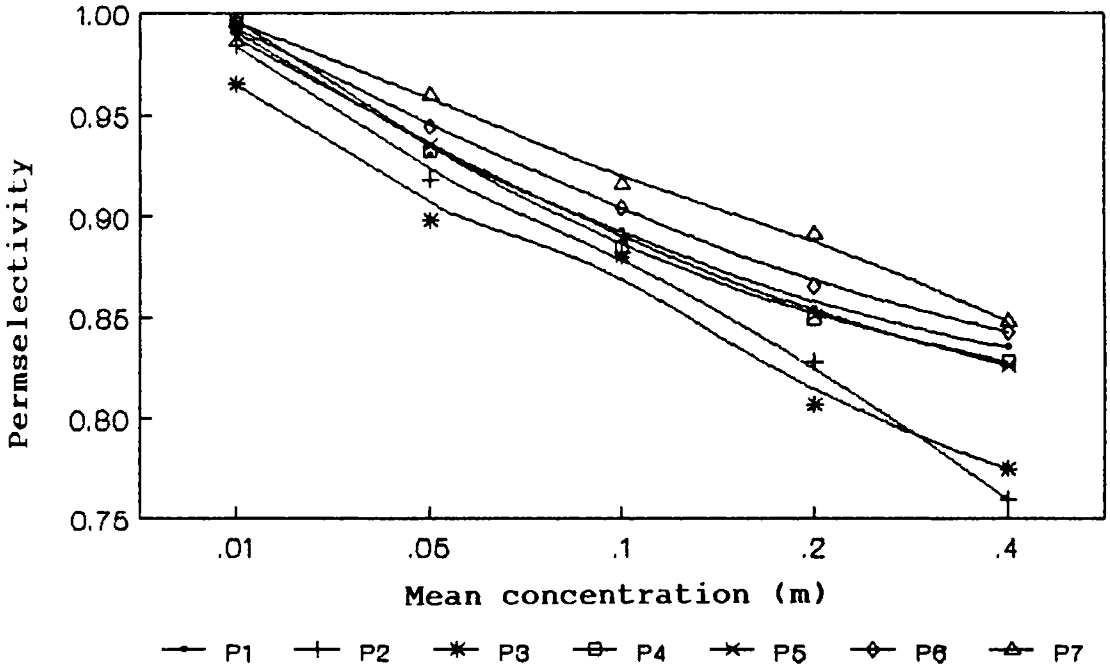


Figure 3.10 Permselectivity values of PSMA-PVA membranes at different mean concentrations of NaCl.

in Tables 3.8 to 3.10 and Figures 3.8 to 3.10 respectively.

In spite of maintaining the ratio of electrolyte concentrations constant, the membrane potential, transport number and permselectivity values were found to vary with mean concentration; it decreased significantly with increasing mean concentration. Variation of membrane potential with concentration even when concentration ratio was kept constant indicated a change in the membrane characteristics as a result of which counterion transport is affected. In an ideal ion-exchange membrane coion transfer does not take place at all. The higher value of transport number (>0.99) at lower concentration of sodium chloride indicates that PSMA membranes are nearly ideal. However, with increase in concentration there is a marked reduction in the transport number of the counterion. Permselectivity values also show the same pattern of change with mean concentration, indicating that the membranes deviate from ideal behaviour at high electrolyte concentrations. Intrusion of coions and water transport within the membrane to varying degrees, seems responsible for the observed alteration in membrane potential characteristics.

Figures 3.11 to 3.13 show the effect of pH on permselectivity. When concentration ratio and mean concentration were kept fixed, the permselectivity was seen to depend on pH of the solution. As the pH increases the membrane potential increases due to dissociation of -COOH groups, reaches a maximum and then decreases in the case of PSMA-Al. The decrease may be due to the decomposition of PSMA-Al due to the amphoteric nature of aluminium facilitating its conversion to soluble aluminate anion at higher pH. Moreover, the transport of anions will be

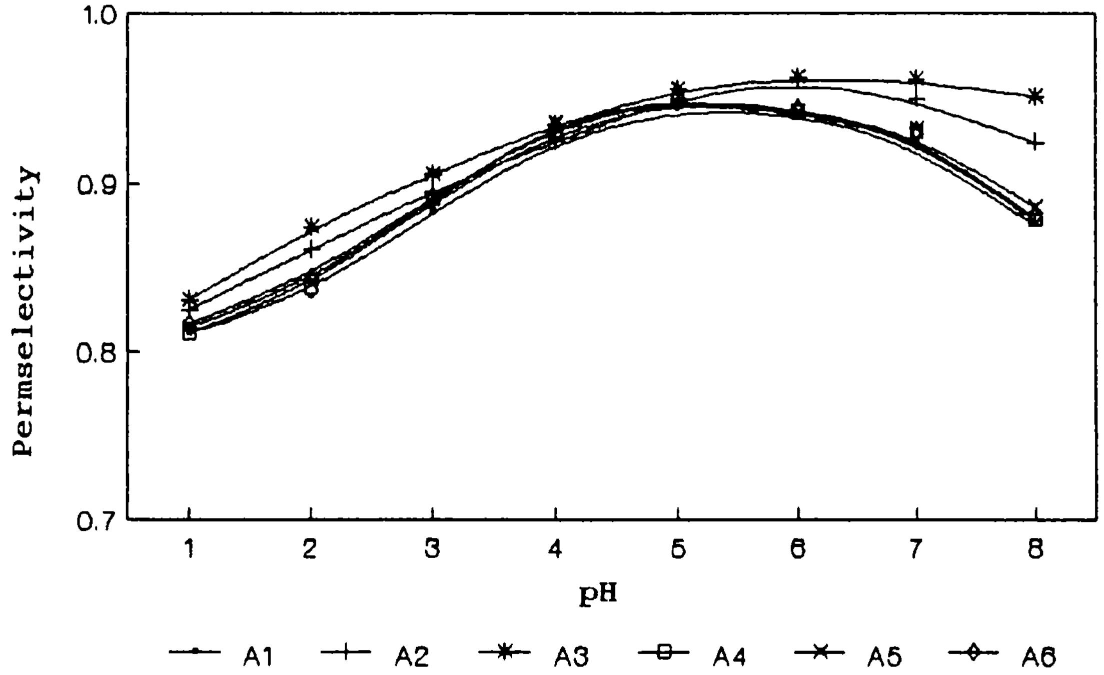


Figure 3.11 Variation of permselectivity of SMA-Al membranes with pH.

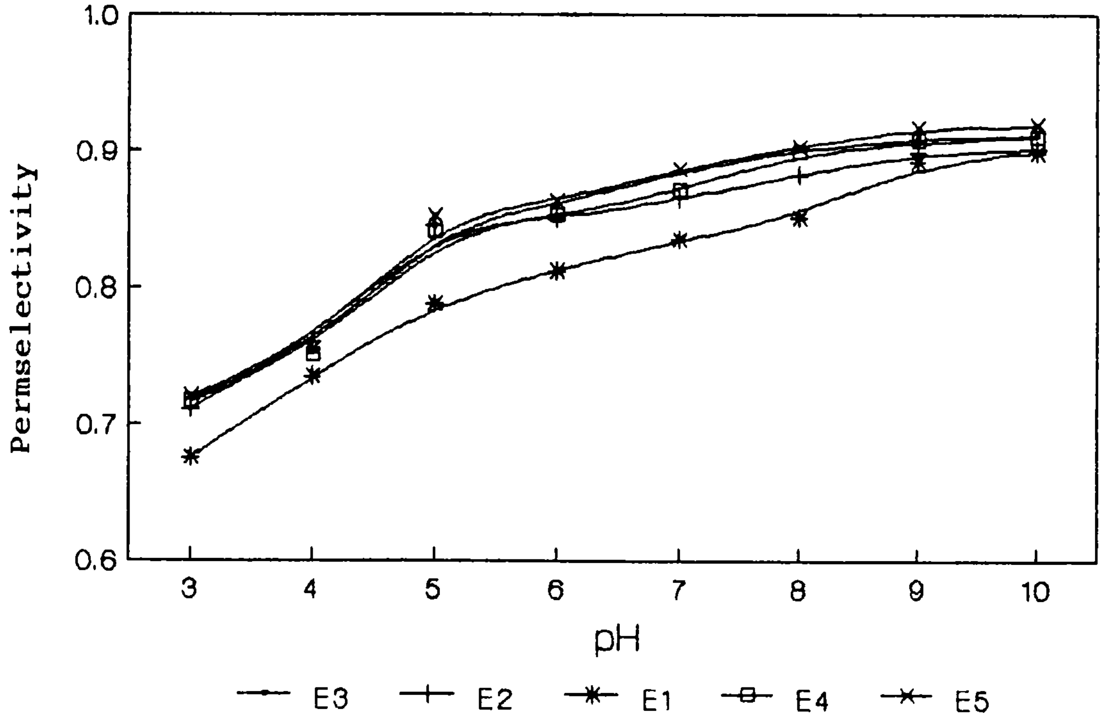
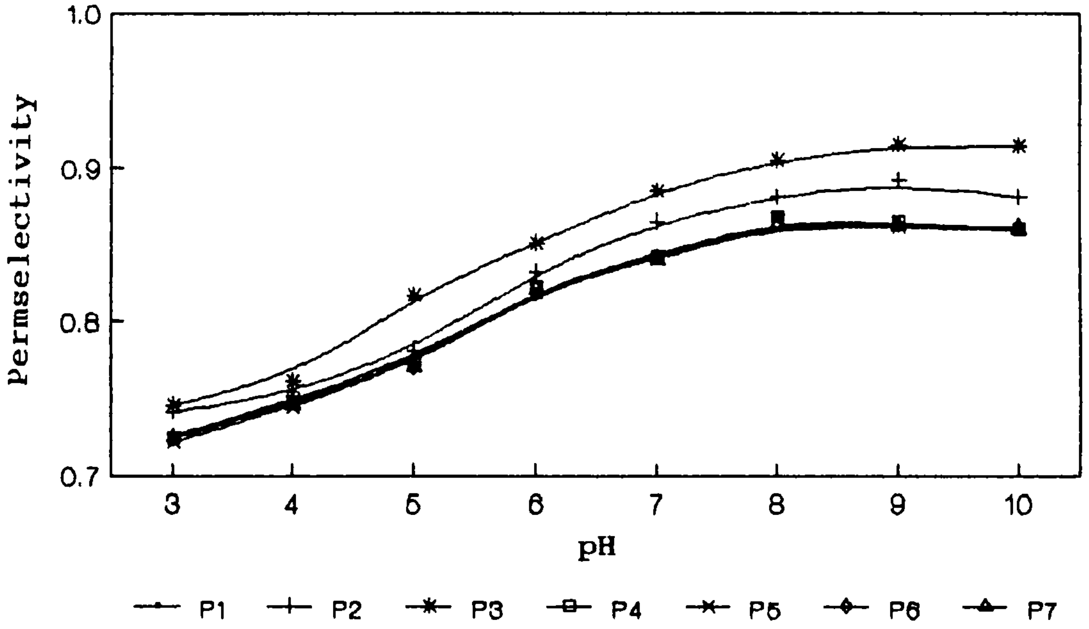


Figure 3.12 Variation of permselectivity of SMA-EDA membranes with pH.



igure.3.13 Variation of permselectivity of SMA-PVA membranes with pH.

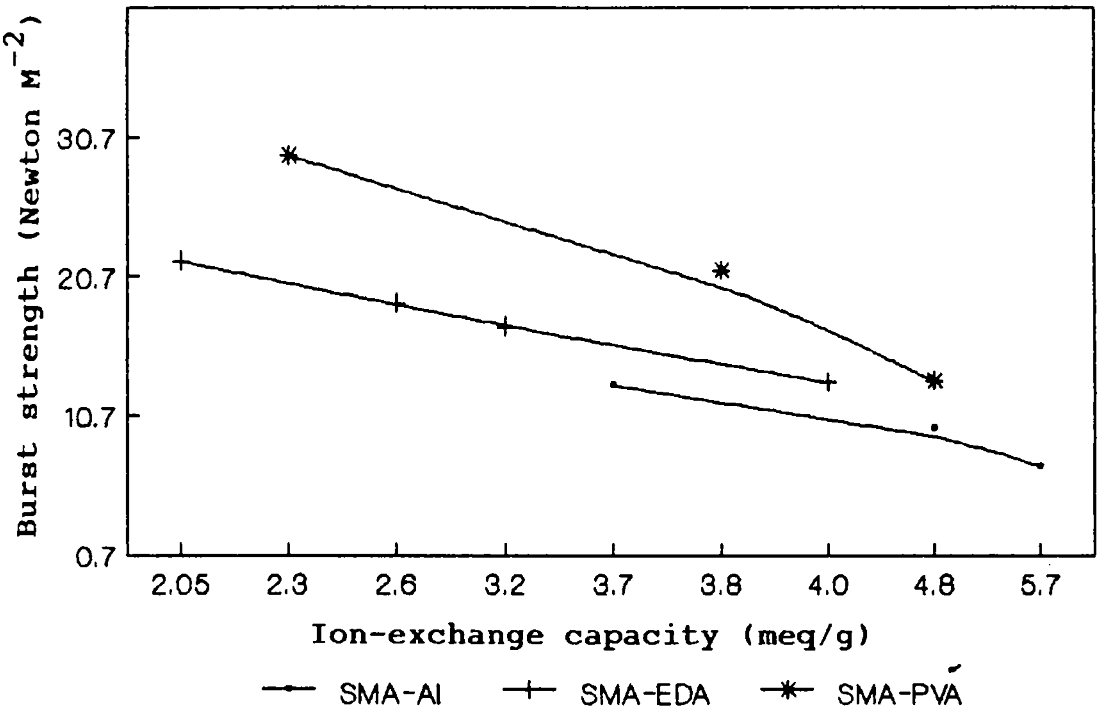
facilitated by the swelling of membranes. The dissociation of -COOH groups will increase the charge density along the polymer backbone. This causes the -COOH moities to repel each other, leading to increased swelling of the membrane. In the case of PSMA-EDA and PSMA-PVA the permselectivity reaches a maximum at higher pH. The cross linking moities in PSAM-EDA and PSMA-PVA are stable at pH 10 under ambient conditions.

(d) Burst strength

Figure 3.14 illustrates the relationship between exchange capacity and burst strength. It is clear from the figure that the yield strength decreases rapidly with increasing capacity. In all the three membranes, the charge group itself is used for cross-linking; membrane with high cross-linking content have low ion-exchange capacity. Hence it is reasonable that membranes with high cross-linking density possess high mechanical strength as observed with cross-linked ion exchangers. With regared to the nature of cross- linking agent the mechanical strength increases in the order aluminium cross-linked < ethylenediamine cross-linked < PVA cross-linked. Aluminium containing membranes are ionically cross-linked while the other two membranes are covalently cross- linked. Hence aluminium membranes rupture at low pressure when compared to other two membranes, PVA membranes are further reinforced by the polymeric backbone of PVA. Hence it shows better mechanical properties.

