

CHAPTER 1

POLYELECTROLYTES: DEFINITION, PROPERTIES AND APPLICATIONS

1.1 Polyelectrolytes: Definition and Properties

A polyelectrolyte, by definition, is a macromolecular species that upon being placed in water or any other ionizing solvent dissociates into a highly charged polymeric molecule. Such dissociation is typically accompanied by smaller oppositely charged counter ions that tend to neutralize the charge on the repeating units of the macromolecule preserving electroneutrality.¹⁻⁶ A polyelectrolyte, in low ionic strength solutions, tends to be in its most extended and uncoiled form due to the intramolecular repulsion of the unscreened charges on each monomeric unit of the macromolecule. On the other hand, when the ionic strength of the solution is increased, a polyelectrolyte tends to become thicker and more coiled due to the screening effects of polymer charges by the excessive presence of smaller salt counterions in solution as is shown in Figure 1.1. This unique physical property will be of major experimental and theoretical significance through the entire content of this dissertation. The degree of charge screening of the polyelectrolyte will be an important factor in tuning the thickness,⁷ uniformity,⁸ stability,⁹⁻¹¹ swelling,¹²⁻¹⁶ permeability¹⁷⁻²¹ and other important variables when studying synthetically modified²²⁻²⁸ as well as naturally occurring polyelectrolytes²⁹⁻³² and their corresponding layer-by-layer ultrathin film composites or assemblies.³³⁻⁴⁰

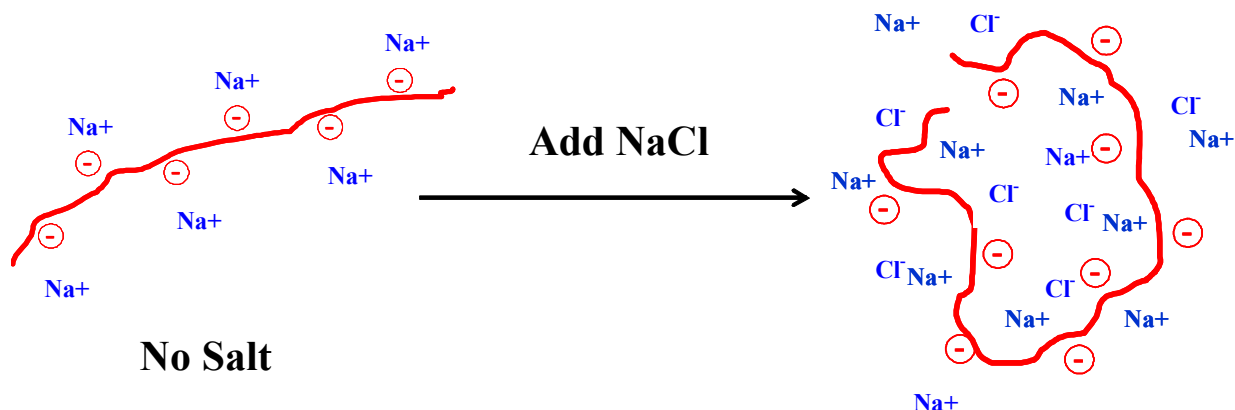


Figure 1.1 Scheme showing the effect of ionic strength on the shape of a polyelectrolyte molecule in solution.

1.2 Polyelectrolytes: Recent Applications

In addition to their essential functions in human physiology and cellular mechanisms in the form of proteins, polypeptides and nucleic acids, polyelectrolytes have found a number of important applications in the major fields of science and engineering such as chemistry, physics, biology, chemical and materials engineering. Their applications in chemistry are mainly centered at the interface of polymer, materials, colloids, surface and analytical chemistry. Recently, polyelectrolytes have found extensive use in a variety of projects and technologies both in the academic and the industrial research and development areas. Polyelectrolytes have been used in the health and personal care industry as thickening reagents,⁴¹ rheology modifiers⁴² and viscosity enhancers for shampoos, conditioners, deodorants and body lotions.^{43,44} They have also been used in water treatment,⁴⁵ waste treatment,⁴⁶ sludge dewatering⁴⁷ and the pulp and paper industry as retention aids as well as flocculating and coagulating agents for solid-liquid separations.⁴⁸ Other polyelectrolytes are used as additives to alter the physical properties of aqueous products.⁴⁸ For instance, they are used for water retention, adhesive strength,

binding power, film formation and protective colloidal, suspending and emulsifying actions.⁴⁸ Recent work by Klibanov et al. has shown that some of these polyelectrolytes are very effective as antibacterial reagents both in solution and as protective coatings on surfaces.⁴⁹ Example of that are the alkylated poly(vinyl pyridines), in which the alkyl chain is between three and eight carbons. The long alkyl tails on the poly(vinyl pyridine) ring tend to burst the bacterial cell wall causing an irreversible reaction that leave the bacterium totally incapacitated. More recently, Shiratori and Sato have designed a thin film coating of polyelectrolytes assembled from chitosan and another polyelectrolyte containing an enzyme which was extracted from bamboo.⁵⁰ The thin film wrap was very effective in preventing decomposition and ripening of fresh fruits such as melons by suppressing their emission of ethylene gas, and thus kept these fruits fresh for long periods of time. In addition to that, assembling these polyelectrolytes into ultrathin film composite membranes is one of the most important applications and has received significant attention and interest recently.⁵¹⁻⁸⁸

