

POLYELECTROLYTE MULTILAYER FILMS FOR ION SEPARATION AND WATER
PURIFICATION

By

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ABSTRACT

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Polyelectrolyte multilayer (PEM) films formed by layer by layer (LbL) adsorption of polycations and polyanions are attractive as the skins of separation membranes because of their simple deposition, minimal thickness, and wide range of transport properties. Variation of the polyelectrolyte type as well as deposition parameters such as supporting electrolyte concentration, polyelectrolyte concentration, duration and temperature of adsorption allow tailoring of films for specific separations. This dissertation examines the effect of ion-exchange sites in PEM films on ion separations as well as removal of model organic pollutants by PEM membranes.

The properties of poly(styrene sulfonate) (PSS)/ poly(diallyldimethylammonium chloride) (PDADMAC) films vary dramatically with the number of polyelectrolyte layers deposited. Attenuated total reflectance infrared spectroscopy shows that coatings with <7 PDADMAC/PSS bilayers do not absorb significant amounts of SCN^- or $\text{Ni}(\text{CN})_4^{2-}$, but films with >7 bilayers exhibit an ion-exchange capacity of about 0.5 moles per L of film. For Si-supported PSS/PDADMAC films terminated with PSS, zeta (ζ) potentials change from negative to positive as the number of adsorbed bilayers increases. These changes in film properties dramatically affect ion transport through $(\text{PSS}/\text{PDADMAC})_n$ PSS-coated alumina membranes. The $\text{Cl}^-/\text{SO}_4^{2-}$ selectivities of these membranes are >30 with $(\text{PSS}/\text{PDADMAC})_4$ PSS films but only 3 with

(PSS/PDADMAC)₆PSS films. Trends in ζ potentials and selectivities with increasing numbers of bilayers are consistent with the exponential growth mechanism where a polycation adsorbs throughout the film to create large numbers of anion-exchange sites, and during polyanion deposition some of the polycation diffuses to the surface of the film to complex with polyanions from solution. Polycation that is not electrically compensated by the polyanion affords anion-exchange sites, and the presence of this fixed positive charge yields decreased $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity.

Deliberate introduction of anion-exchange sites in PEMs can greatly enhance selectivities in cation separations. Immersion of PSS/poly(allylamine hydrochloride) (PAH) membranes in aqueous CuCl_2 or FeCl_3 solutions yields adsorbed Cu^{2+} or Fe^{3+} ions that serve as anion-exchange sites. Remarkably, the $\text{Na}^+/\text{Mg}^{2+}$ selectivity of (PSS/PAH)₄ films on 50 kDa polyethersulfone membranes increases from 17 to 109 after immersion in 5 mM FeCl_3 for 10 min. Moreover, this modification is effective even after 18 h of cross-flow nanofiltration (NF). Reflectance FTIR spectroscopy confirms the formation of anion-exchange sites after Fe^{3+} or Cu^{2+} adsorption. Due to its low pressure requirements, NF is a promising technique for removal of endocrine disrupting and pharmaceutically active compounds from waste water. However, the rejection of small organic compounds by commercial membranes may be too low for effective water treatment. This work shows that coating of commercial NF-90 membrane with a bilayer of poly(acrylic acid)/PAH increases acetaminophen rejection from 65% to 85%. (PSS/PAH)₇ on porous alumina shows a caffeine rejection of 93% along with a solution flux of $1.33 \text{ m}^3/(\text{m}^2 \text{ day})$.

To my husband, Upendra and my son, Rithvik.

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LIST OF ABBREVIATIONS

1,2-BDS	1,2-Benzene Disulfonate
1,3-BDS	1,3-Benzene Disulfonate
1,4-BD	Hydroquinone
AAS	Atomic Absorption Spectroscopy
ACT	Acetaminophen
AFM	Atomic Force Microscopy
AH	Acridine Hydrochloride
ALG	Alginate
AP	Alkyl Phenol
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy
az6ac	1,4,7,10,13,16-hexacarboxymethyl 1,4,7,10,13,16-hexaazacyclo-octadecane
Bs	Benzene sulfonate
CEES	Chloroethyl Ethyl Sulfide
CFN	Caffeine
CHI	Chitosan
CMR	Catalytic Membrane Reactor
DL-HFMR	Dual Layer Hollow Fiber Membrane Reactor
EDC	Endocrine Disrupting Compound
EE2	Ethinylestradiol
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HA	Hyaluronic Acid
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
LbL	Layer by Layer

MCT	Mercury-Cadmium-Telluride
MO	Methyl Orange
MPA	3-mercaptopropionic acid
M _w	Molecular Weight
MWCO	Molecular Weight Cut Off
NF	Nanofiltration
Np	Naphthalene
Ns	Naphthalene 2-sulfonate
P4VP	Poly(4-vinylpyridine)
PAA	Poly (acrylic acid)
PAH	Poly (allylamine hydrochloride)
PAN	Poly (acrylonitrile)
PCBS	Poly(1-[p-(3'-carboxy-4'-hydroxyphenylazo) benzene sulfonamide]-1,2-ethandiyl)
PDADMAC	Poly (diallyl dimethyl ammonium chloride)
PE	Polyelectrolyte
PEG	Poly (ethylene glycol)
PEI	Poly (ethylene imine)
PEM	Polyelectrolyte Multilayer
PES	Polyethersulfone
PET	Poly (ethylene-terephthalate)
PGA	Poly (L-glutamic acid)
Ph	Phenol
PhAC	Pharmaceutically Active Compound
PLL	Poly (L-lysine)
PMP	Poly (4-methyl-1-pentene)
PMMA	Poly (methyl methacrylate)

PRO	protamine sulfate
PS	Polystyrene
PSS	Poly (styrene sulfonate)
PVA	Poly (vinyl amine)
PVS	Poly (vinyl sulfate)
Py	Pyrene
QCM	Quartz Crystal Microbalance
SEM	Scanning Electron Microscopy
TCE	Trichloroethylene
TP	triphenylene
RO	Reverse Osmosis
UF	Ultrafiltration
UV	Ultraviolet
UV/Vis	Ultraviolet/Visible Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
ZVI NP	Zero valent iron nanoparticles

Chapter 1

Introduction and Background

This dissertation describes the growth of polymer films through layer by layer adsorption of polyelectrolytes, and the application of these thin films in anion separations, cation separations, and the removal of pharmaceutically active compounds from water. The research builds on a large body of prior work on adsorption of multilayer polyelectrolyte films and enhancing the selectivity of anion and cation transport through these films. To put my research in perspective, this introduction first discusses the layer by layer (LbL) method for forming multilayer films. Subsequent sections of the chapter review studies of the incorporation of ions and other species into multilayer polyelectrolyte films and previous efforts to use these films as ion-separation membranes. Finally, the introduction gives a brief outline of the dissertation.

1.1. Layer by Layer (LbL) Assembly of Polyelectrolyte Multilayers

Among the many methods for formation of thin films, e.g. spin and dip coating or monolayer adsorption, layer-by-layer (LbL) deposition of complementary polymers has emerged as an especially versatile technique for controlling film thickness and functionality. Figure 1.1 shows the most common form of the LbL method, alternating adsorption of polycations and polyanions. Operationally, this method occurs through simple immersions of a selected substrate in polycation and polyanion solutions, with rinsing to remove excess polymer after each deposition step. Typical polyanions employed for deposition of these films include ionized forms of poly(acrylic acid) (PAA),¹ poly(styrenesulfonate) (PSS),² poly(vinylsulfonic acid),³

alginic acid,^{4,5} hyaluronic acid (HA),⁶⁻⁸ and pectic acid,⁹ whereas most polycations contain quaternary ammonium functionalities^{10, 11} or protonated amines.^{12, 13}

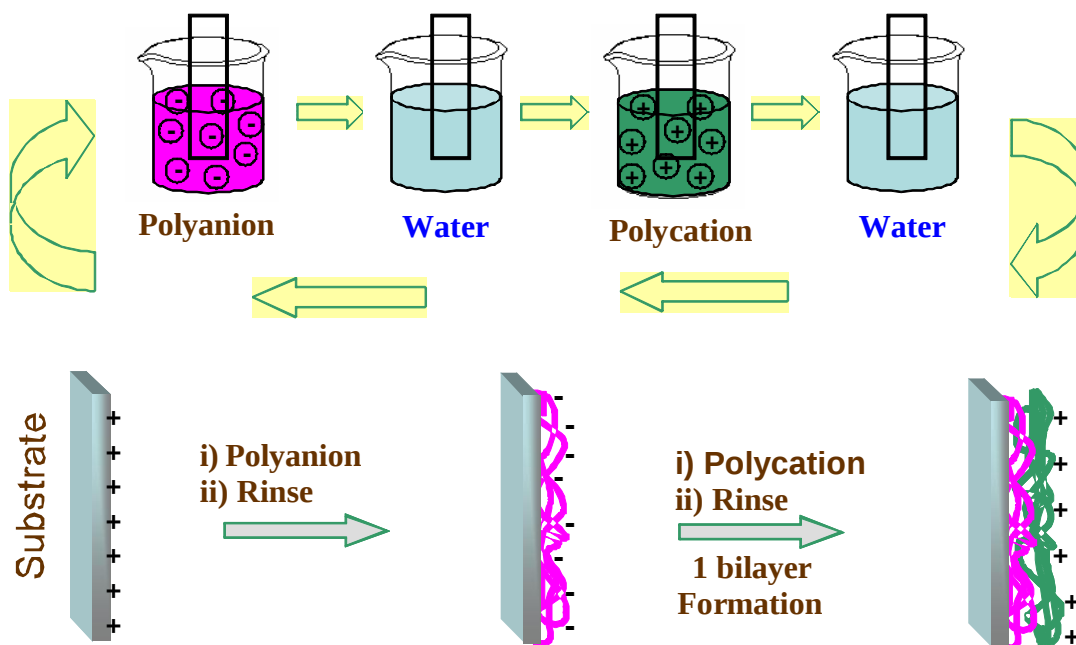


Figure 1.1. Schematic diagram of layer-by-layer adsorption of polyelectrolyte multilayers. (Adapted from *Science*, 1997, 277, 1232-1237). “For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation”

(Figure 1.2 shows some of these polyelectrolytes). Nevertheless, LbL methods can also use a much broader range of multiply charged species including proteins,^{14, 15} viruses,¹⁶ nanoparticles,¹⁷⁻¹⁹ and exfoliated inorganic materials.^{20, 21} I should note that some LbL methods also employ other interactions such as hydrogen bonding²²⁻²⁶ or covalent linkages.²⁷⁻

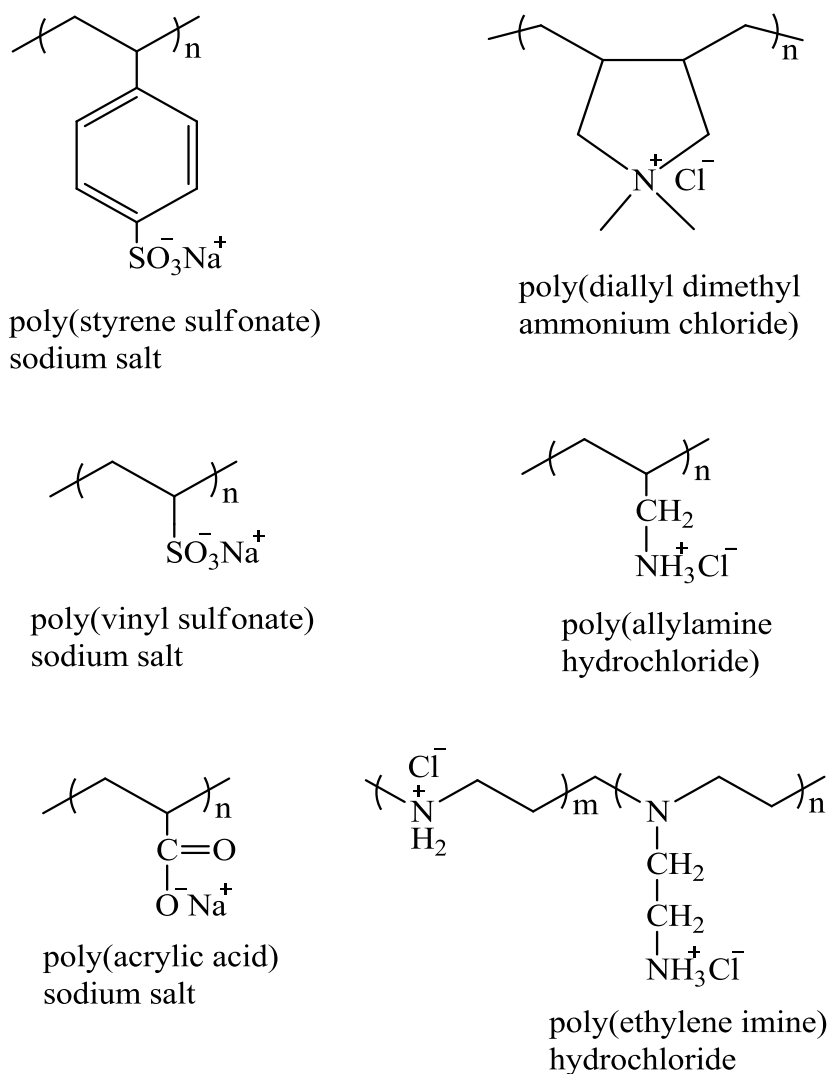


Figure 1.2. Structures of polyelectrolytes frequently used in building multilayers.

The LbL strategy has a number of advantages over most coating techniques. First, because a single adsorption step may deposit as little as a few angstroms (Å) of polymer, this technique offers control over film thickness at the nanometer scale.³¹ Second, conformal adsorption occurs on substrates with a wide range of geometries, allowing coating of 3-dimensional materials such as porous membranes and nanoparticles.^{19, 31-37} Third, the wide range of materials suitable for LbL adsorption and the ability to deposit species in a defined

order should afford a wide range of functional films.^{17, 33, 34, 38-41} Post-deposition reactions such as cross-linking and reduction of metal ions to form nanoparticles provide further ways to modify film properties.⁴²⁻⁴⁷ Prior studies of post-deposition reactions yielded functional films for catalysis,^{35, 48} anti-reflective coatings,⁴⁹ optical shutters,^{40, 50} and superhydrophobic coatings.⁵¹

1.2. Mechanism of Polyelectrolyte Adsorption

The key feature in the adsorption of polyelectrolyte multilayer (PEM) films is charge overcompensation. The initial layer adsorbs onto the substrate either by electrostatic or hydrophilic attractions and creates a charged surface or reverses the substrate surface charge. Adsorption of subsequent layers again overcompensates the charge on the surface to reverse the substrate's charge and allow adsorption of the next layer.⁵²⁻⁵⁴

In many cases, the thickness of multilayer polyelectrolyte films increases linearly with the number of adsorbed layers.⁵⁵⁻⁵⁸ This suggests that the extent of charge overcompensation does not vary greatly with the number of adsorbed layers, so the amount of polyelectrolyte deposited in each step is approximately constant. However, for some polyelectrolyte systems film thickness increases exponentially with the number of layers. Schaaf *et al.* suggested that the exponential growth occurs when one of the polyelectrolytes diffuses “into” the entire film during deposition.⁵⁹⁻⁶¹ Upon addition of the oppositely charged polyelectrolyte, the previously adsorbed polyelectrolyte diffuses “out” of the whole film to form a very thick polyanion-polycation complex at the surface (see figure 1.3). Because one of the polyelectrolytes, usually

one with low charge density and high swelling in water, diffuses into the *entire* film, the thickness of each layer increases with the number of layers.⁶²

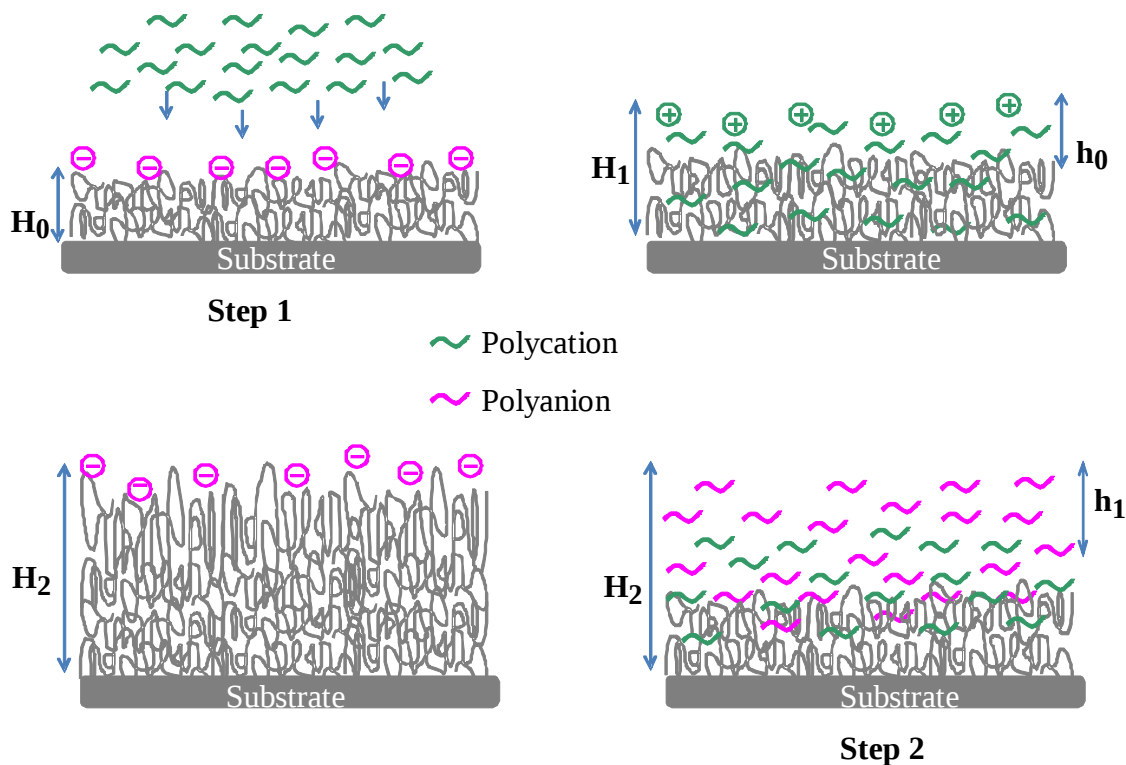


Figure 1.3. Schematic drawing showing the buildup of a polyelectrolyte “bilayer” during exponential growth. Step 1 includes diffusion of a polyelectrolyte (in this case a polycation) into the entire film. During step 2, much of the polycation diffuse out of the film and forms a complex with incoming polyanion. H_0 and H_1 are the film thicknesses at the start and at the end of step 1, and H_2 is the film thickness at the end of step 2. h_0 and h_1 are the increases in film thickness due to the deposition of polycation and polyanion, respectively. (Redrawn from *J. Phys. Chem. B*, 2009 113 (13), 4232-4241.)

1.3. Factors that Affect Film Growth during LbL Polyelectrolyte

Adsorption

In addition to the polyelectrolyte selected for deposition, a number of adsorption parameters such as supporting electrolyte concentration and composition,⁶³⁻⁷⁴ molecular weight of the polyelectrolytes,⁷⁵⁻⁸³ pH of the polyelectrolyte solutions,⁸⁴⁻⁹¹ adsorption time,^{63, 92-97} and temperature⁹⁸⁻¹⁰⁰ also influence the amount of polyelectrolyte deposited in LbL methods. Understanding the mechanisms of PEM formation and the role of process parameters in determining thicknesses and interfacial properties of multilayer films is fundamental for their future applications. Below I discuss the effects of some of these variables on LbL film growth.

1.3.1. Effect of Supporting Electrolyte

1.3.1.1. Effect of Supporting Electrolyte Concentration

A number of groups examined the importance of supporting electrolyte on the growth of polyelectrolyte multilayer films.⁶³⁻⁶⁷ In the absence of added salt, polyelectrolytes are highly extended to maximize the distance between charged repeat units of the polymer. Under these conditions, adsorbed layers are thin and overcompensate the surface charge only slightly (see Figure 1.4).¹⁰¹ For example, the thickness of a 10-bilayer PSS/poly(diallyl dimethyl ammonium chloride) (PDADMAC) film prepared without addition of salt is about 60 Å.⁶³ Thus, the average thickness per layer is only 3 Å.

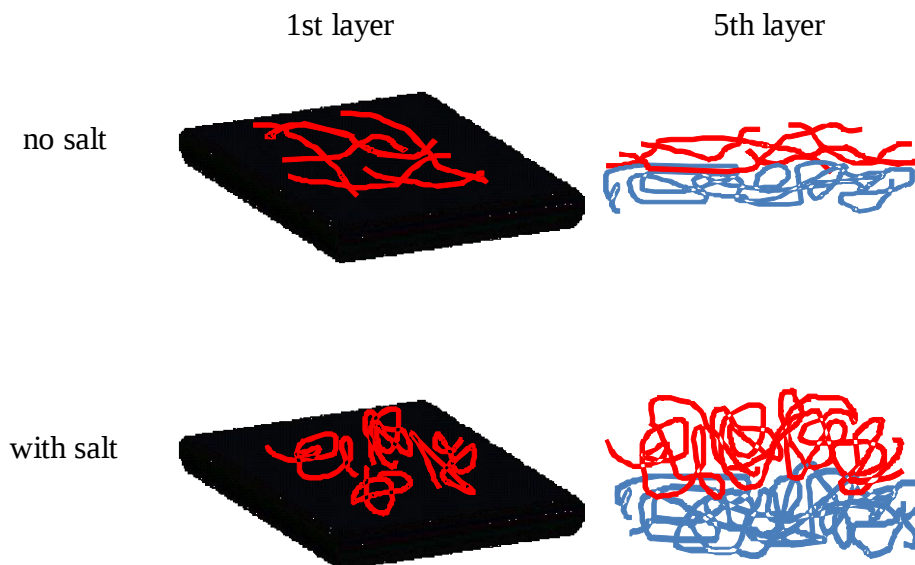


Figure 1.4. Sketch of polyelectrolyte layers adsorbed in the presence and absence of salt. The absence of salt results in thin layers of extended polyelectrolytes, whereas at high ionic strength, coiled polymers form thicker layers. (Redrawn from *Colloids Surf. Physicochem. Eng. Aspects* 2002, 198-200, 293-304.)

Many studies show a dramatic effect of supporting electrolyte concentration on the thickness of PEMs.^{63, 64, 68-74} In Figure 1.5, the thickness of a 10-bilayer PSS/PDADMAC film shows an almost linear dependence on salt concentration between 10^{-2} and 2 M.⁶³ This is in contrast to the early findings of Lvov *et al.*,¹⁰² who reported that the thickness of a layer pair of PSS/poly(allylamine hydrochloride) (PAH) is proportional to the square of the ionic strength in deposition solutions. However in both cases, thickness increases dramatically upon addition of salt to deposition solutions. The reason for the differences in the above-mentioned systems likely stems from the nature of the polyelectrolytes. (PDADMAC has a lower charge density than PAH, and PDADMAC-containing films are prone to very high swelling in some cases.^{53,}

¹⁰³⁻¹⁰⁵) The excess salt presumably screens charges on the polymer chains and allows them to coil and form thicker layers (Figure 1.4). In addition, charge screening may require adsorption of more polyelectrolyte to compensate the opposite charge in the previously adsorbed film.

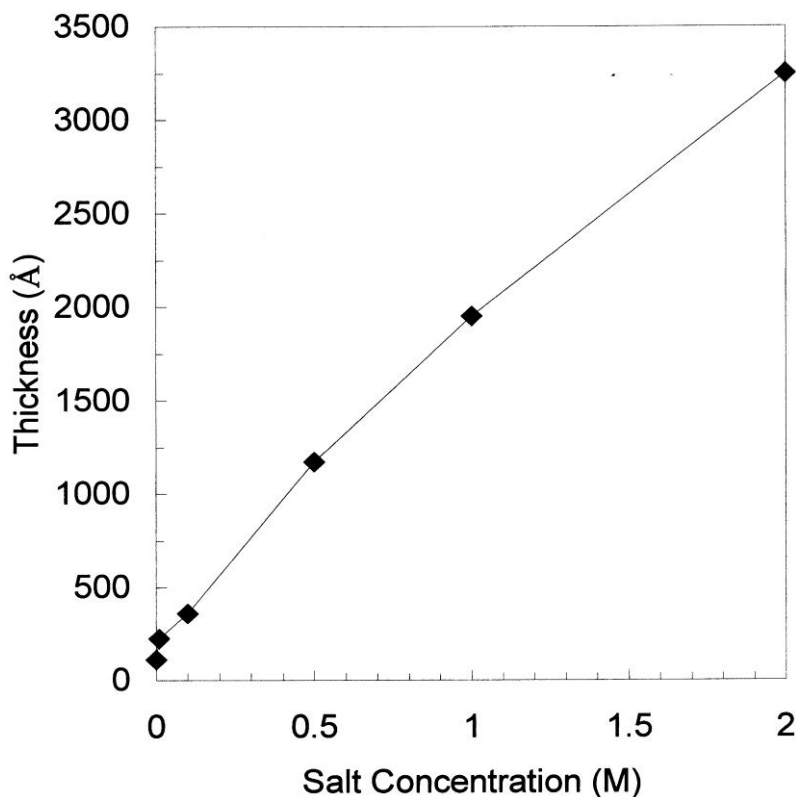


Figure 1.5. Thicknesses of LbL (PSS/PDADMAC)₁₀ films deposited on silicon wafers using a series of NaCl concentrations in the polyelectrolyte deposition solutions. (Reprinted with permission from *Macromolecules* **1999**, 32(24), 8153-8160)

Using atomic force microscopy (AFM), McAloney *et al.* examined the morphology of multilayer PDADMAC/PSS films deposited from solutions with salt concentrations ranging from 10^{-4} to 1.0 M.⁶⁶ The roughness and thickness of (PDADMAC/PSS)₁₀ films deposited from solutions with less than 0.1 M NaCl were approximately constant at 2 nm and 10 nm,

respectively, and the thickness increased linearly with the number of adsorbed bilayers. In contrast, for PDADMAC/PSS films deposited from an ionic strength of 0.3 M or higher, the growth rate rose as the polyelectrolyte attained a coil-like structure and surface roughness also increased. The increase in surface roughness may contribute to the increase in film thickness.⁶⁶ Recently, Lee *et al.* studied the role of salt in the adsorption of DNA films assembled from oligonucleotides composed of two homopolymeric diblocks (polyA_nG_n and polyT_nC_n). A combination of crystal microgravimetry and flow cytometry measurements showed that greater film growth occurred as the salt concentration increased from 0.1 to 1 M.¹⁰⁶ However very high salt concentrations may lead to delamination of the film.¹⁰⁷

1.3.1.2. Effect of Type of Supporting Electrolyte

In addition to the supporting electrolyte concentration, the identity of the supporting electrolyte also affects film thickness. Dubas *et al.* determined the thicknesses of 10-bilayer PDADMAC/PSS films adsorbed from solutions containing different salts. Table 1.1 shows results for a cation series, with a constant anion (chloride). The trends in film thickness from RbCl to LiCl suggest that the least hydrated cations¹⁰⁸ give rise to the thickest polyelectrolyte films. The ion-exchange properties of protons and lithium are similar, which might explain the comparable film thicknesses when adsorbing PEMs from HCl and LiCl solutions. CsCl and RbCl have similar thicknesses even though the hydration number for Rb is lower than Cs. Although in these studies the concentration of the ions also decreases slightly with the degree of hydration to maintain a constant activity of the different salts, this change is not sufficient to account for the large changes in film thickness with varying deposition solutions.¹⁰⁹

Table 1.1. Ellipsometric thicknesses of (PDADMAC/PSS)₁₀ films adsorbed on a Si wafer from solutions containing 1 mM polyelectrolyte (with respect to the repeating unit) and a series of supporting electrolytes with an activity of 0.33. Hydration numbers, n , are also given for each ion. Adsorption occurred for 5 min per layer with 3 min of rinsing after deposition of each layer.

Salt	Concentration, M ^a	n_{cation}	n_{anion}	thickness, ^c Å
HCl	0.43	2.7 ^b	2.0	705
LiCl	0.44	5.2	2.0	820
NaCl	0.48	3.5	2.0	903
KCl	0.50	2.6	2.0	1200
RbCl	0.52	2.4	2.0	1466
CsCl	0.54	2.1	2.0	1420

^aConcentrations were selected based on activity coefficients to maintain a constant activity of 0.33.

^bHydration number for H₃O⁺.

^cEllipsometric thickness, $\pm 3\%$. (**Taken from *Macromolecules* 1999, 32(24), 8153-8160.**)

Several other studies examine how the supporting salt anion in polyelectrolyte solutions affects the growth of PSS/PAH films.¹¹⁰⁻¹¹² In these studies, the supporting electrolytes are all sodium salts, but the nature of the anion varies along the Hofmeister series from cosmotropic to chaotropic anions (F⁻, HCOO⁻, BrO₃⁻, Cl⁻, ClO₃⁻, Br⁻, NO₃⁻, ClO₄⁻).^{112, 113} For all the investigated anions, the PSS/PAH film thickness increases linearly with the number of deposition steps.¹¹⁰ Cosmotropic anions bind strongly to water molecules and induce some structure in the solution that results in “salting-out” of molecules such as proteins. Such anions enhance the hydrogen bonding ability between water molecules to decrease the freedom of motion. Because of their low electronegativity, high polarizability, and weak electrostatic fields,

chaotropic anions destabilize the hydrogen bonding between ion and solvent molecules to increase the solubility of some molecules.¹¹⁴ Figure 1.6 shows that for PSS/PDADMAC multilayers, the chaotropic anions lead to thicker bilayers than cosmotropic anions.¹¹² The chaotropic anions bind strongly to polycations, thus reducing the charge density on the polyelectrolyte. This leads to the formation of coil structure thereby increasing the thickness of the layer.