(e) Dialysis experiments

In dialysis the target solutes are transferred from one solution to another through a membrane down the concentration



igure 3.14 Effect of ion exchange capacity on burst strength of different membranes

gradient. Separation of different solutes is achieved by the difference in the diffusion rate of solutes within the membrane phase, which, in turn, is a function of the hydrodynamic condition of the dialyser (4). The diffusion of any single solute in a dialyser may be considered in two rate controlling steps:- (a) diffusion of the solute through the adjacent fluid films on both faces of the membrane and (b) diffusion of solute into the pores of the membrane. Thus, the diffusion rate in a dialyser may be expressed using the following equation.

$$J = \frac{P\,\Delta C}{b} \qquad (3.7)$$

Where J is the solute flux, P is the permeability co-efficient, ΔC is the driving force for mass transfer, and b is the thickness of the membrane in the wet form. Assuming that the volumes of the solutions in both compartments are equal and do not change (13), and on simplification results in equation (3.8)

$$P = \frac{tg\beta vb}{2q} \quad cm^2 s^{-1} \qquad (3.8)$$

Where $tg\beta$ is the slope of the ln $C_0/(C_0-C_t)$ vs time plot, C_0 is the initial feed concentration (mol dm^{-3}), C_t is the permeate concentration at time t, v is the volume of solution in a compartment (cm^3), and q is the active area of the membrane (cm^2). The exposed area of the membrane samples was 3.14 cm^2 and thickness in the wet form varied from 0.025 to 0.027 cm.

Permeability coefficients obtained are summarized in Tables 3.11 to 3.13. It is observed that for all membranes there is significant difference in the permeability coefficient values for a salt and a base, and a salt and an undissociated species. The difference in permeability coefficient values of the base and

Table 3.11: Permeability coefficients (cm^2s^{-1}) of SMA-Al membranes for NaCl, KCl, NaOH, Na_2SO_4, urea and creatinine.

Membrane	Permeability coefficient(cm^2s^{-1})					
	KCl $x10^{-4}$	NaCl $x10^{-4}$	NaCl $x10^{-4}$	Na_2SO_4 $x10^{-6}$	Urea $x10^{-7}$	Creatinine $x10^{-7}$
A1	3.14	1.12	7.61	2.21	5.21	6.42
A2	3.10	1.11	7.47	2.18	5.17	6.37
A3	3.11	1.21	7.01	2.20	5.15	6.34
A4	3.15	1.11	7.52	2.19	5.18	6.39
A5	3.14	1.12	7.55	2.17	5.20	6.41
A6	3.12	1.12	7.49	2.19	5.19	6.40

Table 3.12 Permeability coefficients (cm^2s^{-1}) of SMA-EDA membranes for NaCl, KCl, NaOH, Na_2SO_4, urea and creatinine.*

Membrane	Permeability coefficient (cm^2s^{-1})					
	KCl $x10^{-4}$	NaCl $x10^{-5}$	NaOH $x10^{-4}$	Na_2SO_4 $x10^{-5}$	Urea $x10^{-7}$	Creatinine $x10^{-7}$
E1	1.02	7.01	7.18	2.19	7.01	6.24
E2	1.15	7.19				
E3	1.45	7.12	7.89	2.78	7.22	6.71
E4	1.52	7.17				
E5	1.55	7.15	8.05	3.14	7.32	7.01

Table 3.13 Permeability coefficients (cm^2S^{-1}) of SMA-PVA membrane for NaCl, KCl, NaOH, Na_2SO_4, urea and creatinine.*

	Permeability coefficient (cm^2S^{-1})					
Membrane	KCl $x10^{-4}$	NaCl $x10^{-4}$	NaOH $x10^{-4}$	$Na2SO_4$ $x10^{-5}$	Urea $x10^{-7}$	Creatinine $x10^{-7}$
P1	4.19	1.85	9.21	1.80	8.61	9.21
P2	3.90	1.83				
P3	3.89	1.12	9.17	1.82	7.03	8.79
P4	3.97	1.71				
P5	4.02	1.70				
P6	4.11	1.84				
P7	4.08	1.83				

* only values for typical membranes are presented.

salt may be due to both electrostatic and geometrical effects of the membranes. The permeability of an electrolyte through a charged membrane is controlled by the mobility of both the ions. Due to the high mobility of the OH^- ions compared to other anions, the permeability coefficient of a hydroxide base will be higher than that of the salts. The low permeability of Na_2SO_4 may be due to the high ionic radius of sulphate ion. The permeability coefficient values for the species studied decrease in the order $NaOH > KCl > NaCl > Na_2SO_4$. The values obtained for urea and creatinine are much lower as expected for the passive transport of neutral solutes through a charged membrane.

(f) Active and selective transport of K+ and Na+

Mass transfer through polymeric membranes is induced by the difference of pressure, concentration and/or electrical potential across the membrane. However, many complex phenomena which can not be understood by physico-chemical mechanisms are found in biomembranes(3). Among them include the selective transport of K^+ and Na^+ ions through the cell membrane against osmotic pressure, concentration and potential gradients(14,15). This transport plays an important role for sustaining the function of life. Active transport in biomembranes have not yet been applied to practical fields but possess the capability of separation and concentration of materials that can not be separated or concentrated by conventional techniques. To a limited extent analogous processes with synthetic membranes can be put to practical use.

Figures 3.15 is an example of the time dependent concentration change of K^+ and H^+ ions on L and R sides of the

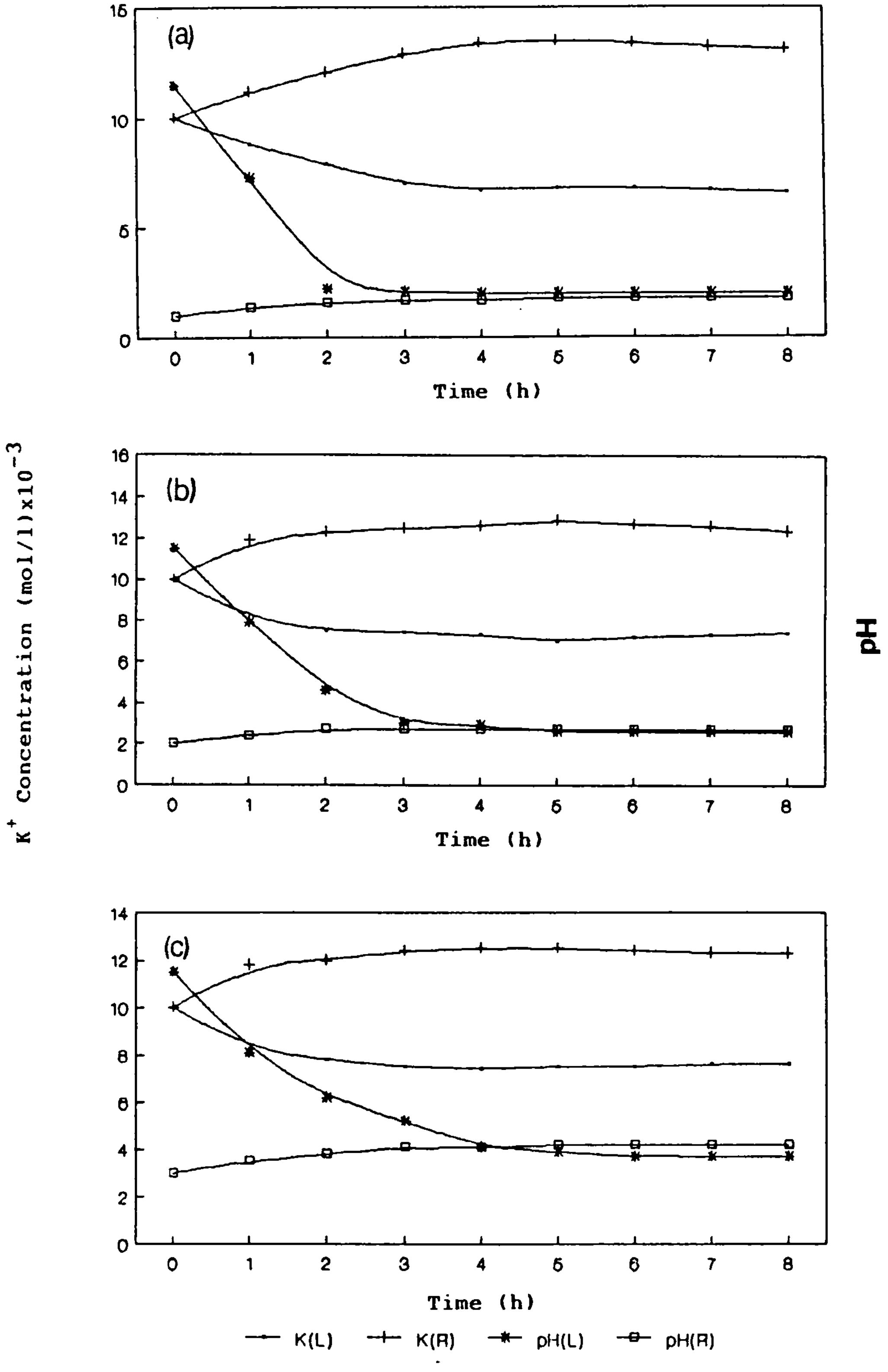


Figure 3.15 Active transport of K^+ through the membrane P1; (a) initial pH in R side 1 (b) initial pH in R side 2 (c) initial pH in R side 3.

membranes. In all systems, the concentration of K^+ ion on R side, which was acidic, increased upto a maximum with time while that on the L side followed just the opposite pattern. Chloride ions were not transferred to any detectable concentration during the experiment. These results suggest that K^+ ions were actively transported across the membrane against its concentration gradient across the sides. When pH was the same on both sides of the membrane, K^+ was not transported to the R side. The rate of active transport of K^+ increased with increasing difference in pH between the two sides. These results suggest that the driving force for the active transport is the transport of H^+ from R side to L side. The membrane swells in alkaline medium, while shrinks in acidic medium. During a long transport period, K^+ concentration remains constant and then decreases after about 4 h as shown in Figure 3.15. This is due to the fact that the pH difference between the two solutions becomes small after some time. A moderate K^+ concentration allows the metal ion to diffuse back to the membrane and to be transported back the L side.

Tables 3.14 and 3.15 shows the effect of initial pH in the R side compartment on the mean transport rate and transport fraction of K^+ which are defined by equations (3.9) and (3.10).

$$\text{Mean transport rate} = \frac{[K^+]_{max} - [K^+]_0}{t_{max}} \qquad (3.9)$$

$$\text{Transport fraction} = \frac{[K^+]_{max} - [K^+]_0 \times 100}{[K^+]_0} \qquad (3.10)$$

where $[K^+]_0$ and $[K^+]_{max}$ are the initial and maximum concentration of K+ on the R side and t_{max} is the transport time for $[K^+]_{max}$. The mean transport rate and the transport fraction decrease with

Table 3.14 Effect of initial pH of solution in the R side on the mean transport rate and transport fraction for the PSMA-PVA (membrane with exchange capacity 4.8 meq/g).

pH	Mean transport rate (mol h^{-1}) x 10^{-4}	Transport fraction (%)
0.5	6.2	40.3
1.0	5.0	25.6
2.0	3.8	19.3
3.0	3.3	15.2

Table 3.15 Effect of initial pH of solution in the R side on the mean transport rate and transport fraction for PSMA-EDA (membrane with exchange capacity 4.01 meq/g).

pH	Mean transport rate (mol h^{-1}) x 10^{-4}	Transport fraction (%)
0.5	4.2	31.2
1.0	3.6	22.7
2.0	2.8	17.4
3.0	1.6	11.5

Table 3.16 Effect of the exchange capacity on mean transport rate and transport fraction for different PSMA-PVA membranes (at R side pH 1.0)

Exchange capacity (meq/g)	Mean transport rate (mol h^{-1}) x 10^{-4}	Transport fraction (%)
2.3	2.40	12.7
3.6	4.75	19.4
4.8	5.00	25.6

Table 3.17 Effect of the exchange capacity on mean transport rate and transport fraction for different PSMA-EDA membrane (R side pH 1.0)

Exchange capacity (meq/g)	Mean transport rate (mol h^{-1} x 10^{-4}	Transport fraction (%)
2.05	1.78	10.18
3.20	2.41	14.20
4.01	3.60	22.71