1.3 Polyelectrolyte Complexes (PECs) and Their Applications

One of the most important physical features of polyelectrolytes is their complexation capabilities when mixed with other polyelectrolytes of the opposite charge. Polyelectrolyte complexes and polyelectrolyte multilayers share similar physical and chemical properties in terms of their internal structure, physical structure and morphology.⁸⁹ Since this dissertation mainly focuses on polyelectrolyte multilayer studies, it is worthwhile to give a brief survey about polyelectrolyte complexes, their formation and applications.

When two relatively high molecular weight polymers are mixed together in dilute aqueous solution, a precipitate is formed which contains almost exact stoichiometric proportions of the component polyions. The precipitate contains none of the counterions initially associated with the individual polymers. This will be referred to as an “*intrinsically compensated*” state in which all the charged units of the polymer chains are internally compensated by oppositely charged units from the other polyelectrolyte. In the presence of external salt solutions, salt ions tend to enter the bulk of the complex and

transform it into an “*extrinsically compensated*” state.⁶⁸ Similar properties are also shared by polyelectrolyte multilayers which are essentially a form of somewhat ordered, automated and reproducible deposition or buildup of polyelectrolyte complexes on different substrates.²⁵ X-ray diffraction studies have shown polyelectrolyte multilayers as highly interpenetrating complexes that are indistinguishable from their corresponding solution complexes at the molecular level due to the absence of Bragg peaks.²⁵ However, due to some unfavorable physicochemical properties of polyelectrolyte complexes, polyelectrolyte multilayers are gaining special appreciation. Such properties include insolubility in common solvents, infusibility and, in general, the lack of processability. On the other hand, the polyelectrolyte multilayer layer-by-layer buildup technique offers solutions to these problems by *in situ* coating of surfaces and substrates of irregular shapes and geometries. Polyelectrolyte solutions can literally reach any crevices, pores or cracks on a substrate and coat them without clogging their openings.² This would be virtually impossible using a ready made solid or colloidal complex. Regardless of their processability problems, polyelectrolyte complexes have found a number of important applications. They were used for dialysis and ultrafiltration membranes. For instance, a 1 mm thick coating of neutral polyelectrolyte complex subjected to 3.5% NaCl at 1500 psi, transmitted 30 liters of water per day per square foot of membrane area. This is roughly 15 times higher than commercial membranes used for reverse osmosis such as regenerated cellulose (cellophane) that were available at that time.⁹⁰ Recent work by Liu and Bruening have shown the water permeability of an ultrathin polyelectrolyte film of (PAH/PSS)₇ to be 82 liters per square foot per day at 70 psi of pressure.²¹ Polyelectrolyte complexes were also used for battery separators, fuel cell membranes,⁹⁰ moisture-breathable plastic composites, electrically conductive coatings, antistatic coatings, medical and surgical prosthetic materials, environmental sensors and chemical detectors.⁹⁰

1.4 Layer-by-Layer Sequential Assembly

As an alternative to using complexed polyelectrolytes to assemble thin film membranes, a new layer-by-layer (LBL) sequential assembly technique is utilized. The

LBL assembly technique was first mentioned by Iler in 1966.⁹¹ In 1991, however, Decher and Hong expanded that technique and brought it to the forefront of materials science and engineering.³⁸ Since then, research in this field has attracted the attention of scientists across the academic and industrial fields. Fifteen hundred publications utilizing this technique were reported by June 2003.⁹² The technique involves alternating rinses of a substrate or a solid support in two oppositely charged polyelectrolytes along with rinse steps in between to remove any extra material that is loosely bound to the surface.^{2,38} Figure 1.2 is a diagram detailing the layer-by-layer assembly process. Thus, one can build as many layers as needed depending on the particular type or requirements of the experiment. Ultrathin films could be built offering high flux and selectivity for membrane separations, filtrations and purifications applications.^{52-56,59} Thicker membranes could also be built offering hydrophobic coatings,²⁵ hydrophilic coatings²⁵ or anti-corrosive coatings.^{93,94} Multilayers reported in the literature had thicknesses that ranged between 10 nm and 10 μm .⁹⁵⁻⁹⁷

1.4.1 Advantages of LBL Assembly Technique

This LBL technique is superior, in many respects, to other deposition techniques that are reported in the literature such as vacuum deposition, solvent casting, spin coating or Langmuir-Blodgett (LB) deposition.^{2,49,98,99} Vacuum deposition requires specialized expensive instrumentation and specific types of substrates. Solvent casting produces thick and non-uniform films. Solvent casting and spin coating do not follow contours well.^{2,49} The earliest technique used to fabricate multilayer films was invented by Langmuir and Blodgett⁹⁸ to make LB films. LB films are highly ordered and have uniform controlled thickness. However, they have several limitations. The requirements for substrates are stringent: they must be smooth, homogeneous⁴⁹ and have regular shape. Further more LB fabrication requires expensive equipment. LB-multilayers have limited stability against solvents and thermal treatments, and defects formed in a given layer are difficult to cover up by subsequent layers. Also, it is a very slow technique.⁹⁹ On the other hand, the LBL assembly technique is a very robust, reproducible, cost effective and environmentally friendly method. It is done at room temperature, so there is no need for any vacuum equipment or special instrumentation. It can be used to assemble various