The film permeability to ions also changes when different salts are present during adsorption. In electrochemical measurements, films consisting of up to 9.5 PSS/PAH bilayers are permeable to hexacyanoferrate(II) ions, $\text{Fe}(\text{CN})_6^{4-}$. However, the peak intensities of anodic and cathodic $\text{Fe}(\text{CN})_6^{3-/4-}$ currents depend on the sodium salt present during deposition, and currents increase in the order $\text{F}^- < \text{Cl}^- < \text{NO}_3^- < \text{ClO}_4^-$. In contrast, PSS/PAH films prepared in the presence of NaF, NaCl, or NaNO_3 are impermeable to $\text{Ru}(\text{NH}_3)_6^{2+}$ after adsorption of the third PAH layer, as both the anodic and cathodic current become zero. These results suggest the presence of excess positive charges in the PSS/PAH multilayer film, which leads to a positive Donnan potential. The stronger binding of PAH with anions as their chaotropic nature increases likely results in a more loopy conformation that leads to less dense films and thus to a high mobility of the $\text{Fe}(\text{CN})_6^{4-}$ ions through the films.¹¹⁰

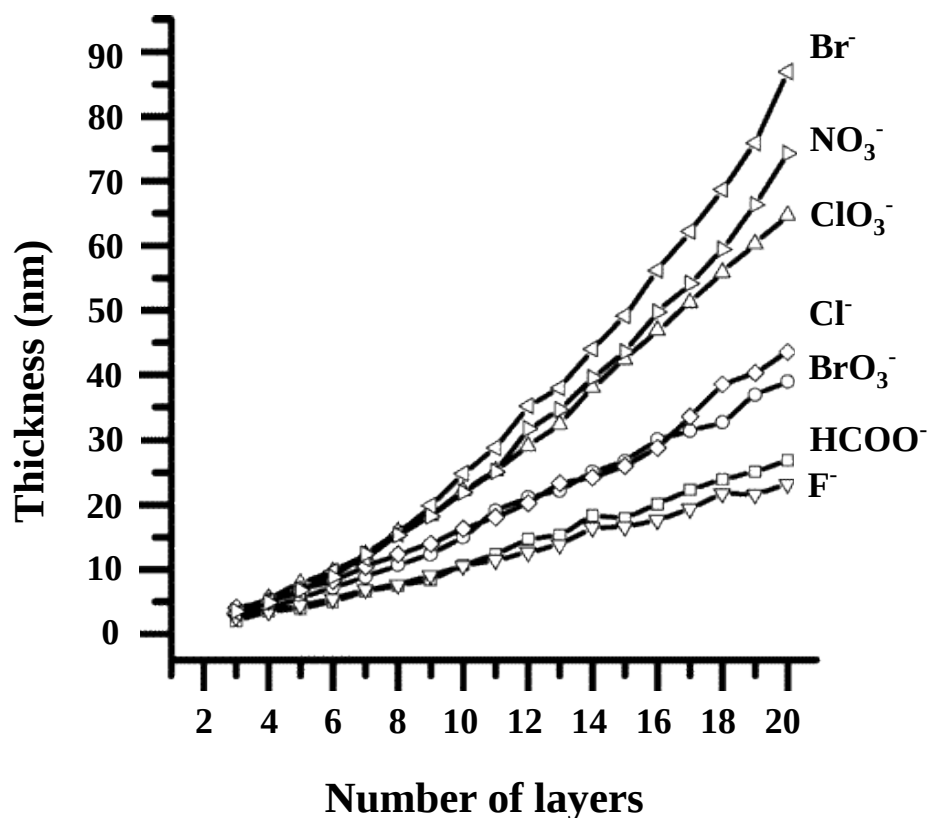


Figure 1.6. Ellipsometric thicknesses of (PSS/PDADMAC)₂₀ films deposited from solutions containing 0.1 M of the sodium salt of the listed anions. (Reprinted with permission from *Langmuir* 2004, 20(9), 3679-3683.)

1.3.2. Effect of Polyelectrolyte on Multilayer Adsorption

A number of polyelectrolyte properties (chemical structure, molecular weight, concentration, and degree of ionization) affect the LbL growth of PEMs. This subsection examines each of these factors in detail.

1.3.2.1. Effect of Polyelectrolyte Type on Multilayer Growth

The mechanism of PEM growth, linear or exponential, depends on the constituent polyelectrolytes as well as the ionic strength of the deposition solutions. PSS/PAH multilayers provide an example of films whose thickness always increases linearly with the number of

adsorbed layers.^{57, 58, 115} In contrast, polyanion/polycation systems that follow an exponential growth mechanism include poly(L-glutamic acid) (PGA)/poly(L-lysine) (PLL),^{59, 61} PGA/PAH,¹¹⁶ PDADMAC/PSS (at high ionic strength)⁶⁶ and HA/chitosan (CHI).^{76, 81} The steady-state incremental thickness increase per bilayer for PSS/PDADMAC⁶³ is 7 times higher than the increment for PSS/PAH¹¹⁷ under the same conditions, which demonstrates the importance of polyelectrolyte type in determining ultimate film thickness. In addition to the chemical structure of the polyelectrolytes, film thickness also varies with polyelectrolyte concentration, molecular weight, and charge density, which often varies with pH. The following sections discuss these factors.

1.3.2.2. Effect of Polyelectrolyte Molecular Weight

Several reports examined the influence of polyelectrolyte molecular weight (M_w) on the thicknesses of PEMS.⁷⁵⁻⁸¹ In early studies Lösche *et al.* showed that the thicknesses of PSS/PAH films are independent of PSS molecular weight.¹¹⁷ Using in situ quartz crystal microbalance (QCM) measurements, Richert *et al.* evaluated the effect of the M_w of CHI on the growth of HA/CHI. The film thickness decreased by a factor of 1.75 when using CHI with a M_w of 460000 rather than 110000.⁸¹ (The HA M_w was 400000 in both cases.)

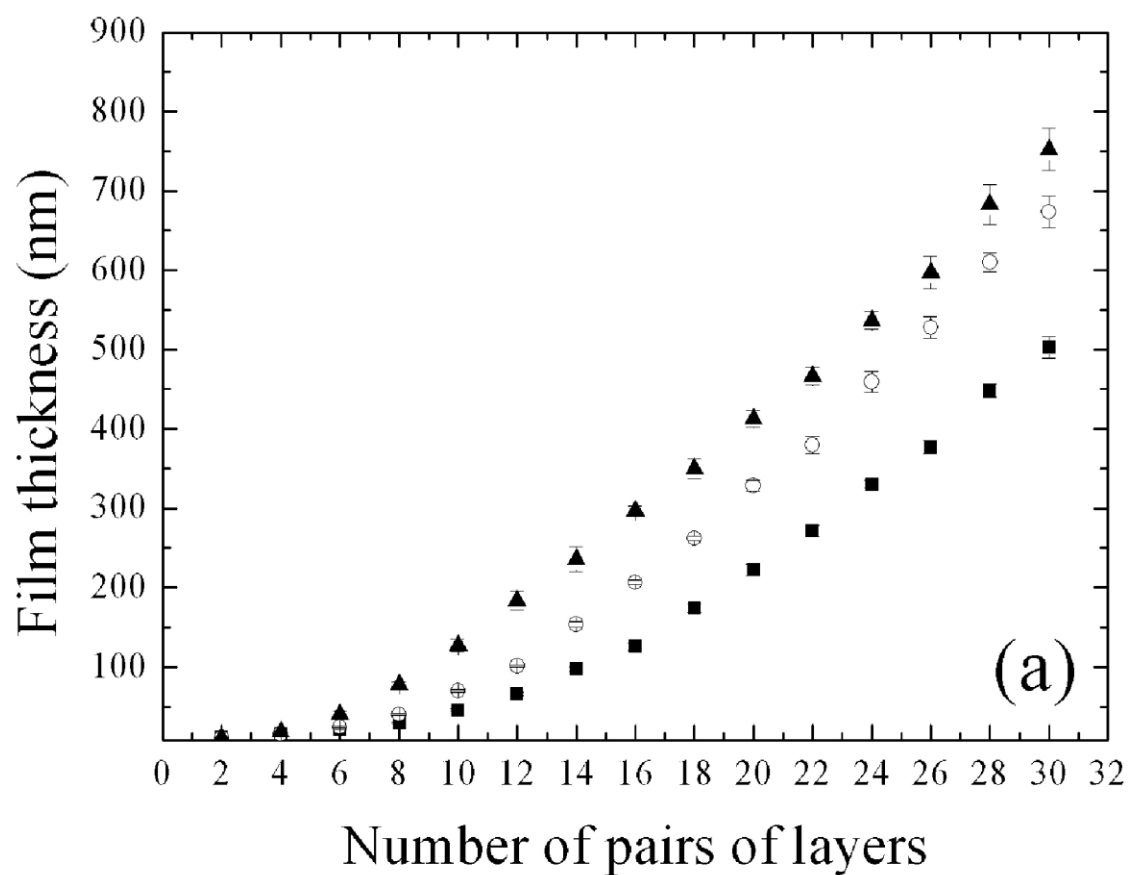


Figure 1.7a. Influence of the molecular weights of HA and PLL on the thickness of (HA/PLL)_n films grown using HA with M_w = 130000 and PLL with M_w values of (■) 20000, (○) 55000, and (▲) 360000. (Reprinted with permission from *Langmuir* 2007, 23(4), 1898-1904.)

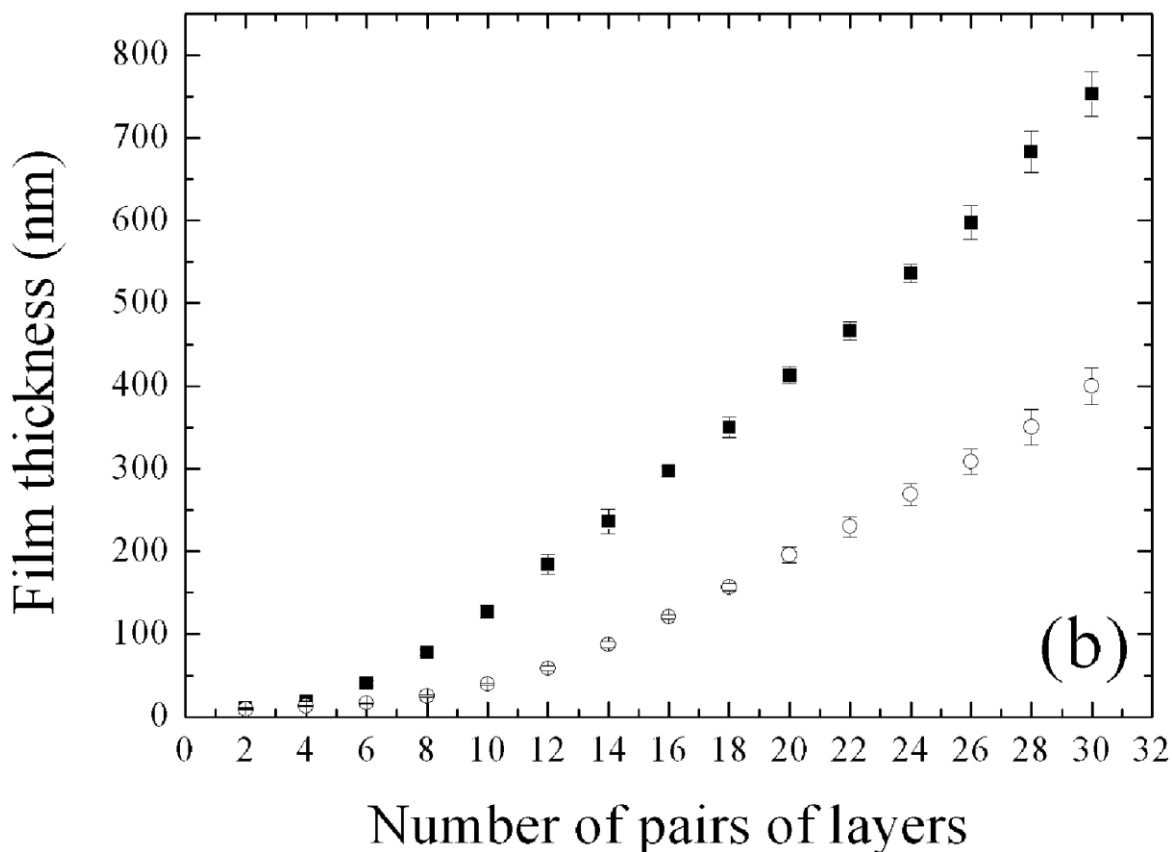


Figure 1.7b. Influence of the molecular weights of HA and PLL on the thickness of $(\text{HA/PLL})_n$ films grown using PLL with $M_w = 360000$ and HA with M_w values of (■) 130000 and (○) 400000. (Reprinted with permission from *Langmuir* 2007, 23(4), 1898-1904.)

Sun *et al.* found that growth rate of PAH/PAA films formed from lower M_w PAA (15000) is greater than the growth rate for films adsorbed using higher M_w (90000) PAA.⁸² Porcel *et al.* similarly examined the adsorption of HA/PLL⁷⁷ and PGA/PAH⁸³ systems by varying the M_w of the polyelectrolytes. The films in both studies were constructed using a spraying method (with rinsing after each layer) and were dried after deposition of every 2 bilayers to measure the ellipsometric thicknesses. In the case of the HA/PLL system, Figure

1.7a, 1.7b show that the thickness increases with the M_w of PLL but decreases with an increase in the M_w of HA.⁷⁷ For the PGA/PAH system the thickness increments were almost independent of the molecular weights of both polyelectrolytes, PGA, 44000 or 100000 and PAH, 15000 or 55000.⁸³ Based on all of these studies, it is difficult to predict how film thickness will vary with polyelectrolyte molecular weight.

1.3.2.3. Effect of Polyelectrolyte Concentration on Film Thickness

Several groups showed that the amount of adsorbed polyelectrolyte in PEM films increases with increasing polyelectrolyte concentration in the deposition solution.^{23, 63, 95, 118,}

¹¹⁹ Figure 1.8 shows that film thickness increases by as much as 30% on increasing polyelectrolyte concentration from 2 to 50 mM when depositing a PSS/PDADMAC film on a Si substrate by spin coating.⁶³ Note that this effect is considerably less than the effect of supporting electrolyte concentration on film thickness. Flerer *et al.* suggest that at high polyelectrolyte concentrations, many polyelectrolyte chains interact with the interface at the same time and each can adsorb on just a few binding sites, which results in relatively thick films. Conversely, at lower polyelectrolyte concentrations, incoming polyelectrolytes will interact with many binding sites at the surface to give thin films.¹²⁰ Baba *et al.* found that the thickness of the PEM changes drastically by varying polyelectrolyte concentrations. Table 1.2 shows the thickness per bilayer for three different combinations of polyelectrolyte concentrations. These thicknesses were calculated from adsorbed mass (obtained from QCM) using Sauerbrey equation.⁹⁴ The difference in thicknesses for the films studied by Dubas *et al.* and Baba *et al.*

adsorbed from 10 mM PSS, PDADMAC might be due to their preparation method (spin coating and dipping).^{63, 94}

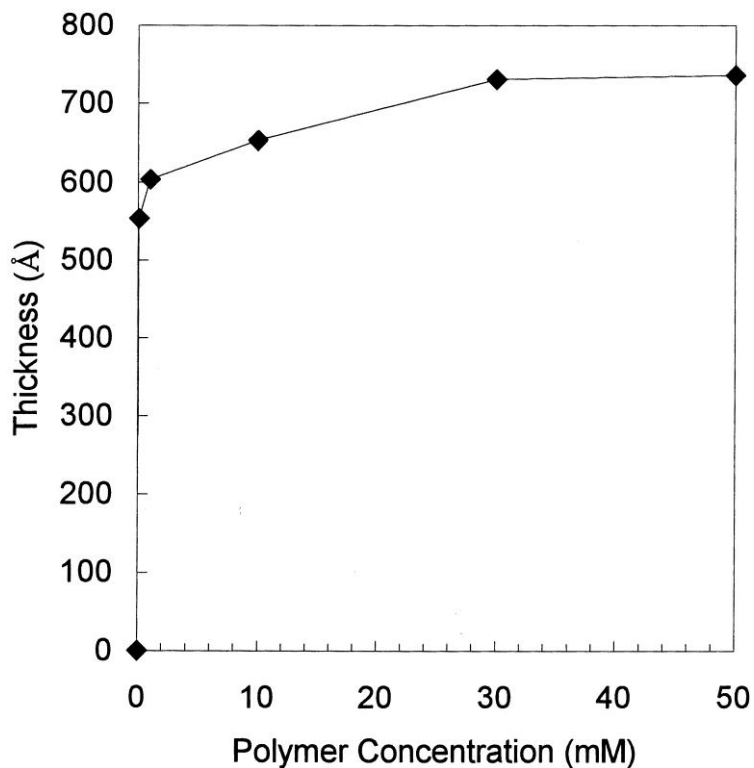


Figure 1.8. Thickness of (PSS/PDADMAC)₅ films as a function of polyelectrolyte concentration. Deposition occurred on a silicon wafer from polyelectrolyte solutions containing 1.0 M NaCl (aq). (Reprinted with permission from *Macromolecules* **1999**, 32(24), 8153-8160.)

Table 1.2. Thickness changes per layer for PDADMAC/PSS films prepared using different polyelectrolyte concentrations. All the films were made with no added salt in deposition solutions. (Taken from *Colloids Surf. Physicochem. Eng. Aspects* 2000, 173(1-3), 39-49.)

	Thickness per layer (nm)
PDADMAC (0.01 M)/PSS (0.01 M)	28.67
PDADMAC (0.01 M)/PSS (0.001 M)	3.09
PDADMAC (0.001 M)/PSS (0.01 M)	7.06

Garg *et al.* studied alternating adsorption of PAH and the polymeric dye poly(1-[p-(3'-carboxy-4'-hydroxyphenylazo)benzenesulfonamido]-1,2-ethandiyl) (PCBS, Figure 1.9) as a function of polyelectrolyte concentration using a quartz crystal microbalance.¹²¹ For films formed at pH 7, the mass adsorbed increased by 50% when the PAH concentration increased from 1 to 5 mM, but the thickness did not increase further on going from a polyelectrolyte concentration of 5 to 10 mM repeat units. This suggests a saturation limit for polymer adsorption rather like an adsorption isotherm plateau.

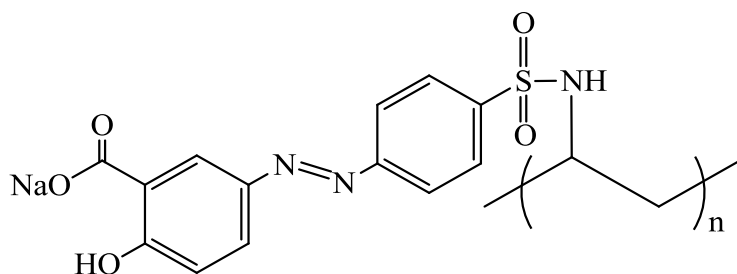


Figure 1.9. Structure of the polymeric dye poly(1-[p-(3'-carboxy-4'-hydroxyphenylazo) benzenesulfonamido]-1,2-ethandiyl) (PCBS).

1.3.2.4. Effect of Deposition pH (or Degree of Polyelectrolyte Ionization) on the Growth of PEMs Containing Weak Polyelectrolytes

The pH of weak polyelectrolyte deposition solutions dramatically affects film thickness along with permeability and morphology.⁸⁴⁻⁸⁸ In weak polyelectrolytes, the ionization of groups such as amines and carboxylic acids, and hence the polymer charge density, is a strong function of pH. An increasing charge density on the adsorbing polymer will lead to thinner adsorbed layers, whereas increasing charge density in the previously adsorbed polymer will favor thicker adsorbed layers. For PAH/PAA films made with the pH of both polyelectrolytes at 2.5, about 70% of the carboxylates of adsorbed PAA are still in the carboxylic acid form. In contrast, when the pH of both polyelectrolyte deposition solutions is 4.5, about 70% of the functional acid groups in the film exist in the ionized carboxylate form. The thicknesses of (PAH/PAA)₃₀ films deposited at pH 2.5 and pH 4.5 are approximately 120 nm and 210 nm, respectively.⁸⁶ Remarkably, for PAA/PAH films the thickness of an adsorbed polycation or polyanion layer can vary from 5 to 80 Å with changes in deposition pH.⁸⁹ However extreme pH values may completely prevent film growth by favoring desorption.⁹⁰

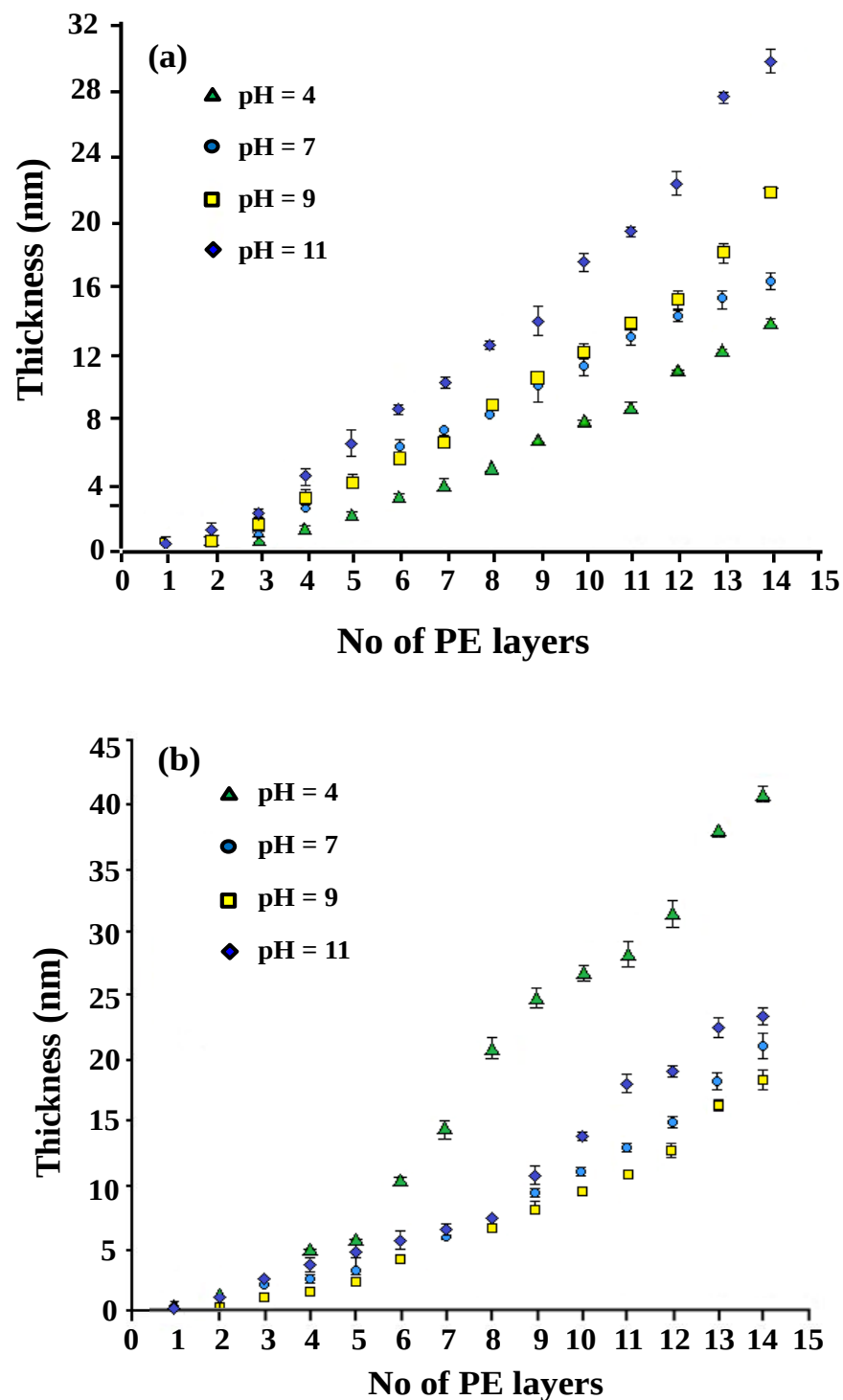


Figure 1.10. Thickness as a function of number of polyelectrolyte (PE) layers for (a) PAH/PSS and (b) PDADMAC/PAA multilayers deposited using different deposition pH values for both polyelectrolytes. (Redrawn from *Colloids Surf. Physicochem. Eng. Aspects* **2008**, 321(1-3), 258-261.)

Changes in charge density due to variations in pH depend on the specific polyelectrolyte system. Figure 1.10a shows that for PAH/PSS the thickest films form under conditions where the charge of the weak polyelectrolyte, PAH, is low (basic pH). In contrast, PDADMAC/PAA films are thicker at low pH (Figure 1.10b), again where the charge density of the weak polyelectrolyte is low. At low charge densities the weak polyelectrolytes will form more coiled conformations due to lower electrostatic repulsion between repeat units. Additionally weaker electrostatic repulsion between adsorbing polyelectrolyte molecules should contribute to the formation of thicker films.⁹¹

1.3.3. Effect of Polyelectrolyte Adsorption Time on the Growth of PEMs

The literature on polyelectrolyte multilayers contains a wide range of estimates (seconds to hours) of the time required to form a layer.^{63, 92-97} This wide range of times likely stems from differences in the structure, molecular weights, and deposition pH values of the polyelectrolytes used to build the multilayer films. Mass transport of polymer to the surface probably limits most of the layer formation, and methods that enhance mass transport such as spin coating can increase the initial rate of layer formation.^{63, 122, 123} Addition of the final 20% or so of the film likely occurs under a slower regime of permeation through surface polymer and rearrangements. Typically, more than 95% of adsorption occurs during the first 1 min after exposure to the polyelectrolyte solution in the case of PAH and PCBS in PAH/PCBS films¹²¹ and in PDADMAC /PCBS films the first order rate constants of adsorption were 1.5 and 2 min for PDADMAC and PCBS respectively.¹²⁴

1.3.4. Effect of Temperature on the Growth of PEMs

Increased deposition temperatures significantly enhance the thicknesses of PAH/PSS and PDADMAC/PSS films, but this effect is stronger for PDADMAC/PSS than for PAH/PSS.^{98, 99} At 55 °C, film thickness increases exponentially with the number of layers for PDADMAC/PSS while it increases linearly for PAH/PSS. Figure 1.11 shows the thicknesses of manually dipped, (PDADMAC/PSS)₁₀ films deposited at temperatures ranging from 10 to 70 °C. (The polyelectrolyte deposition solutions each contained 1 M NaCl.)⁹⁹ The thickness increases in an approximately linear fashion with respect to temperature throughout this range. Recent work by Büscher *et al.* also shows that increasing the temperature of the deposition solution increases the thickness of PAH/PSS deposited in the presence of KCl. Polyelectrolytes tend to precipitate at higher temperatures, which results in the formation of rough, thick multilayers.¹⁰⁰ Secondary interactions like hydrogen bonding, hydrophobicity and van der Waal's forces, which are temperature dependent, also affect the thickness of polyelectrolyte multilayer films.¹²⁵

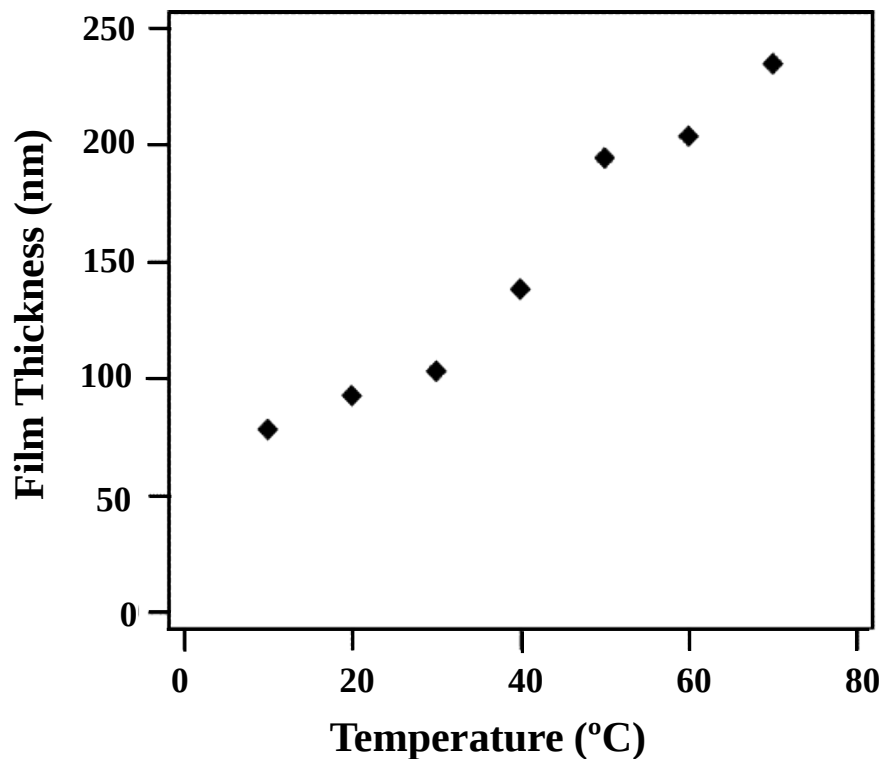


Figure 1.11. Effect of deposition temperature on the thickness of a (PDADMAC/PSS)₁₀ multilayer. (Reprinted with permission from *Langmuir* 2003, 19(22), 9311-9314.)

1.4. Swelling and Doping of Polyelectrolyte Multilayers

In PEM formation, pairing of the charge on a polymer segment with the charge on an oppositely charged polymer segment is termed intrinsic compensation. Conversely, electrical compensation of charges on the polymer segments by counter ions from salt is called extrinsic compensation. Schlenoff termed the introduction of ion-exchange sites by extrinsic compensation as “doping” the film.¹²⁶ The fractions of intrinsic and extrinsic charge compensation have a dramatic effect on film swelling because intrinsically compensated charge cross-links the film, whereas the formation of ion-exchange sites disrupts ionic cross-links and

likely renders the film more hydrophylic. Changes in ambient pH can also affect film swelling through changes in charge compensation and introduction of new charged sites.

Dubas *et al.* reported that the volume swelling coefficients, Q_{swell} (% swelling/salt concentration in the swelling solution), for PAA/PDADMAC and PSS/PDADMAC are about 400 M^{-1} and 20 M^{-1} , respectively, whereas PSS/PAH ($Q_{\text{swell}} \sim 1 \text{ M}^{-1}$) films do not show any change in thickness with increasing salt concentration.¹⁰⁵ Miller *et al.* used ellipsometry and AFM to show that swelling of HA/CHI film is 4-fold higher than the swelling of PSS/PAH films in water. Additionally, with PSS/PDADMAC films prepared from solutions containing 0.1 M NaCl, the composition of the terminating layer does not make any difference in swelling. However, when corresponding coatings are deposited from solutions containing 0.5 M NaCl, films terminated with PDADMAC swell 4 times more than films terminated with PSS.¹⁰⁴ Carrière *et al.* also showed related effects for PSS/PAH films using neutron reflectometry studies, where PAH terminated films swell 25 % less than PSS terminated films.¹²⁷

Using attenuated total internal reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, Jaber *et al.* found that the number of perchlorate ions that enter PDADMAC/PSS after film formation is 2 times higher than the number that enter PAH/PSS.¹²⁸ Thus, the level of intrinsic compensation is much greater in PAH/PSS than PDADMAC/PSS films. Lebedeva *et al.* used much higher NaCl concentration to study swelling and found that at salt concentrations greater than 3 M, softening of PAH/PSS, occurs probably due to breaking of some ionic crosslinks.¹²⁹

1.5. Applications of Polyelectrolyte Multilayer Films

Multilayer polyelectrolyte films are attractive in a wide range of potential applications such as encapsulation of drugs^{37, 130, 131} and enzymes,^{132, 133} membrane-based separations,^{3, 45, 134-140} antibacterial coatings,^{6, 141-146} fuel cells,¹⁴⁷⁻¹⁴⁹ photovoltaic membranes,¹⁵⁰ and membrane reactors.^{33, 151, 152} Below this introduction briefly explores some of these areas.

1.5.1. Membrane-based Separations

1.5.1.1. Nanofiltration Membranes

Nanofiltration (NF) is a pressure-driven separation technology similar to reverse osmosis (RO), but the membrane has a pore size between 0.5 and 2 nm, and operating pressures are between 5 and 40 bar.¹⁵³ Typically, these membranes allow passage of monovalent ions, but they reject multivalent ions and low M_w organic compounds to a much greater degree. NF applications include water softening, removal of organic pollutants, and filtration of acids and bases, and because NF operates at lower pressures than RO, energy costs are less than for a comparable RO treatment system.