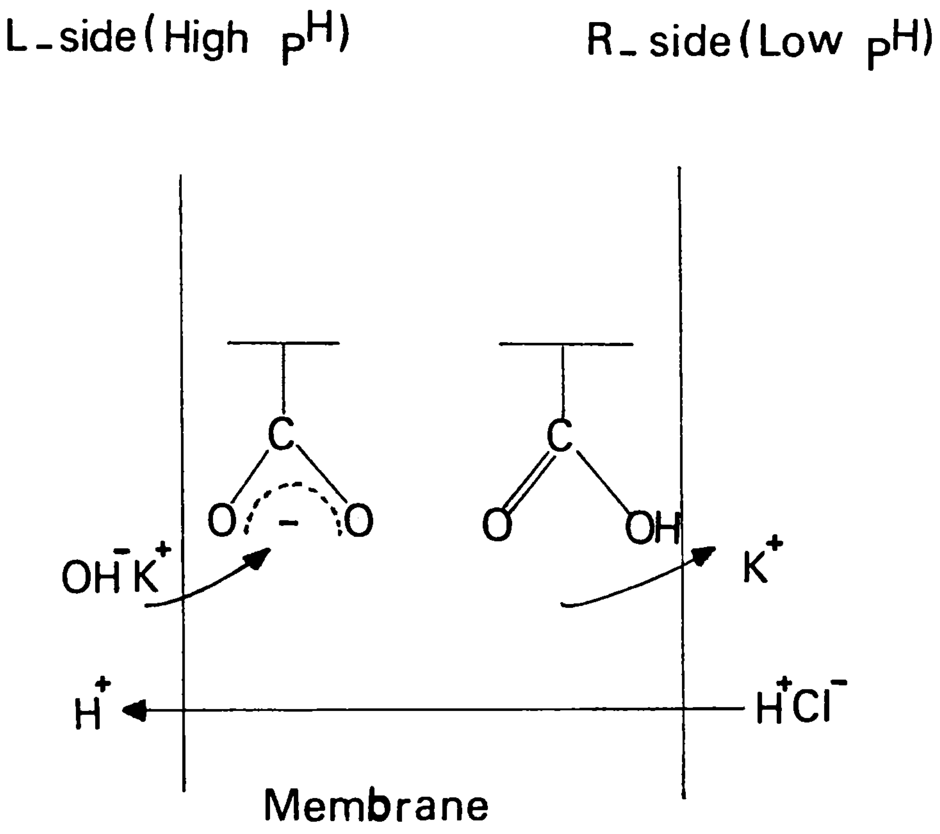
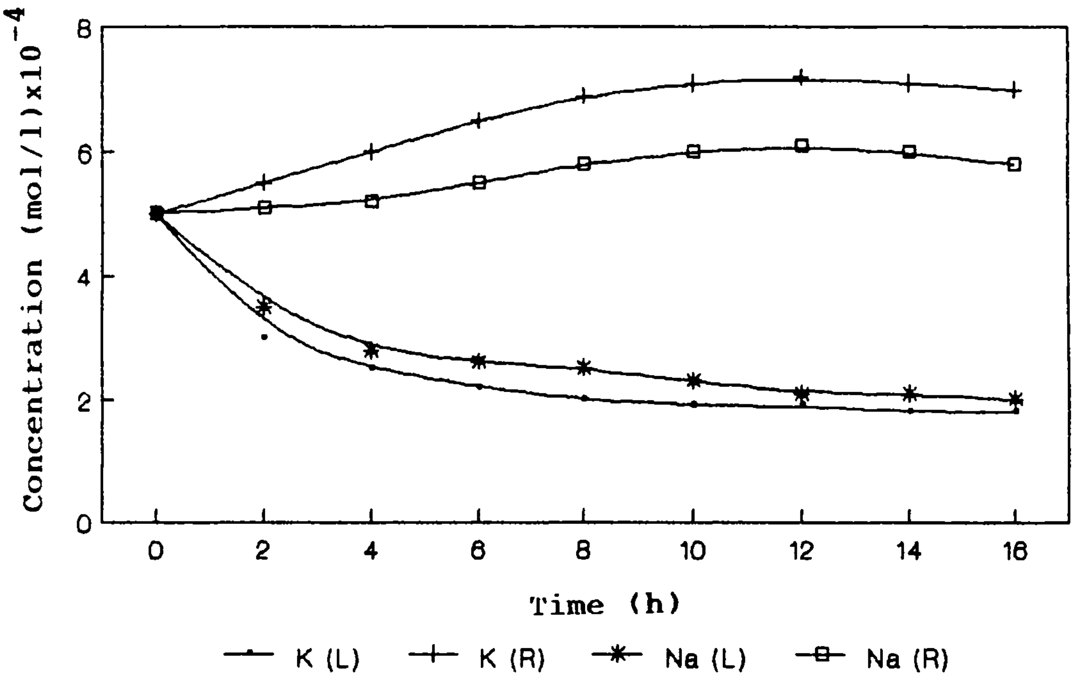


Figure 3.16 Mechanism of active transport of alkali metal through PSMA membrane.

increasing initial pH in the R side compartment.

The variation of mean transport rate and transport fraction with ion exchange capacity (given in Tables 3.16 and 3.17) is attributed to the swelling and contraction of the membrane depending on pH which occur to a significant extent with increasing number of fixed charge group in the membrane.

Figure 3.16 shows the scheme of a tentative transport mechanism operative during the active transport of metal ions through the membrane(15). When one side is alkaline and the other side acidic across the membrane, the carboxyl groups in the membrane dissociate in alkaline side, and metal ions are incorporated into the membrane by the ion exchange between H^+ ion of the carboxylic group and the metal ions on the alkaline side. The metal ions migrate by a cooperative relay mechanism suggested for the migration of protons in a solid state protonic conductor (16). The carboxylic groups fixed to the membrane matrix assist such a corporative transport. On the other hand, the dissociation of the carboxyl groups on the acidic side is very low. Therefore, the membrane surface on the acidic side is very dense, and consequently permeation of metal ions and, in particular, Cl^- into the membrane becomes very difficult. However H^+ ions can be easily transferred from the acidic side to the alkaline side through the membrane by the relay mechanism. When H^+ ions reach the region where metal carboxylate exists, metal ions are released by the exchange between metal ions of the metal carboxylate and H^+ ions. The released metal ions are transferred to the acidic side by a potential gradient between the acidic and alkaline sides. The alkali metal ions released in exchange for protons, increase their concentration on the R side. Protons transported through



gure 3.17 Changes in K^+ and Na^+ concentrations with time through P1 at pH 1.

Table 3.18 Effect of the initial pH of the solution on R side on the selectivity of K+ over Na+ for P 1 membrane.

pH	Selectivity
1.0	1.18
2.0	1.15
3.0	1.11

Table 3.19 Effect of the initial pH of the solution on R side on the selectivity of K+ over Na+ for E 1 membrane.

pH	Selectivity
1.0	1.21
2.0	1.14
3.0	1.09

the membrane to the L side are neutralized by the hydroxide ions. In fact, a rapid decrease of pH in the L side compartment is observed as shown in figure 3.15.

Figure 3.17 shows the changes in alkali metal ion concentration on both sides of the membrane with time, when the initial pH on the L side was 1.0. It is found that K^+ permeates faster than Na^+ and this seems to depend on the diameter of the hydrated ions. Na^+ ion when hydrated is known to be larger in radius than K^+ ion, and the ions must go through the constricted channels of the membrane to be released to the R side. The transport selectivity, K^+/Na^+, was calculated using the equation (3.11).

$$\text{Selectivity} = \frac{[K^+]_{R,t}/\ [K^+]_{R,t}}{[Na^+]_{R,t}/\ [Na^+]_{L,0}} \qquad (3.11)$$

where R,t is the concentration on the R side at time t, and L,O is the initial concentration on the L side. The selectivity for alkali metal ion transport after 12 h at different initial pH in the R side is given in Tables 3.18 and 3.19. The selectivity values are larger than unity and decreases with increasing the initial pH on the R side. At higher pH membrane swells and interaction between the fixed charge groups on the membrane and the permeating cations decreases and the cations simply diffuse through the expanded channels of the membrane.

REFERENCES

1. H. K. Lonsdale, J. Membr. Sci., 1982, 10, 81.
2. H. Strathmann, in Ullman's Encyclopedia of Industrial Chemistry, ed. B. Elvers, S. Hawkins, G. Schulz, 1990, A 16, VCH, FRG.
3. E. Piskin, A. S. Hoffmann, Polymeric Biomaterials, 1986, Martinus Nijhoff Publishers, The Netherlands.
4. R. E. Kesting, Synthetic Polymeric Membranes, 1971, New York, McGraw, Hill Book Company.
5. A. C. Habert, C. M. Burns , R. Y. M. Huang, J. Appl. Polym. Sci., 1979, 24, 801.
6. P. Mears, Chem. and Ind., 1992, 6, 21.
7. O. Sanli , L. Aras, Brit. Polym. J., 1990, 22, 155.
8. Annual Book of ASTM Standards, 1977, 31, D 374, D 774, D 2096, D 2187 , E 380.
9. J. O'. M. Bockris & F. B. Diniz, Electrochim. Acta, 1989, 34, 567.
10. W. F. Graydon, R. J. Stewart, J. Phys. Chem., 1955, 59, 86.
11. S. Williams (Ed.), Official Methods of Analysis, 4th Edn. 1984, AOAC INC, Virginia.
12. N. Lakshminarayanaiah, Transport Phenomena in Membranes 1969, Academic Press, New York.
13. R. Wysick , W. M. Troshimczuk, J. Membr. Sci. 1992, 65, 141.
14. A. Katchalsky, R. Spangler, Q. Rev. Biophys., 1986, 1, 127.
15. T. Uragami, S. Watanabe, R. Nakamura, F. Yoshida , M. Sugihara, J. Appl. Polym. Sci. 1983, 28, 1613.
16. S. Chandra, Superionic Solids - Principles and Applications, 1981, North Holland, Amsterdam.

CHAPTER IV

POLY(STYRENE-CO-MALEIC ACID) BASED FLOCCULANTS

ABSTRACT

Flocculation studies were carried out on dilute suspensions of the hydroxides of iron, copper and uranium using polyelectrolytes. The polyelectrolytes used in the study include poly(styrene-*co*-maleic acid) with varying acid content and its hydroxamic acid derivative. The two-portion mixing procedure was adopted in studying flocculation. A sharp dependence of flocculation efficiency on the acid content of the polymer and the pH of the medium was observed. The flocculation efficiency was strongly influenced by the mixing process of the sol and flocculant. The optimum polymer dosage for different flocculants varied with pH. The critical concentration of electrolyte for flocculation was found to depend on the valency of the counterion and the polymer dosage. The characteristics of the flocs were evaluated by sedimentation.

4.1 INTRODUCTION

Separation of particulate matter from the water phase and dewatering of the sludge are essential steps in most of the waste water treatment processes. These operations are facilitated if the particles are aggregated into structures that allow rapid settling and release of water. For these purposes, both inorganic coagulants and flocculants have found extensive use. In such applications a number of important characters of the candidate material can be identified. The flocs formed should be large and dense to settle properly. They should also be strong enough to withstand disruptive hydrodynamic forces appearing in different stages of operation. In practice it may be difficult to achieve good characteristics with regard to all of the aforementioned requirements with a certain flocculant. Polyelectrolytes offer significant advantages over their inorganic counterparts in flocculation efficiency (1).

Polyelectrolytes serve as floccculants by two different mechanisms. Firstly the polyelectrolyte can act as a primary coagulant in neutralizing the double layer directly and allowing aggregation to take place. Secondly, the polyelectrolytes can bring about flocculation through a bridging mechanism (2). La Mer and co-workers(3,4), Michaels(5), and Ruehrwein and Ward(6) have contributed in developing an acceptable model which explains the ability of polymers to flocculate suspensions. The theory assumes that a colloidal particle may attach to one or more adsorption sites on the long polymer chain with the remainder of the chain extending out into the bulk of the solution. Other particles may also become attached to the chain at other sites, and hence the polymer molecule serves as a bridge. The particles thus become bound into flocs and grow in size. An increase in polymer concentration in solution will promote increased bridging up to the point where adsorption sites are no more available, and then particles become coated with the polymer preventing their close approach to form aggregates.

The removal of the suspended metal species at low concentrations from water is an important step in the clarification of industrial effluents and in the recovery of metal values. Common separation processes become ineffective here because of the small particle size and the stabilizing effect of surface charge on particles. The context is ideal for the application of polyelectrolytes as flocculants. In this study the flocculation of the hydroxides of Fe(III), Cu(II) and U(VI) using poly(styrene-*co*-maleic acid) was attempted. The choice of target materials was prompted by their significance in water purification, effluent treatment and recovery of strategic materials from lean sources.

4.2 EXPERIMENTAL

4.2.1 Materials

Poly(styrene-*co*-maleic acid) (PSMA) with varying monomer content and its hydroxamic acid (PSMH) derivative were prepared as described in section 2.2.1.

Metal hydroxide sol

Hydroxides of Fe(III), Cu(II) and U(VI) were precipitated by adjusting the pH of metal salt solutions using aqueous NaOH. Metal salt solutions were prepared by dissolving ammonium iron(III) sulphate, copper(II) sulphate and uranyl nitrate in distilled water (7). Fe(III) solution was maintained acidic using HCl. Fe(III) was precipitated at pH 7 while Cu(II) and U(VI) at pH 9. The suspension formed in the alkaline medium was stirred for 24 h, filtered, washed with water and then redispersed in a required amount of water and adjusted the pH to the desired level.

4.2.2 Methods

(a) Adsorption measurements

Adsorption measurements were conducted as follows(8). Stock solutions of polymer (20 ml) were introduced into an adsorption tube which contained 30 ml of metal hydroxide sol. After rotating the tube end-over-end for 1 h, the suspended particles were separated from solution by centrifugation (5000 rpm, 20 min) and the residual polymer concentration was determined by measuring the COD of the supernatant (9). From these measurements, the amount of polymer adsorbed per unit weight of the sol was calculated.

(b) Flocculation experiments

Flocculation studies were carried out by a two-portion mixing procedure (10), in which one part of the sol (V_1 ml), salt solution, ($NaCl$, $CaCl_2$, or $AlCl_3$) [5 ml] and polymer solution (5 ml) were carefully brought together in the mixing tube in the order given above. The components were mixed by slowly inverting the tube end-over-end six times after closing. After the contact time, t_2 (15 min) the second portion of the sol (V_2 ml) was added. The tube was rotated end-over-end during the flocculation time, t_2 (1 h). The extent of flocculation was noted by measuring the absorbance of the suspension at 450 nm after centrifugation under mild conditions (2 min at 600 rpm). At this wave length the system has maximum absorbance and absorbance is proportional to the amount of material left in the supernatant liquid. Sol concentration (C_{sol}), salt concentration (C_s), polymer concentration (C_p) and flocculation time (t_2) were varied to get optimum conditions.

(c) Sedimentation studies

Sedimentation time, the time required for the complete settling, was obtained from absorbance vs time plot. Sedimentation time was taken as the time above which no change in absorbance was observed. The rate of subsidence of the solid phase was observed by recording the volume of the solid phase as a function of time, in a graduated cylinder filled to the mark with suspension under examination.

4.3 RESULTS AND DISCUSSION

The Characteristics of flocculants are summarized in Table 4.1.

Table 4.1 Characteristics of polymers used in flocculation studies.

Flocculant	Functional group	Molecular weight$\times 10^{-6}$	Acid content (meq/g)
F1	COOH	2.4	7.8
F2	COOH	3.1	5.6
F3	COOH	2.1	3.2
F4	CONHOH, COOH	2.4	3.6

4.3.1 Flocculation of iron (III) hydroxide

Iron (III) hydroxide is known to form several solid phases(11) like α-,β-,τ-FeO(OH), α-Fe_2O_3 and active and inactive forms of amorphous $Fe(OH)_3$. There is no evidence that any definite hydroxide $Fe(OH)_3$ exists(12), and the red brown precipitate commonly called ferric hydroxide is best described as hydrous ferric oxide, Fe_2O_3 nH_2O . The form in which Fe(III) hydroxide precipitates depends on conditions such as pH, temperature and anions present in solution. The stoichiometry remains unchanged over a pH range 4 to 11. Usually the amorphous form transformed slowly into α-FeO(OH), and aging for one hour leads to complete transformation.

(a) Adsorption measurements

In the present study, chemical oxygen demand (COD) was used to measure the amount of polymer left in the supernatant after adsorption. COD is defined as the amount of oxygen, expressed in mg/l consumed under specified conditions in the oxidation of organic and oxidizable inorganic matter (9). Since the only oxidizable species present in the test solution is the residual concentration of the polymer used, the COD of the supernatant is a measure of the total amount of polymer left. The COD of standard solutions of the polymers were determined and the residual concentrations are expressed on the basis of the COD of such standard solutions.