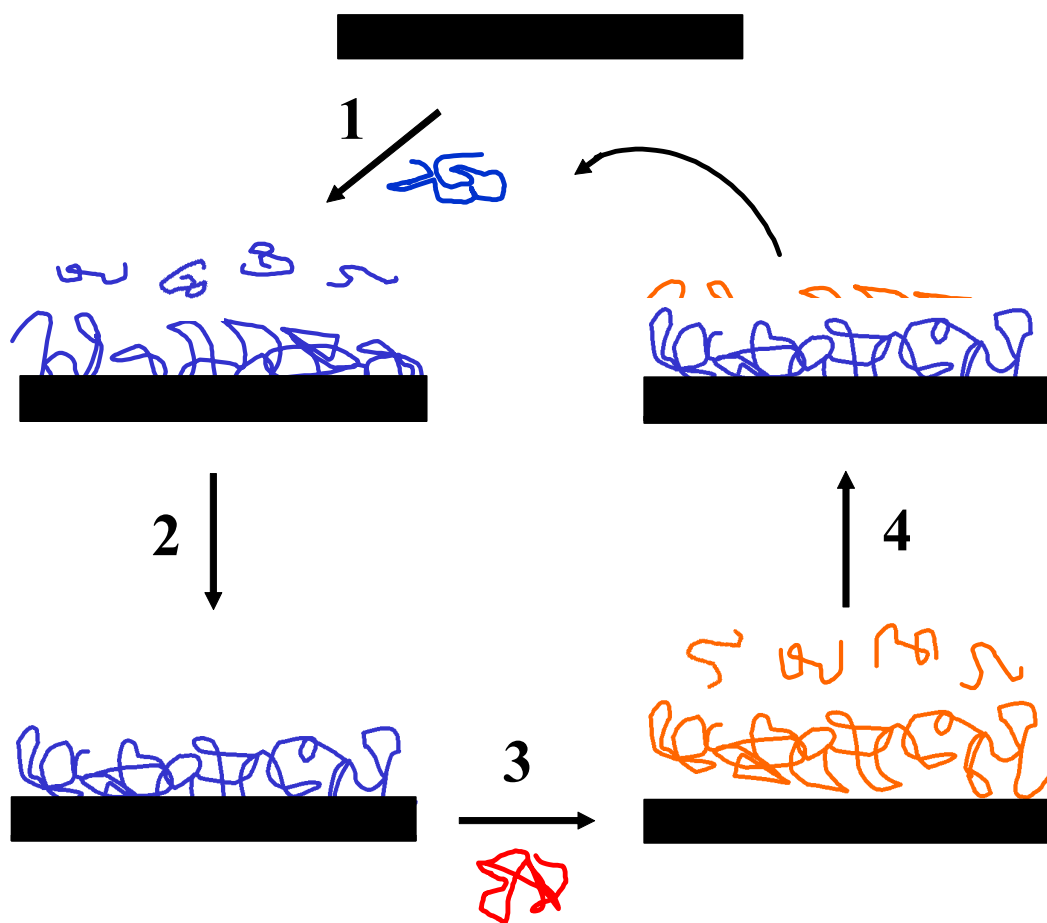


Figure 1.2 Scheme showing the layer-by-layer assembly procedure. Step 1 represents the deposition of the first positively charged polyelectrolyte on the negatively charged substrate. Step 2 represents subsequent rinsing to remove any polymer that is loosely bound to the surface. Step 2 was repeated three times. Step 3 represents the addition of the next negatively charged layer. Step 4 represents rinsing and was repeated three times. The complete cycle 1-2-2-2-3-4-4-4 can be repeated multiple times to get the desired thickness or number of layers.

various types of materials,¹⁰⁰ polymers,¹⁰¹ composites,¹⁰² clay,¹⁰³ proteins,³³ dyes,¹⁰⁴ carbon nanotubes¹⁰⁵ or nanoparticles.^{106,107} This is a limitation of other techniques because they only work for special kinds of materials. Also, it can be coated on various kinds of substrates such as silicon, gold, platinum, plastic, glass, quartz, stainless steel, clay, nanoparticles, blood cells and colloidal particles.¹⁰⁸ The whole process can be automated making the coating procedure less time consuming and applicable for commercial applications where productivity and labor are major problems. Above all, this technique offers very precise control over the thickness and unprecedented uniformity of the coating or the membrane built, down to the subnanometer scale.