Similar to RO membranes, NF membranes are asymmetric materials that contain a thin selective layer on a highly permeable support. Several studies show that LbL adsorption of oppositely charged polyelectrolytes on porous supports is a suitable method for forming NF membranes for the separation or removal of ions,¹⁵⁴⁻¹⁵⁶ sugars,^{157, 158} and dyes.¹⁵⁹ In particular, the high surface charge of many PEM films makes them attractive for separating

monovalent and divalent ions. The performance of a membrane is reported in terms of rejection, R and selectivity, S which are defined by equations 1.1 and 1.2,

$$R = \left(1 - \frac{C_{perm}}{C_{feed}} \right) \times 100\% \quad \text{----- (1.1)}$$

$$S = \frac{C_{A,perm}}{C_{A,feed}} \frac{C_{B,feed}}{C_{B,perm}} = \frac{100 - R_A}{100 - R_B} \quad \text{----- (1.2)}$$

where C_{feed} and C_{perm} are the concentrations of solute A or B in the feed and the permeate, respectively, and R_A and R_B are the rejections of solute A and B.

The solution flux, J, is calculated from the measured volume V of the permeate flowing across the membrane of area A in the time period Δt as shown in equation 1.3

$$J = \frac{V}{A\Delta t} \quad \text{m}^3/(\text{m}^2 \text{ day}) \quad \text{----- (1.3)}$$

Harris *et al.* showed that a (PAH/PSS)₅ film deposited on porous alumina exhibits a $\text{Cl}^-/\text{SO}_4^{2-}$ transport selectivity of 7 and a $\text{Cl}^-/[\text{Fe}(\text{CN}_6)]^{3-}$ selectivity of 310 in diffusion dialysis.¹⁶⁰

Similarly, Krasemann *et al.* showed that a 60-bilayer film of PAH/PSS membrane has a transport diffusion dialysis selectivity of 45 for NaCl over Na_2SO_4 , but using such a large number of layers is not practical for large-scale membrane fabrication.¹⁶¹

Deposition of hybrid PSS/PAH/PAA films on alumina supports and cross-linking of PAA/PAH at 115 °C for 2 h enhances the ion-transport selectivity of layered polyelectrolyte membranes to give an average diffusion dialysis $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity as high as 360.⁴⁵ In nanofiltration, Hong *et al.* achieved a $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity of 26 and a solution flux of $2.7 \text{ m}^3/(\text{m}^2 \text{ day})$ at 4.8 bar with a

(PSS/PDADMAC)₃PSS film on alumina. By terminating films with the polyanion PSS, and depositing this layer from a solution containing 1.0 M NaCl to increase surface charge, multivalent anions are electrostatically repelled from the membrane more than monovalent anions.¹³⁹

Balachandra *et al.* examined templating of films with Cu²⁺ to enhance the negative charge in PAA/PAH films and increase anion-transport selectivity. Deposition of polyelectrolytes from solutions containing Cu²⁺ ions and subsequent removal of the Cu²⁺ from the carboxylate groups to which they are bound ultimately leaves negatively charged COO⁻ groups in the interior of the film.¹⁶² The presence of excess negative charge in the film leads to a fourfold increase in Cl⁻/SO₄²⁻ selectivity.

Optimization of cation separations with PEM films, particularly sodium and magnesium separations, is a less thoroughly explored area than anion separations. Krasemann *et al.* showed that in diffusion dialysis, a (PAH/PSS)₅ membrane exhibits a selectivity of 31.3 for NaCl/MgCl₂ permeation, whereas (PAH/PSS)₆₀ membranes show a selectivity of 112.5. Interestingly, these membranes terminated with PSS and still exhibit high NaCl/MgCl₂ permeation selectivities.¹⁶¹ Jin *et al.* studied rejections of chloride and sulfate salts of sodium and magnesium using 60-bilayer poly(vinyl amine) (PVA)/poly(vinyl sulfate) (PVS) films on poly(acrylonitrile) (PAN)/poly(ethylene terephthalate) (PET) supporting membranes. The rejection of NaCl increased with applied pressure but was independent of feed concentration. As pressure was raised from 5 bar to 40 bar for 0.01 M Na₂SO₄, the rejection increased from 96.4% to 98.5%.¹¹

Of course, the large number of polyelectrolyte layers led to a very low film permeability. Ouyang *et al.* optimized the PSS/PAH PEM system to achieve a $\text{Na}^+/\text{Mg}^{2+}$ NF selectivity as high as 22 and a solution flux of $0.85 \text{ m}^3/(\text{m}^2 \text{ day})$ at 4.8 bar.¹⁶³

Toutianoush *et al.* increased the $\text{Na}^+/\text{Mg}^{2+}$ selectivity of 60-bilayer PVS/PVA films from 45 to 55 by adsorbing Cu^{2+} ions in the film. They concluded that the copper ions in the membrane form a complex with the amino groups of PVA, thereby increasing the crosslink density in the membrane.¹⁶⁴ However, the Cu^{2+} adsorption may also increase the amount of positive charge in the membrane to enhance cation exclusion. Using 60-bilayer hexa-p-sulfonato-calix[6]arene/PVA and PSS/PVA films the same group achieved $\text{Na}^+/\text{Mg}^{2+}$ selectivities of 71.9 and 37.2 in diffusion dialysis.¹⁶⁵ They also reported that membranes containing 60 bilayers of PVA and 1,4,7,10,13,16-hexacarboxymethyl 1,4,7,10,13,16-hexaazacyclo-octadecane (az6ac) exhibit a separation factor of 28 for $\text{NaCl}/\text{MgCl}_2$ permeation in diffusion dialysis.¹⁶⁶

Jin *et al.* investigated the transport of phenol (Ph), hydroquinone (1,4-BD), naphthalene (Np), pyrene (Py), triphenylene (Tp), alkali metal salts of benzene sulfonate (Bs), naphthalene 2-sulfonate (Ns), methyl orange (MO), and isomeric benzene disulfonates (1,2-, 1,3-BDS) compounds across PDADMAC/PSS and PAH/PSS multilayer membranes.¹⁶⁷ They achieved separation factors of $\alpha(\text{Ph}/\text{Py}) \approx 13$ using $(\text{PDADMAC}/\text{PSS})_{60}$ and $\alpha(\text{Ph}/\text{Np}) \approx 28$, $\alpha(\text{Bs}/\text{Ns}) \approx 4$ and $\alpha(\text{Bs}/1,3\text{-BDS}) \approx 65$ using $(\text{PAH}/\text{PSS})_{60}$ membranes.¹⁶⁷ For neutral compounds separation is based on size-selective transport and for charged compounds separation is based on size and charge of the aromatic compounds. Size-based separation depends on the

effective pore size of the membrane, which in turn varies with the type of polyelectrolyte in the film.

1.5.1.2. Gas Separation Membranes

Stroeve *et al.* alternately adsorbed PAH and PSS on porous polypropylene supports and on highly permeable dimethyl silicone membranes to examine the gas separation properties of PAH/PSS films.¹⁶⁸ The CO₂/N₂ selectivity on the polypropylene membrane was 23.8 for a (PAH/PSS)₂₀ film at 50 °C. A (PAH/PSS)₅₀-coated silicone membrane showed CO₂/N₂ selectivities that were 1.25 times the selectivity of the bare silicon membrane.

Leväsalmi *et al.*¹⁶⁹ deposited (PAH/PSS)₂₀₀ on an oxidized poly(4-methyl-1-pentene) (PMP) support. After film formation, the O₂/N₂ selectivity of the PMP increased 4-fold, the H₂/N₂ selectivity increased 10-fold and the H₂/O₂ selectivity doubled. Van Ackern *et al.*¹³⁴ also demonstrated that the CO₂/N₂ selectivity of (PAH/PSS)₆₀ films on etched ion-track polycarbonate supports was 2.42, which is due to greater solubility of CO₂ than N₂ in the PAH/PSS film. However, the selectivity for CO₂ over N₂ was only 1.5 with (poly(4-vinylpyridine) (P4VP)/PSS)₆₀ as the separation layer.¹⁷⁰ In another study, Blumstein *et al.* prepared polyelectrolyte multilayers from poly(N-octadecyl-2-ethynylpyridinium bromide) and PSS on Nafion and achieved an O₂/N₂ separation factor of 3.5.¹⁷¹ Overall these studies demonstrate that polyelectrolyte films are defect free and show some selectivity in gas separations. However, in most cases the selective membranes contain large numbers of bilayers, which is not attractive for large-scale membrane fabrication.

1.5.1.3. Pervaporation Membranes

A number of studies demonstrated effective pervaporative separations of liquid-liquid mixtures using polyelectrolyte membranes.^{136,137,170} Krasemann *et al.* compared ethanol-water separations by polyelectrolyte multilayer membranes with different polycations, and separation factors varied between 1.9 for (PDADMAC/PSS)₆₀ and 12.0 for poly(ethylene imine) (PEI)/PSS)₆₀.¹⁷⁰ Tieke *et al.* improved the separation efficiency for ethanol-water mixtures by using membranes made of polyelectrolytes of high charge density. A maximum water-ethanol separation factor of 700 occurred with (PVA/PVS)₆₀ on a PAN/PET support.³ Meier-Haack *et al.* used polyamide supports and achieved water-ethanol separation factors as high as 1400 after adsorption of (PEI/PAA)₆.¹³⁷

Very recently Zhang *et al.* reported composite membranes with a separation factor of 304 and a permeation flux of $0.512 \text{ kg m}^{-2} \text{ h}^{-1}$ for pervaporation of 95 wt% ethanol-water mixtures at 75 °C. The membranes used in this study were prepared by depositing PEI on hydrolyzed PAN ultrafiltration (UF) membranes under a DC electric field. These films gave fairly good flux values and high separation factor as a very uniform and dense film was formed due to rapid migration of positively charged PEI towards negatively charged PAN under the influence of the electric field.¹⁷² In other work, PDADMAC/PSS, PDADMAC/PAA and PEI/PAA membranes deposited in an electric field separated isopropanol-water mixtures (90/10, w/w) very efficiently. The separation factor and permeation flux of a (PEI/PAA)₄PEI membrane assembled in an electric field were 1289 and $1.71 \text{ kg m}^{-2} \text{ h}^{-1}$ at 50 °C. The PEMs formed in an electric field

have a high selectivity and low permeability compared to normal PEM with the same number of bilayers.¹⁷³

1.5.1.4. Membranes for Protein Separation and Purification

Membrane-based processes are also beginning to play critical roles in the separation and purification of biotechnological products, and polyelectrolyte films in porous supports can serve as novel membranes for protein capture. Müller *et al.* reported that PEI/PAA multilayers selectively bind one protein from a mixture of concanavalin A and lysozyme. At pH 7.3 (PEI/PAA)₃ preferentially adsorbed positively charged lysozyme and (PEI/PAA)₂PEI adsorbed negatively charged concanavalin A.¹⁷⁴ PEM films formed in the pores of membrane terminated with a polyanion have cation-exchange sites as shown in Figure 1.12. These cation-exchange sites bind positively charged proteins like lysozyme, and the lysozyme-binding capacities of (PSS/PEI)₃PSS films increase with the ionic strength of capping layer to values as high as 16 mg/mL of membrane.¹⁷⁵

Several studies examined the interactions between proteins and polyelectrolyte multilayers. In the case of human serum albumin and PAH/PSS multilayers, the protein adsorbs on both PAH- and PSS-terminated films. However, on PSS-terminated multilayers a dense protein monolayer forms, whereas on PAH-ending multilayers, adsorbed protein films have thicknesses as high as four times the largest native protein dimension.¹⁷⁶ Salloum *et al.* studied the adsorption of serum albumin, fibrinogen, and lysozyme on different PEM films. The adsorption of the proteins depends on the surface charge, protein charge and thickness of the PEM film.¹⁷⁷

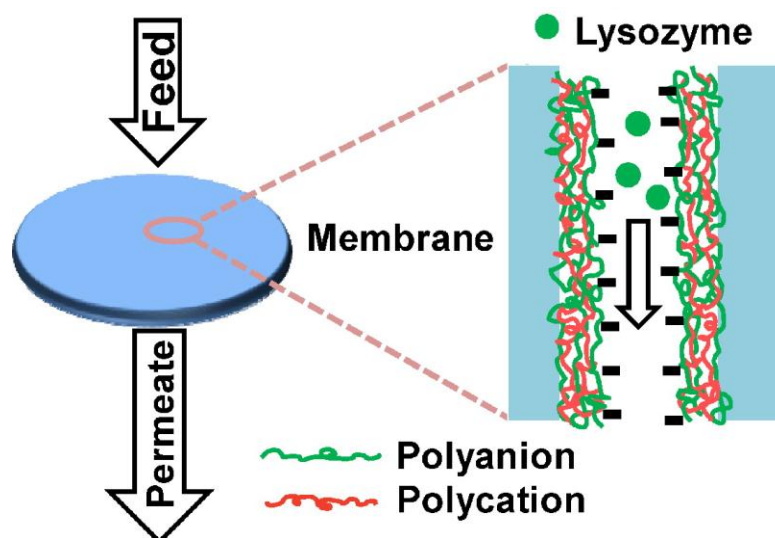


Figure 1.12. Schematic diagram showing the binding of positively charged lysozyme to a PEM film terminated with a polyanion. Charges are only shown for the terminal layer. (Reprinted with permission from *J. Membr. Sci.* **2010**, 354(1-2), 198-205.)

1.5.2. Encapsulation of Drugs and Enzymes

LbL technology is also attractive for encapsulation of proteins and other bioactive compounds. Encapsulation occurs by either directly coating the drug microcapsules with polyelectrolyte multilayers, or by removing a template to form hollow polyelectrolyte microcapsules and then loading the biomolecules into the capsules. Careful selection of the encapsulating polyelectrolytes, including the incorporation of functional polyelectrolytes or nanoparticles, allows tailoring of capsule properties for controlled and triggered release and responsiveness to temperature, pH, light and magnetic fields. Micro-encapsulation by LbL adsorption shows potential applications in biochemistry, pharmacy, controlled release, cosmetics and catalysis.^{178, 179}

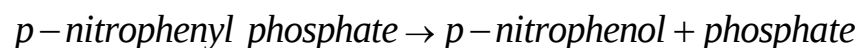
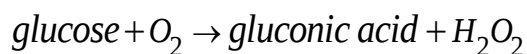
As examples, Caruso *et al.* encapsulated an enzyme (catalase) through LbL adsorption onto enzyme crystal templates.¹⁸⁰ Encapsulated enzymes maintain a high activity because the polyelectrolyte films restrict enzyme denaturation and degradation. Multilayer films of protamine sulfate (PRO) and PSS formed on ibuprofen-loaded CaCO_3 microparticles¹⁸¹ and acridine hydrochloride (AH) deposited in CHI/alginate (ALG) nanocapsules¹⁸² were used for sustained drug release by Wang *et al.* The porous CaCO_3 particles are useful for loading drugs in an amorphous state, and the polyelectrolyte multilayer films coated on these particles help control drug release.¹⁸¹ The CHI/ALG multilayers were formed on polystyrene (PS) nanoparticles which were later dissolved by tetrahydrofuran. Positively charged AH was deposited due to electrostatic interactions with negatively charged residual PS copolymer with styrene sulfonate units in the capsule.¹⁸²

1.5.3. Catalytic Membrane Reactors

When applied in porous supports, LbL adsorption of polyelectrolytes and either enzymes or precious metal nanoparticles provides a convenient method of forming catalytic membranes. Such catalytic membrane reactors (CMRs) are attractive because they allow flow-through reactions and avoid the need to separate the catalyst from reaction mixture.¹⁸³ Dotzauer *et al.* showed that the adsorption of nanoparticle/polyelectrolyte films in either polymeric or alumina membranes effectively immobilizes the gold nanoparticles without inhibiting access to catalytic sites (Figure 1.13). The rate constants for nanoparticle-catalyzed 4-nitrophenol reduction in solution and in membranes were essentially identical. Alumina membranes modified with

nanoparticle/polyelectrolyte films catalyze the reduction of >99% of 0.4 mM 4-nitrophenol in membrane residence times of 6.1 ms.³³

Weimann *et al.* encapsulated a biocatalyst, lipase B from *Candida antarctica* in a PAH/PSS film on CaCO₃ colloid particles. A slight increase (32%) in the enzyme catalytic performance for esterification of caprylic acid and 1-octanol in n-hexane was observed because immobilization results in better dispersion of the enzymes in organic solvents.¹⁵² Smuleac *et al.* fabricated enzyme-containing PEMs inside membrane pores to achieve high loading of biomolecules with minimum loss of activity.¹³³ Specifically, adsorbed glucose oxidase and alkaline phosphatase catalyzed the reactions shown below.



Electrostatic immobilization of glucose oxidase in a PLL/PSS/PAH-modified membrane resulted in a maximum loading of 699 µg of enzyme and 76% enzyme activity relative to enzyme activity obtained in a homogeneous phase. Similarly, alkaline phosphatase retained 71% of its activity after immobilization in a membrane. The advantage of using immobilization in membranes is the convective flow, which eliminates diffusion limitations and transports the product away from the catalytic site during operation.¹³³

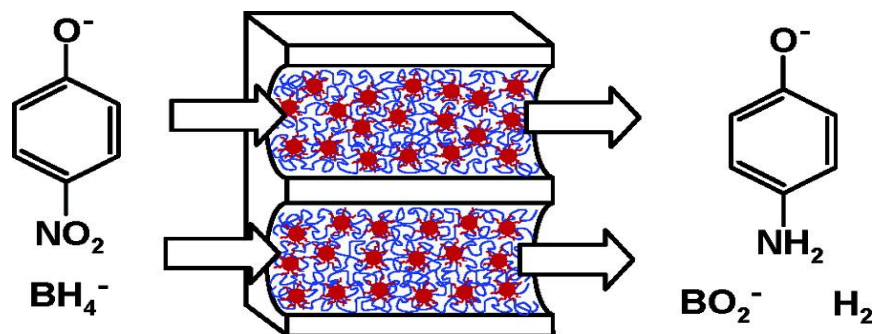


Figure 1.13. Schematic diagram of gold nanoparticle (●) / polyelectrolyte (~) films immobilized in membranes for 4-nitrophenol reduction. (Reprinted with permission from *Nano Lett.* 2006, 6(10), 2268-2272.)

Increasing concern over the use of chemical warfare, combined with more frequent potential exposure of soldiers and emergency care providers to toxic chemicals has heightened the need for new protective measures. Reactive textile coatings that selectively degrade toxic chemicals, including chemical warfare agents and environmental toxins such as NO_x and SO_x , while still affording the wearer a high degree of water vapor permeability and thus greater comfort, are attractive for protection against low to moderate exposures to toxic chemicals. A recently developed PDADMAC/ TiO_2 LbL coating provides a reactive barrier with more than 99% efficiency against a saturated environment of the sulfur mustard simulant compound chloroethyl ethyl sulfide (CEES) in the presence ultraviolet radiation.¹⁸⁴

1.5.4. Antibacterial Coatings

Klevens *et al.* estimated that approximately 64% of hospital-acquired infections worldwide stem from attachment of viable bacteria to medical devices and implants,¹⁸⁵ and these infections have an associated annual mortality of 100 000 persons in the US alone.¹⁸⁶

Among various methods for combatting the formation of bacterial films, PEMs provide numerous opportunities for designing surfaces that either inhibit bacteria attachment and growth or kill bacteria.^{6, 143, 145, 187}

Recently, Boulmedais *et al.*¹⁴⁴ constructed anti-adhesive multilayer films via the LbL method with pegylated polypeptides. Films with one PLL/PGA-graft-poly(ethyl glycol) (PEG) and three PLL/PGA-g-PEG bilayers reduced the adhesion of *E. coli* by 72% and 92%, respectively, compared with bare substrates. Fu *et al.* alternately deposited CHI and heparin onto aminolyzed PET films to construct anti-adhesive and antibacterial multilayer films.¹⁴⁶ The multilayer films not only reduced the bacterial adhesion significantly, but also killed a part of the bacteria that adhered to the surface.

More recently Malcher *et al.* designed a new antibacterial coating made of PLL/HA multilayer films and liposome aggregates loaded with AgNO_3 .¹⁴² Release of Ag^+ ions should kill bacteria through disruption of crucial metabolic proteins and enzymes. After 120 min of contact with such AgNO_3 -containing coatings the number of *E. coli* bacterial in a bacterial suspension decreased by a factor of 10,000 relative to the initial bacterial population.

1.5.5. Environmental Applications

Industrial effluents constitute a major source of contaminated water with a wide range of toxic pollutants, and membrane technologies such as reverse osmosis, ultrafiltration, and nanofiltration may prove effective in treating such waters.^{11, 188, 189} Polyelectrolyte membranes could potentially be tailored for removal of specific contaminants at low operating pressures. Catalytic polyelectrolyte films may also be effective in wastewater treatment. Huang

et al. assembled PAA/PAH multilayers on glass beads or carbon grids and immersed these materials in FeSO_4 solution for 30 min to allow ferrous cations to complex with available free carboxylate groups on PAA. The substrates were then immersed in 10 mM NaBH_4 solution to reduce ferrous ions to Fe^0 nanoparticles. The resulting zero valent iron nanoparticles (ZVI NPs) can degrade trichloroethylene (TCE), a compound representative of a major class of chlorinated organic contaminants.¹⁹⁰ Mass-normalized rate constants for pseudo-first-order degradation of TCE are as high as $0.016 \text{ Lhr}^{-1} \text{ mg}^{-1}$ for $(\text{PAA/PAH})_{15}$ assembled at pH 2.5. Xiao *et al.* immobilized ZVI NPs on PAA/PDADMAC multilayers deposited on cellulose acetate nanofibers. The decoloration efficiency of the ZVI NP-modified polymer nanofibers for acid fuchsin, a model contaminant, was 86.8% in 40 min.¹⁹¹ Priya *et al.* recently studied the use of multilayer ultrathin composite films containing nanosized titanium dioxide particles and polyelectrolytes (PAH or PSS) in photodegradation of rhodamine B under ultraviolet (UV) irradiation. They achieved 100% degradation efficiency in 4 h with a $\text{PAH}/(\text{PSS}/\text{TiO}_2)_{20}$ film.¹⁵¹

Compounds that disrupt the normal functionality of endocrine (endocrine-disrupting compounds, EDCs) in humans or other animals are commonly present in municipal wastewaters.¹⁹² They include pharmaceuticals such as ethynylestradiol (EE2), plasticizers such as bisphenol A and phthalates, surfactants such as the alkylphenols (APs), and organochlorine pesticides. Health effects due to EDCs include a range of reproductive problems, changes in hormone levels, early puberty, brain and behavior problems, impaired immune functions, and

various cancers.^{193, 194} Pharmaceutically active compounds (PhAC) are also common constituents of municipal waste water. Although the toxicological effects posed by residual PhACs are still unknown, the presence of these compounds may induce unwanted effects in the environment.¹⁹⁵ In aquatic systems, PhACs may affect lower animals with identical or similar target organs, tissues or cells as humans.^{196, 197} Several groups examined the removal of EDCs and PhACs by NF membranes¹⁹⁸⁻²⁰⁰ some of which were modified by grafting,^{201, 202} but no literature describes the use of LbL films for PhAC or EDC removal. Hoshi *et al.* showed that Pt electrodes coated with PAH/PVS or PAH/PSS films successfully exclude acetaminophen, a PhAC,²⁰³ So such films could be attractive as membranes for removal of such compounds.

1.6. Dissertation Outline

This dissertation focuses on the characterization of polyelectrolyte multilayers and their use in ion separations and water purification. Chapter 2 provides the experimental details for film formation and characterization as well as the methods for examining separation efficiencies with these membranes. Chapter 3 examines why the separation performance of PSS/PDADMAC membranes varies dramatically with the number of layers deposited on the underlying porous substrate. ATR-FTIR spectroscopy shows that the ion exchange capacity in the films changes with number of layers and reaches a maximum value, 0.5 M, after deposition of 7 bilayers. Moreover, streaming potential measurements demonstrate that the surface charge of PSS-terminated films changes from negative to positive as the number of layers increase. These changes in film properties dramatically affect ion transport through

(PSS/PDADMAC)_nPSS-coated alumina membranes. Nanofiltration properties such as rejections of sulfate initially increase with the number of adsorbed layers, reach a maximum and then decrease with more layers.

Chapter 4 demonstrates a new method for enhancing the selectivity of PAH/PSS films for cation separations. Immersing the films in aqueous FeCl₃ generates fixed positive charges in the film to greatly increase Na⁺/Mg²⁺ selectivity. FTIR spectroscopy shows the presence of counterions in the multilayers, which presumably stems from the anion-exchange sites that enhance selectivity in Na⁺/Mg²⁺ separations.

Chapter 5 examines the removal of acetaminophen and caffeine from water using NF with commercial membranes and polyelectrolyte multilayer membranes. This work studies the effect of the number of PEM bilayers, polyelectrolyte concentration and type of polyelectrolyte on the rejections of acetaminophen. Commercial NF-90 membranes modified with only one bilayer of PSS/PAA show 85% rejection of acetaminophen, whereas unmodified NF-90 membranes exhibit a 65% acetaminophen rejection. This work also examines the rejections of caffeine using commercial NF membranes and PEM membranes. (PSS/PAH)₇ films have caffeine rejections of 94% and a solution flux that is 1.5 times higher than that of NF-90.

The final chapter of the thesis presents a summary of the research and its impact as well as future directions for the work.

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Chapter 2

Methods and Techniques

2.1. Polyelectrolyte Multilayer Nomenclature and Deposition

This dissertation employs the $(A/B)_X$ nomenclature for polyelectrolyte multilayers, where A is the initially deposited polyelectrolyte that is in direct contact with the substrate, B is the oppositely charged polyelectrolyte, and X represents the number of bilayers. Integer values of X indicate films that terminate with B, whereas $n+0.5$ values of X, where n is an integer, indicate films that terminate with A. In some cases, we also use the terminology $(A/B)_XA$ to denote a film containing X bilayers and an additional, terminating layer of A.

Deposition of PEM films on Si and Ge crystals or PES membranes begins by exposing the top of the substrate to a solution containing 0.02 M polycation and then rinsing for 1 min with deionized water from a squirt bottle (concentrations of polyelectrolytes are always given with respect to the repeating unit). Subsequent adsorption of polyanions occurs similarly, and repetition of the entire process yields the multilayer films. For Au-coated wafers, a monolayer of 3-mercaptopropionic acid (MPA) on the Au wafer serves as an adhesion layer between Au and a polycation, which is the first deposited polyelectrolyte. Adsorption of PEMs on alumina membranes takes place similarly to deposition on Si, except the starting layer is PSS. The pH and supporting salt concentrations in deposition solutions are mentioned in each chapter for specific experiments.

2.2. Determination of Film Thickness by Ellipsometry and Scanning Electron Microscopy

2.2.1. Ellipsometry¹

Ellipsometry is a rapid, convenient method for determining the thicknesses of smooth films whose thicknesses range from nanometers to a few microns. This technique measures a change in the polarization of light as it reflects or transmits from an interface. The polarization change is typically described by the ratio, ρ , of reflection coefficients for the transverse magnetic and transverse electric modes. This ratio can be expressed as a function of both the amplitude ratio, Ψ , and the phase difference, Δ , of the two reflection coefficients as shown in equation 2.1.

$$\rho = \tan(\psi) e^{i\Delta} \quad \text{-----} \quad (2.1)$$

The measured values of Ψ and Δ depend on both the optical properties and thickness of a film, so in principle ellipsometry allows determination of both film thickness and optical constants. For thin films, the Cauchy model, equation 2.2, effectively describes the variation of refractive index with wavelength, λ ,

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad \text{-----} \quad (2.2)$$

where the three terms A, B, and C are adjusted to fit the refractive index of the material. Determination of optical constants is difficult for ultrathin films, however, because in this realm the values of Ψ and Δ vary only weakly with refractive index. Because ellipsometry assumes a smooth film and substrate, the validity of this technique diminishes for rough films.

Ellipsometry studies were performed with a J.A. Woollam model M-44 rotating analyzer ellipsometer to determine the thicknesses of PEM films on Si wafers. The thicknesses of dry

films were determined using literature values of refractive indices for Si and SiO₂ and assuming a PEM refractive index of 1.5. After deposition, films were dried with a stream of nitrogen, and the dry thickness was determined at several points on each wafer.

2.2.2. Scanning Electron Microscopy (SEM)

For films with thicknesses >50 nm, cross-sectional SEM images provide a measure of film thickness and roughness. Film-coated Si wafers were fractured immediately after exposure to liquid nitrogen and subsequently sputter-coated (Pelco model SC-7 auto sputter coater) with gold on the cross section of the wafer to minimize charging during SEM. PES membranes coated with polyelectrolyte multilayers were cut with scissors, and the surface of the membrane was sputter-coated with 5 nm of gold prior to imaging. SEM images were obtained with a Hitachi S-4700 II field-emission scanning electron microscope.

2.3. Molecular Spectroscopy

2.3.1. Reflectance Fourier Transform Infrared (FTIR) Spectroscopy

External reflection FTIR spectra were obtained with a Nicolet Magna 560 FTIR spectrometer using a PIKE grazing angle (80°) attachment. This instrument contains a Mercury-Cadmium-Telluride (MCT) detector and a KBr beam splitter and has a spectral range of 4000 cm⁻¹ - 700 cm⁻¹. The MCT detector is vital to achieve the sensitivity needed for reflectance spectroscopy. All spectra were recorded using 128 scans at 4 cm⁻¹ resolution, and a spectrum of a gold wafer in air served as a background.

2.3.2. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR)

Spectroscopy

ATR-FTIR spectroscopy relies on absorption of the evanescent wave at the surface of the ATR crystal. Figure 2.1 show an in situ ATR-FTIR setup where the crystal is covered with solution. Total reflection, which results in the formation of an evanescent wave, occurs when light propagates from an optically denser medium to a rarer medium and when the angle of incidence is greater than critical angle, θ_c .² Equation 2.3 defines the critical angle

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right) \quad \text{-----} \quad (2.3)$$

where n_1 is the refractive index of the dense medium (ATR crystal) and n_2 is the refractive index of the rare medium (polymer film). Equation 2.4 gives the magnitude of the electric field, E , of the evanescent wave as a function of the distance, z , from the surface where

$$E = E_0 e^{-z/d_p} \quad \text{-----} \quad (2.4)$$

E_0 is the incident electric field amplitude, and d_p is the penetration depth or the distance at which the amplitude of the evanescent wave drops to $1/e$ times its amplitude at the crystal/film or crystal/solution interface.^{3, 4} For a particular wavelength, λ , equation 2.5 describes the penetration depth,

$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2 \theta - n_2^2)^{1/2}} \quad \text{-----} \quad (2.5)$$

where θ is the angle of incidence (45° in our experiments), n_1 is the refractive index of the Ge crystal (4.0) and n_2 is the refractive index of the film.⁵ Significant absorption in an ATR-FTIR

experiment occurs only within 2-3 penetration depths of the surface because at greater distances, the electric field is <10% of its initial amplitude. Moreover, the light intensity and absorption are proportional to the square of the electric field.