The adsorption of the polymer is obviously a key factor in understanding how it functions as a flocculant. The adsorption data were plotted corresponding to Henry, Langmuir and Freundlich

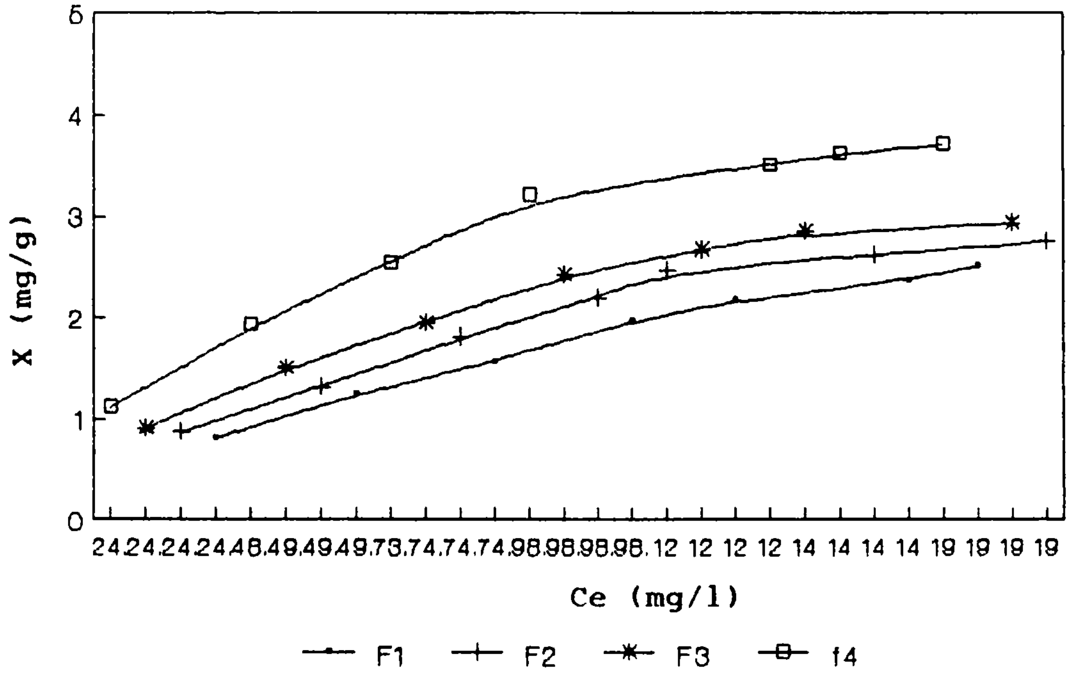


Figure 4.1 Adsorption isotherm of PSMA and PSMH on Fe(III) at pH 4

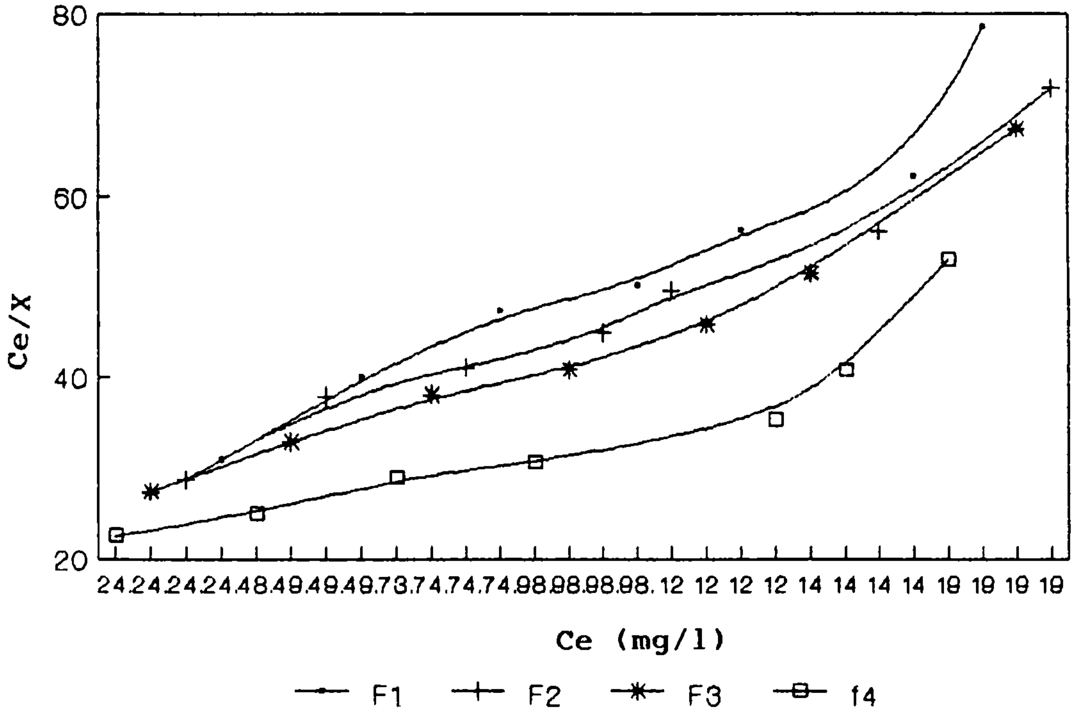


Figure 4.2 Langmuir plot of adsorption of PSMA and PSMH on Fe(III) at pH 4.

isotherms, of which the more interesting plots are presented in the figures. Figures 4.1 and 4.2 show typical adsorption isotherms of different flocculants used in the study. In the low concentration ranges; Henry's isotherm is valid and at intermediate concentrations the adsorption conforms to Langmuir isotherm. However, at higher concentrations large deviations are observed on the Langmuir plot indicating the operation of non-adsorptive forces. The absorption studies were carried out at concentrations much larger than those employed in the flocculation studies due to the lack of sensitivity and accuracy in the measurement of flocculant concentrations at lower levels. Hence it is reasonable to assume that essentially the Henry's isotherm is applicable for the adsorption of the polyelectrolytes on the metal hydroxide sols.

Table 4.2 Maximum amount of polymer adsorbed on iron (III) hydroxide at different pH

pH	Amount of polymers adsorbed (mg/g)			
	F1	F2	F3	F4
4.0	2.2	2.4	2.6	3.2
6.0	2.6	2.5	2.8	3.4
8.0	3.0	3.4	3.1	3.6
10.0	4.9	4.7	3.8	3.9

Maximum amount of polymer adsorbed on the iron hydroxide sol at different pH is summarized in Table 4.2. It is evident that the maximum amount of polymer adsorbed depends on the charge content on the polymer. At lower pH the amount adsorbed increases with decreasing functional group content on the polymer and the highest amount adsorbed is on the hydroxamic acid

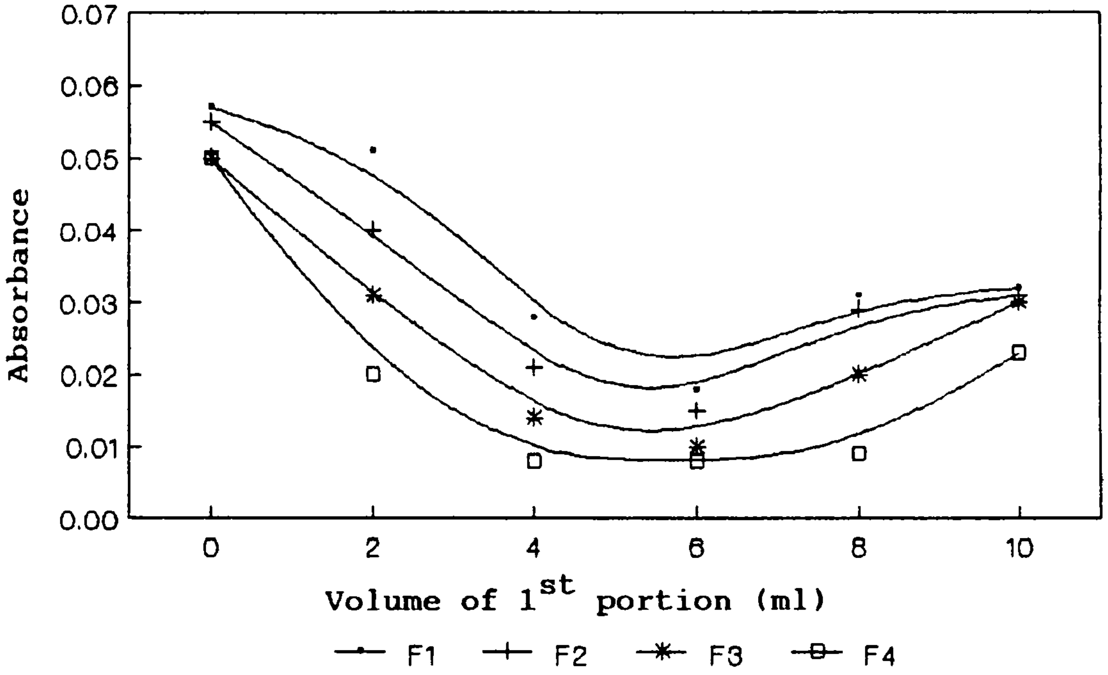


Figure 4.3 Effect of the mode of mixing on flocculation efficiency:

C_{sol} = 2.0 mg/l of Fe, C_s = 1mmol/l of $CaCl_2$,

t_1 = 15 min, t_2 = 1h, pH = 4

flocculant (F4). The amount of polymer adsorbed on the sol increases considerably for F1 compared to F4 on an increase in pH. Maximum amount of F1 has been adsorbed on the sol at pH 10 . Such results might be due to the effect of functional groups in the interaction of the polymers with iron (III) hydroxides (14). The effect is further discussed in section 4.3.1c.

(b) Mode of mixing

The effect of the mode of mixing of the sol and the flocculant is shown in Figure 4.3, where the absorbance of the supernatant is plotted as a function of the volume of the first sol portion (V1) for different flocculants. The absorbance for all the flocculant samples show a minimum when the two volumes, V(1) and V(2) are equal since absorbance gives the amount of sol left behind after flocculation. A minimum on the absorbance plot represents the effectiveness of flocculation at that concentration.

The occurrence of a flocculation optimum as a function of volume of sol can be explained on the basis of the distribution of the polymer over the particle surface in the first portion and the solution. The flocculation is optimal at a particular mixing ratio because the extension of the loops on its adsorption on the particles in the first portion is maximum and the concentration of the polymer in solution is negligibly small. It is evident from the graph that lowering or raising of V1 makes flocculation less effective. On lowering V1, too much of polymer remains in solution and on raising V1, loops of polymer chain are not sufficiently extended for bridging (10). In further studies, the two-portion mixing method,

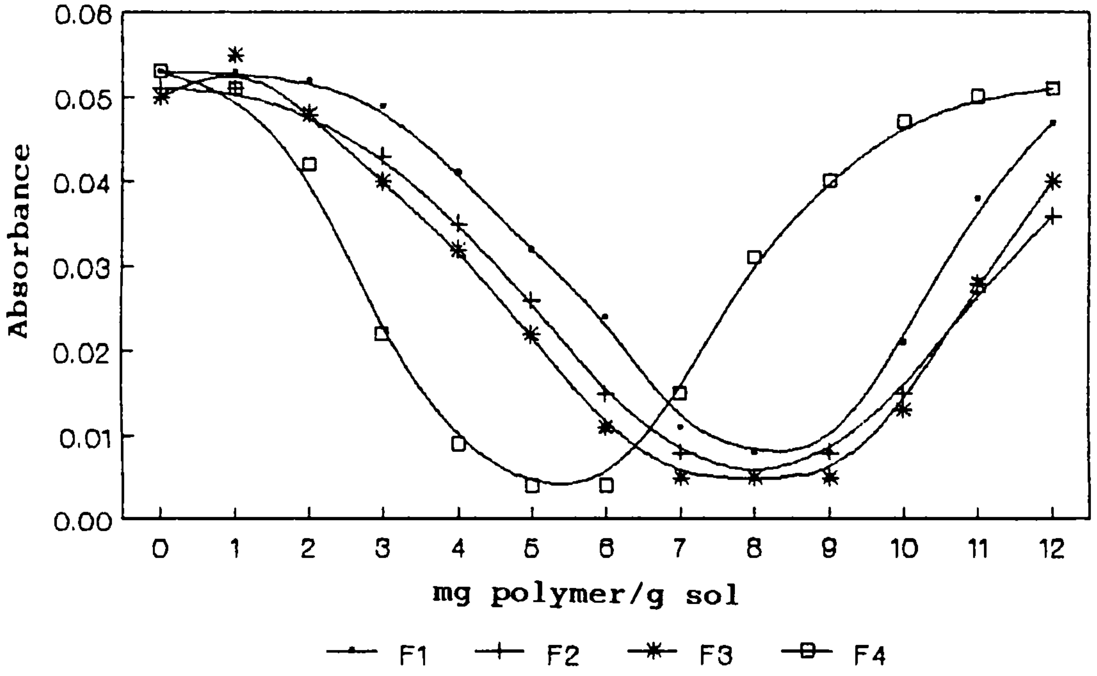


Figure 4.4 Flocculation as a function of polymer dosage at optimum mixing condition: $V_1 = V_2 = 5$ ml, $C_{sol} = 2$mg/l of Fe, $C_s = 1$ mmol/l $CaCl_2$,$t_1 = 15$ min, $t_2 = 1$ h, pH = 4.

where $V_1 = V_2 = 5$ ml was utilized.

(c) Optimum polymer dosage

Figure 4.4 is a typical case showing the absorbance of the supernatant liquid after flocculation as a function of polymer dosage. Absorbance decreases, attains a minimum and increases as the polymer dosage increases. The polymer concentration which gives a minimum absorbance value is taken as the optimum polymer dosage. This is because at this region minimum amount of suspended matter was left in the liquid. Addition of polymer to a suspension will lead to adsorption and promote bridging leading to flocculation. When the adsorption sites are saturated the particles become coated with polymer to such an extent that they are prevented from coming together close enough to allow aggregation. This is probably the reason for the stabilization (increase in absorbance) of the suspension beyond optimum polymer dosage.

Table 4.3 Optimum polymer dosage for different polymers: $C_{sol} = 2$ mg/l Fe^{+3}, $C_s = 1$ mmol/l of $CaCl_2$, $t_1 = 15$ min $t_2 = 1$ h

pH	Dosage of polymer (mg/g of sol)			
	F1	F2	F3	F4
4.0	8.5	8.0	7.4	5.5
6.0	7.6	7.2	7.1	5.4
8.0	6.0	6.6	6.4	5.3
10.0	4.4	5.0	5.3	5.2

The optimum polymer dosage obtained at various pH are given in Table 4.3. The optimum polymer dosage decreases with increasing pH. The effect is more pronounced for F1, that is the polymer with maximum acid content. For the hydroxamic acid polymer, the pH dependency is minimum, and the other two come in the intermediate range.