1.5 Ultrathin Polyelectrolyte Films: Membrane Applications

Diffusion of molecules, ions, gases, dissolved species, liquids, drugs and vitamins through biological and synthetic membranes is a very interesting phenomenon. For example, the sodium-potassium gated channels in human cells are a natural demonstration of the importance of gated permeabilities,¹⁰⁹ controlled release and membrane separation of species of different sizes, charges and functional groups.¹⁰⁹

There is a large number of synthetic or biological membranes reported in the literature.^{40,110} In this Introduction, the discussion will be mainly limited to ultrathin film membranes that are built from synthetic, semi-synthetic, naturally occurring polyelectrolytes, polyzwitterions or polyampholytes using the layer-by-layer sequential assembly technique. Such membranes are used for separation of ions,^{52,54,60,62,63,65,69,71,75} enantiomers,²⁴ liquids,^{20,57,58} neutral compounds,¹¹¹ drugs¹¹² and gases.^{59,72} Significant control over their flux and selectivity have been demonstrated which makes them very good candidates for commercial applications such as nanofiltration for water softening and reverse osmosis for desalination.⁵⁵ Other sulfonated perfluorinated polyelectrolytes and sulfonated polyimides were used as effective proton conducting membranes for fuel cell applications.¹¹³

The content of this dissertation will be devoted to studying polyelectrolytes synthesis, structure-property relationships and their applications in surface modifications, ultrathin film membranes and analytical separations. Membranes assembled from these

polyelectrolytes will be referred to as *polyelectrolyte multilayers (PEMUs)* throughout the rest of this dissertation.

PEMUs were introduced in 1991. Recently, they have played an important role in research involving membrane and chromatographic separations. In this section, some of the most important achievements and applications will be presented.

One of the earliest uses of multilayer thin film assemblies as membranes for separations was reported in 1997.⁸³ Crooks et al. reported the use of pH-switchable, ultrathin permselective membranes prepared from multilayer polymer composites. In the same year, Levasalmi and McCarthy⁷² reported using (PAH/PSS) combinations on surface-modified poly(4-methyl-1-pentene) film with the objective of creating an asymmetric gas separation membrane consisting of a thin skin multilayer coating on a more permeable support polymer film. Poly(4-methyl-1-pentene) film was first surface-oxidized to introduce carboxylic acid functionality to the surface in preparation for depositing the first layer. Alternating PAH and PSS depositions, ultrathin multilayer films were obtained. Thin film multilayers of PAH and PSS were found to be 18000 times more blocking to nitrogen than bare poly(4-methyl-1-pentene). A selectivity of 15 was reported for O₂:N₂ using (PAH/PSS)₁₀₀ deposited on top of oxidized poly(4-methyl-1-pentene). On the other hand, the alternating deposition of polyaniline and PSS did not change the permeability properties of the film, suggesting a loose packing of polymer segments in the membrane.

In 1998, Krasemann and Tieke⁸⁸ reported the use of polyelectrolyte thin films as membranes for pervaporation applications as well as gas separations. They described ethanol-water pervaporation using new composite membranes made of a polyethylene terephthalate (PET) fleece coated with a thin layer of polyacrylonitrile (PAN) and an ultrathin polyelectrolyte complex separating layer that is assembled on top of the PAN/PET support. The polyelectrolytes used were PAH and PSS. They found that the separation capability increased dramatically if the membranes were annealed at temperatures above 60°C. On the other hand, the flux decreased. Similar results were obtained when the number of polyelectrolyte bilayers was increased. The highest separation factor of 70 was found at a low feed water content of 6.2% (w/w). Water was permeating at a higher rate than ethanol. The corresponding flux was 230 g m⁻² h⁻¹. In

another study, the same group reported using an alternating sequence of cationic and anionic compounds (polyelectrolytes and bolaamphiphiles) as gas separation membranes. (PAH/PSS)₂₀ at PAN/PET membranes were sufficient to reduce the argon flow to 7% of the initial value, while 60 bilayers reduced the flow to 0.1%. Gas flow rates of oxygen, nitrogen and argon were also studied and found to be the same. On the other hand, the flow rate of carbon dioxide was higher by a factor of 2.4.

Soon afterwards, Bruening et al. started using these alternating polyelectrolyte coatings as anticorrosive coatings as well as ultrathin films for membrane applications.^{81,82} Ultrathin, passivating films are attractive for protecting metal surfaces without completely masking substrate properties. Using layered PAA/PAH films on aluminum produced ultrathin coatings that protect aluminum from chloride induced corrosion. On the other hand, high-flux composite membranes were made by depositing ultrathin, defect-free films on highly permeable supports. LBL deposition of polyelectrolytes on porous alumina produced such membranes. Electron microscopy shows that (PAH/PSS)₅ were sufficient to cover the porous alumina substrate and that underlying pores were not clogged during the deposition process. Selectivity increased linearly with the number of layers until the substrate was totally masked. Selectivity values up to 310 for chloride over ferricyanide were obtained. According to the authors, selectivity in both of these systems likely resulted from Donnan inclusion/exclusion mechanism.