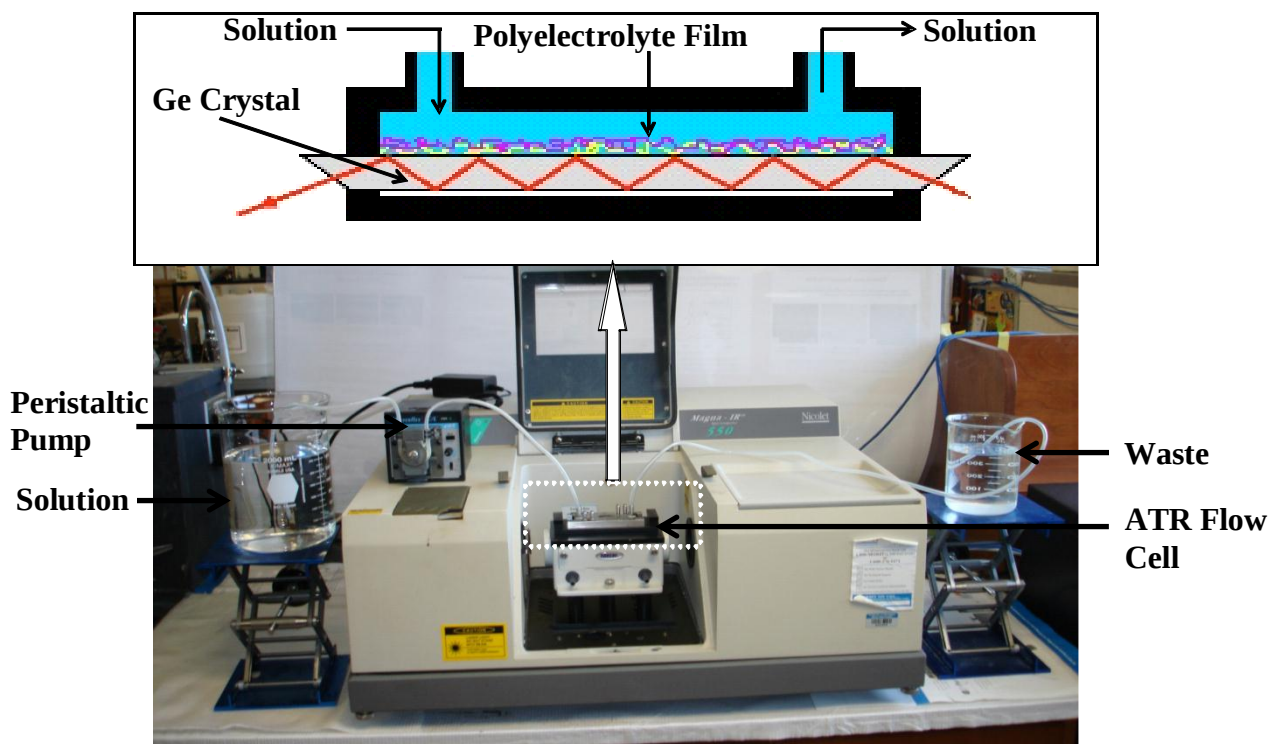


Figure 2.1. ATR-FTIR flow cell for the measurement of diffusion of ions in the polymers. (The sample compartment was closed during measurements.) The inset shows a schematic diagram of the ATR crystal in the flow cell.

A Nicolet Magna 550 FTIR spectrophotometer was used to monitor the diffusion of ions into polyelectrolyte multilayers. A flow cell with a volume of 550 μL , and a 70 mm x 10 mm x 6 mm 45° germanium crystal from Specac were used in these studies. All spectra were recorded using 32 scans at 4 cm^{-1} resolution, and a spectrum of a bare germanium crystal in water was typically used as a background. The germanium crystal was cleaned by rinsing sequentially with

1 M CaCl₂ and water and then wiping the crystal with a tissue soaked in methanol or isopropanol.^{6, 7} Cleaning was verified by the absence of sulfonate absorbances in ATR-FTIR spectra taken with air as a background.

2.3.3. UV/Vis Spectroscopy⁸

A Perkin Elmer Lambda 40 spectrophotometer was used to record UV/Vis spectra for analysis of acetaminophen and caffeine. According to Beer's law which is given by equation 2.6,

$$A = \epsilon bC \quad \text{-----} \quad (2.6)$$

where A is the absorbance, ϵ is the molar absorptivity coefficient or molar extinction coefficient in Lmol⁻¹cm⁻¹, b is path length in cm and C is the concentration in molL⁻¹ or M. When the extinction coefficient and the path length are constant, absorbance is directly proportional to the concentration.

2.4. Ion Chromatography

Concentrations of anions were determined by ion chromatography with conductivity detection using a Dionex 600 Ion Chromatograph with an Ionpac AS16 column. Samples are first passed through a shorter and less expensive guard column to protect the separator column from potentially damaging sample material. The eluent is 20 mM NaOH, the anions are separated based on their tendency to bind to ion-exchange sites, and the concentrations are then determined using conductivity measurements. For anion detection, an ASRS-Ultra anion self-regenerating suppressor (4 mm) is used to reduce the background conductivity of the eluent

because the concentration of anions is very low. Chromatograms are collected using a 1.0 mL/min flow rate, and the sample loop has a volume of 25 μ L. Eluents and all sample solutions are prepared with deionized water of resistivity 18.2 M Ω cm.

2.5. Atomic Absorption Spectroscopy and Inductively Coupled Plasma

Optical Emission Spectroscopy

Atomic Absorption Spectroscopy allows the determination of trace concentrations of elements, usually metals, through monitoring of light absorption due to specific electronic transitions of atoms. The light source is a hollow cathode lamp that is element specific, and atoms in the sample are vaporized in a high temperature source such as a flame or graphite furnace. This work employed a Varian Spectra Atomic Absorption-200 Spectrometer to analyze metals like Na and Mg.

A Varian 710-ES ICP Optical Emission Spectrometer was used for analysis of the iron in polyelectrolyte multilayer films. In this case, plasma is used to excite the atoms and ionize a sample, and the emission of light from specific elements is used along with a calibration curves to determine their concentration.

2.6. Streaming Potential Measurements

In a system with flow across a surface, convective transport of the excess charge in the diffuse electrical double layer creates a streaming potential such that no net current flows through the system. Based on the assumption that the currents due to convection of the diffuse double layer and to migration stemming from the streaming current must be equal in magnitude and opposite in direction, equation 2.7 provides an expression for the streaming potential, U .⁹

$$U = \frac{\varepsilon_o \varepsilon_r}{\mu K_b} \Delta P \zeta \quad \text{----- (2.7)}$$

In this equation, ΔP is the pressure drop across the capillary of length L , μ is the fluid viscosity, K_b is liquid conductivity, ε_o is the permittivity of vacuum, ε_r is the dielectric constant of the solvent, and ζ is the zeta potential, which is the potential at the interface of the Stern layer, where ions are firmly bound to the surface, and the diffuse layer where ions are mobile (See Figure 2.2).

Streaming potential measurements were performed with a Brookhaven Instruments Electro Kinetic Analyzer using a clamping cell (Anton Paar, Graz, Austria) as shown in figure 2.3. In this cell, the test sample is placed flush against a 10 mm by 20 mm piece of grooved poly(methyl methacrylate) (PMMA) spacer. The clamping cell includes Ag/AgCl electrodes and inlet/outlet tubing which introduce the test solutions (1 mM KCl and 1 mM MgCl₂ in this work) into the rectangular channels of the PMMA spacer.^{9, 10} PES membranes with dimensions of 5 cm x 5 cm (cut from a flat sheet of 100 kDa membrane from Pall Corporation, Port Washington, NY), served as substrates for streaming potential measurements. These membranes were initially soaked in 0.1 M NaOH for 1 hour and rinsed with deionized water prior to polyelectrolyte adsorption.

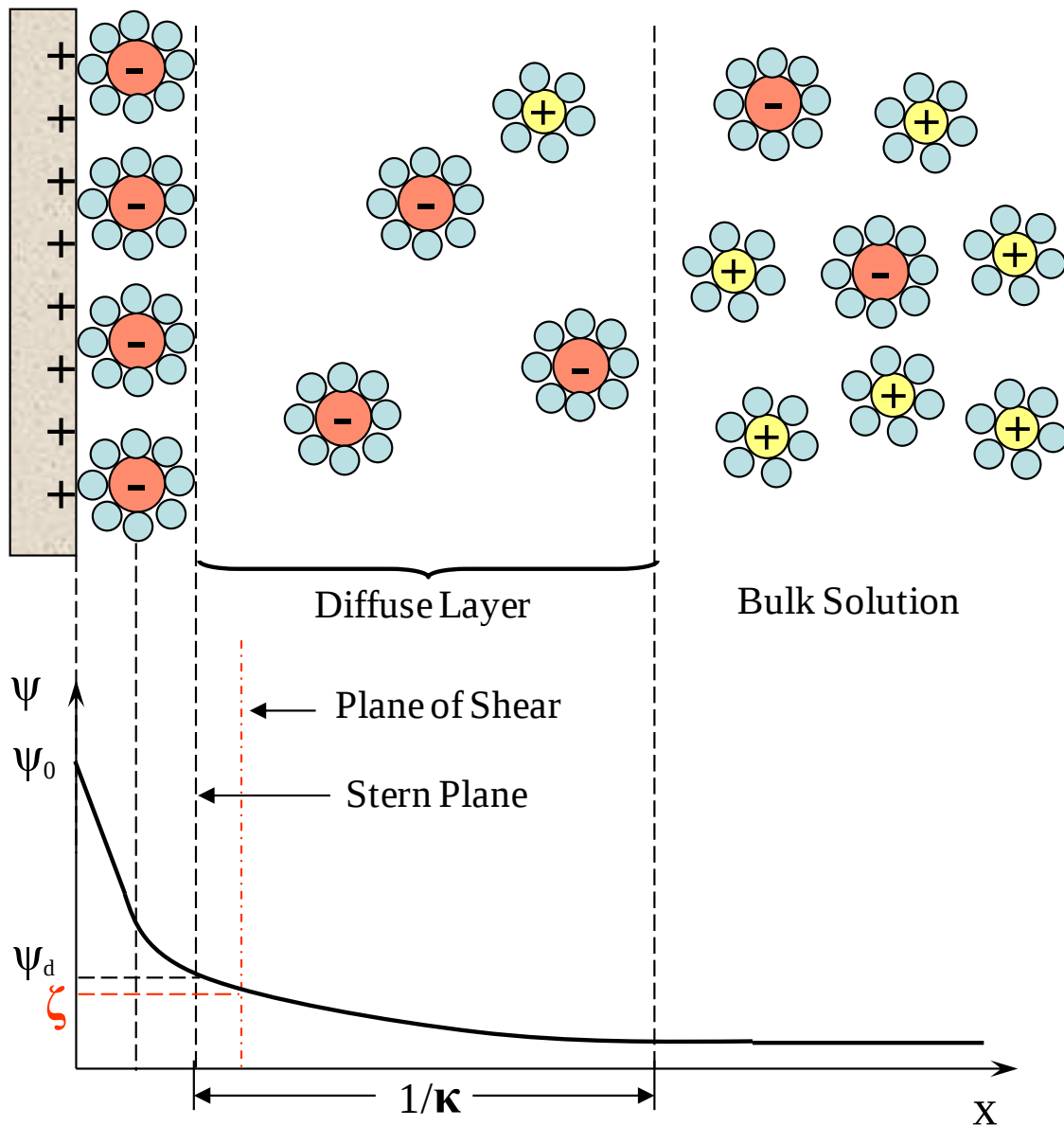


Figure 2.2. Schematic representation of electrical double layer and ζ potential.¹¹

The ζ potentials were measured with both a sheet of PMMA and the membranes. The measurement with the PMMA provides the value of the spacer zeta potential. Even with the membrane in place, the PMMA spacer still contributes to the streaming potential, so the ζ potential of the sample is calculated from the ζ potential that is measured during the experiment, ζ_{average} , using equation 2.8.⁹

$$\zeta_{sample} = 2\zeta_{average} - \zeta_{spacer} \quad \text{----- (2.8)}$$



Figure 2.3. Electro Kinetic Analyzer flow cell setup for zeta potential measurements.

2.7. Nanofiltration Experiments

Nanofiltration experiments were performed with a home built cross-flow apparatus (Figure 2.4) that was pressurized with Ar at 4.8 bar, as described previously.¹² A centrifugal pump circulated the analyte solution through the apparatus and across the membrane, which had an exposed area of 1.5 cm². The exposed area was measured by nanofiltration with 0.1% Congo red dye.¹² The flow rate across the membrane was set to 18 mL/min and controlled by a flow meter located between the pump and membrane cells. This flow rate was selected to minimize any concentration polarization in the nanofiltration cell. After 18 h of filtration, four permeate samples were collected for time periods ranging from 5 to 30 min each, depending on the flux

through the membrane, and the feed was analyzed at the end of the experiment to calculate rejections. The volume of the feed was 6- to 8-fold greater than the total volume of permeate, so the feed concentration was relatively constant. The flux measurements reported are the average of several steady-state solution flux measurements after the initial 18 h of filtration.

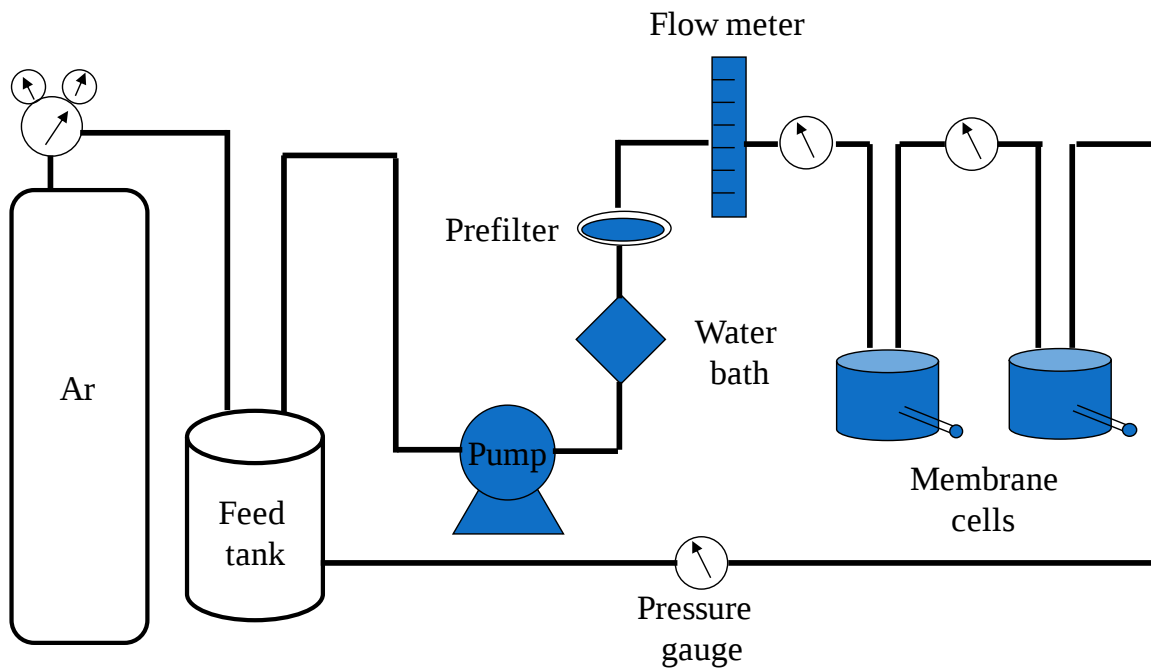


Figure 2.4. Schematic drawing of the experimental NF apparatus.¹²

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2.8. References

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Chapter 3

Variation of Ion-exchange Capacity, Zeta Potential, and Ion-transport Selectivities with the Number of Layers in a Multilayer Polyelectrolyte Film

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3.1. Introduction

Alternating adsorption of polycations and polyanions is a simple, versatile technique for forming functional thin films.¹⁻⁵ The thicknesses of these films can be controlled by varying the number of deposited layers, and a wide range of materials including synthetic polymers, proteins, inorganic sheets, and nanoparticles can be incorporated into such coatings to tailor them for specific applications.⁶⁻¹³ In some potential uses of multilayer polyelectrolyte films, e.g. membrane-based separations¹⁴⁻²² and encapsulation of drugs²³⁻²⁵ and enzymes,^{26, 27} control of transport through the film, which can be achieved by changing deposition conditions and polyelectrolytes, is vital. Adsorption of different polyelectrolytes yields films with a wide range of swelling and transport properties, and even the mechanism of film growth varies among polyelectrolyte pairs.²⁸⁻³⁶

Film permeability and the amount of polyelectrolyte deposited per adsorption step can also vary dramatically with the number of layers in a multilayer polyelectrolyte film.^{20, 37-40} Hong *et al.* recently found that the Cl^-/F^- nanofiltration selectivities of PSS/PDADMAC films on porous alumina membranes reach a maximum value of 3.4 for (PSS/PDADMAC)₄PSS films and

then decline to essentially unity with (PSS/PDADMAC)₆PSS films.^{35, 41} The research described here focuses on better understanding the changes that occur in PSS/PDADMAC films as the number of adsorbed layers increases.

Schlenoff *et al.* proposed a model for ion transport through polyelectrolyte multilayers in which the ions hop between ion-exchange sites.⁴² Thus, one of the film properties that this manuscript investigates is the ion-exchange capacity of PSS/PDADMAC films as a function of the number of deposited layers. Although several techniques were employed to determine whether counterions are present in multilayer polyelectrolyte films,^{10, 43-47} attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy is particularly attractive for examining the absorption of counterions that have suitable infrared absorbances.^{48, 49} By focusing on specific IR absorption bands in the ion, ATR-FTIR spectroscopy can sensitively distinguish between polymers and solutes, and this technique also reveals chemical interactions between solutes and polymers through shifts in peak absorbances.⁵⁰ In this chapter, we use ATR-FTIR spectroscopy to examine the absorption of both a monovalent ion, SCN^- , and a divalent ion, $\text{Ni}(\text{CN})_4^{2-}$, in PSS/PDADMAC films as a function of the number of bilayers. These studies show that the number of anion-exchange sites in PSS/PDADMAC films increases dramatically after deposition of 6 bilayers in the film.

We also investigate the zeta potentials of PSS/PDADMAC films as a function of the number of deposited layers. Zeta potentials are indicative of the net film charge, which can increase ion-transport selectivities by heavily excluding the partitioning of multivalent ions into the film (Donnan exclusion³⁹). A number of studies show that the sign of the zeta potentials of

polyelectrolyte films oscillates between positive and negative depending on whether the film terminates with a polycation or a polyanion.^{33, 51-53} In contrast, in the case of PSS/PDADMAC, the situation is more complex and the trend in zeta potential changes as more layers are deposited.

Finally, this chapter examines the separation of monovalent and divalent ions by nanofiltration through PSS/PDADMAC films deposited on highly permeable supports. Trends in monovalent ion/divalent ion transport selectivities as a function of the number of deposited PSS/PDADMAC layers correlate well with corresponding trends in zeta potentials and ion-exchange capacities, and remarkably high selectivities can only be achieved only with the optimal number of bilayers.

3.2. Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70\,000$ Da), poly(diallyl dimethylammonium chloride) (PDADMAC, $M_w = 200\,000 - 350\,000$), KSCN, and NaSCN were purchased from Sigma-Aldrich, and Figure 3.1 shows the structures of the polyelectrolytes. Reagent grade KCl, NaCl, and Na_2SO_4 were obtained from Jade Scientific, and $\text{K}_2\text{Ni}(\text{CN})_4$ was purchased from Spectrum. Porous alumina supports (0.02- μm Whatman Anodisk filters) were UV/ O_3 cleaned (Boekel UV-Clean Model 135500) with the feed side up for 15 min before film deposition, and deionized water (Millipore purification system, 18.2 $\text{M}\Omega\text{cm}$) was used for membrane rinsing and preparation of the polyelectrolyte solutions. We utilized alumina membranes with 20 nm-diameter surface pores to avoid significant deposition of polyelectrolytes in membrane pores.^{29, 54}

Polyethersulfone (PES) membranes with molecular weight cutoffs of 50 and 100 kDa were kindly provided by Pall Corporation (Port Washington, NY) and were initially soaked in 0.1 M NaOH for 1 hour, then soaked in DI water for 24 hours and rinsed with deionized water. Silicon wafers (100 orientation) were obtained from Silicon Quest International (Santa Clara, CA), and after 15 min of UV/Ozone cleaning, the ellipsometric thickness of the SiO₂ layer on the surface of the wafer was 2 nm.

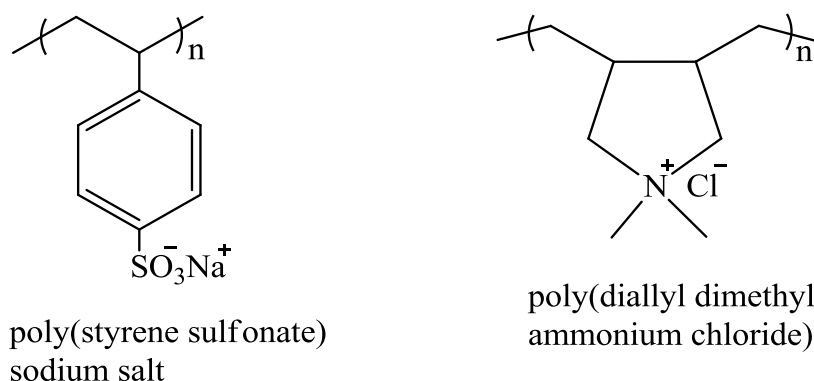


Figure 3.1. Structures of the polyelectrolytes used in this study.

Film Deposition. Polyelectrolyte films were deposited using a procedure described previously.^{28, 29} Briefly, deposition of PSS occurred by exposing the top of the substrate to 0.02 M PSS in 1.0 M NaCl for 5 min and rinsing for 1 min with deionized water. Deposition of PDADMAC occurred similarly. The pH of PDADMAC and PSS deposition solutions was adjusted to 7.4 with 0.1 M NaOH. After deposition of the desired number of polyelectrolyte layers, membranes were stored in water until use.

Ellipsometry. Ellipsometry studies were performed with a J.A. Woollam model M-44 rotating analyzer ellipsometer to determine the thicknesses of PDADMAC/PSS films on Si wafers. This technique is described in more detail in chapter 2.

Scanning Electron Microscopy. Cross-sectional images of silicon wafers coated with polyelectrolyte multilayers were taken using a Hitachi S-4700 II field-emission scanning electron microscope (FESEM) as described in Chapter 2.

ATR-FTIR Studies. Attenuated total internal reflection FTIR spectroscopy was used to monitor the diffusion of ions into polyelectrolyte multilayers (see Chapter 2). Multilayer formation was accomplished by alternately passing the polyelectrolyte solutions and deionized water over the ATR crystal in the flow cell for the times mentioned above.

Streaming Potential Studies. Streaming potential measurements were performed with a Brookhaven Instruments Electro Kinetic Analyzer using a clamping cell (see Chapter 2). A 1 mM KCl solution served as the electrolyte for these measurements.

Transport Studies. Nanofiltration experiments were performed as described in section 2.6. For $\text{Cl}^-/\text{SO}_4^{2-}$ separations, feed solutions contained 1000 ppm SO_4^{2-} and 1000 ppm Cl^- prepared by dissolving Na_2SO_4 and NaCl in deionized water. Anion concentrations were determined using ion chromatography (Dionex 600 Ion Chromatograph with an Ionpac AS16 column) with conductivity detection, and all reported transport results are the averages of experiments with two different membranes. The plus and minus values are the standard deviations of several measurements on two different membranes.

In the case of $\text{SCN}^-/\text{Ni}(\text{CN})_4^{2-}$ and $\text{Cl}^-/\text{Ni}(\text{CN})_4^{2-}$ experiments, $\text{Ni}(\text{CN})_4^{2-}$ concentrations were determined by Ni atomic absorption spectroscopy (Varian Spectra Atomic Absorption-200 Spectrophotometer). The SCN^- or Cl^- concentrations were determined with conductivity measurements (Orion 115 Conductivity meter), where conductivities were converted into concentrations using a calibration curve with a small correction for $\text{Ni}(\text{CN})_4^{2-}$

concentration. The correction, which was small because of the low permeability of Ni(CN)_4^{2-} , was based on a separate conductivity-concentration calibration curve for $\text{K}_2\text{Ni(CN)}_4$ and the Ni analysis. For $\text{SCN}^-/\text{SO}_4^{2-}$ experiments, the SCN^- and SO_4^{2-} concentrations were determined using ion chromatography.

3.3. Results and Discussion

3.3.1. Film Formation and Characterization

Figure 3.2 shows the ellipsometric thicknesses of PDADMAC/PSS films on Si wafers as a function of the number of PDADMAC/PSS bilayers. (The Si wafers contain a 2 nm layer of SiO_2 on their surface, and the films are adsorbed from solutions containing 1 M NaCl.) Similar to literature data, the thicknesses of the PDADMAC/PSS multilayer films increase nonlinearly with the number of bilayers,³⁷ and the thickness per bilayer is as high as 60 nm. Films with more than 10 bilayers are visually inhomogeneous and rough, so it is difficult to determine their thicknesses using ellipsometry.

The initial nonlinear and very rapid growth of PDADMAC/PSS films may occur by the “exponential growth” mechanism suggested previously.^{37, 40, 55-57} In this mechanism, one of the polyelectrolytes, frequently the polycation, absorbs throughout the polyelectrolyte multilayer. Upon deposition of the next layer, the previously deposited polyelectrolyte diffuses to the surface and forms a thick layer of the polyanion/polycation complex.

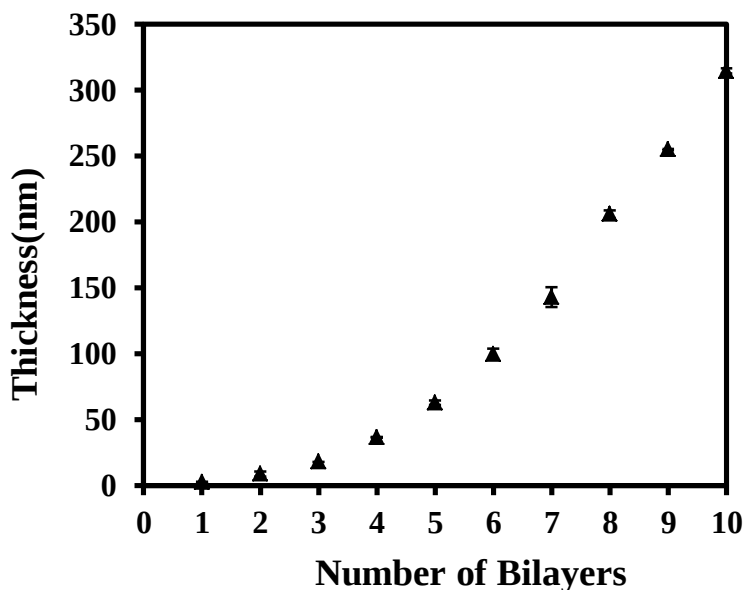


Figure 3.2. Ellipsometric thicknesses of (PDADMAC/PSS)_n films on silicon wafers. Polyelectrolytes were adsorbed from solutions containing 1 M NaCl.

Figure 3.3 shows SEM images of the cross sections of 10-bilayer and 30-bilayer PDADMAC/PSS films on Si. The average thicknesses of these films are 400 nm and 1750 nm, respectively. The ellipsometric thickness of the 10-bilayer film is 25% less than the SEM thickness, which could be due to the film roughness or the fracturing of the film for SEM. ATR-FTIR spectra such as those in Figure 3.4 provide a means to examine the layer by layer adsorption of PDADMAC/PSS films on a Ge ATR crystal. Increases in the height of the sulfonate absorbances at 1008 and 1033 cm⁻¹ indicate the adsorption of PSS.^{49, 58}

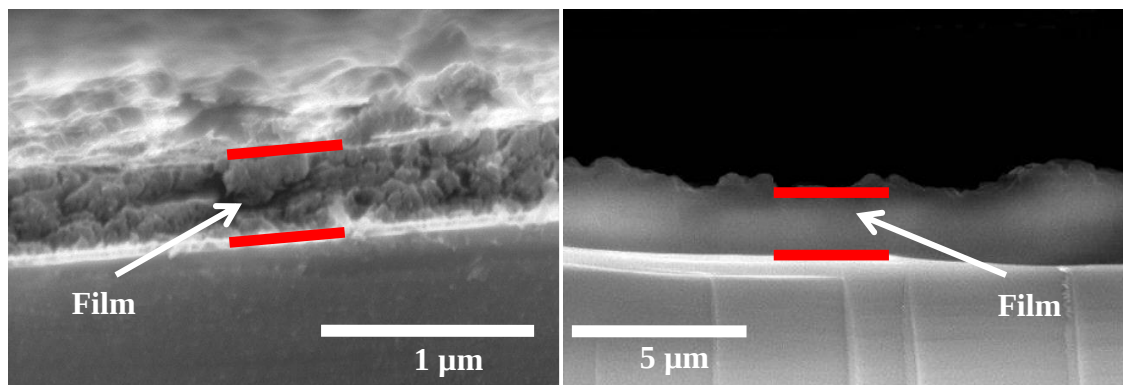


Figure 3.3. Cross-sectional SEM images of Si wafers coated with 10-bilayer (left) and 30-bilayer (right) PDADMAC/PSS films.

The intensities of the sulfonate peaks initially increase rapidly as more layers are deposited and then level off after deposition of about 12-15 bilayers (Figure 3.5). This plateau in absorbance suggests that the thickness of the film is at least 2-3 times the penetration depth of the evanescent IR beam after deposition of 15 layers. The penetration depth at 1033 cm^{-1} for a film with a refractive index of 1.44 is $0.62\text{ }\mu\text{m}$. (Dry PDADMAC/PSS films have a refractive index around 1.55, and the refractive index of water is about 1.33, so a refractive index of 1.44 represents approximately 100% swelling in water.) Thus, for films with 100% swelling, a thickness of 2-3 times the penetration depth is equivalent to a swollen film thickness of $1.2\text{-}1.9\text{ }\mu\text{m}$. In agreement with these IR studies, AFM data taken by Schlenoff *et al.* show that the wet thickness of (PDAMAC/PSS)₁₅ films prepared with solutions containing 1M NaCl is about $1.2\text{ }\mu\text{m}$.^{31, 49}

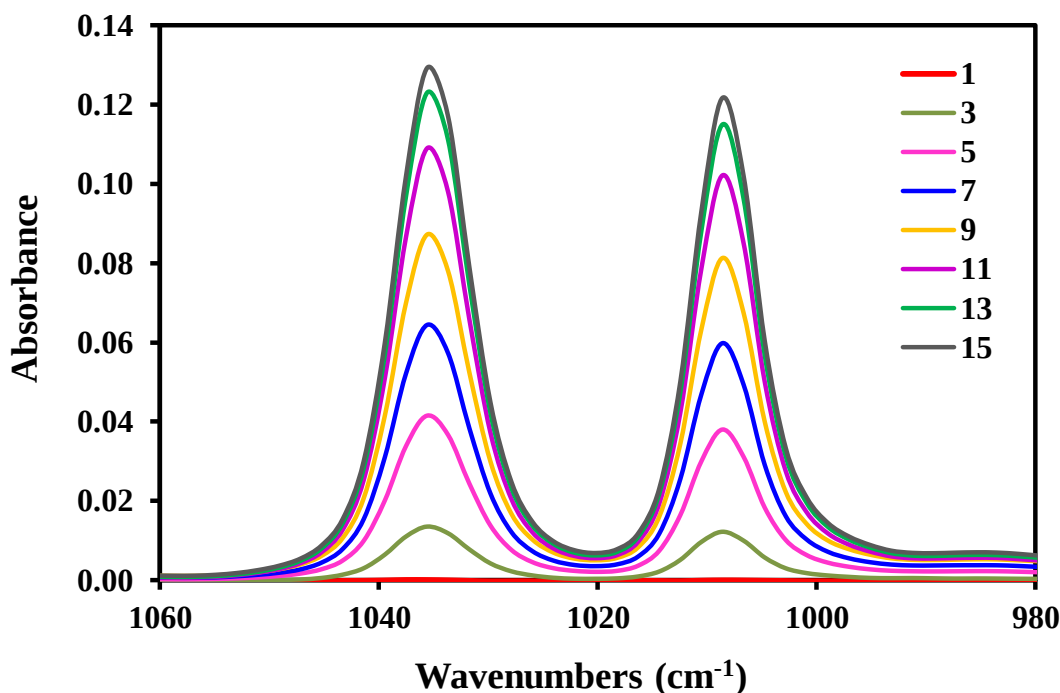


Figure 3.4. ATR-FTIR spectra of (PDADMAC/PSS)_nPDADMAC films adsorbed on a Ge ATR crystal. The numbers in the legend represent *n*, and the peaks at 1008 cm⁻¹ and 1033 cm⁻¹ are due to the sulfonate groups of PSS. The films were immersed in deionized water while the spectra were taken, and the background spectrum was that of deionized water on a clean crystal.