The decreasing sensitivity of the hydroxamic acid polymer to variation in pH, perhaps, culminates from the intrinsic nature of the hydroxamic acid group. In the pH range studied the -CONHOH is not sensitive to pH dependent ionization. Moreover, hydroxamic acid function can coordinate with the metal ion(19). Energetically the coordination is more favourable than adsorption and hence the driving force for the action can be derived from coordination.

All these results show that ion content on the polymer and external pH exert significant influence on flocculation. The solution pH affects both flocculant chemistry and rheology and the surface chemistry of the particle(15). Here iron (III) hydroxide was selected as a model target since the stoichiometry remains unchanged in the pH range studied (11). The variation is with the flocculants rather than with the metal hydroxide sol. At low pH the flocculants are in the unionized form. As the pH increases, the carboxylic groups get dissociated forming negative charge on polymer molecules. The presence of carboxylate moieties along the polymer will change the rheology to a significant extent. It will extend the polymer chain due to the electrostatic repulsion between adjacent carboxylate groups. Thus the functional groups on the polymer chain have two functions in bringing about flocculation. It has the capacity to adsorb onto the particle surface forming bridges to produce aggregates. The other function of the carboxylate group is to uncoil the polymer chain in solution by electrostatic repulsion enabling bridging to take place more easily. The effectiveness of the hydroxamic acid polymer at lower pH compared to the carboxylic acid polymers is due to stronger interaction of the former with suspended particles. The presence of coordinating as well as hydrogen bonding sites on the hydroxamic acid polymer makes it effective in the low pH range. An increase in pH facilitates ionization of -COOH groups which in turn will change the polymer rheology by uncoiling the chain facilitating bridging. The significant difference in the optimum polymer dosage for flocculation with an increase in pH using F1 (acid content 7.8 meq/g) and F4 (acid content 3.8 meq/g) can be explained on the basis of this reasoning. For F4 a change in pH will not cause any significant effect on the polymer rheology and hence its flocculation efficiency remains unchanged. The other two flocculants F2 and F3 perform in the intermediate range corresponding to the availability of -COOH groups on the polymer chain.

(d) Effect of electrolytes

In order to provide further insight into the flocculation process, it is desirable to find the effect of low molecular weight electrolytes. On the basis of the influence of the mixing mode on optimum polymer dosage, it is also desirable to quantify such influences.

The effect of NaCl, $CaCl_2$ and $AlCl_3$ on flocculation efficeny was evaluated and is given in Figure 4.5, where the

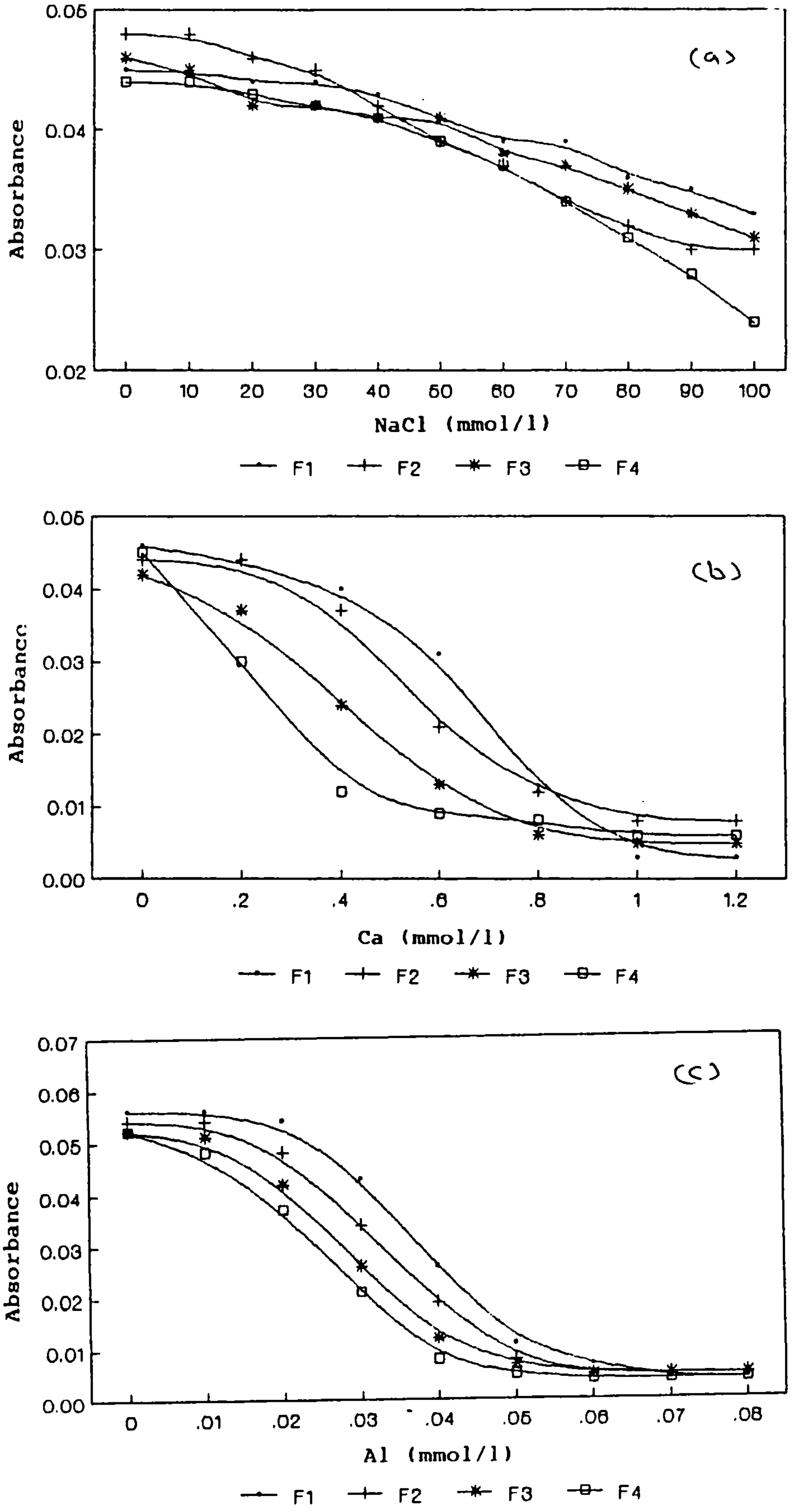


Figure 4.5 Effect of salt concentration on flocculation efficiency: C_{sol} = 2 mg/l, C_p = Optimum polymer dose (5 ml), t_1 =15 min, t_2 = 1 h, pH = 4

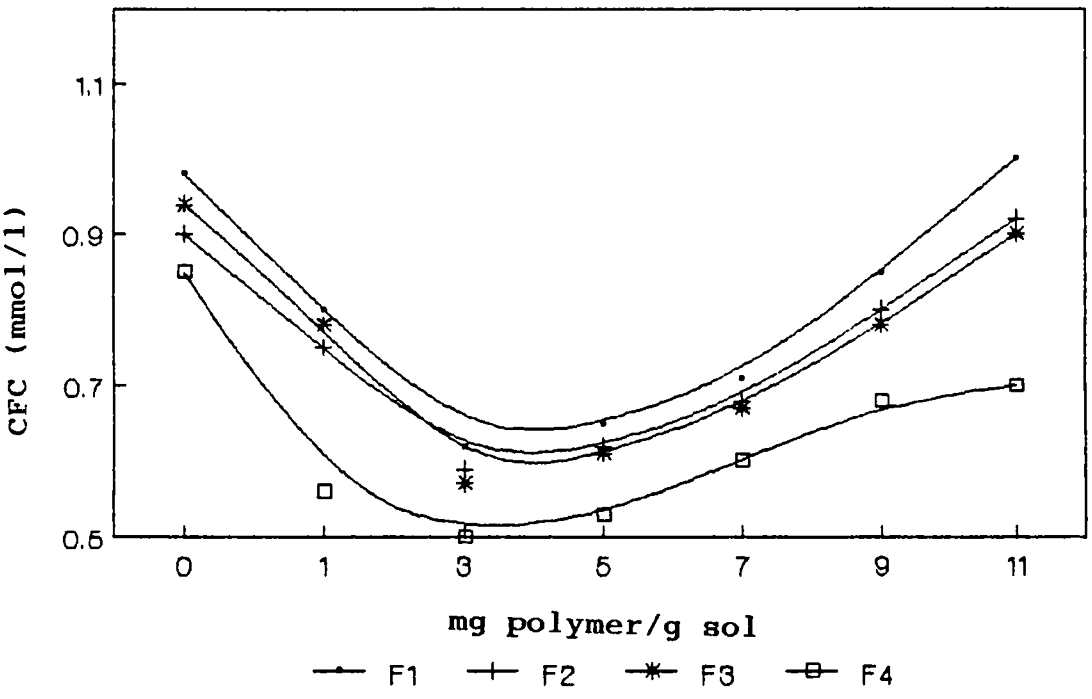
(a) NaCl (b) $CaCl_2$ (c) $AlCl_3$

Table 4.4 Critical salt concentration of different electrolytes:

C_p = Optimum polymer dosage, C_{sol} = 2mg/l Fe^{+3},
t_1 = 15 min, t_2 = 1h

Salt	CSC (mmol/l)			
	F1	F2	F3	F4
NaCl	46.4	44.2	38.1	32.3
$CaCl_2$	0.68	0.60	0.30	0.36
$AlCl_3$	0.076	0.062	0.54	0.041

absorbance of of supernatant is plotted against electrolyte concentration. A salient feature of the results is that the extent of flocculation increases from negligible to almost complete over a narrow range of electrolyte concentration. Apparently a certain critical concentration of salts (CSC) is required to obtain flocculation, which is defined as that concentration at which half of the material is flocculated(16). The critical concentration of different salts for flocculation is given in Table 4.4. The CSC depends strongly on the valency of the counter ion. For the effective bridging of the particles it is necessary that the particles approach each other closely enough. The distance at which bridging is possible will be of the order of the thickness of the polymer layer (17). So long as the double layer repulsion is strong the particle do not approach close enough for bridging and the system remains stable. The same is the case in the presence of adsorbed layers. The primary role of the electrolyte is to suppress the electrical double layer outside the polymer layer. As the valency of the counter ion increases the effect



igure 4.6 Dependence of CSC of $CaCl_2$ on polymer concentration:

C_{sol} = 2 mg/l, t_1 = 15 min, t_2 = 1h, pH = 4 become more pronounced. Another possibility is that the free acid group present on the polymer get deactivated by salt formation.

Table 4.5 Critical concentration of $CaCl_2$ at different pH:
C_p = Optimum polymer dosage C_{sol} = 2 mg/l Fe(III)
t_1 = 20min, t_2 = 1h

pH	CSC (mmol/l)			
	F1	F2	F3	F4
4.0	0.68	0.66	0.65	0.51
6.0	0.61	0.61	0.58	0.48
8.0	0.59	0.59	0.48	0.46
10.0	0.50	0.49	0.43	0.42

This effect will become more pronounced with multivalent metals. The polyvalent metal ion can cross-link two or more polymer chains, thereby forming insoluble salts. This will considerably enhance the flocculation efficiency. The explanation outlined conforms to the order of flocculation efficiency observed for these metal ions: [Al(III) > Ca(II) > Na(I)]

The effect of polymer dosage on the CSC for $CaCl_2$ is given in Figure 4.6. For all the flocculants, initially a strong decrease of CSC is observed and beyond a minimum the CSC increases. With increase in polymer dosage the CSC increases again because the second portion of the sol becomes totally covered by the polymer and the flocculation by bridging is gradually changed into protection against salt. The CSC of $CaCl_2$ for different flocculants at various pH are summarized in Table 4.5. The CSC strongly depends on the charge content on the polymer. It decreases with decreasing charge content in the polymer. There is a slight decrease in CSC with increase in pH. It is observed that as the pH increases the adsorption of the polymer on the sol increase. That is, more number of carboxylic groups are involved in protecting particles by covering and the availability of the carboxylic groups for cross-linking is diminished.

(e) Effect of sol concentration and time of flocculation

A number of experiments were done using the two-portion mixing procedure. The results of these experiments supplement the conclusion arrived at by earlier investigations. Critical salt concentration for the polymer were measured at different sol concentrations (C_{sol}) and time of flocculation (t_2). The results obtained are summerised in Tables 4.6 to 4.9. The following trends have been observed. At a given t_2, flocculation becomes much more efficient with increasing C_{sol}. The strong dependence of CSC on C_{sol} is a consequence of the mode of measuring, in which CSC is determined at a point where half the material is flocculated. Increasing the flocculation time at a given C_{sol} results in more number of collisions and thus to a greater extent of flocculation. If C_{sol} is increased the number of Brownian encounters per second increases, leading to a higher proportion of flocculated material in a given period.

(f) Sedimentation experiment

When the conditions for optimum flocculation are established, the selection of a separation technique such as

Table 4.6 Critical salt concentration for F1 at different C_{sol} and t_2 :

C_p = 7.6 mg/g of sol

C_{sol} (mg/l)	CSC (mmol/l)					
	NaCl		$CaCl_2$		$AlCl_3$	
	t_2=1 h	t_2=30/C_{sol} h	t_2=1 h	t_2=30/C_{sol} h	t_2=1 h	t_2=30/C_{sol} h
2.0	46.4	27.4	0.68	0.41	0.076	0.047
5.0	22.7	17.8	0.42	0.31	0.041	0.024
10.0	15.2	10.1	0.27	0.22	0.024	0.018

and t_2 :

c_p = 7.2 mg/g of sol

C_{sol} (mg/l)	CSC (mmol/l)					
	NaCl		$CaCl_2$		$AlCl_3$	
	t_2=1 h	$t_2=30/C_{sol}$ h	t_2=1 h	$t_2=30/C_{sol}$ h	t_2=1 h	$t_2=30/C_{sol}$ h
2.0	44.2	30.1	0.60	0.47	0.062	0.046
5.0	23.2	16.1	0.38	0.40	0.040	0.021
10.0	14.7	10.3	0.16	0.14	0.026	0.016

Table 4.8 Critical salt concentration for F3 at different C_{sol} and t_2 :

C_p = 7.1 mg of sol

C_{sol} (mg/l)	CSC (mmol/l)					
	NaCl		$CaCl_2$		$AlCl_3$	
	t_2=1 h	t_2=30/C_{sol} h	t_2=1 h	t_2=30/C_{sol} h	t_2=1 h	t_2=30/C_{sol} h
2.0	38.1	20.2	0.30	0.19	0.054	0.038
5.0	17.4	10.6	0.19	0.14	0.038	0.021
10.0	10.2	8.1	0.11	0.08	0.019	0.012

Table 4.9 Critical salt concentration for F4 at different

C_{sol} and t_2 :

C_p = 5.4 mg/ of sol

C_{sol} (mg/l)	CSC (mmol/l)					
	NaCl		$CaCl_2$		$AlCl_3$	
	t_2=1 h	$t_2=30/C_{sol}$ h	t_2=1 h	$t_2=30/C_{sol}$ h	t_2=1 h	$t_2=30/C_{sol}$ h
2.0	32.3	18.6	0.36	0.17	0.061	0.022
5.0	15.1	9.5	0.18	0.14	0.029	0.014
10.0	8.2	4.7	0.12	0.11	0.014	0.010

filtration, sedimentation, etc. follows. The selection is based on the properties of the floc formed, the extent of separation needed, the volume to be handled, etc. The most important factors affecting a solid-liquid separation process are:

1. The nature of particles ie size, shape, specific gravity, surface properties and chemical properties.
2. The concentration ratio of solid to liquid in the suspension.