Since 2000, a significant number of studies have been reported using the layer-by-layer assembly technique of polyelectrolytes to assemble thin film coatings for membrane separations.⁵⁰⁻⁸⁸ Some reported using polyelectrolyte thin films for separation of gases and dissolved species.^{59,72} Others reported using them for separation of neutral species and other drug-like molecules.¹¹⁰⁻¹¹² Several factors have been shown to affect the permeability and the selectivity of the assembled membranes. In a related study, pH was used to control the charge density on the repeat units of weak polyelectrolyte brushes and thus control their permeability. For instance, Zhang and Ito used PAA and cystamines for self-assembly on a gold-coated membrane.⁸⁴ They found that the amount of assembled polyelectrolytes significantly depended on the solution pH. Water permeability through the membrane was reversibly regulated by pH. The permeability was high at low pH and

low at high pH, and an increase in ionic strength increased the permeability at high pH. At low pH the polyelectrolyte was protonated and that caused the brushes to shrink and open the pores. At high pH, the opposite process took place. The ionic strength screened the electrostatic repulsion between like charges and caused the pores to shrink. Thus, pH-responsive permeability depended on the pH of the permeating solution. In addition to pH, ionic strength, number of layers, the nature of the polyelectrolyte and thickness of the film were important factors as well.

Multilayered polyelectrolyte combinations provide a versatile platform for the synthesis of ultrathin coatings and membranes with tunable ion transport properties. Electrochemical studies show that ion transport through multilayered polyelectrolyte films varies with the number of layers in the film and the deposition conditions. Crosslinking of poly(acrylic acid)/poly(allylamine hydrochloride) films through heat-induced amidation results in the formation of blocking films, and these ultrathin coatings provide modest corrosion protection for aluminum.⁸¹ Deposition of films on porous alumina substrates results in ultrathin membranes that completely cover substrate pores without filling them, and such membranes allow rapid transport of monovalent ions, while largely rejecting multivalent species. According to the study, increasing the extrinsic charge in these membranes by templating with Cu^{2+} enhances membrane selectivity and suggests that Donnan exclusion is an important part of the selectivity mechanism.⁶³ Transport can also depend greatly on the charge at the surface of the membrane, as changing this surface from a polyanion to a polycation sometimes results in large decreases in $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity. Variation of the surface structure through changes in the constituent polyelectrolytes allows control over selectivity and yields $\text{Cl}^-/\text{SO}_4^{2-}$ selectivities greater than 1000. The ability to tune the ion permeability of polyelectrolyte films may allow their application in areas such as metal corrosion protection and water recycling.^{62,63}

In this dissertation, a variety of more than 20 different polyelectrolytes, polyzwitterions, polyampholytes, conjugated polyelectrolytes and perfluorinated polyelectrolytes were synthesized and characterized. Each group of these synthetic polymeric -mostly water soluble- materials was engineered to satisfy the requirements of different types of applications, thus demonstrating a very strong correlation between

Table 1.1 Different types of synthetic, semisynthetic and natural polyelectrolytes and their applications.

POLYELECTROLYTES SYNTHESIZED	APPLICATIONS
Strong Polyelectrolytes	Controlled release, gated permeabilities, and membrane separations
Weak Polyelectrolytes	Electroosmotic flow control in microchannels, microfluidics
Polyzwitterions	Colloidal suspensions and coatings, porous coatings, water-soluble PECs
Polyampholytes	Protein resistant coatings and surfaces
Perfluorinated Polyelectrolytes	Fuel cells, ultra hydrophobic surfaces, corrosion protection
Hydrophobically-Modified Polyelectrolytes	Modification of Surface and Bulk properties of polymeric coatings
Conjugated Polyelectrolytes	Corrosion protection
Water-Soluble Zwitterionic Conducting Polyelectrolytes	Anti static and conducting surfaces
Chiral Polyelectrolytes	Enantiomeric membrane and chromatographic separations

the structure and property of the polymer as is shown in Table 1.1.

Among these applications were novel approaches for optimizing the ion filtering and separations of these ultrathin polyelectrolyte films assembled using the LBL technique. A thorough study of the effect of the hydrophobicity, the water content and the structure-property relationships inside these thin film coatings will be of significant importance in predicting the permeation and selective behavior of these films both theoretically and experimentally. Figure 1.3 shows a diagram of a target ultrathin film polyelectrolyte membrane that is capable of complete separation of singly and triply charged ions.¹¹⁴

In another approach, varying the pH of the solution and incorporating ionizable pH-sensitive molecules was equally interesting. By controlling the protonation state of some vitamins and drugs,¹⁹ precise permeation and selectivity measurements were achieved. Instead of using conventional weak polyelectrolytes for building the separation membranes, strong polyelectrolytes were used. Weak polyelectrolytes were shown to undergo phase transitions and form micro and nano porous membranes when they sense a change of solution pH or ionic strength.¹¹⁵⁻¹¹⁷ On the other hand, strong polyelectrolytes did not experience that behavior and were extraordinarily stable to pH extremes when assembled into thin film membranes.