The oscillations in Figure 3.5 likely stem from different percent swelling values for PSS-terminated and PDADMAC-terminated films. As discussed in Appendix A the PDADMAC-terminated films swell by 400% and have a refractive index of ~1.34 whereas films terminated by PSS swell by 100% and have a refractive index of ~1.44. In more swollen films, the sulfonate groups are on average farther from the ATR crystal surface, and this give rise to lower IR peak intensities.

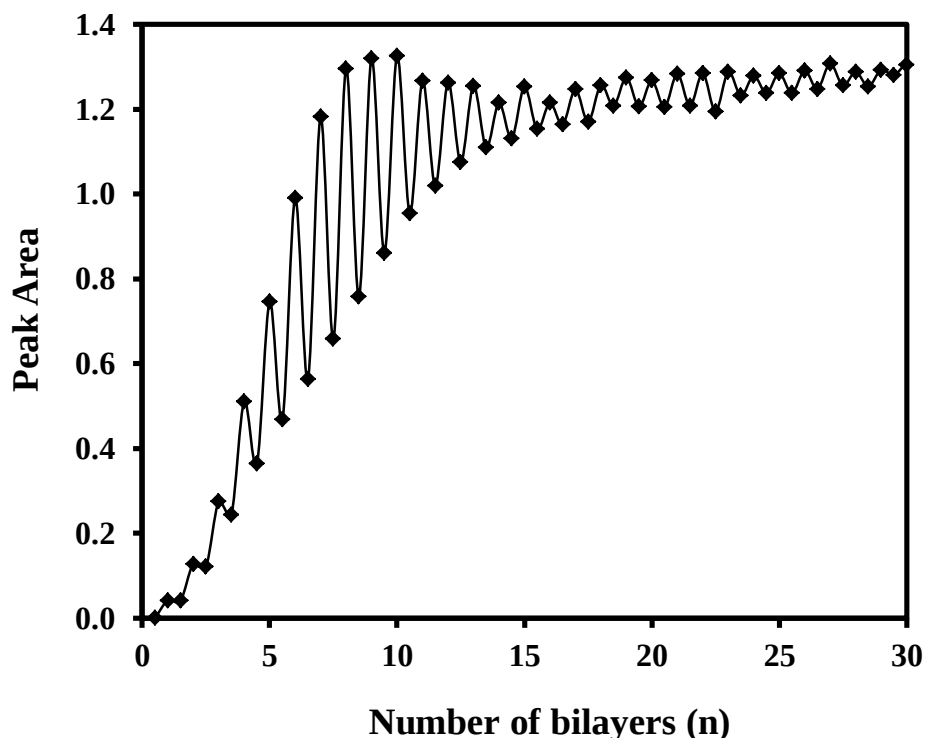


Figure 3.5. Peak area of the -SO_3^- absorbance centered at 1033 cm^{-1} in the ATR-FTIR spectra of $(\text{PDADMAC/PSS})_n$ multilayer films deposited on a Ge crystal. Films were deposited from a solution containing 1 M NaCl. The wide oscillations between the areas of peaks in PSS- and PDAMAC-terminated films are likely due to differences in the swelling of these films. The more swollen PDADMAC-terminated films exhibit lower absorbances.²⁸ Films with an integer number of bilayers terminate with PSS, while films with an additional 0.5 bilayer terminate with PDADMAC.

3.3.2. ATR-FTIR Studies of SCN^- Absorption in $(\text{PDADMAC/PSS})_{30}\text{PDADMAC}$ films

In an effort to better understand ion absorption and transport in PDADMAC/PSS coatings, we utilized ATR-FTIR spectroscopy to examine partitioning of SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ into PDADMAC/PSS films on Ge crystals. We studied these two anions because they have

different valences as well as distinct, strong IR stretches that appear in a region of the spectrum (2000 to 2100 cm^{-1}) where there is minimal interference from absorbances due to other functional groups. In initial absorption studies, we employed (PDADMAC/PSS)₃₀PDADMAC films that have a dry thickness (1750 nm) that is >5-times the penetration depth of the IR beam at 2058 cm^{-1} (assuming a film refractive index of 1.55). Swollen films should be 2- to 5-fold thicker than dry films and have a thickness >10 penetration depths. (The penetration depth at 2058 cm^{-1} for a film with a refractive index of 1.34 is 0.31 μm . The refractive index is taken as 1.34 as these are PDADMAC terminated films and swell by 400%.) Thus, IR signals will only be due to species in the film, not species in solution.

Figure 3.6 shows the ATR-FTIR spectrum of aqueous 0.5 M NaSCN on a bare Ge crystal along with the spectrum of SCN^- absorbed into a (PDADMAC/PSS)₃₀PDADMAC film from 1 mM NaSCN. Upon absorption in the film, the SCN^- peak absorbance that is due to a C=N stretching vibration⁵⁹ shifts from 2065 cm^{-1} (bare crystal exposed to NaSCN solution) to 2058 cm^{-1} , which may be due to a lower permittivity in the film than in water or to interaction of SCN^- with the film.⁶⁰⁻⁶³ Moreover, the area of the peak due to SCN^- absorbed from a 1 mM solution is 17% greater than that of 0.5 M NaSCN on the bare crystal, indicating that the concentration of SCN^- absorbed in the film is much higher than its 1 mM concentration in the solution from which it is absorbed.

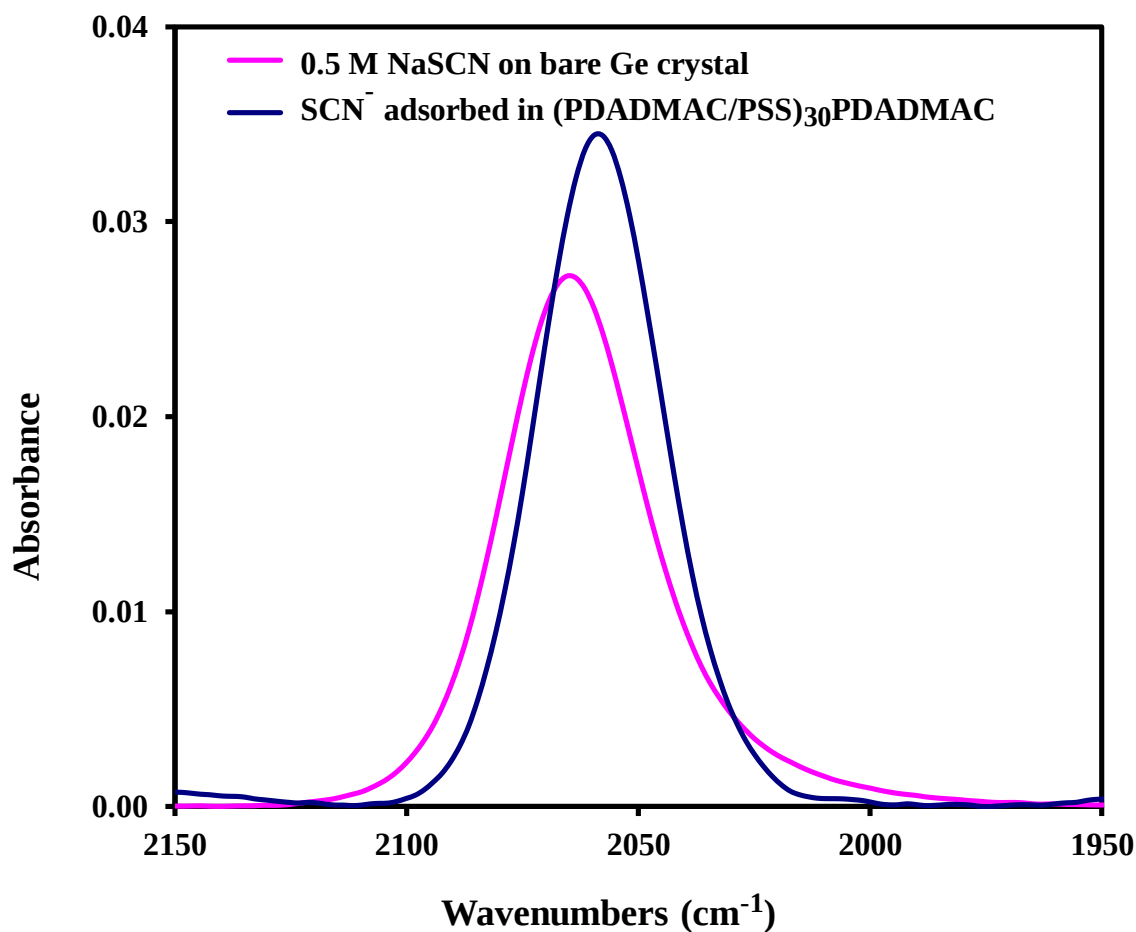


Figure 3.6. FTIR spectra of aqueous 0.5 M NaSCN on a bare Ge crystal (pink) and of SCN⁻ adsorbed in a (PDADMAC/PSS)₃₀PDADMAC film on a Ge crystal (blue). The SCN⁻ was absorbed for 6 h from a solution containing 1 mM NaSCN, and the blue spectrum was taken while the film was still covered with the NaSCN solution.

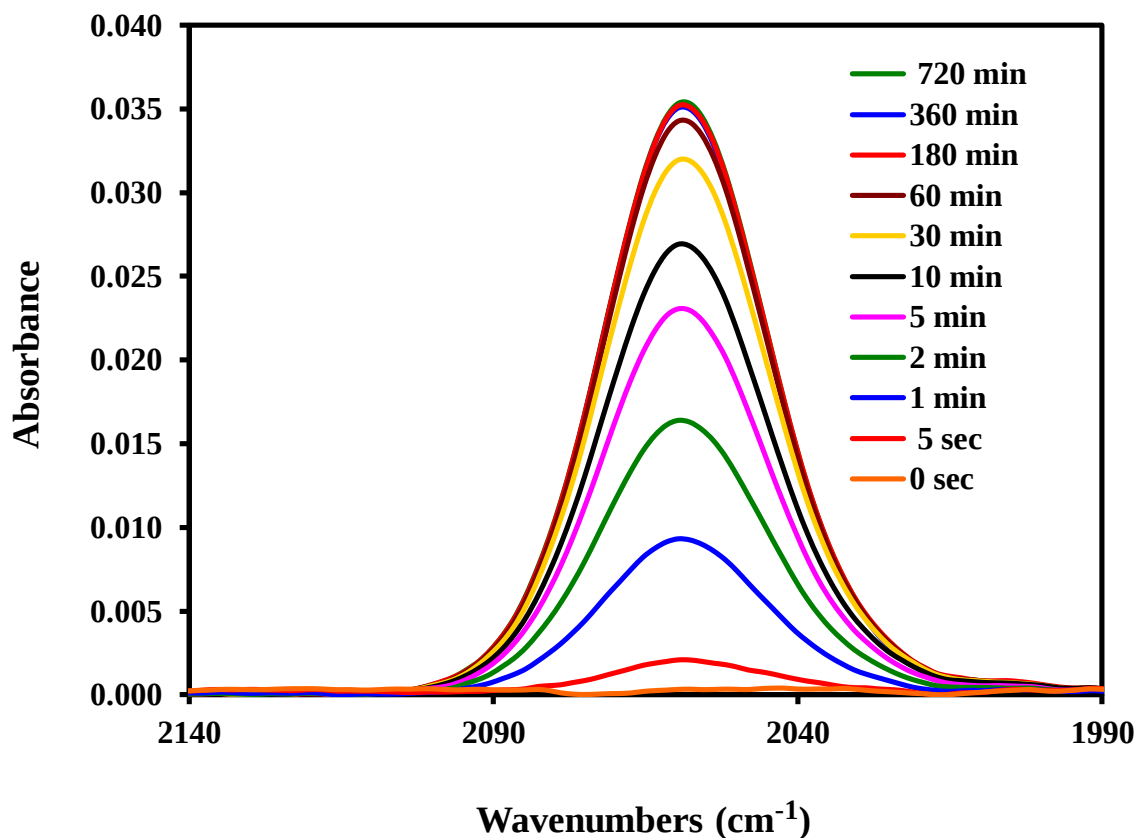


Figure 3.7. ATR-FTIR spectra of a (PDADMAC/PSS)₃₀PDADMAC film during exposure to a 0.01 M NaSCN solution for varying lengths of time. The absorbance in this region is due to the C=N stretch of SCN⁻. The spectra overlap after 180 min of exposure.

Figure 3.7 shows the increase in the SCN^- peak (2058 cm^{-1}) with time after exposure of a (PDADMAC/PSS)₃₀PDADMAC film to 0.01 M NaSCN, and Figure 3.8 shows how the area of this peak evolves with time after exposure of a (PDADMAC/PSS)₃₀PDADMAC film to different concentrations of SCN^- . The SCN^- peak areas in Figure 3.8 are normalized with respect to the sulfonate peak of PSS at 1033 cm^{-1} to minimize any variations in absolute absorbance due to changes in swelling and refractive index upon SCN^- absorption.⁴² As Figure 3.8 shows, the time required to achieve equilibrium absorption decreases with an increasing concentration of SCN^- in solution. Higher concentrations of anions in solution should increase the rates of both ion-exchange and diffusion into the film to decrease the time required to saturate the anion-exchange sites. Attempts to model the data in Figure 3.8 with equations for simple diffusion into the film did not give a good fit to the data.⁶⁴

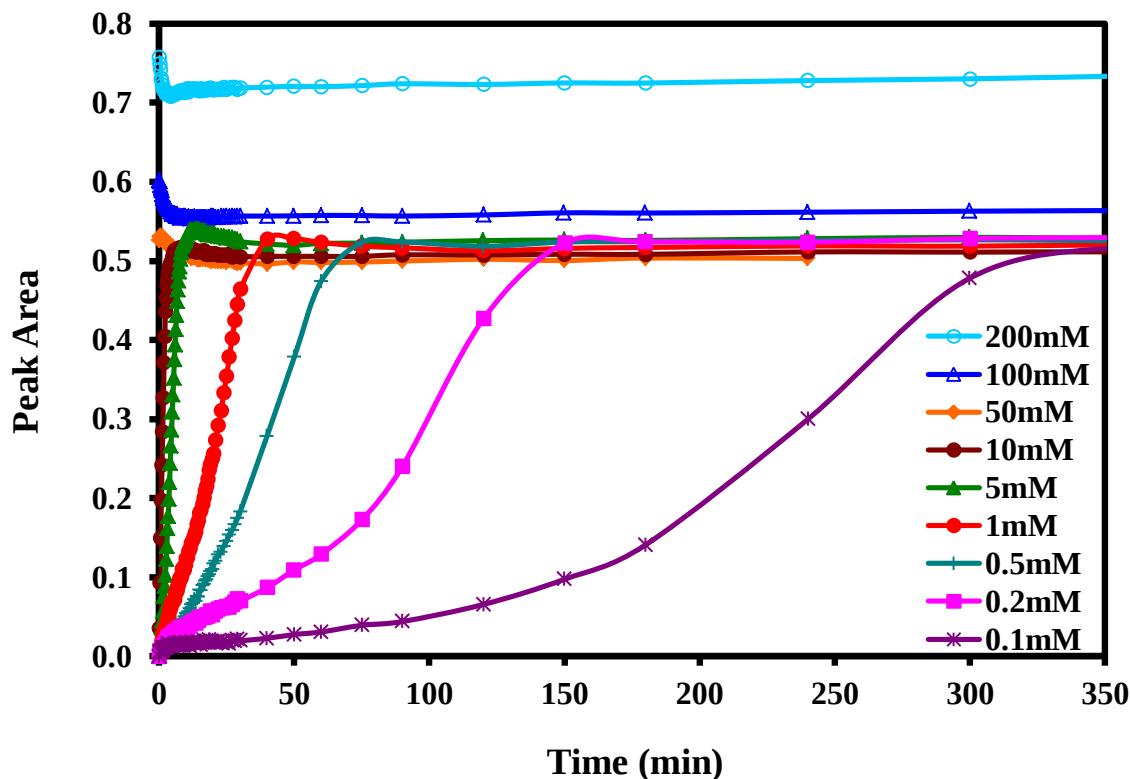


Figure 3.8. Normalized area of the SCN^- peak (2058 cm^{-1}) in ATR-FTIR spectra of a $(\text{PDADMAC/PSS})_{30}\text{PDADMAC}$ film exposed to different concentrations of NaSCN for various periods of time. The film was deposited on a Ge ATR crystal, and after measurements of spectra at a given NaSCN concentration, the film was rinsed with 0.5 M NaCl to remove SCN^- prior to changing the NaSCN concentration. The SCN^- peak area was normalized to the area of the $-\text{SO}_3^-$ peak at 1033 cm^{-1} .

At all solution NaSCN concentrations $\leq 50\text{ mM}$, the equilibrium peak areas for absorbed SCN^- are similar. To quantify the amount of SCN^- in the film, we obtained ATR-FTIR spectra of a series of aqueous NaSCN solutions on a bare Ge crystal and used a calibration method that takes into account differences in film and solution dielectric constants. (The Appendix A

describes this method in detail.) Figure 3.9 shows that the equilibrium concentration of absorbed SCN^- in the film is 0.5 M for all solution concentrations of $\text{NaSCN} \leq 50$ mM.

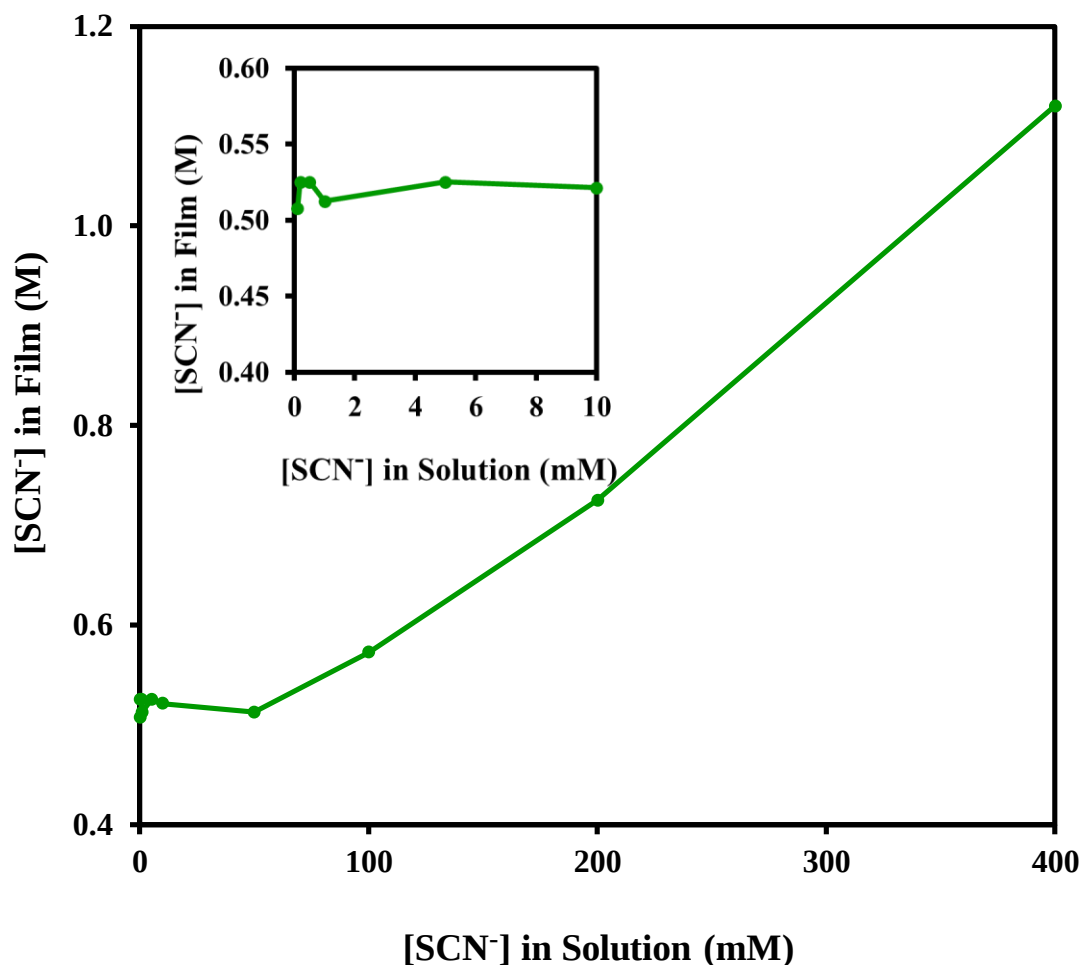
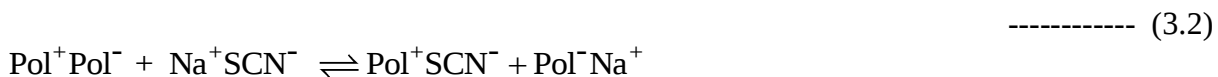
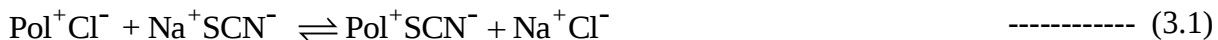


Figure 3.9. Equilibrium SCN^- concentrations in a $(\text{PDADMAC}/\text{PSS})_{30}\text{PDADMAC}$ film exposed to different concentrations of NaSCN . The inset shows an expanded view at lower solution concentrations.

The data in Figure 3.9 suggest that there is a high concentration of ion-exchange sites in the film and that at solution concentrations of $\text{SCN}^- \leq 50$ mM, SCN^- absorption primarily results from displacement of Cl^- by SCN^- at ion-exchange sites in the film as shown in reaction 3.1. In

this reaction, Pol^+ represents anion-exchange sites that are presumably due to PDADMAC quaternary amines that are not charge-compensated by a neighboring sulfonate of PSS.



There are two possible explanations for the increase in the concentration of SCN^- in the film at solution concentrations of $\text{NaSCN} > 50 \text{ mM}$. One is that a significant number of $\text{Pol}^+ \text{Pol}^-$ pairs dissociate to create anion-exchange, Pol^+ , and cation-exchange, Pol^- , sites as shown in reaction 3.2.^{42, 65} Another explanation could be simple partitioning of NaSCN into the solvent-swollen film, which should be more significant at higher NaSCN concentrations in solution.

Rinsing of films with deionized water does not remove the SCN^- that is absorbed from solutions containing $\leq 50 \text{ mM NaSCN}$. However, a deionized-water rinse of a film exposed to 400 mM NaSCN decreases the amount of absorbed SCN^- to the levels seen after exposure of the film to $\leq 50 \text{ mM NaSCN}$ (Figure 3.10). Hence if new ion-exchange sites are created at high ionic strength, they do not remain when the concentration of NaSCN in solution decreases.

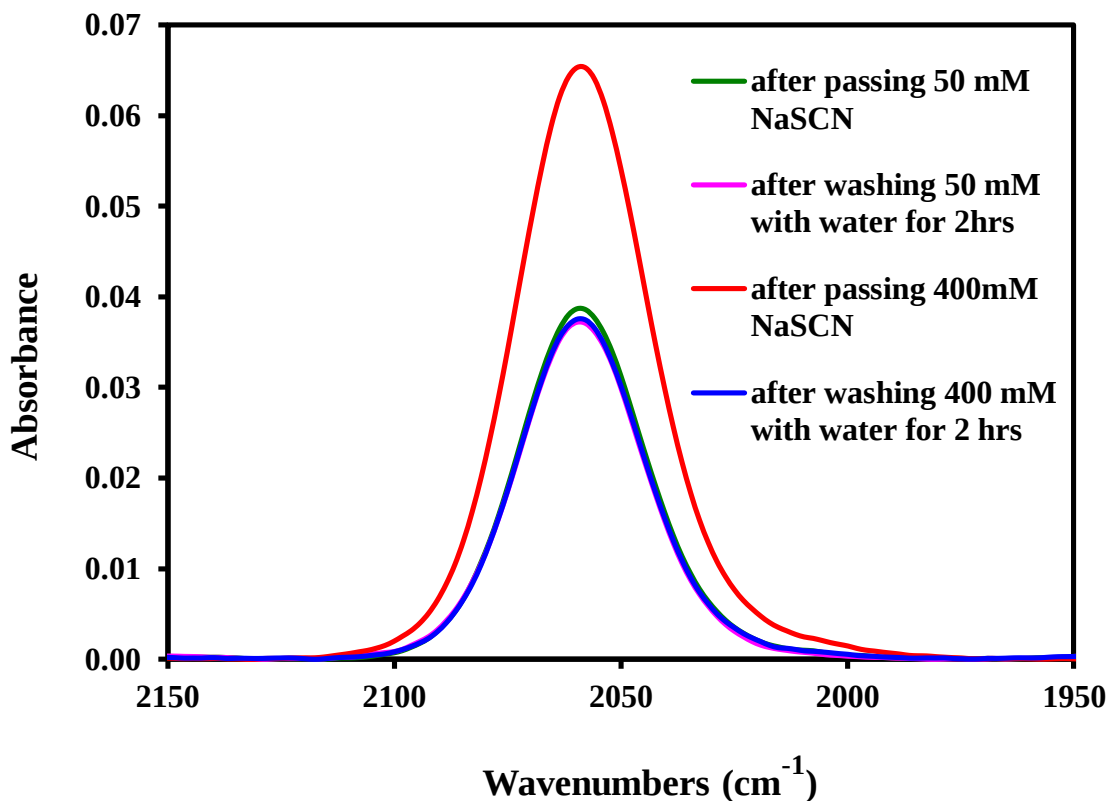


Figure 3.10. ATR-FTIR spectra of absorbed SCN^- (peak at 2058 cm^{-1}) in a $(\text{PDADMAC/PSS})_{30}\text{PDADMAC}$ film after a 6 h exposure to an aqueous solution of 50 mM (green) or 400 mM (red) NaSCN, and after rinsing of these films with deionized water for 2 h (blue or pink). The pink spectrum is difficult to see because it overlaps the blue one.

3.3.3. Competitive ion exchange

Competitive binding experiments, where a $(\text{PDADMAC/PSS})_{30}\text{PDADMAC}$ film is exposed to a solution containing both 0.5 mM NaSCN and 0.5 mM $\text{K}_2\text{Ni}(\text{CN})_4$, demonstrate initial rapid binding of SCN^- (peak at 2060 cm^{-1}) followed by displacement of SCN^- by $\text{Ni}(\text{CN})_4^{2-}$ (peak at 2123 cm^{-1}) (Figure 3.11). Figure 3.12 shows the normalized areas of the

SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ peaks from the ATR-FTIR spectra in Figure 3.11. The data suggest that SCN^- diffuses into the film more quickly than does $\text{Ni}(\text{CN})_4^{2-}$, although binding of the doubly charged $\text{Ni}(\text{CN})_4^{2-}$ is energetically favored.

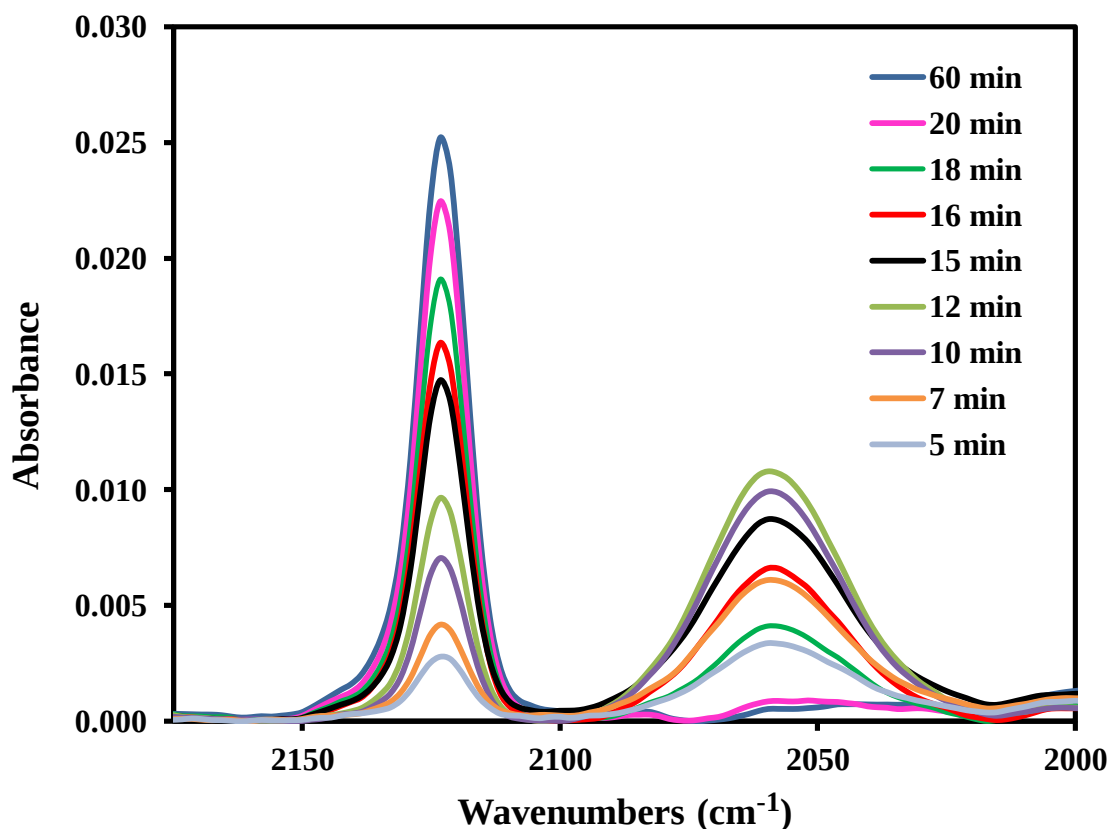


Figure 3.11. ATR-FTIR spectra of a $(\text{PDADMAC/PSS})_{30}\text{PDADMAC}$ film during exposure to a solution containing 0.5 mM NaSCN and 0.5 mM $\text{K}_2\text{Ni}(\text{CN})_4$. The peaks are due to SCN^- (2060 cm^{-1}) and $\text{Ni}(\text{CN})_4^{2-}$ (2123 cm^{-1}). There was no change in SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ peaks after 60 min of exposure to the solution.