In the present study sedimentation was selected because of its simplicity of operation. Experiments were designed so as to get an idea about the nature of sedimentation of the flocs formed using polyelectrolytes

Figure 4.7 shows the time dependent change in sediment volume after flocculation. This represents "Phase settling" type flocs, where settling occurs when a suspension of the flocculated particles reach a concentration that causes them to contact each other obstructing the free settling paths of individual particles (18). The result is that the solid phase as a whole assumes a common settling rate, as the individual particles within it move about at varying velocities and directions, while the liquid "channels" move upwardly through it.

Sedimentation time and volume percentage settled after 30 minutes are given in Tables 4.10 and 4.11. It was observed that in all cases the settling takes around 60 minutes. There is a slight decrease in settling time with increase in pH.

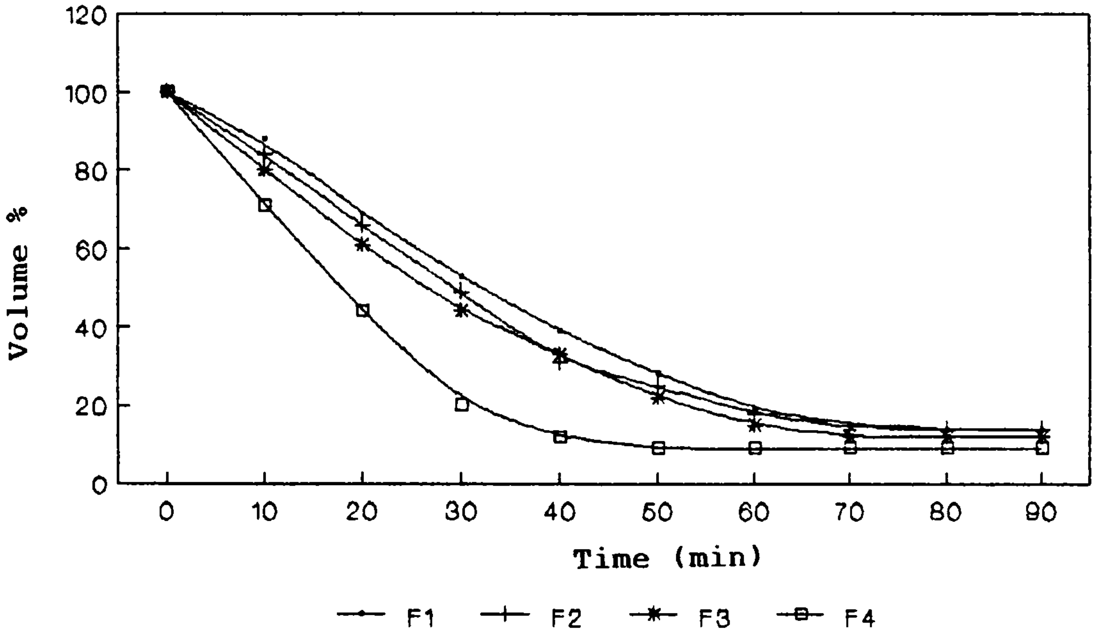


Figure 4.7 Volume percentage of solid as a function of time at optimum flocculation:

C_{sol} = 2mg/l, C_s = 1 mmol of $CaCl_2$, C_p = Optimum polymer dosage, pH = 4.

Table 4.10 Sedimentation time of Fe(III) hydroxide using different flocculants:

C_{sol} = 2 mg/l, C_s =1 mmol/l of $CaCl_2$, C_p = optimum polymer dosage, t_2 = 1 h.

pH	Sedimentation time (min)			
	F1	F2	F3	F4
4.0	74	74	76	61
6.0	70	69	72	62
8.0	60	69	62	60
10	54	62	61	59

Table 4.11 Percentage of settled solids: C_{sol} = 2 mg/l of Fe, C_s = 1 mmol/l $CaCl_2$, C_p = optimum polymer dosage, t_2 = 1 h

pH	Volume percentage(%)			
	F1	F2	F3	F4
4.0	53	79	72	83
6.0	49	63	70	77
8.0	44	72	66	72
10.0	30	67	58	62

4.3.2 Application to other systems

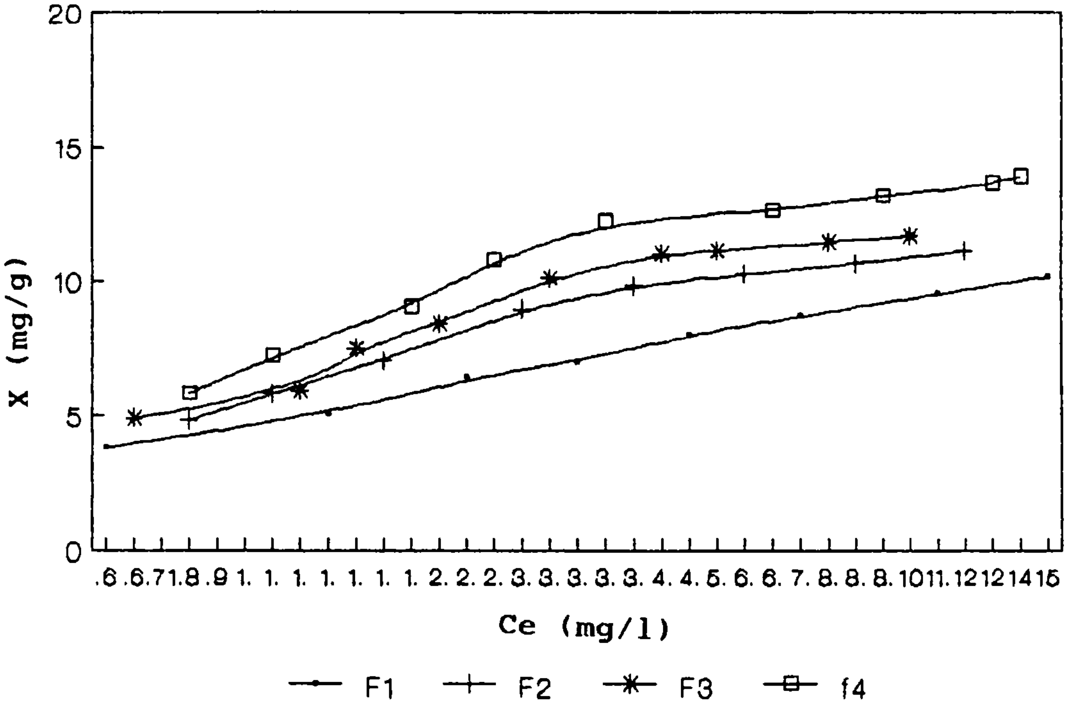
In the forgoing section the efficiency of the flocculation of $Fe(OH)_3$ by polyelectrolytes has been explained on the basis of the irreversibility of polymer adsorption. This irreversibility is generally found for polymer adsorption and it is worth probing the applicability of the procedure to similar systems of industrial and environmental concern. Application of polymer flocculant in the recovery and removal of copper and uranium from lean source are described in the following subsections.

(a) Flocculation of Cu (II) hydroxides

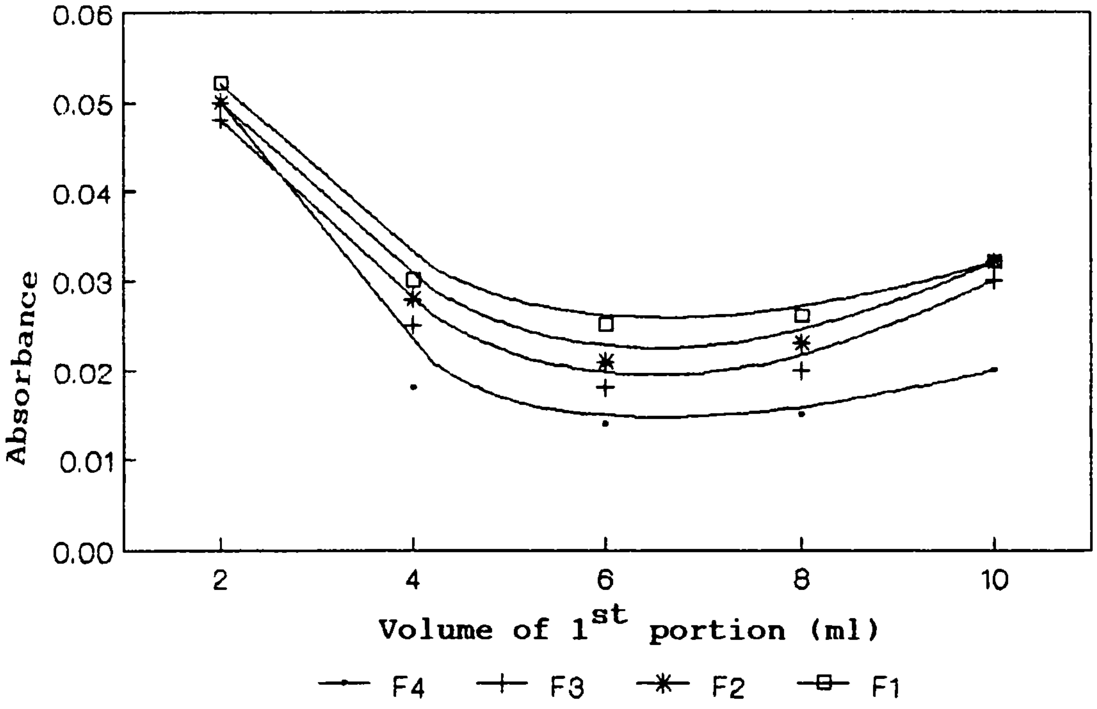
The hydroxide obtained as blue bulky precipitate on addition of alkali hydroxide to cupric solution has been characterized as $Cu(OH)_2$ (12). Its structure and solution chemistry are well established (11, 12). It is insoluble in the pH range 8.85 to 10.5.

The isotherm obtained for the adsorption of different flocculants on $Cu(OH)_2$ suspensions are given in Figure 4.8, where the amount of polymer adsorbed (X) is plotted against equilibrium concentration (Ce)of the polymer. As in the case of iron(III) hydroxide, the plots are found to be nearly linear in all the cases in the low concentration ranges. At higher concentration deviations are observed as in the case of $Fe(OH)_3$.

The effect of the mode of mixing of the metal hydroxide and the polymer was studied as in the case of iron(III) hydroxide and the results are presented in Figure 4.9. Here also a strong



igure 4.8 Adsorption isotherm of PSMA and PSMH on Cu(II) at pH 9



gure 4.9 Effect of the mode of mixing on flocculation efficiency

C_{sol} = 2.0 mg/l of Cu, C_s = 1mmol/l of $CaCl_2$,

t_1 = 15 min, t_2 = 1h, pH = 9

dependence of mixing mode on flocculation efficiency was observed. Effective flocculation occurs when the volume of the two fractions of the sol are equal.

Table 4.12 Optimum polymer dosage to flocculate $Cu(OH)_2$ with different flocculants at different C_{sol}:
C_s = 1 mmol/l of $CaCl_2$, t_2 = 1 h, pH = 9.0

C_{sol} (mg/l)	Optimum polymer dosage (mg/g of sol)			
	F1	F2	F3	F4
2.0	6.5	7.5	7.0	6.0
5.0	4.8	5.1	5.2	4.8
10.0	4.1	4.0	4.2	4.0

Table 4.13 Critical salt concentration of different electrolytes for the flocculation of $Cu(OH)_2$:
C_{sol} = 2mg/l, C_p = Optimum dosage, t_2 = 1 h, pH = 9.0

Electrolyte	CSC (mmol/l)			
	F1	F2	F3	F4
NaCl	80.0	60.0	70.0	60.0
$CaCl_2$	0.58	0.64	0.66	0.54
$AlCl_3$	0.09	0.08	0.09	0.07

The optimum polymer dosage is given in Table 4.12. The difference in the requirement of the polymer dosage is very small for different polymers. That is all the polymers have equal flocculation efficiency at this pH (9.0). This is accountable when the rheology of polymers in solution is considered. The

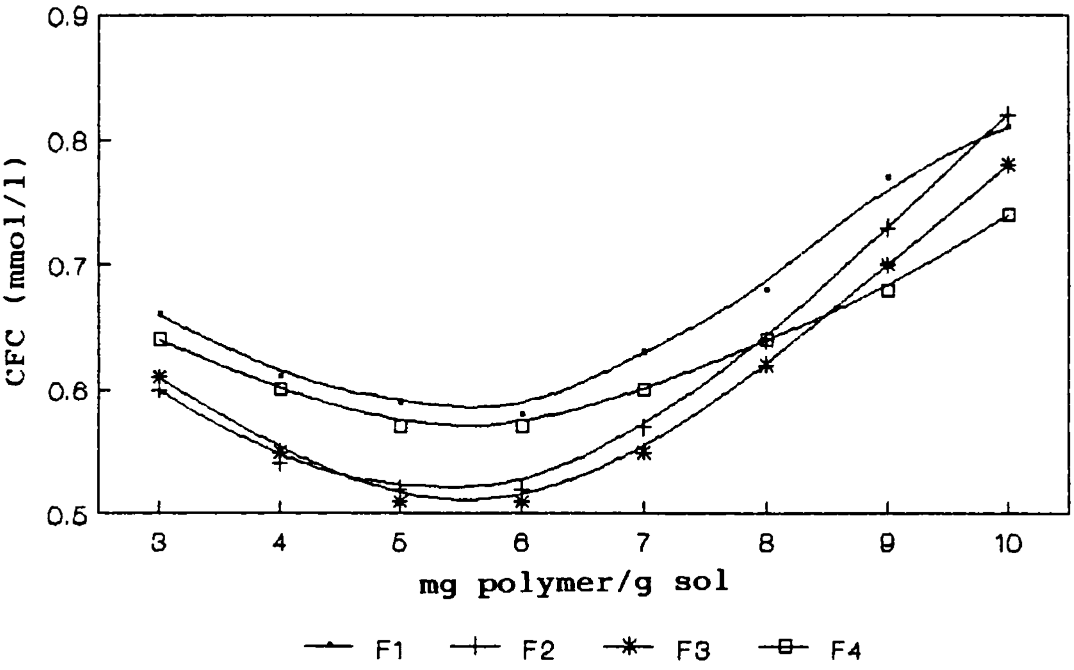


Figure 4.10 Dependence of CSC of $CaCl_2$ on polymer concentration: C_{sol} = 2 mg/l of Cu, t_1 = 15 min, t_2 = 1h, pH = 9.