Ionic strength was also found to have important effects on controlling the permeability and the selectivity of ions of various sizes and charges. The mechanism of permeability will be discussed thoroughly in Chapters 5, 6 and 7. In brief, the mechanism of permeability was found to be very different from a Donnan inclusion/exclusion mechanism that governs the behavior of crosslinked conventional ion exchangers. The permeability mechanism through polyelectrolyte multilayer coatings was referred to as the “reluctant exchange” mechanism. The intrinsic nature of the as-made dry multilayers discussed here makes it extremely hard for salt and probe ions to penetrate and diffuse through these films. Extrinsic sites are created by contacting the multilayer with solutions of high ionic strength.⁵⁴ The formation of extrinsic sites is an important factor in creating ion exchange sites which make the membrane more selective and permeable to ions of lower charge and smaller size.

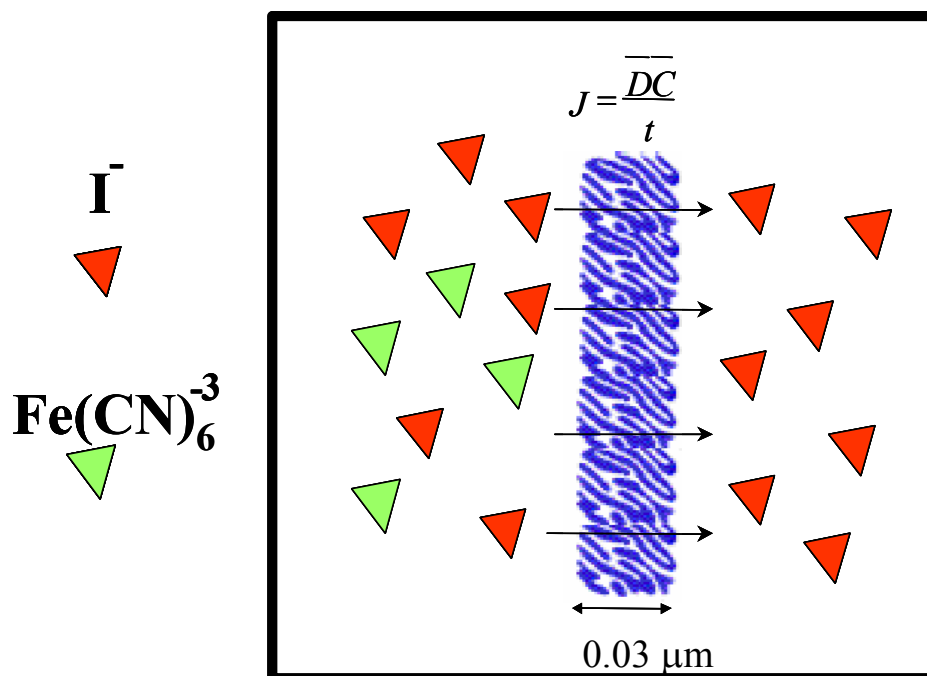


Figure 1.3 A target ultrathin polyelectrolyte membrane showing complete separation of singly and triply charged ions when used as a coating on a rotating disk electrode voltammetry.

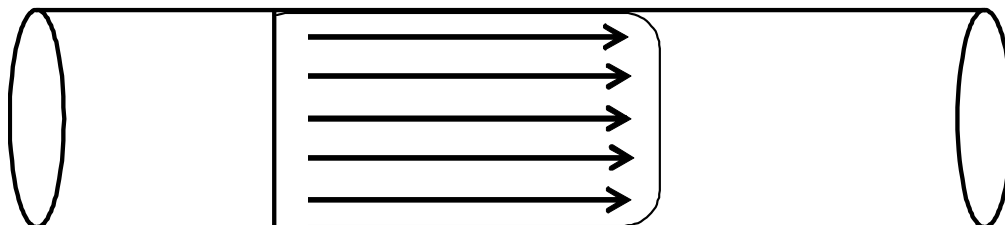
1.6 Polyelectrolyte Thin Film Coatings for Chromatographic Separations

Polyelectrolyte coatings were also used for chromatographic separations.¹¹⁸⁻¹²⁸ Chromatography is a well-known technique that is widely used for the identification and isolation of drugs, pharmaceuticals, proteins, peptides, amino acids, stereoisomers and chemicals.^{129,130} Typical chromatographic separations utilize columns that are packed with derivatized porous silica particles, known as stationary phases. Different solutes interact differently with the coatings on the particles and therefore different molecules migrate at different rates through the column. Such differences in the rates of migration or “retention time” allow separation of the components of a mixture. These components can be isolated and identified if interfaced to mass spectrometry, UV-Vis spectroscopy or refractive index detectors. In a similar vein, electrophoretic separations use the same principles as liquid chromatographic separations. However, instead of using pressure to push the solutes through the column, an applied voltage will pull the buffer solution in which the solutes are dissolved from the inlet to the outlet to achieve the desired separation. Separation efficiencies in electrophoretic chromatograms are much higher than chromatographic ones. The plug flow profile in electrophoretic separations minimizes band broadening that is usually observed when doing chromatographic separations as is shown in Figure 1.4.