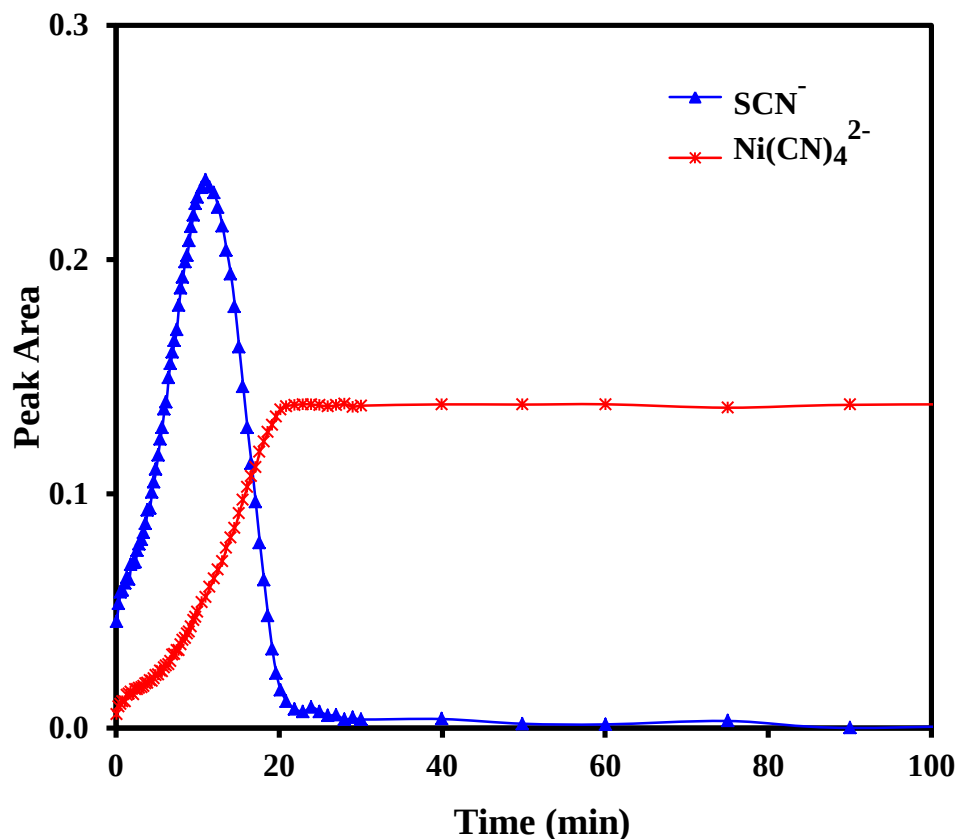


Figure 3.12. Normalized areas of the SCN^- (2060 cm^{-1}) and $\text{Ni}(\text{CN})_4^{2-}$ (2123 cm^{-1}) peaks in ATR-FTIR spectra of a $(\text{PDADMAC}/\text{PSS})_{30}\text{PDADMAC}$ film during exposure to a solution containing 0.5 mM NaSCN and $0.5\text{ mM K}_2\text{Ni}(\text{CN})_4$.

Figure 3.13 presents the equilibrium concentrations of SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ in a $(\text{PDADMAC}/\text{PSS})_{30}\text{PDADMAC}$ film as a function of the SCN^- to $\text{Ni}(\text{CN})_4^{2-}$ ratio in the solution. The concentration of NaSCN in solution was varied from 0.05 to 400 mM while the concentration of $\text{Ni}(\text{CN})_4^{2-}$ was kept constant at 0.5 mM . The data show that at high solution NaSCN concentrations, the SCN^- does displace $\text{Ni}(\text{CN})_4^{2-}$ from the film. At solution concentrations of $\text{NaSCN} \leq 50\text{ mM}$, where the overall absorption is dominated by intrinsic ion

exchange (new adsorption sites are not created upon addition of salt and negligible free salt is present in the film), the exchange reaction between SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ should be represented by reaction 3.3.

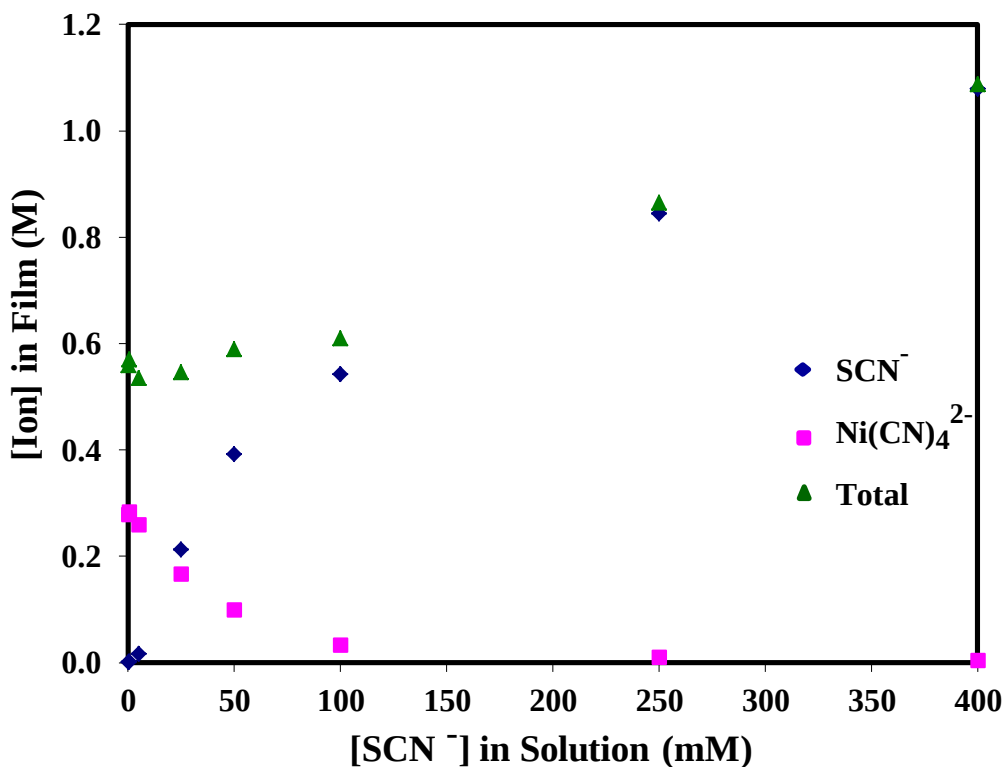
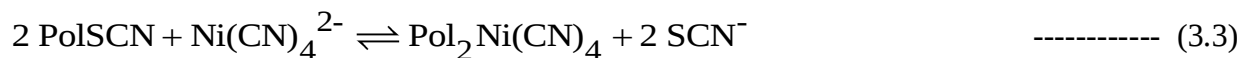


Figure 3.13. Equilibrium SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ concentrations in a (PDADMAC/PSS)₃₀PDADMAC film exposed to solutions containing 0.5 mM $\text{K}_2\text{Ni}(\text{CN})_4$ and varying concentrations of NaSCN. The total absorption (green triangles) is the sum of the $\text{Ni}(\text{CN})_4^{2-}$ concentration in the film multiplied by 2 and the SCN^- concentration in the film.

Based on the three data points in Figure 3.13 where the solution concentration of SCN^- is ≤ 50 mM and the concentration of SCN^- in the film is measurable, the equilibrium constant for reaction 3 is around 4. Attainment of equal concentrations of the two anions in the film requires a solution $\text{SCN}^-/\text{Ni}(\text{CN})_4^{2-}$ ratio of about 50 when the solution concentration of $\text{Ni}(\text{CN})_4^{2-}$ is 0.5 mM.

3.3.4. Ion binding as a function of the number of adsorbed PDADMAC/PSS bilayers

Polyelectrolyte multilayer properties such as permeability and swelling can vary greatly with the number of layers in a film,^{66, 67} so we also examined anion absorption as a function of the number of layers in PDADMAC/PSS coatings. Table 3.1 summarizes the results of these studies. There is no detectable binding of ions in films with <6 bilayers, but the concentration of absorbed ions in 7-bilayer films ranges from 0.04 to 0.07 M. Film thickness, in contrast, increases by only 30% upon the addition of the seventh bilayer. (Even though the film thickness is less than the IR penetration depth, because the concentrations of SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ in solution are low, they do not give rise to a detectable signal.) On going from 7 to 10 PDADMAC/PSS bilayers, the concentrations of absorbed ions in the film typically increase by a factor of 3-4, but the total absorbed ion concentrations for films with 10 and 30 bilayers differ by less than a factor of 2. Consistent with ion-exchange, in single-salt absorption, the concentration of SCN^- in the film is about double the concentration of $\text{Ni}(\text{CN})_4^{2-}$. In competitive ion absorption, the ratio of SCN^- to $\text{Ni}(\text{CN})_4^{2-}$ in the film decreases as the number of deposited layers increases. This may occur due to changes in ζ potentials (see below).

Table 3.1. Equilibrium ion concentrations^a in (PDADMAC/PSS)_n films exposed to solutions containing 2.5 mM NaSCN, or 2.5 mM K₂Ni(CN)₄, or 2.5 mM of both salts.^b

number of bilayers, n	NaSCN in solution	K ₂ Ni(CN) ₄ in solution	Mixture of NaSCN and K ₂ Ni(CN) ₄ in solution	
	[SCN ⁻] in film (M)	[Ni(CN) ₄ ²⁻] in film (M)	[SCN ⁻] in film (M)	[Ni(CN) ₄ ²⁻] in film (M)
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.01
7	0.07	0.04	0.04	0.04
10	0.31	0.15	0.02	0.15
30	0.46	0.27	0.00	0.28

^aThe concentration of the ions in the films was calculated from ATR-IR spectra of films on a Ge crystal as described in Appendix A.

^bExperiments with absorption of KSCN and NaSCN showed that the cation did not affect the absorbed ion concentration.

For comparison, Table 3.2 shows the concentrations of ions in the film when PDADMAC is the top layer. In this case, the surface is positively charged, so in thin films (4.5 bilayers, for example), many of the observed ions may be adsorbed at the film surface. The concentrations of ions in the film increase as the number of bilayers increases from 4.5 to 10.5, which shows that not only are ions adsorbed on the surface but they also are absorbed at ion-exchange sites within the polyelectrolyte multilayer. These ion-exchange sites evidently increase in concentration as more layers are added to the film. The concentration of absorbed ions in the film with 30.5 bilayers is about 15% less than that in the 7.5-bilayer film, perhaps partly because the penetration depth is reached and the extra ions adsorbed on the positively charged surface of the 30.5-bilayer film are no longer observable. For 30 and 30.5-bilayer films, the concentrations of absorbed ions

are essentially independent of whether the top layer is PSS or PDADMAC (compare Tables 3.1 and 3.2).

Table 3.2. Equilibrium ion concentrations in (PDADMAC/PSS)_nPDADMAC films exposed to solutions containing 2.5 mM NaSCN, or 2.5 mM K₂Ni(CN)₄, or 2.5 mM of both salts.

number of bilayers ^a	NaSCN in solution	K ₂ Ni(CN) ₄ in solution	Mixture of NaSCN and K ₂ Ni(CN) ₄ in solution	
	[SCN ⁻] in film (M)	[Ni(CN) ₄ ²⁻] in film (M)	[SCN ⁻] in film (M)	[Ni(CN) ₄ ²⁻] in film (M)
4.5	0.40	0.21	0.01	0.19
5.5	0.42	0.24	0.03	0.21
6.5	0.50	0.27	0.03	0.22
7.5	0.55	0.29	0.05	0.24
10.5	0.60	0.32	0.01	0.31
30.5	0.51	0.26	0.00	0.28

^aThe extra 0.5 bilayer indicates that films are terminated with PDADMAC.

3.3.5. Streaming Potential Measurements

The results in Table 3.1 show that the concentration of ion-exchange sites increases dramatically on going from 6 to 7 and 7 to 10 bilayers in (PDADMAC/PSS)_n films where n is an integer. Such increases should also be reflected in changes in the ζ potentials of the films, so we measured streaming potentials on multilayer coatings deposited on both silicon wafers and PES membranes.

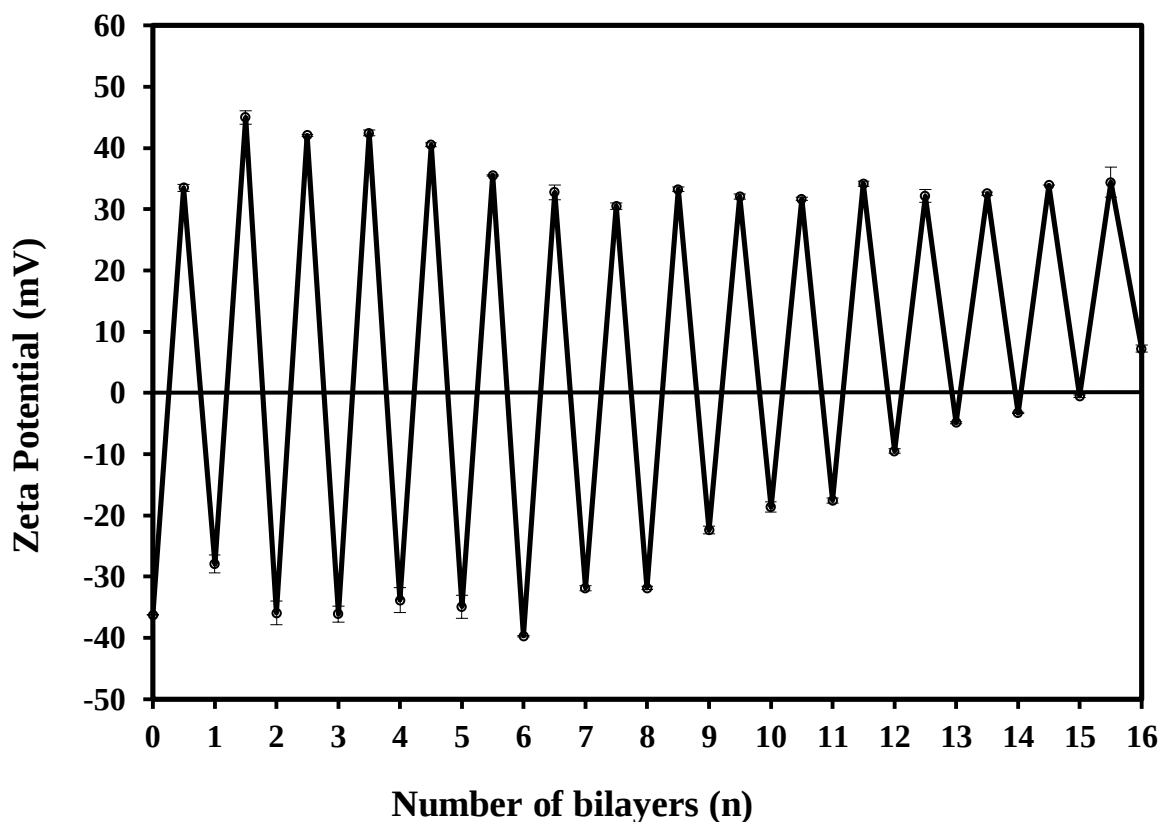


Figure 3.14. Zeta Potentials of Si wafers coated with (PDADMAC/PSS)_n films. Integer numbers of bilayers represent films terminated with PSS, while films with an extra 1/2 bilayer are terminated with PDADMAC.

Figure 3.14 shows ζ potentials of PDADMAC/PSS films on silicon wafers as a function of the number of bilayers. As seen in a number of previous studies,⁶⁸⁻⁷⁰ the ζ potential shifts between positive and negative values, respectively, as PDADMAC and PSS are added. However, the magnitude of the ζ potential for PSS-terminated films begins to decrease after the deposition of about 6 bilayers, and 16-bilayer films no longer have a negative ζ potential.

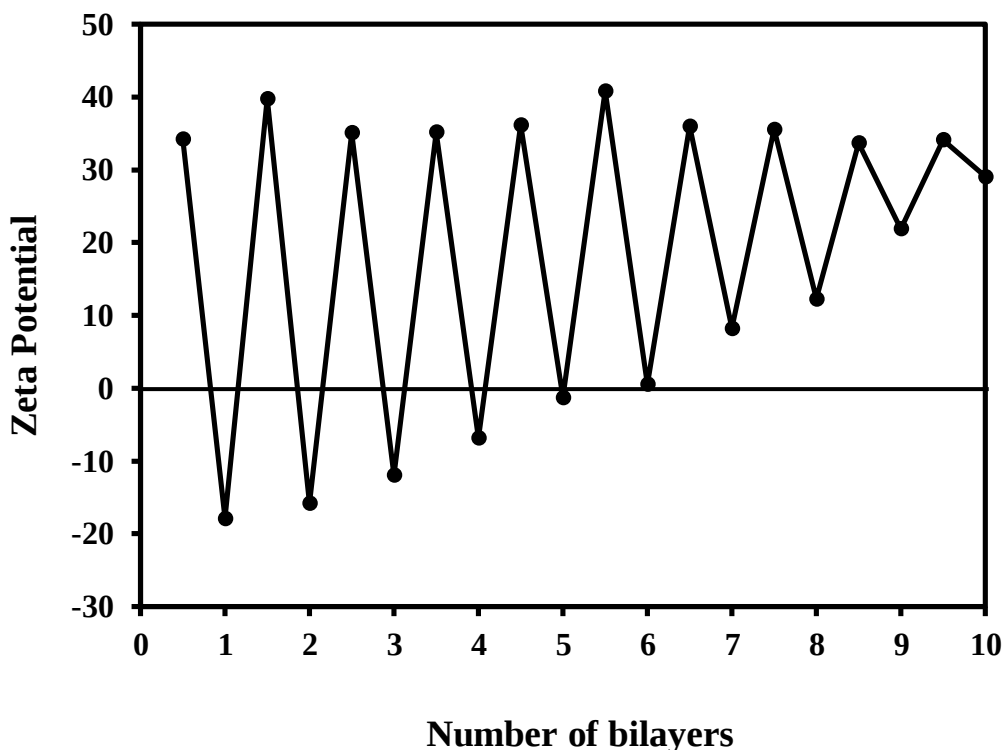


Figure 3.15. Zeta Potentials of 100 kDa PES membranes coated with (PDADMAC/PSS)_n films. Integer numbers of bilayers represent films terminated with PSS, while films with an extra ½ bilayer are terminated with PDADMAC.

The ζ potentials of PDADMAC/PSS films on 100 kDa PES membranes (Figure 3.15) exhibit a similar trend to films on silicon, but the ζ potentials of PSS-terminated films on PES become positive after deposition of only 7 bilayers. Changes in ζ potentials may also affect the selectivity of ion exchange. With 7-bilayer PDADMAC/PSS on Ge, the negative zeta potential of the film likely provides some preferential electrostatic exclusion of $\text{Ni}(\text{CN})_4^{2-}$ to offset the stronger binding of $\text{Ni}(\text{CN})_4^{2-}$ to anion exchange sites in the film. Hence the amounts of bound SCN^- and $\text{Ni}(\text{CN})_4^{2-}$ in 7-bilayer films are about the same (Table 3.1). As the zeta potential becomes less negative when more bilayers are adsorbed, $\text{Ni}(\text{CN})_4^{2-}$ becomes the anion

predominantly absorbed in the film. This trend also agrees with the nanofiltration results presented below.

The SEM images in Figure 3.3 confirm that film growth continues to occur even when the surface potential does not become negative after deposition of PSS. This variation of zeta potential is consistent with the exponential growth mechanism mentioned earlier, where large amounts of PDADMAC enter the film during polycation adsorption and these polymers migrate to the surface and complex with PSS during the PSS deposition step.^{71, 72} Although the PDADMAC surface charge is not fully compensated during PSS adsorption, more PDADMAC diffuses into the film during the next adsorption step. Such a growth mechanism, while not operative at low ionic strengths, seems to occur when PSS/PDADMAC films are deposited from 1 M NaCl.⁷³

3.3.6. Nanofiltration Properties of PSS/PDADMAC films as a function of the number of bilayers

Changes in ζ potential and ion absorption should also greatly affect transport through multilayer polyelectrolyte films, so we investigated the nanofiltration properties of PSS/PDADMAC coatings on both porous alumina substrates and PES ultrafiltration membranes. (All films terminate with PSS to enhance divalent anion rejection.) Table 3.3 shows results for films on alumina, where the initially deposited layer in the polyelectrolyte film is PSS because alumina is positively charged below pH 8.^{74, 75} The results are reported in terms of rejection, R , which is defined in equation 3.4, where C_{perm} and C_{feed} are the solute concentrations in the permeate and feed, respectively. The selectivity, S , for transport of solute A over solute B is

defined by equation 3.5, which can also be expressed in terms of rejections for solute A and solute B as shown. In some cases, negative rejection of Cl^- occurs when the combination of a high flux of Na^+ and a high SO_4^{2-} rejection requires enhanced Cl^- transport to maintain electrical neutrality in the permeate. In such cases the concentration of Cl^- in the permeate can actually exceed that in the feed.

$$R = \left(1 - \frac{C_{perm}}{C_{feed}} \right) \times 100\% \quad \text{-----} \quad (3.4)$$

$$S = \frac{C_{A,perm}}{C_{A,feed}} \frac{C_{B,feed}}{C_{B,perm}} = \frac{100 - R_A}{100 - R_B} \quad \text{-----} \quad (3.5)$$

With both (PSS/PDADMAC)₃PSS and (PSS/PDADMAC)₄PSS films on alumina, SO_4^{2-} rejection is about 97%, while $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity is above 30, similar to the results we saw previously.³⁵ (Membranes containing (PSS/PDADMAC)₂PSS films show a selectivity of around 1 because the film does not completely cover the substrate, data not shown.) After adsorption of 4.5 bilayers, the addition of more bilayers results in a rapid decline in selectivity. Film thickness still increases with the number of bilayers deposited, as shown by decreases in flux with adsorption of additional PDADMAC/PSS bilayers, but SO_4^{2-} rejection and $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity decline. This is consistent with both the drop in ζ potential after deposition of about 4 bilayers on PES supports and the rapid increase in anion adsorption seen after deposition of 6 to 7 PDADMAC/PSS bilayers on the Ge ATR crystal. The presence of excess positive charge in the membrane probably results in less electrostatic exclusion of the divalent SO_4^{2-} . Faster hopping of SO_4^{2-} between the highly concentrated ion exchange sites could provide a second

mechanism for decreased SO_4^{2-} rejection.⁴² Films with more layers may also be more swollen with water.⁶⁶

Table 3.3. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PSS/PDADMAC)_nPSS-coated porous alumina membranes and feed solutions containing 1000 ppm Cl^- and 1000 ppm SO_4^{2-} .^a

number of bilayers ^b	ellipsometric thickness, ^c nm	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	Cl^- rejection, %	SO_4^{2-} rejection, %	$\text{Cl}^-/\text{SO}_4^{2-}$ selectivity
3.5	18.0±0.1	1.7±0.1	-16±2	96.9±0.2	37±2
4.5	36.6±0.4	1.15±0.06	-11±1	96.7±0.5	34±5
5.5	63±2	0.99±0.06	-5±3	93±1	15±3
6.5	100±4	0.83±0.04	3±2	86±2	6.8±0.6
7.5	143±7	0.65±0.03	2±1	68±6	3.2±0.7

^aSolutions were prepared with NaCl and Na_2SO_4 .

^bThe extra half bilayer indicates that coatings were terminated with PSS.

^cThicknesses were measured with films deposited on Si wafers.

To better correlate ζ potentials and transport, we performed nanofiltration with the same PES membranes used for streaming potential measurements. (Commercial porous alumina membranes are too small for the streaming potential apparatus.) Using 100 kDa PES supports (Table 3.4), flux decreases with the number of adsorbed PDADMAC/PSS bilayers, but SO_4^{2-} rejection and $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity peak after deposition of 6 bilayers. The polymeric substrates are probably less charged than alumina, and thus it may take a few more layers to achieve complete coverage and maximum selectivity. Previously we achieved a maximum $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity of 32 for 4.5-bilayer PSS/PDADMAC films on a 50 kDa PES membrane from

Millipore.⁶⁷ However, those films were deposited from a 0.5 M NaCl solution, rather than a 1 M solution, which could greatly affect selectivity. Variations in the support can also change selectivity. With a 50 kDa PES support from Pall Corporation, we achieved a maximum selectivity of 13 using PDADMAC/PSS films deposited from 1 M NaCl as shown in Table 3.5.

Table 3.4. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PDADMAC/PSS)_n-coated 100 kDa PES membranes and feed solutions containing 1000 ppm Cl⁻ and 1000 ppm SO₄²⁻.^a

number of bilayers,n	solution flux, m ³ /m ² -day	Cl ⁻ rejection, %	SO ₄ ²⁻ rejection,%	Cl ⁻ / SO ₄ ²⁻ selectivity
3	7.5±1.7	-1.0±0.4	7±4	1.1±0.1
4	2.4±0.5	-6±2	59±2	2.6±0.2
5	0.95±0.05	-16.8±0.6	79±4	6±1
6	0.82±0.03	-13±3	85±3	8±1
7	0.73±0.02	-2±8	80±4	5±1
8	0.67±0.01	0.7±4	70±4	3.1±0.2

^aSolutions were prepared with NaCl and Na₂SO₄.

As a final correlation between transport and ion absorption, we examined nanofiltration of SCN⁻/Ni(CN)₄²⁻ mixtures using PSS/PDADMAC films prepared on alumina supports. The trend is similar to that for Cl⁻/SO₄²⁻ separations as shown in Table 3.6, with selectivity peaking after deposition of 4.5-bilayers. However, the maximum selectivity is only 2.

Table 3.5. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PDADMAC/PSS)_n-coated 50 kDa PES membranes and solutions containing 1000 ppm Cl⁻ and 1000 ppm SO₄²⁻.^a

number of bilayers,n	solution flux, m ³ /m ² -day	Cl ⁻ rejection, %	SO ₄ ²⁻ rejection,%	Cl ⁻ / SO ₄ ²⁻ selectivity
4	2.17±0.09	-12±3	69±14	5±2
5	1.28±0.04	-1±6	87±4	8±3
6	0.97±0.02	-13±2	91±3	13±3
7	0.79±0.03	0.6±3	90±3	10±3
8	0.69±0.02	0.6±1	81±5	5±1

^aSolutions were prepared with NaCl and Na₂SO₄.

Table 3.6. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PSS/PDADMAC)_nPSS-coated alumina membranes and feed solutions containing 1000 ppm SCN⁻ and 1000 ppm Ni(CN)₄²⁻.^a

number of bilayers ^b	solution flux, m ³ /m ² -day	SCN ⁻ rejection, %	Ni(CN) ₄ ²⁻ rejection,%	SCN ⁻ / Ni(CN) ₄ ²⁻ Selectivity
3.5	2.5±0.2	1±2	33±9	1.5±0.2
4.5	1.51±0.05	2.6±0.9	50±7	2.0±0.3
5.5	1.09±0.03	2±3	41±6	1.7±0.2
6.5	0.76±0.01	-3±4	32±3	1.5±0.1
7.5	0.66±0.02	-17±5	21±7	1.5±0.1

^aSolutions were prepared with KSCN and K₂Ni(CN)₄.

^bThe extra half bilayer indicates that films terminate with PSS.

Table 3.7. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PSS/PDADMAC)₄PSS-coated porous alumina membranes and feed solutions containing different combinations of 1000 ppm anions .

	solution flux, m ³ /m ² -day	monovalent ion rejection, %	divalent ion rejection,%	selectivity
Cl ⁻ /SO ₄ ²⁻ ^a	1.15±0.06	-11±1	96.7±0.5	34±5
SCN ⁻ /Ni(CN) ₄ ²⁻ ^b	1.51±0.05	2.6±0.9	50±7	2.0±0.3
SCN ⁻ /SO ₄ ²⁻ ^c	0.76±0.04	-39±3	94.5±0.2	25±1
Cl ⁻ / Ni(CN) ₄ ²⁻ ^d	1.1±0.2	3±3	45±2	1.8±0.1

^a Solution was prepared with NaCl and Na₂SO₄.

^b Solution was prepared with KSCN and K₂Ni(CN)₄.

^c Solution was prepared with NaSCN and Na₂SO₄.

^d Solution was prepared with KCl and K₂Ni(CN)₄.

To understand why the SCN⁻/Ni(CN)₄²⁻ selectivity was so low compared to the Cl⁻/SO₄²⁻ selectivity, we performed nanofiltration of different combinations of ions with a series of different membranes. As Table 3.7 shows, these experiments reveal that the rejection of Ni(CN)₄²⁻ is quite low compared to that of SO₄²⁻, even though both are divalent ions. The low rejection of Ni(CN)₄²⁻ yields Cl⁻/ Ni(CN)₄²⁻ and SCN⁻/Ni(CN)₄²⁻ selectivities of 2 or less, while both Cl⁻/SO₄²⁻ and SCN⁻/SO₄²⁻ selectivities are 25 or more.

We also sequentially examined Cl⁻/SO₄²⁻, SCN⁻/Ni(CN)₄²⁻, and Cl⁻/SO₄²⁻ selectivities in NF with the same membrane (Table 3.8). The initial Cl⁻/SO₄²⁻ selectivity was 26, and the SCN⁻/Ni(CN)₄²⁻ selectivity was 3, similar to previous experiments. However, when the Cl⁻

SO_4^{2-} selectivity was determined after the $\text{SCN}^-/\text{Ni}(\text{CN})_4^{2-}$ nanofiltration, the selectivity decreased to 10, suggesting that $\text{Ni}(\text{CN})_4^{2-}$ changes the film properties by making it more permeable to SO_4^{2-} .

Table 3.8. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PSS/PDADMAC)₄PSS-coated porous alumina membranes and solutions containing different combinations of 1000 ppm anions. The experiments were performed sequentially (from top to bottom) using the same two (PSS/PDADMAC)₄PSS-coated alumina membranes.

	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	monovalent ion rejection, %	divalent ion rejection, %	selectivity
$\text{Cl}^-/\text{SO}_4^{2-}$ ^a	1.00±0.03	-16.5±0.8	95.4±0.2	26±1
$\text{SCN}^-/\text{Ni}(\text{CN})_4^{2-}$ ^b	1.21±0.03	-26±1	52±9	2.7±0.6
$\text{Cl}^-/\text{SO}_4^{2-}$ ^a	1.07±0.03	-20.4±0.6	88.0±0.5	10.0±0.4

^aSolution was prepared with NaCl and Na₂SO₄.

^bSolution was prepared with KSCN and K₂Ni(CN)₄.

Similar results were observed when sequentially examining $\text{SCN}^-/\text{SO}_4^{2-}$, $\text{Cl}^-/\text{Ni}(\text{CN})_4^{2-}$, and $\text{SCN}^-/\text{SO}_4^{2-}$ separations. The first $\text{SCN}^-/\text{SO}_4^{2-}$ selectivity was 28, while the second was only 12 as shown in Table 3.9. Although we do not understand the effect of $\text{Ni}(\text{CN})_4^{2-}$ on the film, it obviously alters film structure to decrease selectivity. Tieke and coworkers also showed effects of ion absorption on selectivity.^{76, 77}

Overall, the trends in transport with the number of deposited layers are consistent with a film that becomes less selective after deposition of 4 to 6 bilayers. This corresponds with the

point at which films rapidly increase in thickness and gain anion-exchange sites. These additional anion-exchange sites likely reduce selectivity by decreasing Donnan exclusion, increasing hopping pathways for divalent ions, or increasing swelling.