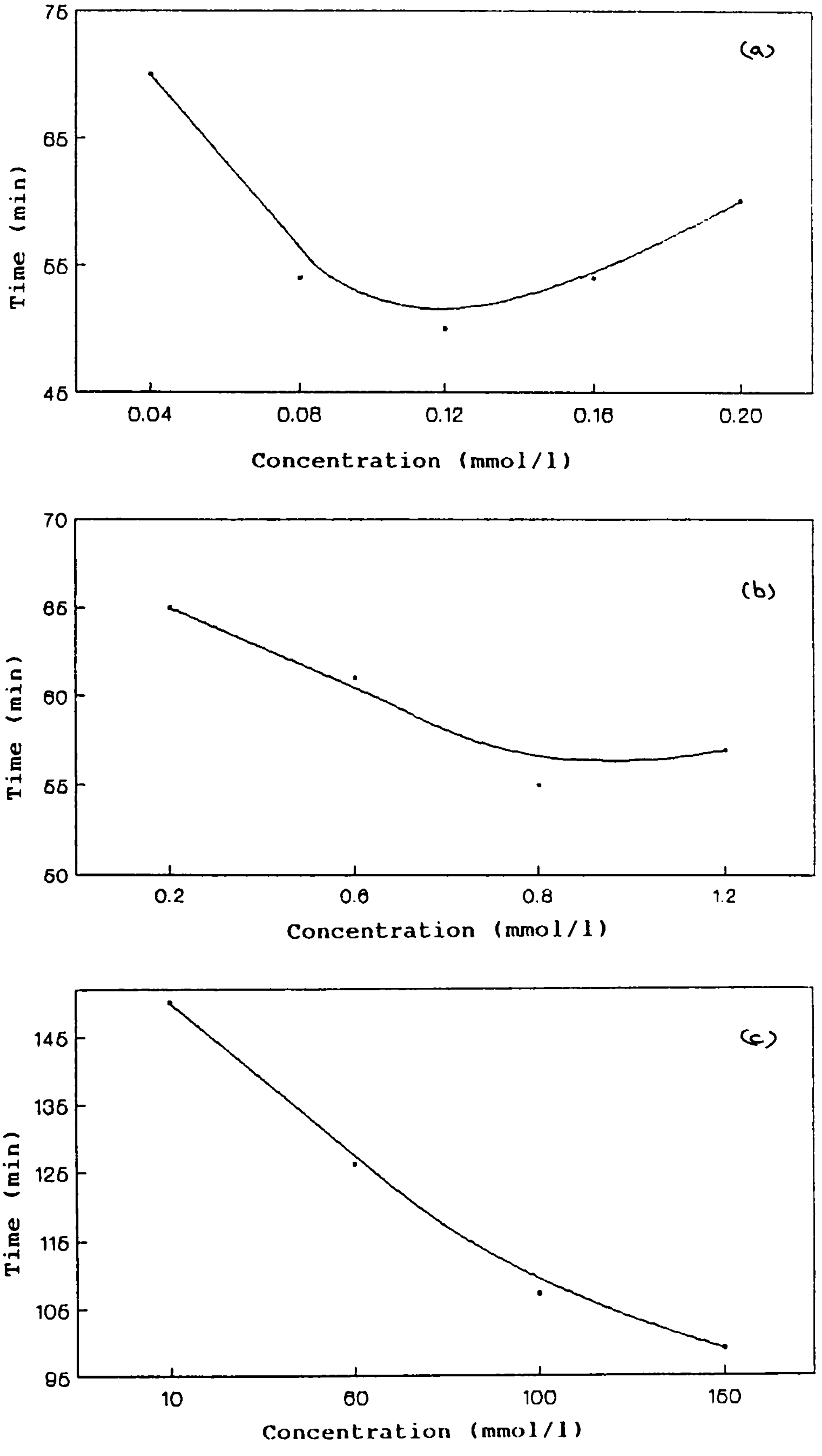


Figure 4.11 Effect of salt concentration on sedimentation time

(a) $AlCl_3$ (b) $CaCl_2$ (c) NaCl

flocculation efficiency is comparable to that obtained that for Fe(III) in the same pH range. Optimum polymer dosage decreases with increasing C_{sol}. The critical concentration of different salts for flocculation is summarized in Table 4.13. Here also the valency of the counter ion strongly affects the CSC. The CSC decreases with an increase in valency. Figure 4.10 shows the dependence of polymer concentration on the CSC of $CaCl_2$. The CSC increases with increasing polymer dosage.

The time required for the complete sedimentation of the flocs formed using different polymers with varying dosage is given in Figure 4.11. It decreases, attains a minimum and then increase with increasing concentration of polymers. This is also explained on the basis of the bridging mechanism. The stabilization of suspensions beyond optimum polymer dosage prevents aggregation. Particles with larger size settle faster than smaller ones. It is evident that the bridging mechanism controls not only the floc formation but also the separation characteristics of the floc formed. It is evident that there is an optimum electrolyte concentration over which the sedimentation time increases. The effect is more pronounced for aluminum chloride. This may be due to its high counter ion valency that significantly influences charge distribution on flocs. Increasing the amount of electrolyte will lead to a charge reversal on the particles that causes restabilization of suspension. This results in increased sedimentation time after an optimum electrolyte concentration.

Effect of different electrolytes on the settling characteristics of the flocs formed is given in Figure 4.12, where the volume percentage of solids is plotted against time. A strong dependence of counterion valency on the volume settled is

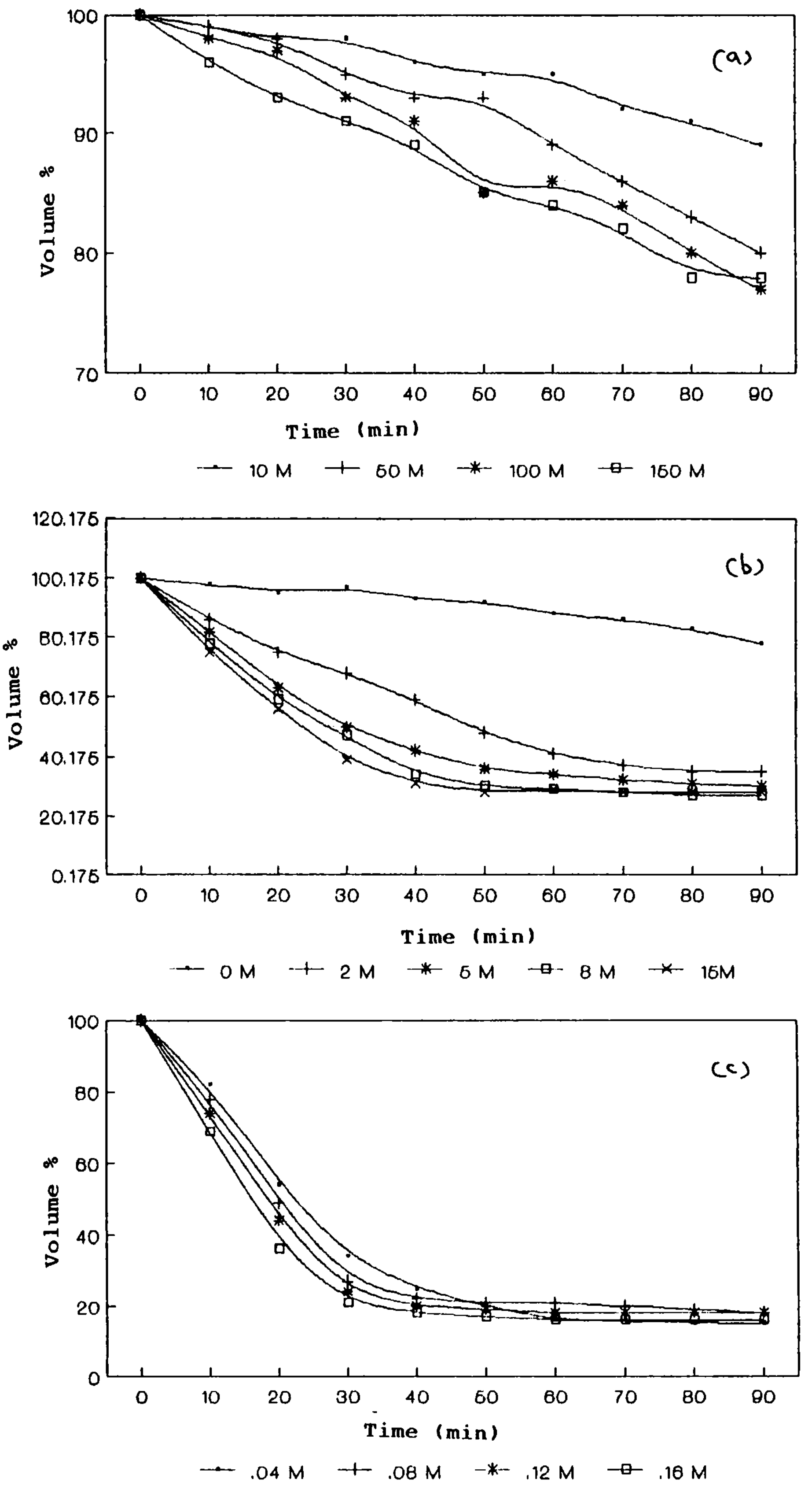


Figure 4.12 Effect of salt concentration on volume percentage of settled solid as a function of time:

C_{sol} = 2 mg/l, C_p = 8 mg/g of F1

(a) NaCl (b) $CaCl_2$ (c) $AlCl_3$

observed. It is evident that the flocs formed using Al^{+3} salts show better separation characteristics.

Figures 4.13 and 4.14 show the effect of different flocculants on the volume percentage of settled solids. Settling improved with an increase in the polymer dosage, as seen from the change in the slope of the curves. From the nature of the graphs it can be concluded that the flocs formed are of the phase settling type.

(b) Flocculation of U(VI) at high pH

The material obtained by the addition of NaOH to uranyl nitrate $[UO_2(NO_3)_2]$ solution is usually termed sodium diuranate. This is mainly the hydrate, $UO_2(OH)_2H_2O$ (11,12).

The optimum dosage of polymer for flocculation is given in Table 4.14. The values are quite agreeable with those obtained for Fe(III) and Cu(II). The flocculants F1 and F4 are found to be

Table 4.14 Optimum polymer dosage for the flocculation of U(VI) at pH 9.0 with different flocculants at different C_{sol}: C_s = 1 mmol/l $CaCl_2$, t_2 = 1 h.

C_{sol} (mg/l)	Optimum polymer dosage (mg/g of sol)			
	F1	F2	F4	F4
2.0	5.0	5.5	5.5	4.0
5.0	3.2	3.3	4.0	2.9
10.0	2.7	2.7	3.1	2.5

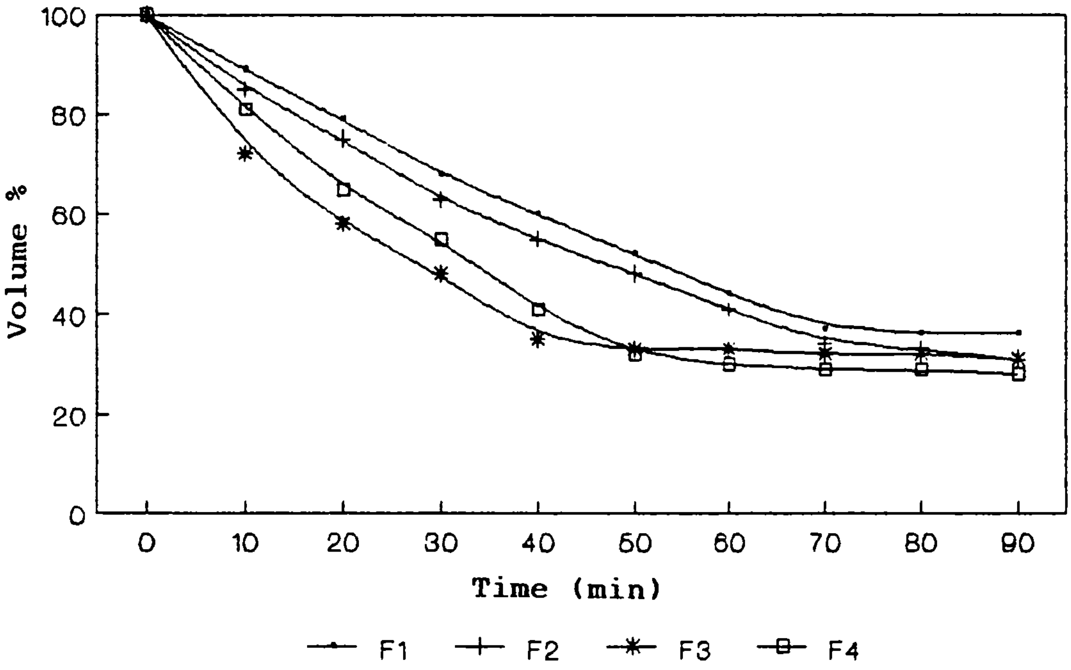


Figure 4.13 Volume percentage of settled solid as a function of time for different flocculants

C_{sol} = 2 mg/l, C_p = 8 mg/g of sol, C_s = 1 mmol/l.