Capillary electrochromatography (CEC) is a recently discovered technique that is a hybrid of liquid chromatography (LC) and capillary zone electrophoresis (CZE).¹³¹⁻¹³³ It involves chromatographic particles as stationary phases for packing in a capillary. In other words, CEC is CZE with a stationary phase. Electroosmotic flow causes the buffer and the solutes to flow from one side of the capillary to the other. CEC offers enhanced separation efficiencies compared to liquid chromatography. The plug flow which is typical for electrophoretic separations allows for highly resolved peaks due to minimal band broadening which is caused by diffusion. Each solute will reach the detection window at one instant of time rather than an interval or distribution of time which is the case for the laminar or pressure flow. There are two types of CEC, packed and open tubular.¹³¹⁻¹³³

Most of the work done on CEC utilizes packed capillaries. Packed CEC is

Capillary tube (Plug Flow)



LC Column (Laminar Flow)

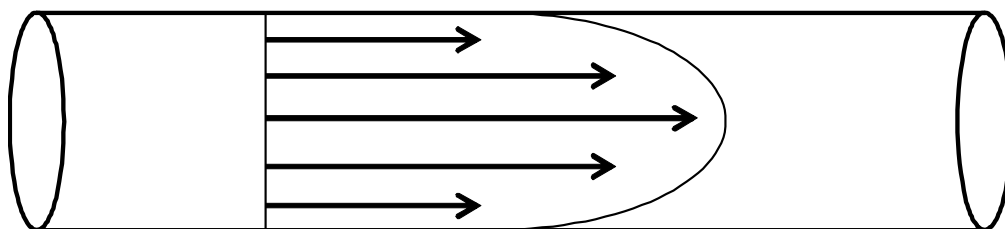


Figure 1.4 Plug flow and laminar flow in electrophoretic and pressure driven chromatographic separations.

advantageous to open tubular CEC as a result of high stationary phase surface to volume ratio. Thus, larger injection volumes will be allowed which eventually improves the concentration limit of detection.¹³⁴ It allows for the separation of neutral species which cannot be done using CZE. Also, improved EOF reproducibility is observed. Packed CEC has a number of inherent problems. One has to deal with bubble formation inside the column, making the frits to hold the stationary phases in place inside the capillary and the time consuming process of packing the capillary.¹²⁸ On the other hand, open tubular CEC minimizes these problems and offers another alternative for achieving decent and quick separations with comparable efficiencies and resolution. However, using open tubular capillary electrochromatography (OT-CEC) has its own challenges. Increasing the thickness of the coating has profound effects on retention time, selectivity, band broadening, electroosmotic flow and resolution as is shown in Chapter 7. The inner diameter of the capillary should be very small and the coated stationary phase should be thick enough so that band broadening problems could be minimized. Miyabe et al. studied the kinetics of mass-transfer of C₁₈-silica stationary phases at room temperature.¹³⁵ At high flow rates, axial dispersion and diffusive migration across the C₁₈-silica skeleton contribute much to band broadening, suggesting that it remains important to reduce the effect of eddy diffusion and the mass-transfer resistance in the stationary phase to achieve fast separations and high efficiencies. Typical diffusion coefficient values were of the order $10^{-7} \text{ cm}^2\text{s}^{-1}$.¹³⁵ The values of the diffusion coefficients decreased with increasing retention of sample compounds. PEMU stationary phases offer comparable values of diffusion coefficients for singly charged and low molecular weight species.¹⁹ However, they still suffer from problems of band broadening which is a result of poor mass transfer between the mobile phase and the multilayer that is coated on the inner walls of the capillary.^{24,123} Also, OT-CEC has poor limits of detection when using UV as a detector. The path length of light crossing through the window of detection is too short and this will lower the absorbance signal for a given species.¹¹⁸

There are many published studies that examined CZE and CEC for chromatographic separations.¹³⁶⁻¹³⁸ Early reports investigated dynamic coatings of polyelectrolyte multilayers for chemical control of electroosmotic flow in capillary electrophoresis microchips.¹³⁹⁻¹⁴¹ However, the dynamic coating required a continuous supply of

polyelectrolyte solution which might be infeasible if using synthetic polyelectrolytes, proteins or polypeptides.¹³⁹⁻¹⁴¹ An alternative would be to coat the inner diameter of the capillary using layer-by-layer assembly of thin film polyelectrolytes.³⁸ Using the rinse function on the capillary electrophoresis system, the layer-by-layer buildup was done automatically to reach the number of desired layers. Such coatings were used to separate neutral molecules,^{24,118,123} proteins,¹²³ chiral molecules,^{24,118} structural isomers¹¹⁹ and functional derivatives.^{119,128}

Katayama et al. used multiple ionic layers to perform capillary zone electrophoretic experiments.^{126,127} Graul and Schlenoff extended that technique and performed capillary electrochromatography (CEC) using a multilayer coating approach.¹²³