Table 3.9. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PSS/PDADMAC)₄PSS-coated porous alumina membranes and solutions containing different combinations of 1000 ppm anions. The experiments were performed sequentially (from top to bottom) using the same two (PSS/PDADMAC)₄PSS-coated alumina membranes.

	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	monovalent ion rejection, %	divalent ion rejection, %	selectivity
$\text{SCN}^-/\text{SO}_4^{2-}$ ^a	0.85±0.03	-41.0±0.6	94.9±0.1	27.7±0.8
$\text{Cl}^-/\text{Ni}(\text{CN})_4^{2-}$ ^b	1.01±0.03	0.7±1.8	44±6	1.8±0.2
$\text{SCN}^-/\text{SO}_4^{2-}$ ^a	0.91±0.03	-26.8±0.6	89.6±0.2	12.2±0.2

^a Solution was prepared with NaSCN and Na₂SO₄.

^b Solution was prepared with KCl and K₂Ni(CN)₄.

3.4. Conclusions

The properties of PDADMAC/PSS films vary dramatically with the number of layers in the film. (PDADMAC/PSS)_n films on a Ge ATR crystal do not absorb significant amounts of SCN^- or $\text{Ni}(\text{CN})_4^{2-}$ when n is an integer less than 7, but films with ten bilayers have a concentration of anion-exchange sites of about 0.5 M. Consistent with anion-exchange, $\text{Ni}(\text{CN})_4^{2-}$ is the predominantly absorbed species from equimolar mixtures of SCN^- and $\text{Ni}(\text{CN})_4^{2-}$, even though SCN^- initially exchanges into the film more rapidly than $\text{Ni}(\text{CN})_4^{2-}$.

Streaming potential measurements suggest that the high ion-exchange capacities of films with more than 5-6 bilayers stem from excess positive charge due to more ammonium than sulfonate groups in the film, even when PSS is the terminal layer. These data explain why transport through PDADMAC/PSS films is such a strong function of the number of layers in the film. $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity peaks after adsorption of 4-6 bilayers because a minimum number of layers are required to fully cover the support, and deposition of additional layers results in a more positively charged film with decreased SO_4^{2-} rejection. This knowledge is vital for designing PSS/PDADMAC membranes.

Appendix

3.5. Appendix A

Calculation of Ion Concentrations in Polyelectrolyte Films

We plot ATR-IR spectra as absorbance, $-\log(I/I_0)$, where I is the intensity of the light reaching the detector when a SCN^- -containing film or solution is on the surface of the ATR crystal and I_0 is the intensity of the light reaching the detector when no SCN^- is in the film or solution. To convert the SCN^- ATR-IR absorbance to SCN^- concentration in a film, we use ATR-IR spectra of aqueous NaSCN solutions for calibration. However, because I/I_0 is a complicated function of both film thickness and dielectric constant, the calibration requires calculation of I/I_0 using Fresnel reflection coefficients.

For a single bounce on an ATR crystal covered with a SCN^- solution as shown in Figure A1, the ratio of reflected intensity, I_R , to incident intensity, I_{in} can be calculated using equation A.1, where E_{in} is the amplitude of the incident electric field, E_R is the amplitude of the reflected field, r_{12} is the Fresnel reflection coefficient at the crystal (medium 1)/solution (medium 2) interface, and r_{12}^* is the complex conjugate of this reflection coefficient.

$$I_R / I_{\text{in}} = \frac{E_R^2}{E_{\text{in}}^2} = r_{12} r_{12}^* \quad \text{----- (A.1)}$$

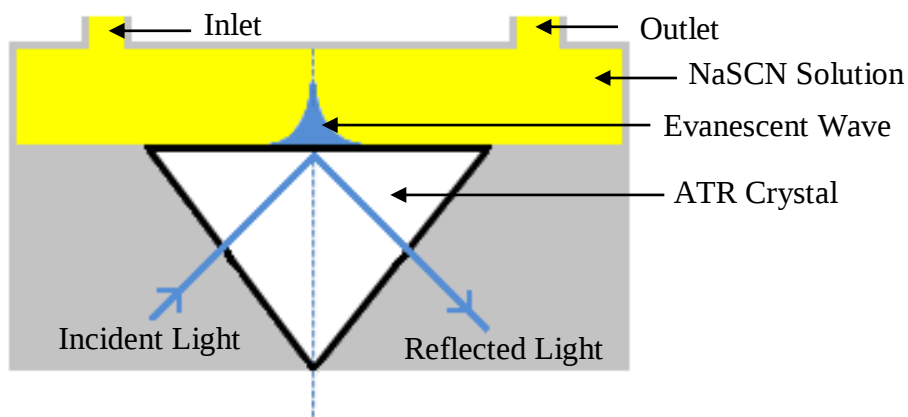


Figure A1. Single-reflection ATR-FTIR experiment with a crystal exposed to a NaSCN solution.⁷⁸ The actual apparatus in this work employed 6 reflections.

The values for r_{12} depend on polarization and can be calculated using the Fresnel equations shown in equation A.2, where n_1 and n_2 are the refractive indices of the crystal and the solution, respectively, and θ_i and θ_t are the angles of incidence and refraction. (Snell's law, $n_1 \sin \theta_i = n_2 \sin \theta_t$ is used to calculate the value of $\cos \theta_t$.)

$$r_{12}^{\parallel} = \frac{n_2 \cos \theta_i - n_1 \cos \theta_t}{n_2 \cos \theta_i + n_1 \cos \theta_t}$$

$$r_{12}^{\perp} = \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \quad \text{----- (A.2)}$$

Note that for light-absorbing solutions or films, n_2 is a complex number ($n_2 + ik_2$) as is $\cos \theta_t$.

For an unpolarized IR beam and N bounces in the ATR crystal, the total absorbance, A_{tot} , is given by equation A.3,

$$A_{\text{total}} = -\log[(I_{\parallel} + I_{\perp}) / (I_{o\parallel} + I_{o\perp})] = -\log[(I_{o\parallel} 10^{-NA_{\parallel}} + I_{o\perp} 10^{-NA_{\perp}}) / (I_{o\parallel} + I_{o\perp})] \quad \text{----- (A.3)}$$

where $A_{\parallel}$ and $A_{\perp}$ are the values of $-\log(I/I_0)$ for a single bounce of radiation polarized parallel and perpendicular to the plane of incidence, respectively^{79, 80}. The I/I_0 values for a single bounce are calculated by dividing I_R/I_{in} for the solution or film containing SCN^- by the I_R/I_{in} value in the absence of SCN^- , which is 1. Thus, $A_{\parallel}$ and $A_{\perp}$ are simply $-\log(I_R/I_{in})$ values for SCN^- absorption in parallel and perpendicular polarizations, respectively. Equation A.3 can be rewritten as equation A.4,

$$A_{total} = -\log[x10^{-NA_{\parallel}} + (1-x)10^{-NA_{\perp}}] \quad \text{----- (A.4)}$$

where x represents the fraction of incident light that is polarized parallel to the plane of incidence.^{79, 80} The x value of 0.375 was calculated using a polarizer to determine the relative intensities of the IR beam polarized perpendicular and parallel to the plane of incidence.

Calculation of $A_{\parallel}$ and $A_{\perp}$ and, hence, A_{total} requires values for the angle of incidence, the refractive index of the crystal, and the complex refractive index of the solution or film. Because the solutions or films were relatively dilute with respect to SCN^- , the real part of the refractive index was assumed to be that of the pure swollen film or pure solvent (see below for further discussion of this point), while the value of k was used to fit the absorbance. The value of k is directly proportional to SCN^- concentration, C , and determination of k at several solution concentrations with no film on the crystal afforded the constant of proportionality Q shown in equation A.5. Use of equation A.5 and the value of Q determined from spectra of standard solutions on a bare crystal allows calculation of the SCN^- concentration in the film from the value of k in the film.

$$C = k / Q \quad \text{-----} \quad (\text{A.5})$$

For a film whose thickness is much greater than the penetration depth of the evanescent wave, determination of SCN^- concentration is relatively straightforward. Equations A.1-A.4 allow iterative calculation of k from absorbance. The real part of the film refractive index determined using in situ ellipsometry was taken as 1.442 for PSS-terminated films in water and 1.345 for PDADMAC-terminated films in water, and k_2 was varied to fit the absorbance. These refractive indices of the water-swollen films at 2058 cm^{-1} (4859 nm) were estimated from the Cauchy model used to fit the refractive index of swollen films on Si at the wavelengths of the ellipsometer (414 – 736.1 nm). Refractive indices determined for swollen 4 and 4.5-bilayer PDADMAC/PSS films were applied to all films terminated with the same polyelectrolyte. The refractive index of the aqueous solutions at around 2058 cm^{-1} was 1.323.⁸¹

In the case of films with <10 bilayers, film thickness is also an important parameter for determining absorbed ion concentrations (see below). The thicknesses of 4- to 5.5-bilayer PDADMAC/PSS films in water were determined using in situ ellipsometry as described in reference 28. Table A1 summarizes the results for 4-, 4.5-, and 5.5-bilayer PDADMAC/PSS films on Si wafers. The percent swelling of PSS-terminated films is around 150% while the PDADMAC-terminated films swell around 400%.

Table A1. Ellipsometric thicknesses and %swelling of PDADMAC/PSS films on silicon wafer immersed in water.

number of bilayers ^a	dry thickness (nm)	wet thickness (nm)	% swelling
4	37.7±0.7	95.0±1.9	152±5
4.5	59.7±1.1	291.8±8.2	389±18
5.5	86.9±1.8	465.2±30.3	435±32

^aThe extra 0.5 bilayer indicates that films are terminated with PDADMAC.

Swollen thicknesses for films with more than 5.5 bilayers could not be obtained because the films were rough and the ellipsometric model did not give good fits. For films with 5 to 10.5 bilayers, dry ellipsometric thicknesses (Figure 3.1) along with the swelling factors in Table A1 were used to obtain swollen thicknesses. Figure 3.5 suggests, however, that differences in swelling of PSS and PDADMAC-terminated films decrease for films with more than about 8 bilayers, so the application of refractive indices determined for 4- or 4.5-bilayer films to films with as many as 30 or 30.5 bilayers could cause errors in calculated concentration values for the thicker films. However, the difference in calculated concentrations obtained using refractive indices of 1.345 and 1.442 is <12%. Even in the case of (PDADMAC/PSS)₇PDADMAC films, where both thickness and refractive index are input parameters, calculated values of absorbed ion concentrations differ by only 5% when assuming 150% swelling and $n=1.442$ rather than 400% swelling and $n=1.345$. The effect of large differences in assumed swelling on calculated concentrations is relatively small because even a 150% swollen 7.5-bilayer film would have a thickness of 1.5 penetration depths, and the lower refractive index and higher thickness have opposite effects on calculated concentrations.

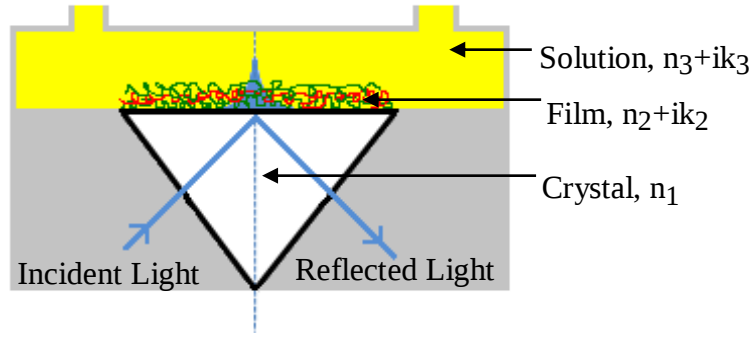


Figure A2. Schematic drawing of an optical system containing three layers (crystal, swollen film, and solution).

Calculation of absorbed ion concentrations is more complicated for films with thicknesses less than 2 or 3 penetration depths than for thicker films. In this case the optical system consists of three layers as shown in Figure A2. The absorbance for a single bounce is determined by the overall reflection coefficient, which is the term in brackets in equation A.6.

$$I_R / I_{in} = \frac{E_r^2}{E_i^2} = \left[\frac{r_{12} + r_{23} \exp(-2i\delta)}{1 + r_{12}r_{23} \exp(-2i\delta)} \right] \left[\frac{r_{12} + r_{23} \exp(-2i\delta)}{1 + r_{12}r_{23} \exp(-2i\delta)} \right]^* \quad \text{----- (A.6)}$$

$$\delta = 2\pi \frac{d}{\lambda} n_2 \cos \theta_2$$

In this equation, r_{12} is the Fresnel reflection coefficient for the crystal/film interface, r_{23} is the Fresnel reflection coefficient for the film/solution interface, d is the swollen film thickness, and λ is the wavelength of interest. The values of $\cos \theta_2$ and $\cos \theta_3$ needed for calculating r_{12} and r_{23} are determined using Snell's law.

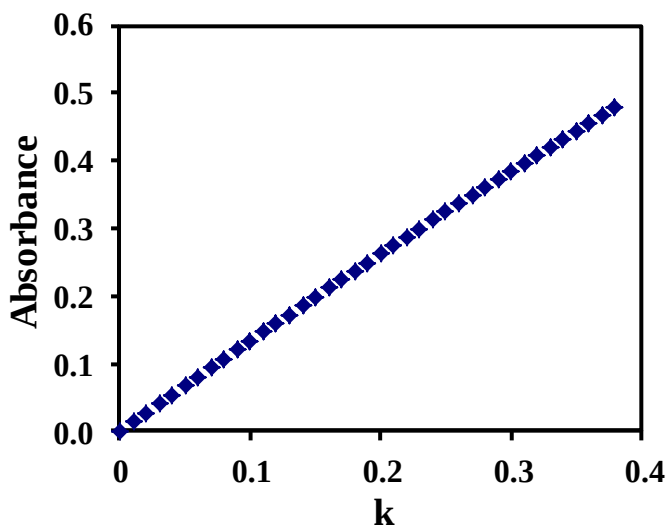


Figure A3. Simulated values of absorbance at 2058 cm^{-1} as a function of k using equation A.6. Refractive index and thickness of the film are taken as 1.345 and 260 nm, respectively. The water above the film had a refractive index of 1.323.

Because the concentration of SCN^- in the film is much greater than the SCN^- concentration in the solution, k_3 is negligible, and n_3 is simply the refractive index of water. (If needed, the concentration-dependent k_3 determined from solution studies with the ATR crystal could be included.) The thickness and refractive index of the film can be estimated from in situ ellipsometry of films on Si wafers so the only remaining unknown is k_2 , which can be iteratively calculated from a value for the overall absorbance. Again, k_2 is converted to concentration using equation A.5 with the Q value determined from standard aqueous solutions.

The above discussion uses the absorbance at a given wavelength to determine concentration. However, ideally we would like to determine the concentration of a species in a film based on the area of a peak, particularly when peak wavelengths show small shifts.

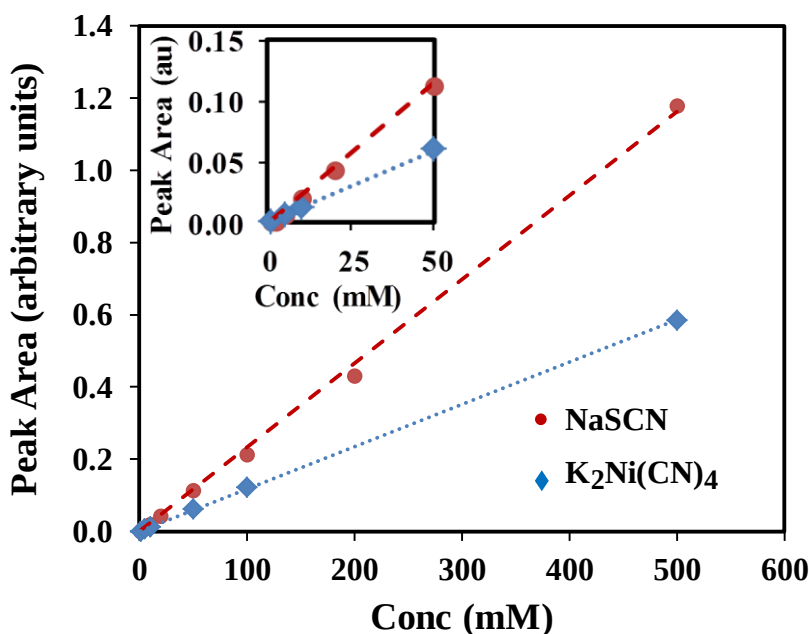


Figure A4. Peak Area versus the concentration of salt in a solution contacting the ATR crystal for solutions containing NaSCN and K₂Ni(CN)₄. The inset shows data for low concentrations.

We can show by simulation that for low absorbances ($k(\lambda) < 0.38$), at each wavelength the absorbance is proportional to $k(\lambda)$ (Figure A3). Thus, the overall peak area is proportional to the k values at each wavelength, and these k values should vary linearly with concentration. Figure A4 shows a plot of peak area versus the concentration of salt in a solution contacting the ATR crystal for both NaSCN and K₂Ni(CN)₄. The plots are linear as expected. For each peak, we can calculate an average absorbance, A_{avg} , such that peak area = $A_{\text{avg}}\Delta\nu$, where $\Delta\nu$ is the width in wavenumbers over which the peak is integrated. From this A_{avg} , we can calculate a k_{avg} using the overall reflection coefficient and make a plot of k_{avg} versus concentration. Over the integration range, the value of λ does not make a significant difference (<3%) in the calculated value of A for a given k and thickness. The effect of the dispersion in the refractive index of

SCN^- should be small because the concentrations of SCN^- in the film or solution are low enough that the refractive index of the composite should not be greatly affected.

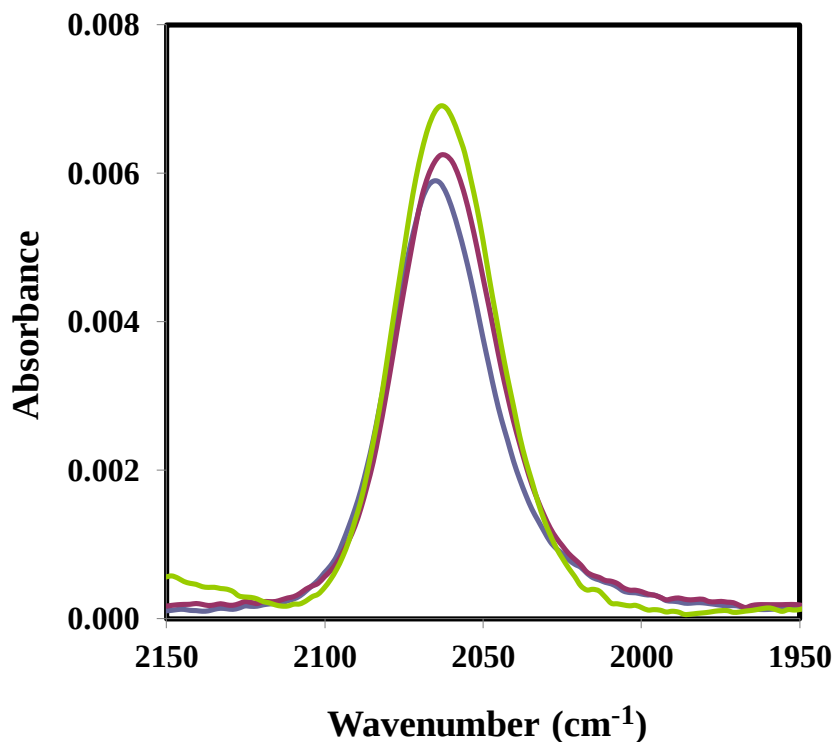


Figure A5. ATR-FTIR spectra of 0.1 M NaSCN in aqueous (purple) and 80% ethanol in water (green) solutions containing 0.2 M PDADMAC. The ATR-FTIR spectrum of 0.1 M NaSCN in water without PDADMAC is shown in blue.

To determine the concentration of the species in a film with a thickness much greater than the penetration depth, we determine A_{avg} using the same width for the integration as in solution spectra and calculate a k_{avg} using the reflection coefficient equation A.1 and equation A.4. Concentration can be determined using equation A.5 where Q is calculated from k_{avg} values for solutions containing different concentrations of SCN^- . The situation is slightly more

complicated with thinner films. We again determine A_{avg} and calculate the k_{avg} value, but this time the overall reflection coefficient (equation A.6) must be used to take into account the three-phase (crystal-film-solution) interface. With a k_{avg} for the film in hand, we can use equation A.5 to calculate the concentration in the film.

One major question that arises in this method is whether the value of k_{avg} for a given concentration is the same in water and in the film. Simple expressions such as the Maxwell Garnett mixing rule would suggest that changes in k due to the changes in refractive index between water ($n=1.323$) and the film ($n=1.44$, for example) would be less than 6%. However, such expressions neglect specific interactions that may occur. To assess changes in k as a function of both dielectric constant and interactions, we measured the spectra of 0.1 M NaSCN in deionized water and in solutions containing 0.2 M PDADMAC in water, and 0.2 M PDADMAC in 80% ethanol in water (v:v). As shown in Figure A5, compared to the spectrum of 0.1 M NaSCN in pure water, the peak position for SCN^- in solutions containing 0.2 M PDADMAC changes from 2065 cm^{-1} to 2062 cm^{-1} , and the peak area increases by 5% on going from water to aqueous 0.2 M PDADMAC and by 8% on going from aqueous 0.2 M PDADMAC to 0.2 M PDADMAC in 80% ethanol. From simulation, the absorbances for solutions with the same k values and refractive indices of 1.323 (pure water at 2058 cm^{-1}) and 1.355 (80% ethanol in water, refractive index estimated from the difference in water and 80% ethanol refractive indices at 589.3 nm) should differ by about 4%, which agrees reasonably well with the spectra for NaSCN in 0.2 M PDADMAC in water and 80% ethanol. Overall these data suggest that film

concentrations of SCN^- calculated from ATR-FTIR spectra could differ by a maximum of 10-20% from the true value.

We note that Jaber and Schlenoff utilized a powerful method for calculating the ratios of different species in films with thicknesses greater than 2 or 3 penetration depths.⁶⁵ They simply used the ratio of the areas of peaks in solution as a calibration and then determined the ratios of species in the film from their peak areas. This method does not give an absolute concentration, however, unless the concentration of one of the species in the film is known.⁷⁹

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3.6. References

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Chapter 4

Enhancing the $\text{Na}^+/\text{Mg}^{2+}$ Transport Selectivity of Polyelectrolyte Multilayer Films Through Adsorption of Cu^{2+} or Fe^{3+}

4.1. Introduction

Nanofiltration (NF) is an effective method for selectively removing divalent ions from water streams in applications such as water softening.¹⁻⁷ Typical NF membranes are more permeable than reverse osmosis membranes, and high permeability along with the low monovalent ion rejections in NF allow water treatment at much lower pressures than in reverse osmosis.⁸ This research examines methods for increasing the selectivity of NF membranes prepared by layer-by-layer (LbL) adsorption of multilayer polyelectrolyte films on polymeric substrates. The polyelectrolyte films serve as a selective membrane “skin”, and the LbL method is attractive because it allows fine control over the skin thickness through variation of the number of deposited layers. Minimizing the thickness of the PEM is critical for achieving high membrane permeabilities, but the skin should be thick enough to cover the substrate without defects.

Water softening by NF involves selective rejection of Ca^{2+} and Mg^{2+} in the presence of monovalent cations such as Na^+ , and several groups examined the $\text{Na}^+/\text{Mg}^{2+}$ and $\text{Na}^+/\text{Ca}^{2+}$ selectivities of membranes containing a polyelectrolyte multilayer film as a selective skin.⁹⁻¹² (For NF and diffusion dialysis (DD), selectivity is simply the ratio of the fluxes of the ions of interest.) In particular, polyelectrolyte deposition at high ionic strength can increase ion-transport selectivity, presumably through an increase in surface charge that leads to enhanced

exclusion of divalent ions.¹³⁻¹⁵ Fixed ionic charges present within the film also increase the rejections of charged ions.^{16, 17} Toutianoush *et al.* studied the alternating permeation of NaCl and BaCl₂ through (PVA/PVS)₆₀ and found that after 6 measurements for 180 min each, the NaCl/BaCl₂ selectivity changes from 8.6 to 17.5, and the permeation rate increases by about 10%.¹⁷ This work aims to further increase the Na⁺/Mg²⁺ selectivities of multilayer polyelectrolyte membranes through deliberate adsorption of transition metal cations throughout the film.

Xiao *et al.* reported the formation of zero valent iron nanoparticles in PAA/PDADMAC multilayers adsorbed on cellulose acetate nanofibers by immersing the PEM film in 0.18 M ferrous chloride for 30 min and subsequently reducing the adsorbed Fe²⁺.¹⁸ Several other papers also demonstrated metal-ion adsorption in polyelectrolyte films.^{19, 20} This chapter describes a similar method to adsorb Fe³⁺ or Cu²⁺ in membranes and introduce anion exchange sites into these films. The adsorption of these ions yields remarkable improvements in Na⁺/Mg²⁺ selectivities during NF through (PSS/PAH)_n membranes. Even mM concentrations of FeCl₃ are sufficient to create ion-exchange sites and give high separation factors.

4.2. Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS, M_w = 70 000 Da), poly(allyl amine hydrochloride) (PAH, M_w = 56 000 Da), CuCl₂, FeCl₃, and 3-mercapto propionic acid (MPA)

were purchased from Sigma-Aldrich, and reagent grade MgCl_2 and NaCl were obtained from Columbus Chemical Industries. Figure 4.1 shows the structures of the polyelectrolytes. Polyethersulfone (PES) membranes (50 kDa, Millipore catalog number PBQK02510) were soaked in deionized water for 1 hour and rinsed with water prior to deposition of polyelectrolytes.

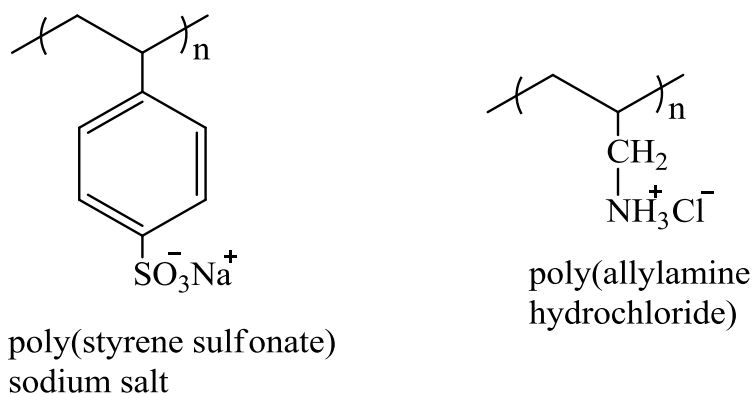


Figure 4.1. Structures of the polyelectrolytes used in this study.

Preparation of PEM Films and modification with Cu^{2+} or Fe^{3+} . Polyelectrolyte deposition followed a literature procedure.^{21, 22} Briefly, adsorption of PSS occurred by exposing the top of the substrate to 0.02 M PSS in 0.5 M NaCl for 2 min and rinsing for 1 min with deionized water. (Concentrations of polyelectrolytes are always given with respect to the repeating unit). The polycation layer was adsorbed during exposure of the substrate to 0.02 M PAH in 1.0 M NaCl for 5 min prior to rinsing with water for 1 min. The pH of PSS and PAH deposition solutions was adjusted to 2.3 with 0.1 M HCl . Polyanion and polycation adsorption steps were repeated to give the desired number of polyelectrolyte layers, and the membranes were stored in water until

use. Unless otherwise noted, the top side of the PEM film was exposed to 0.5 M CuCl_2 or FeCl_3 for one hour and rinsed with water to modify the membranes with Cu^{2+} or Fe^{3+} .

Characterization of doped PEM films. A monolayer of MPA on the Au wafer served as an adhesion layer between Au and PAH.²³ After deposition, films were dried with nitrogen, and the thicknesses were determined at several points on each piece of coated wafer. External reflection Fourier-transform infrared (FTIR) spectra of films on Au-coated Si were obtained with a Nicolet Magna 560 FTIR spectrometer using a PIKE grazing angle (80°) attachment. A UV/ozone-cleaned gold wafer was used to obtain the background spectrum.

To analyze the amount of iron in the films, the membranes were immersed in 1 M sulfuric acid for 1 h (to make sure all the iron was extracted) and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian 710-ES ICP Optical Emission Spectrometer). Top view images of PES membranes coated with polyelectrolyte multilayers were taken using a Hitachi S-4700 II field-emission scanning electron microscope (FESEM). The surface of the membrane was sputter-coated (Pelco model SC-7 auto sputter coater) with 5 nm of gold prior to imaging.

Transport Studies. Nanofiltration experiments were performed with a cross-flow apparatus that was pressurized with Ar at 4.8 bar, as described previously.¹³ For $\text{Na}^+/\text{Mg}^{2+}$ separations, feed solutions contained 1000 ppm Na^+ and 1000 ppm Mg^{2+} prepared by dissolving NaCl and MgCl_2 in deionized water. For $\text{Cl}^-/\text{SO}_4^{2-}$ separations, feed solutions contained 1000 ppm SO_4^{2-} and 1000 ppm Cl^- prepared by dissolving Na_2SO_4 and NaCl in deionized water. Cation concentrations were determined using atomic absorption spectroscopy (Varian Spectra Atomic

Absorption-200 Spectrometer), and anion concentrations were determined using ion chromatography (Dionex 600 Ion Chromatograph with an Ionpac AS16 column) with conductivity detection. All the reported values are averages of several measurements on at least two different membranes.

4.3. Results and Discussion

4.3.1. Adsorption of Cu^{2+} and Fe^{3+} in PEM Films

This work aims to employ Cu^{2+} or Fe^{3+} adsorption in multilayer polyelectrolyte films to enhance the ion-transport selectivity of membranes capped with these films. Thus, the first step in this research is to show that adsorption occurs and creates anion-exchange sites that may increase selectivity. The most direct way to demonstrate ion adsorption is to dissolve the adsorbed ions for subsequent analysis, and Table 4.1 shows the results of such studies. After exposure of (PAH/PSS)₄PAH films on gold wafers to 0.5 M or 0.005 M FeCl_3 and subsequent rinsing with DI water, a 1.2 cm^2 film contains approximately $0.002 \text{ } \mu\text{mol}$ of Fe^{3+} . The ellipsometric thickness of the (PAH/PSS)₄PAH films prior to Fe^{3+} adsorption is about 20 nm, so assuming that the density of the film is 1 g/cm^3 and that PSS accounts for 50% of the adsorbed polyelectrolyte, the film should contain around $0.014 \text{ } \mu\text{mol}$ of $-\text{SO}_3^-$ groups. Thus, the ratio of $-\text{SO}_3^-$ to Fe^{3+} in the film is 0.1-0.2. However, this number should be viewed with some caution because the concentration of Fe^{3+} eluted from the film is near the detection limit of ICP-OES.

Table 4.1. Concentrations of Fe^{3+} and $-\text{SO}_3^-$ in (PAH/PSS)₄PAH films after immersion of the film in an FeCl_3 solution and rinsing.

Substrate	Fe^{3+} (μmol)	$-\text{SO}_3^-$ (μmol) ^a	$-\text{SO}_3^-/\text{Fe}^{3+}$
(PAH/PSS) _{4.5} - 0.005 M Fe^{3+} (Au wafer one sided)	0.002	0.014	0.14
(PAH/PSS) _{4.5} - 0.5 M Fe^{3+} (Au wafer one sided)	0.003	0.014	0.21

^aThe $-\text{SO}_3^-$ concentration was calculated from the film ellipsometric thickness using the assumptions described in the text.