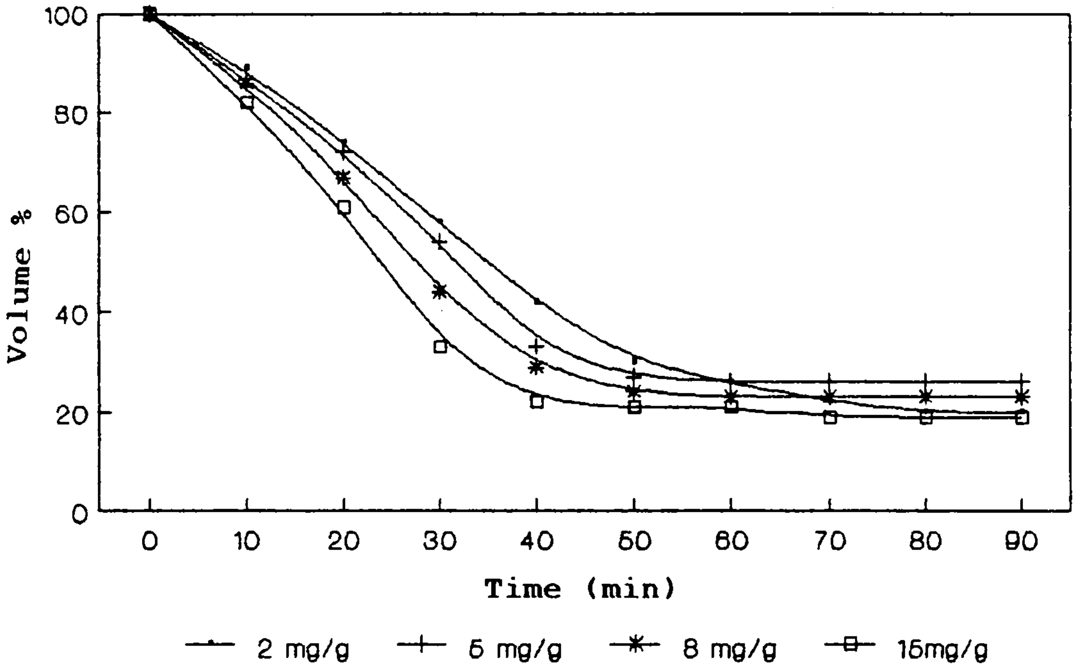


Figure 4.14 Volume percentage of settled solid as a function of time for different F1 concentration

C_{sol} = 2 mg/l, C_s = 1 mmol/l $CaCl_2$

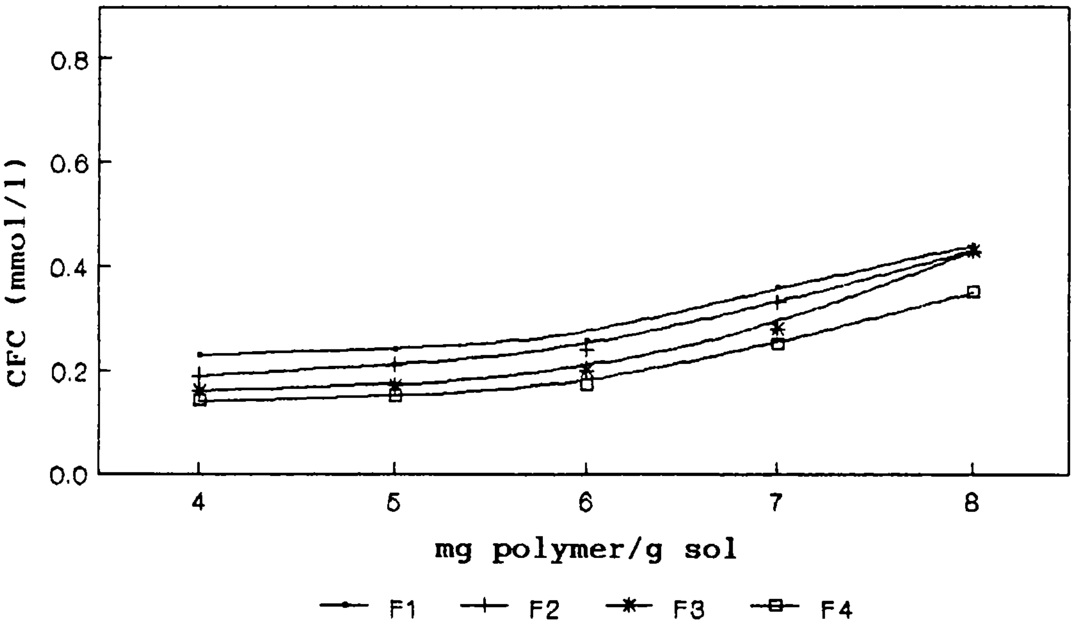


Figure 4.15 Dependence of CSC of $CaCl_2$ on polymer concentration: C_{sol} = 2 mg/l of U(VI), t_1 = 15 min, t_2 = 1h, pH = 9.

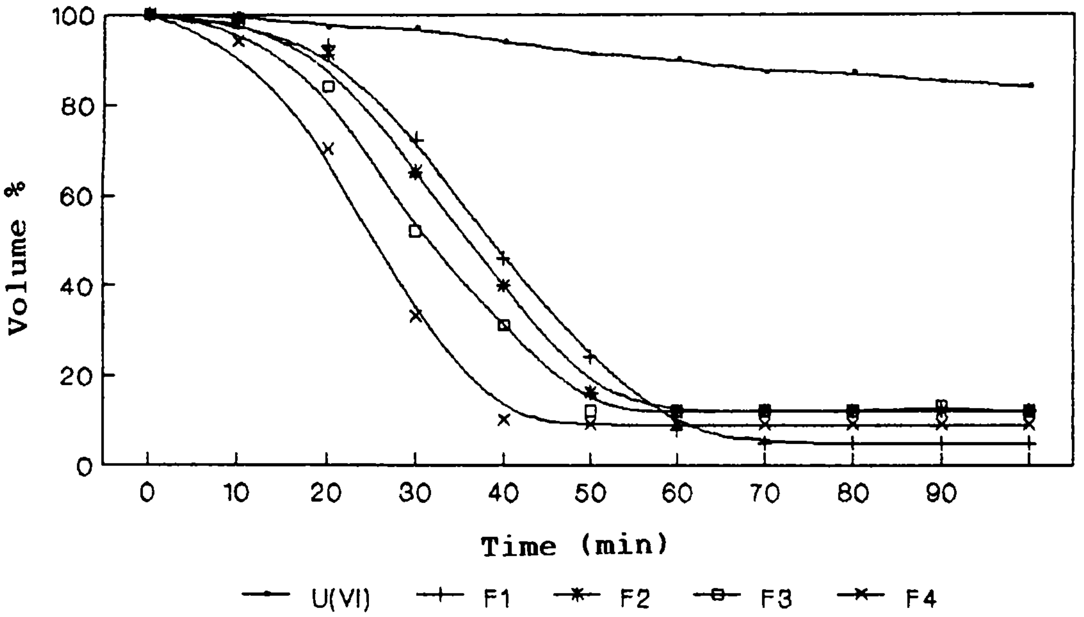


Figure 4.16 Volume percentage of settled solid as a function of time for different flocculants
C_{sol} = 2 mg/l U(VI), C_p = Optimum dose, C_s = 1 mmol/l.

Table 4.15 Time of sedimentation of U(VI) flocs formed with different flocculants at pH 9:

C_{sol} = 1mmol/l, C_p = Optimum polymer dose, t_2 = 1 h.

C_{sol} (mg/l)	Time (min)			
	F1	F2	F3	F4
2.0	68	62	64	49
5.0	47	45	49	34
10.0	31	28	30	26

the most effective. This is reasonable since the former has a high ionic content and the latter has a chelating group.

The dependence of CSC of $CaCl_2$ on polymer dosage is given in Figure 4.15. The explanations given for the effect of polymer dosage on CSC in the flocculation of iron and copper suspensions fits here also. The settling characteristics of the flocs formed are presented in Figure 4.16 and Table 4.15.

The observations presented in this chapter clearly make out the optimum experimental conditions and polymer characteristics required for the efficient flocculation of three typical metal hydroxides. Attempts have also been made to explain the observations in terms of the characteristics of the polymers and the metal hydroxides.

REFERENCES

1. L. Svarovsky, Solid-Liquid Separation, 1977, Butterworth, London.
2. W. W. Shuster, L. K. Wang, Separation and Purification Methods, 1977, 6, 153.
3. V. K. La Mer, J. Colloid Sci., 1964, 19, 291.
4. V. K. La Mer, T. W. Healy, Rev. Pure and Appl., Chem., 1963, 13, 112.
5. A. S. Michaels, Ind. Eng. Chem., 1954, 46, 1485.
6. R. A. Ruehrwein, D. W. Ward, Soil Sci., 1992, 73, 485.
7. R. D. Vold, M. J. Vold, Colloid and Interferace Chemistry, 1983, Addison-Wesley Publishing Company, Inc., Massachusetts.
8. K. Furusawa, Y. Tezuka, N. Watanabe, J. Colloid Interface Sci., 1980, 73, 21.
9. Annual Book of ASTM Standards, 1974, 31, D 1252.
10. G. J. Fleer, J. Lyklema, J. Colloid Interface Sci., 1974, 46, 1.
11. J. Kargton, Atlas of Metal-Ligand Equilibria in Aqueous Solution, 1978, Ellis Horwood Limited, New York.
12. F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 1976, Willey Eastern Limited, New Delhi.
13. S. D. Faust, O. M. Aly, Adsorption Processes for Water Treatment, 1987, Butterwoth Publishers, Stonham.
14. K. Kandori, A. Kitahara, K. Kon-no, Bull. Chem. Soc. Jpn., 1983, 56, 1581.
15. J. M. G. Cowie, Polymers: Chemistry and Physics of Modern Materials, 1973, International Text book Company Limited, Aylesbury.
16. A. Kitahara, A. Watanabe, Electrical Phenomena at Interfaces:

Fundamentals, Measurements and Applications, 1984, Marcel Decker, New York.

17. G. J. Fleer, L. K. Koopal, J. Lyklema, Kolloid Z. Z. Polym., 1972, 250, 689.

18. W. L. K. Schwoyer, Polyelectrolytes for Water and Wastewater Treatment, 1981, CRC Press Inc., Florida.

19. R. Mendez, Studies on Polymer Complexones, Ph.D thesis, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, 1990.

CHAPTER V

SUMMARY AND CONCLUSIONS

Poly(styrene-*co*-maleic acid) samples having different ratio of the monomers were prepared and characterized by physico-chemical techniques. The polyelectrolyte samples were found to be effective flocculants for dilute suspensions of metal hydroxides. Flocculation conditions were optimized to achieve effective separation of flocs. Membranes cast from the polymer act as selective barriers. The ion-exchange membranes so formed were evaluated for their performance in dialysis and transport of metal ions under active conditions. The results obtained in this study lead to the following conclusions:

1. Dilute solution viscosity measurements of poly(styrene-*co*-maleic acid) (PSMA) in water confirms its polyelectrolyte nature. Reduced viscosity decreases with increasing concentration. pH and added electrolytes have pronounced effect on the rheology of polyelectrolytes. Viscosity increases with pH, owing to the increasing ionization of -COOH groups and their electrostatic repulsion. The hydroxamic acid derivative (PSMH) of the polymer shows non-ionic behaviour and its reduced viscosity increases with concentration.
2. Cross-linking of PSMA leads to a decrease in its solubility in water. Films formed by partial cross-linking with Al^{+3}, ethylenediamine and PVA perform as stable ion-exchange membranes. As expected the ion-exchange capacity depends on

the extent of cross-linking, decreasing with increasing cross-linking content. Mechanical stability measured as burst-strength increases with cross-linking content. Mechanical strength also depends on the nature of the cross-linking agent. It decreases in the order PVA > EDA > Al^{+3}.

3. The membranes reported here possess good electrical properties. Electrical conductivity increases with external pH due to the dissociation of -COOH groups. Membrane potential studies reveal high permselectivity towards cations. Transport number values of cations calculated from membrane potential data were found to decrease with increase in electrolyte concentration as predicted by Donnan exclusion principle. Permselectivity is affected by external pH due to the change in the electrical property of the membranes.

4. The membranes are permeable to KCl, NaOH, NaCl, Na_2SO_4 and to a limited extent to urea and creatinine. The difference in the limiting permeability coefficients is due to the difference in the size of the hydrated ions, and electrical and geometrical effect of the membranes. Sodium hydroxide has the highest permeability coefficient due to its high counter ion mobility. KCl moves faster than NaCl due to the difference in the size of the hydrated cationic spicies. Sodium sulphate has comparatively low permeability coefficient value among salts due to the low mobility of SO_4^{2-} ions. Urea and creatinine have still lower permeability coefficient values, which can be accounted for in terms of the permeation of neutral species through charged membranes.

5. The membranes exhibit active and selective transport of metal

ions. In the active transport of metal ions, H^+ controls the physical and chemical structure of the membrane and its concentration provides the driving force. In the selective transport of metal ions, the selectivity depends on both the size of the hydrated ions, and the interaction between the charge groups on the membrane and the metal ion. The mean transport rate increases with increasing exchange capacity of the membrane and difference in pH between the two compartments. Ion-exchange capacity has a profound effect on the mean transport rate and selectivity of the membrane to the metal ions.

6. Polyelectrolytes, PSMA and PSMH are soluble in water and can act as effective flocculants for metal hydroxide sol at low concentrations. The efficiency of flocculation can be explained on the basis of a bridging mechanism, where polymeric chain is adsorbed onto the particle surface in such a way that long loops of segments protrude into the liquid phase. Other particles may also become attached to the chain at other sites, and hence the polymer molecule serves as a bridge.
7. The isotherms for polymer adsorption on metal hydroxides are of the Langmuir type at moderate concentrations and of the Henry type at very low concentrations. The maximum amount of polymer adsorbed depends on the charge content on the polymer and the pH of the medium.
8. The study shows that the mode of mixing is an important parameter in controlling the flocculation of hydrophobic sols by polymers. In experiments using two portion method of mixing, flocculation is much more effective when the volumes

of the two portions are equal at the concentrations employed. The efficiency of the mode of mixing has been explained on the basis of the irreversibility of adsorption of the polymer.

9. The optimum dosage of polymer depends on the pH of the medium, sol concentration and the acid equivalent of the polymer. It is observed that PSMH acts as a non-ionic polymer and shows minimum pH dependence while PSMA exhibits a large pH dependence. This supports the idea that uncoiling of the polymer chain affects the activity. The flocculant F_1 which is highly anionic in nature is found to be effective above pH 9.0, while F_4 (hydroxamic acid) is effective at lower pH.
10. In the two portion method, a low but non-zero concentration of electrolyte is still needed to produce flocculation. The critical salt concentration (CSC) as measured by the amount of salt needed to flocculate half of the suspension strongly depends on the valency of the metal ion. CSC varies with polymer dosage and gives a minimum value at optimum polymer dosage.

A part of the work presented in this thesis has been published in journals/ presented in conferences/ communicated in the following form.

1. Preparation, Characterization and Alkali Metal Ion Permeation through Cross-linked Poly(styrene-*co*-maleic acid) membranes.
K. C. Philip, and V. N. Sivasankara Pillai
Accepted for publication Polymer International, 1993.

2. Synthesis and Characterization of Ionically Cross-linked Poly(styrene -*co*-maleic acid) Membranes.
K. C. Philip and V. N. Sivasankara Pillai
Paper No. 154, **EUROMEMBRANE/ 92 CONGRESS**, 5-8 October, 1992, paris, France.

3. Flocculation of Fe(III), Cu(II) and U(VI) Suspensions by Styrene-Maleic Anhydride Copolymers.
K. C. Philip and V. N. Sivasankara Pillai
(Under communication)