Despite some of the challenges in (OT-CEC), a number of studies have been reported with promising efficiencies and resolution.¹²⁸ Fused silica capillaries were coated with thin films of charged polymers for capillary electrophoretic separations. The coating was a polyelectrolyte multilayer, constructed *in situ* by alternating rinses with positively and negatively charged polymers.^{123,126,127} The thickness of the multilayer and amount of surface charge was controlled by the concentration of salt in the deposition solutions.⁷ The direction of the electroosmotic flow oscillates as the multilayer's surface charge alternates in polarity during buildup.¹²²⁻¹²⁵ The apparent surface charge, deduced from the electroosmotic mobility, is considerably less than the nominal surface charge of the film. The multilayer-coated columns exhibit many desirable features in addition to their ease of construction and reproducible electroosmotic flow: Stable flow rates are achieved immediately on exposure of the column to running buffer, and reversed flow is possible.^{123,124} Columns also are stable to extremes of pH and ionic strength, and to dehydration/rehydration.¹²⁴ Basic proteins are separated with good efficiency,¹²³ demonstrating column resistance to irreversible protein adsorption.¹²³ Partitioning and separation of neutral solutes using thicker films were also demonstrated.^{24,119,123}

In a more recent study, Kapnissi et al. used molecular micelles to separate phenols and benzodiazepines using open tubular CEC.¹⁴² They investigated the utility of using a polymeric surfactant (molecular micelle) for open tubular CEC. The PEMU coating is constructed *in situ* by alternating rinses with positively and negatively charged polymers, where the negatively charged polymer is a molecular micelle. This can offer a number of

advantages for separation and identification of a variety of hydrophobic analytes. Poly(diallyldimethylammonium chloride) was used as the cationic polymer and poly(sodium N-undecanoyl-L-glycinate) was used as the anionic polymer for coating. The performance of the modified capillaries as a separation medium was evaluated by use of seven structural derivatives of benzodiazepines as analytes.¹¹⁸ The run-to-run, day-to-day, week-to-week and capillary-to-capillary reproducibilities of electroosmotic flow were very good with relative standard deviation values of less than 1% in all cases. In addition, the chromatographic performance of the monomeric form of the molecular micelle was compared for the separation of these analytes. No selectivity was observed when using the monomeric form of the micelle. The multilayer coated capillary was also robust with more than 200 runs accomplished in this study.¹¹⁸

In a separate approach, Loscasio et al. utilized thin film polyelectrolyte coatings to control electroosmotic flow in microchannels.^{122,125} Electroosmotic flow (EOF) is utilized in microfluidics on a regular basis. Because the direction of the EOF can be determined by the substrate surface charge, control of the surface charge offers the potential, in addition to voltage control, to direct the flow in microfluidic channels. They reported the use of polyelectrolyte multilayers to alter the surface charge and control the direction of flow in polystyrene and acrylic microfluidic devices. Relatively complex flow patterns with simple arrangements of applied voltages were reported and analyzed. In addition, flow in opposite directions in the same channel was feasible. A positively derivatized plastic substrate with a negatively charged lid was used to achieve top-bottom opposite flows. Derivatization of the two sides of a plastic microchannel with oppositely charged polyelectrolytes was used to achieve side-by-side opposite flows. The flow was characterized by using fluorescence imaging and particle velocimetry.^{122,125}

Recently, Sui and Schlenoff used layer-by-layer assembly of polyampholyte-polyelectrolyte pairs to achieve *in situ* control of the direction of the electroosmotic flow without any need for extra rinse or additional coating as was the case in earlier studies.¹²⁴ This was possible by switching the solution pH *in situ* which creates negatively charged sites inside the bulk of the multilayer. Charge extrusion to the surface switches the charge on the surface and thus the electroosmotic flow is reproducibly reversed. This is potentially useful for electrophoretic separations of basic and acidic proteins

simultaneously without any need for adding additional polyelectrolyte layers of the opposite charge. A simple flush in a solution of the desired pH will be able to achieve that goal.¹²⁴

Chapter 7 of this dissertation will investigate using optically active polyelectrolyte multilayer coatings for enantiomeric separations of ascorbic acid stereoisomers. Also, the effect of film thickness and number of layers on retention time, selectivity and resolution will be discussed.

1.7 Polyelectrolyte Interactions: Electrostatic versus Secondary

Most researchers utilizing polyelectrolyte coatings for membrane and chromatographic separations consider electrostatic interactions as the main driving forces for multilayer coatings and buildup.^{9-11,40,108} A number of different interactions for multilayer assembly mechanisms have been reported in literature. Multilayer thin films can be assembled via multiple interactions such as stereoregular recognition incorporating syndiotactic polymers,¹⁴³⁻¹⁴⁵ hydrogen bonding,¹⁴⁶⁻¹⁵³ charge transfer¹⁵⁴⁻¹⁵⁷ and electrostatic interactions.¹⁵⁸⁻¹⁶² In Chapter 5, secondary interactions such as “hydrophobic interactions” will be shown to overwhelm electrostatic interactions and become the primary interactions instead.

In the polyelectrolyte systems described in this dissertation, the interaction between the negatively and the positively charged polyelectrolytes are mainly controlled by either electrostatic or hydrophobic interactions or a combination of both. The following chapters will describe the synthesis and characterization of a variety of polyelectrolytes that were carefully designed and tailored to meet the specific requirements of certain applications. They will be used as ultrathin film membranes for surface and membrane separation of ions, dissolved species, vitamins and drugs.