FTIR spectra can demonstrate the presence of anions in polyelectrolyte films and confirm the formation of anion-exchange sites.^{24, 25} Unfortunately, Cl^- ions do not absorb IR radiation, so we exchanged SCN^- for Cl^- to facilitate counterion analysis. However, the SCN^- may adsorb to the film to a greater extent than Cl^- because it exhibits significantly stronger ion-exchange interactions.²⁴

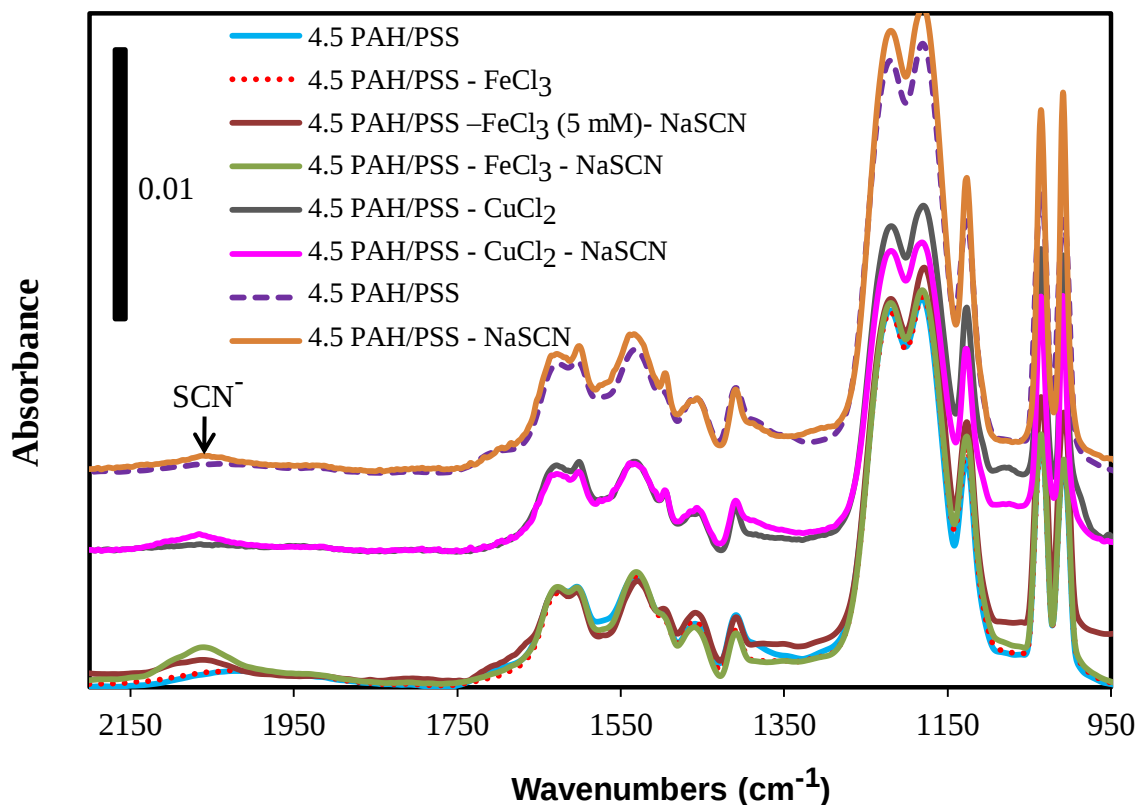


Figure 4.2. Reflectance FTIR spectra of (PAH/PSS)₄PAH-coated Au wafers before and after a 1-h immersion in 0.5 M FeCl₃ or 0.5 M CuCl₂ or 0.5 M NaSCN followed by rinsing with water, and the spectra of the CuCl₂ or FeCl₃-treated films, including a film immersed in 5 mM FeCl₃, after a 1 h immersion in 0.5 M NaSCN followed by rinsing. Some of the spectra are offset for clarity.

Figure 4.2 shows FTIR spectra of (PAH/PSS)₄PAH films before and after exposure to aqueous FeCl₃, CuCl₂, or NaSCN solutions and after exposure of Fe³⁺- or Cu²⁺-treated films to a solution containing NaSCN. The dominant peaks in the spectrum between 1750 and 950 cm⁻¹ stem from PSS and PAH,^{26, 27} and there is no significant change in the IR spectrum of the

multilayer film after exposure to a solution of FeCl_3 or CuCl_2 . After immersion in the NaSCN solution and rinsing with water, both $(\text{PAH/PSS})_4\text{PAH}$ films and Fe^{3+} - or Cu^{2+} -treated $(\text{PAH/PSS})_4\text{PAH}$ films show a new peak at 2058 cm^{-1} due to SCN^- adsorption. However, with immersion in 0.5 M FeCl_3 and subsequent exposure to NaSCN , the area of the SCN^- peak is about 2.5-fold the area of the corresponding peak for an untreated film that was immersed in 0.5 M NaSCN , suggesting that Fe^{3+} adsorption increases the number of ion-exchange sites in the film 2.5-fold. The relatively large SCN^- peak even without Fe^{3+} adsorption probably appears because SCN^- adsorbs to the terminal polycationic layer of the film. We employed polycation-terminated coatings both to avoid Fe^{3+} adsorption at a polyanion-terminated surface and to increase $\text{Na}^+/\text{Mg}^{2+}$ selectivities. The FTIR spectra of 5 mM Fe^{3+} -treated $(\text{PAH/PSS})_4\text{PAH}$ after exposure to SCN^- also shows a peak at 2058 cm^{-1} , but the peak area is only 1.5 times the area for the untreated $(\text{PAH/PSS})_4\text{PAH}$ after immersion in aqueous NaSCN . The corresponding SCN^- peak area after treatment with 0.5 M CuCl_2 and immersion in 0.5 M NaSCN is only 1.3-fold that for the untreated film, which suggests fewer ion-exchange sites in the Cu^{2+} -treated films than in Fe^{3+} -treated films.

Figure 4.3 shows SEM images of the top face of a bare PES membrane, and PES membranes coated with $(\text{PSS/PAH})_4$ with and without subsequent treatment with 0.5 M FeCl_3 and rinsing. On 4-bilayer PSS/PAH films treated with 0.5 M FeCl_3 (Figure 4.3c and 4.3d), the

surface contains a number of particles, which may be $\text{Fe}(\text{OH})_3$ formed by reaction between FeCl_3 and water (the membranes are stored in water until use in SEM or nanofiltration studies). No such particles are present on bare PES and PES coated with 4-bilayer PSS/PAH films. To determine if the formation of $\text{Fe}(\text{OH})_3$ occurs during storage, a 4-bilayer PSS/PAH film immersed in 0.5 M FeCl_3 was dried immediately after rinsing and stored briefly in air. The SEM image of this membrane shows no particles on the surface. Moreover, membranes treated with 0.005 M FeCl_3 show no particles on the surface, even after storage in water.

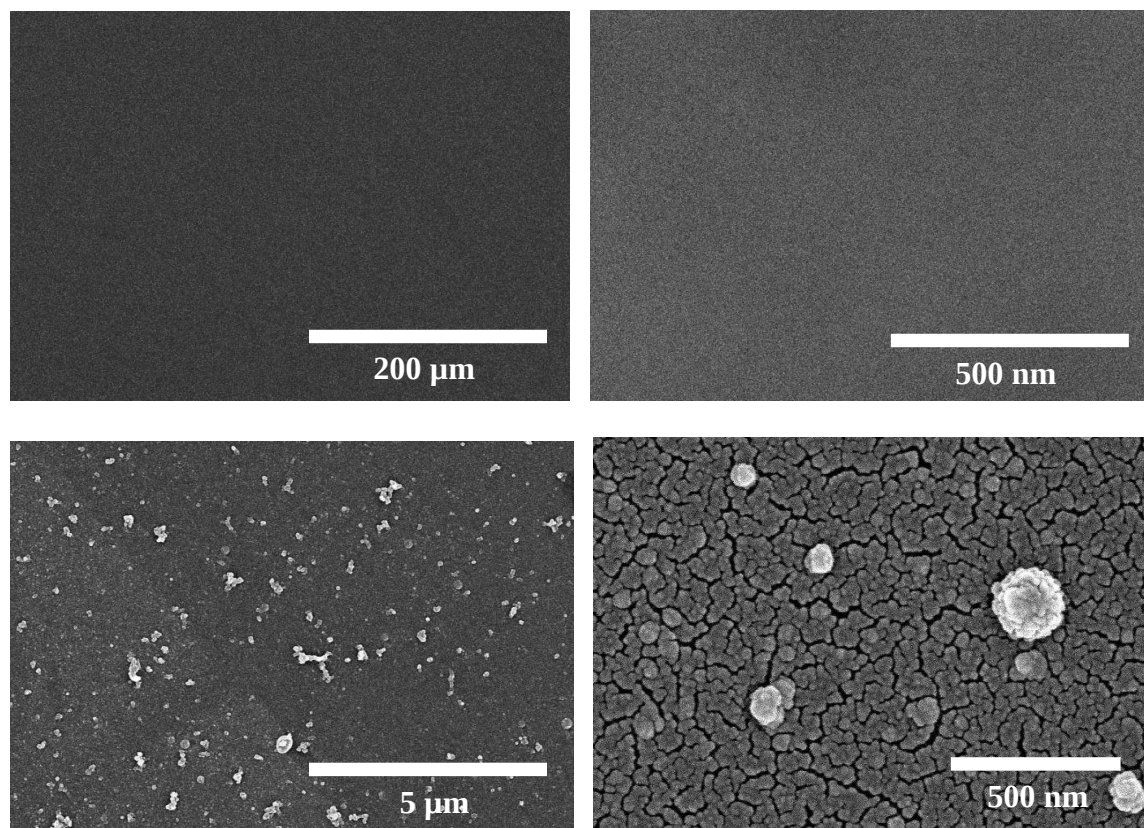


Figure 4.3. SEM images of 50 kDa PES membranes after (a) no treatment, (b) adsorption of a $(\text{PAH}/\text{PSS})_4$ film and (c, d) after $(\text{PAH}/\text{PSS})_4$ adsorption followed by immersion in 0.5 M FeCl_3 and rinsing with water.

4.3.2. Effects of Metal Ion Adsorption on the Nanofiltration Properties of (PSS/PAH)_n

Films on PES membranes

4.3.2.1. Mixed Salt Solutions

Deposition of PSS/PAH coatings on PES 50 kDa ultrafiltration membranes yields ultrathin membrane skins on a highly permeable support.²⁸ Most of our previous studies examined deposition of polyelectrolyte films on porous alumina,^{13, 27, 29-33} but polymeric supports are less brittle and typically less expensive than ceramic supports. We begin the polyelectrolyte deposition with a PSS layer that likely adsorbs to the membrane surface through hydrophobic interactions, and all membranes terminate in PAH to provide a positively charged surface that enhances Na⁺/Mg²⁺ selectivity. Upon deposition of a (PSS/PAH)₄ film, the pure water flux through the membrane at a transmembrane pressure drop of 4.8 bar decreases from 7.7 m³ m⁻² day⁻¹ to 0.9 m³ m⁻² day⁻¹, showing that the ultrathin film provides the bulk of the hydraulic resistance in the membrane.

Table 4.2 presents data for nanofiltration of NaCl/MgCl₂ solutions in terms of cationic rejection, R , which is defined in equation 4.1, where C_{perm} and C_{feed} are the solute concentrations in permeate and feed, respectively. Equation 4.2 defines the selectivity, S , for transport of solute A over solute B, which is also a function of the rejections for solute A and solute B.

$$R = \left(1 - \frac{C_{perm}}{C_{feed}} \right) \times 100\% \quad \text{----- (4.1)}$$

$$S = \frac{C_{A,perm}}{C_{A,feed}} \frac{C_{B,feed}}{C_{B,perm}} = \frac{100 - R_A}{100 - R_B} \quad \text{-----} \quad (4.2)$$

Table 4.2. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PSS/PAH)_n films deposited on 50 kDa PES membranes and feed solutions containing 1000 ppm Na⁺ and Mg²⁺.^a The transmembrane pressure was 4.8 bar.

Membrane	solution flux, m ³ /m ² -day	Na ⁺ rejection, %	Mg ²⁺ rejection, %	Na ⁺ / Mg ²⁺ Selectivity
(PSS/PAH) ₄	0.51±0.03	-4.2±7.1	93.5±1.7	17.3±5.4
(PSS/PAH) ₄ - Cu ²⁺ ^b	0.48±0.02	6.9±3.4	96.6±0.3	27.0±2.5
(PSS/PAH) ₄ - Fe ³⁺ ^c	0.58±0.04	15.9±2.5	99.1±0.1	93.0±9.5
(PSS/PAH) ₅	0.42±0.03	-4.9±4.2	95.3±0.1	22.4±1.2
(PSS/PAH) ₅ - Fe ³⁺ ^c	0.62±0.02	4.2±1.9	99.0±0.1	99.4±6.4

^aSolutions were prepared with NaCl and MgCl₂.

^bThe membrane was exposed to 0.5 M CuCl₂ and rinsed with deionized water.

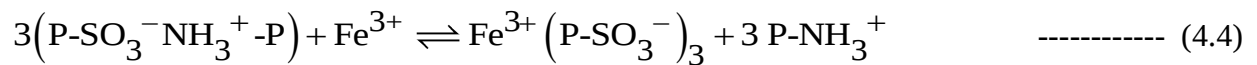
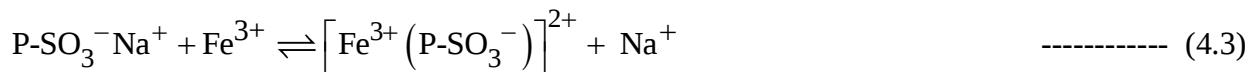
^cThe membrane was exposed to 0.5 M FeCl₃ and rinsed with deionized water.

For (PSS/PAH)₄ films on PES, the Mg²⁺ rejection and Na⁺/Mg²⁺ selectivity values of 94% and 17, respectively, agree reasonably with previous work in our group.¹⁴ Flux decreases with adsorption of an additional PSS/PAH bilayer, whereas Mg²⁺ rejection and Na⁺/Mg²⁺ selectivity increase slightly for (PSS/PAH)₅ relative to (PSS/PAH)₄. Immersion of the (PSS/PAH)₄ membrane in a 0.5 M CuCl₂ solution followed by rinsing with water increases Mg²⁺ rejection to 97% and Na⁺/Mg²⁺ selectivity to 27. More remarkably, similar treatment

with Fe^{3+} leads to a 99% Mg^{2+} rejection and a 5-fold increase in $\text{Na}^+/\text{Mg}^{2+}$ selectivity.

Moreover, after treatment with the FeCl_3 solution, the fluxes through $(\text{PSS}/\text{PAH})_4$ and $(\text{PSS}/\text{PAH})_5$ increases by 14 and 48%, respectively, even with the increased rejection.

We presume that the increased $\text{Na}^+/\text{Mg}^{2+}$ selectivity after Fe^{3+} adsorption stems from an increase in the number of ionic exchange sites in the film, which is consistent with the FTIR spectra discussed above. Binding of Fe^{3+} to the films via ionic interactions with sulfonate groups likely gives rise to the high stability of this modification. Even after 18 h of cross-flow filtration in a solution containing no Fe^{3+} and 1000 ppm Na^+ and Mg^{2+} , the membrane retains its selectivity. The Fe^{3+} ions may adsorb to the film through ion exchange with Na^+ according to equation 4.3, or they may actually disrupt ionic cross-links between sulfonate and ammonium groups as shown in equation 4.4. Disruption of cross-links might be responsible for the increase in flux after the FeCl_3 treatment.



To provide evidence that the increase in $\text{Na}^+/\text{Mg}^{2+}$ selectivity stems primarily from an increase in the number of anion-exchange sites in the film, we also examined the $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity in nanofiltration of solutions containing NaCl and Na_2SO_4 . Table 4.3 shows that the polycation-terminated $(\text{PSS}/\text{PAH})_4$ films show minimal $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity before and after

treatment with Fe^{3+} . If adsorption of Fe^{3+} were inducing size-based discrimination among ions, we would expect to see an increase in $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity for membranes treated with FeCl_3 solutions, but this is not the case. In fact the $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity decreases slightly after adsorption of Fe^{3+} , which is consistent with an increase in the positive charge in the film. Adsorption of SO_4^{2-} might explain the smaller than expected difference in flux between the Fe^{3+} -treated and untreated membranes. In fact the flux through these membranes is even higher than the pure water flux of $0.9 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$.

Table 4.3. Rejections, solution fluxes, and selectivities from nanofiltration experiments with $(\text{PSS}/\text{PAH})_4$ films deposited on 50 kDa PES membranes and feed solutions containing 1000 ppm Cl^- and SO_4^{2-} .^a

Membrane	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	Cl^- rejection, %	SO_4^{2-} rejection, %	$\text{Cl}^-/\text{SO}_4^{2-}$ Selectivity
$(\text{PSS}/\text{PAH})_4$	1.20 ± 0.05	9.4 ± 1.0	20.2 ± 2.2	1.14 ± 0.02
$(\text{PSS}/\text{PAH})_4 - \text{Fe}^{3+\text{b}}$	1.24 ± 0.02	13.1 ± 3.0	20.5 ± 2.7	1.09 ± 0.01

^aNanofiltration solutions were prepared with NaCl and Na_2SO_4 .

^bThe membrane was exposed to 0.5 M FeCl_3 and rinsed with deionized water.

4.3.2.1.1. Effect of immersion time and Fe^{3+} concentration on NF properties of membranes treated with FeCl_3 .

The NF properties of $(\text{PSS}/\text{PAH})_x$ films exposed to FeCl_3 solutions vary with both the concentration of Fe^{3+} in the solution and the exposure time. As Table 4.4 shows, flux through $(\text{PSS}/\text{PAH})_4$ -modified PES membranes is around 30% higher for films exposed to 0.5 M FeCl_3 than for films exposed to 5 mM or 50 mM FeCl_3 . Only with 0.5 M FeCl_3 is the flux higher than that through an unmodified membrane (see Table 4.4). This suggest that breaking of ionic cross-links as described by equation 4.4 requires a high Fe^{3+} concentration.³⁴ The Na^+ and Mg^{2+} rejections also increase with the concentration of FeCl_3 in the modification solutions, but differences in selectivity among the various modifications are not statistically significant because rejection increases for both ions.

Table 4.4. Rejections, solution fluxes, and selectivities from nanofiltration experiments with $(\text{PSS}/\text{PAH})_4$ films on 50 kDa PES membranes after treatment of the membranes by immersion in FeCl_3 . The feed solutions contained 1000 ppm Na^+ and Mg^{2+} .^a

FeCl_3 concentration in treatment solution	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	Na^+ rejection, %	Mg^{2+} rejection, %	$\text{Na}^+ / \text{Mg}^{2+}$ Selectivity
5 mM	0.43±0.02	-6.9±7.8	98.3±0.4	78.9±17.3
50 mM	0.45±0.03	-5.7±3.0	98.8±0.1	86.4±3.7
0.5 M	0.58±0.04	15.9±2.5	99.1±0.1	93.0±9.5

^aNanofiltration solutions were prepared with NaCl and MgCl_2 .

Table 4.5. Rejections, solution fluxes, and selectivities from nanofiltration experiments with (PSS/PAH)₄ films on 50 kDa PES membranes with and without treatment of the membranes by immersion in 5 mM FeCl₃ for different times. The feed solutions contained 1000 ppm Na⁺ and Mg²⁺.^a

Doping time (min)	solution flux, m ³ /m ² -day	Na ⁺ rejection, %	Mg ²⁺ rejection, %	Na ⁺ / Mg ²⁺ Selectivity
0	0.51±0.03	-4.2±7.1	93.5±1.7	17.3±5.4
5	0.50±0.03	-4.5±3.0	94.4±0.3	18.8±0.8
10	0.42±0.02	-5.3±1.8	99.0±0.1	109.4±10.1
30	0.43±0.02	-5.8±2.1	98.6±0.1	75.8±2.5
60	0.43±0.02	-6.9±7.8	98.3±0.4	78.9±17.3

^aNanofiltration solutions were prepared with NaCl and MgCl₂.

We investigated the effect of exposure time on membrane modification using the lowest FeCl₃ concentration, where the rate of membrane modification should be lowest. As Table 4.5 shows, full modification of the membrane requires about 10 min, and further exposure to 5 mM FeCl₃ may even lead to small decreases in selectivity and Mg²⁺ rejection. We also studied the effect of adsorption of Fe³⁺ on separation properties using a commercial NF-270 membrane (Table 4.6). The rejections and selectivity of the unmodified membrane are similar to those reported in literature,^{14, 35} but the FeCl₃ treatment leads to only modest increases in Mg²⁺ rejection and Na⁺/Mg²⁺ selectivity.

Table 4.6. Rejections, solution fluxes, and selectivities from nanofiltration experiments with NF-270 membranes before and after immersion in 0.5 M FeCl₃ for 60 min. The feed solutions contained 1000 ppm Na⁺ and Mg²⁺.^a

Membrane	solution flux, m ³ /m ² -day	Na ⁺ rejection, ^b %	Mg ²⁺ rejection, ^b %	Na ⁺ / Mg ²⁺ Selectivity
NF-270	0.92±0.04	14.4±2.2	48.5±2.7	1.8±0.1
NF-270 - Fe ³⁺	0.79±0.08	10.9±3.0	59.9±6.6	2.4±0.4

^aSolutions were prepared with NaCl and MgCl₂.

^bSolutions were analyzed using ICP-OES.

4.3.2.2. Single Salt Experiments

To better understand the higher selectivities and fluxes for the modified membranes, we performed nanofiltration of solutions containing single salts (Table 4.7). Na⁺ and Mg²⁺ rejections and fluxes for (PSS/PAH)₄ films are similar to results reported by Ouyang *et al.*¹⁴ Solution flux through the (PSS/PAH)₄ membrane is less for MgCl₂ than for NaCl because of the higher MgCl₂ rejection and the higher overall concentration of ions in the MgCl₂ solutions. After treatment with 5 mM or 0.5 M FeCl₃, sodium rejection increases from 40% to 50-55 % whereas magnesium rejection increases from 95% to 99 %. Thus the salt passage decreases more than 5-fold for MgCl₂ and at most 25% for NaCl, which is consistent with exclusion of Mg²⁺ due to increased fixed positive charges in the film. The flux of the NaCl solution is higher for the Fe³⁺-doped films compared to the original PSS/PAH film, again suggesting the possibility of breaking the ionic cross-links in polymer chains at high concentrations of Fe³⁺.

The flux of MgCl_2 solutions does not change significantly after Fe^{3+} treatment, perhaps because of Mg^{2+} adsorption in films.

Table 4.7. Rejections and solution fluxes from single-salt nanofiltration experiments with $(\text{PSS}/\text{PAH})_4$ and Fe^{3+} -modified (60 min) $(\text{PSS}/\text{PAH})_4$ films deposited on 50 kDa PES membranes. The feed solutions contained 1000 ppm Na^+ or 1000 ppm Mg^{2+} .^a

Membrane	Na^+		Mg^{2+}	
	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	rejection, %	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	rejection, %
$(\text{PSS}/\text{PAH})_4$	0.78 ± 0.03	40.3 ± 2.1	0.41 ± 0.02	95.0 ± 1.2
$(\text{PSS}/\text{PAH})_4$ - 0.5 M Fe^{3+}	1.02 ± 0.02	55.0 ± 1.7	0.44 ± 0.02	99.1 ± 0.1
$(\text{PSS}/\text{PAH})_4$ - 5 mM Fe^{3+}	0.96 ± 0.04	48.6 ± 1.7	0.42 ± 0.03	99.4 ± 0.3

^aSolutions were prepared with NaCl or MgCl_2 .

4.4. Conclusions

Doping PEMs through exposure to solutions containing FeCl_3 or CuCl_2 introduces ion-exchange sites into the film. Immersion of a $(\text{PSS}/\text{PAH})_4$ film on a 50 kDa PES membrane in as little as 5 mM FeCl_3 yields a 5-fold increase in the $\text{Na}^+/\text{Mg}^{2+}$ selectivity of the membrane with a minimal decrease in permeability compared to untreated $(\text{PSS}/\text{PAH})_4$ films. Remarkably, the membranes maintain their modification for at least 18 h of cross-flow nanofiltration with solutions that do not contain Fe^{3+} . Increases in the density of anion-exchange sites in the

membrane give rise to exclusion of divalent Mg^{2+} but not divalent SO_4^{2-} , as would be expected for an ion-exchange membrane. The high $\text{Na}^+/\text{Mg}^{2+}$ selectivities and low operating pressures of these membranes make them attractive for water softening applications.

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Chapter 5

Polyelectrolyte Multilayer Films for Removal of Pharmaceutically Active Compounds from Water

5.1. Introduction

Pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) in environmental waters are an increasing problem for animals and aquatic life, although the effect of these chemicals on humans is still debatable.¹⁻⁷ Many water-treatment techniques such as biological methods,⁸⁻¹⁰ chlorination,¹¹⁻¹³ reverse osmosis^{14, 15} and nanofiltration (NF)¹⁶ can modify or isolate EDCs and PhACs in water. Among these treatment options, NF is attractive because it removes a wide range of dissolved organic pollutants from water using relatively low pressures.¹⁷⁻²¹

Unfortunately, however, the small-molecule rejections of commercial NF membranes are often too low for effective treatment of streams containing EDCs and PhACs. Kimura *et al.* reported 44% rejection of caffeine by a commercial SC-3100 NF membrane (MWCO 200–300 Da).¹⁵ Yangali-Quintanilla *et al.* studied the rejections of acetaminophen (ACT) and caffeine (CFN) using NF-90 membranes from DOW and found a steady state rejection of 71% for ACT and 81% for CFN.²² Yoon *et al.* performed dead-end, stirred-cell NF using a pressure of 7.5 bar and obtained ACT and CFN rejections less than 40% for a NF membrane from ESNA, Hydranautics, USA.²³ Zazouli *et al.* studied the influence of solution pH, ionic strength and

transmembrane pressure on ACT rejection. Rejections of ACT with SR3 membranes from Koch, USA increased with the solution pH value because deprotonation of the phenolic group on ACT created a negatively charged species that was more highly rejected by the negatively charged membrane. However, the maximum ACT rejection was only 60%.²⁴

This research examines the rejections of ACT and CFN by NF membranes prepared through layer-by-layer (LbL) adsorption of multilayer polyelectrolyte films on permeable substrates. For comparison, we also study the ACT and CFN rejections of two commercial NF membranes, NF-270 and NF-90. The polyelectrolyte films are attractive because they allow variation of the thickness of the membrane skin through changing the number of deposited layers, and control over the skin thickness permits optimization of the tradeoff between rejection and membrane permeability. Moreover, at high pH, electrostatic repulsions between ACT and terminal polyanion layers in polyelectrolyte membranes should lead to very high rejections. To the best of our knowledge, this is the first work to use LbL films to remove PhACs from water. However, Hoshi *et al.* showed that PAH/PSS films block the access of ACT to electrodes.²⁵

5.2. Experimental Section

Materials. Poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70\,000$ Da), poly(allyl amine hydrochloride) (PAH, $M_w = 56\,000$ Da), poly(acrylic acid) (PAA, $M_w = 90\,000$ Da), and reagent grade ACT and CFN were purchased from Sigma-Aldrich. Figure 5.1 shows the structures of the PhACs, and Table 5.1 provides a summary of their physical properties. Porous alumina supports (0.02- μm Whatman Anodisk filters) were UV/O₃ cleaned (Boekel UV-Clean Model 135500) with the feed side up for 15 min before film deposition, and deionized water (Millipore

purification system, 18.2 MΩcm) was used for membrane rinsing and preparation of the polyelectrolyte solutions. Commercial NF-90 and NF-270 membranes were soaked in deionized water for 1 hour. These membranes were then rinsed with water and used for NF experiments or modified with polyelectrolyte multilayers.

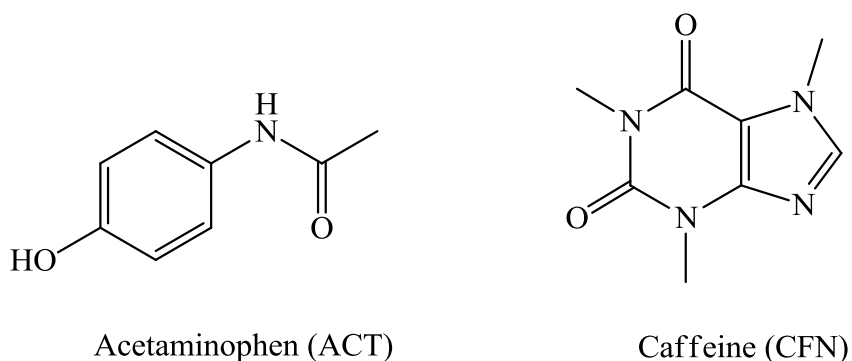


Figure 5.1. Structures of acetaminophen and caffeine.

Preparation of PEM Films. Polyelectrolyte adsorption followed a literature procedure.^{26, 27}

Briefly, deposition of PSS occurred by exposing the top of the substrate to 0.01 M PSS in 0.5 M NaCl for 2 min and rinsing for 1 min with deionized water. (Concentrations of polyelectrolytes are always given with respect to the repeating unit). The polycation layer was adsorbed during exposure of the substrate to 0.01 M PAH in 0.5 M NaCl for 5 min and rinsing with water for 1 min. The pH values of PSS and PAH deposition solutions were adjusted to 2.1 and 2.3, respectively, using 0.1 M HCl. Polyanion and polycation adsorption steps were repeated to give the desired number of polyelectrolyte layers, and the membranes were stored in water until use.

Transport Studies. Nanofiltration experiments were performed with a cross-flow apparatus that was pressurized with Ar at 4.8 bar, as described previously.²⁸ Feed solutions contained 100 ppm

ACT or 100 ppm CFN, prepared by dissolving 0.1 g in 1 liter deionized water (Milli-Q, 18.2 MΩcm). Permeate and feed concentrations of ACT and CFN were determined using UV/Vis spectroscopy (Perkin Elmer Lambda-40 Spectrometer) and a calibration curve. All the reported values are average of several measurements on at least two different membranes.

Table 5.1. Physical and chemical properties of acetaminophen and caffeine.

Compound	Molecular Weight	Water Solubility g/L	pKa at 20°C	Charge at pH 6.4
ACT	151	4.15 ²⁹	9.4 ²⁹	Neutral
CFN	194	11.0 ³⁰	10.4 ³⁰	Neutral

5.3. Results and Discussion

5.3.1. Nanofiltration of ACT with NF-270, NF-90 and PSS/PAH membranes

We employed ACT as the primary compound for evaluating the PhAC rejection properties of polyelectrolyte and commercial NF membranes. Figure 5.2 shows the UV/Vis spectrum of aqueous 20 ppm acetaminophen, and similar spectra of permeate solution allow rapid determination of ACT rejections from the absorbance at $\lambda_{\max}$, 243 nm. Experimental results are expressed in terms of the rejection percentage, R, which is calculated by comparing the permeate and feed concentration using equation 5.1,

$$R = \left(1 - \frac{C_{pi}}{C_{fi}} \right) \times 100\% \quad \text{----- (5.1)}$$

where C_{fi} and C_{pi} are the concentrations of compound i in the feed and the permeate, respectively. Solution flux is the volume flowing through the membrane per unit area and time.

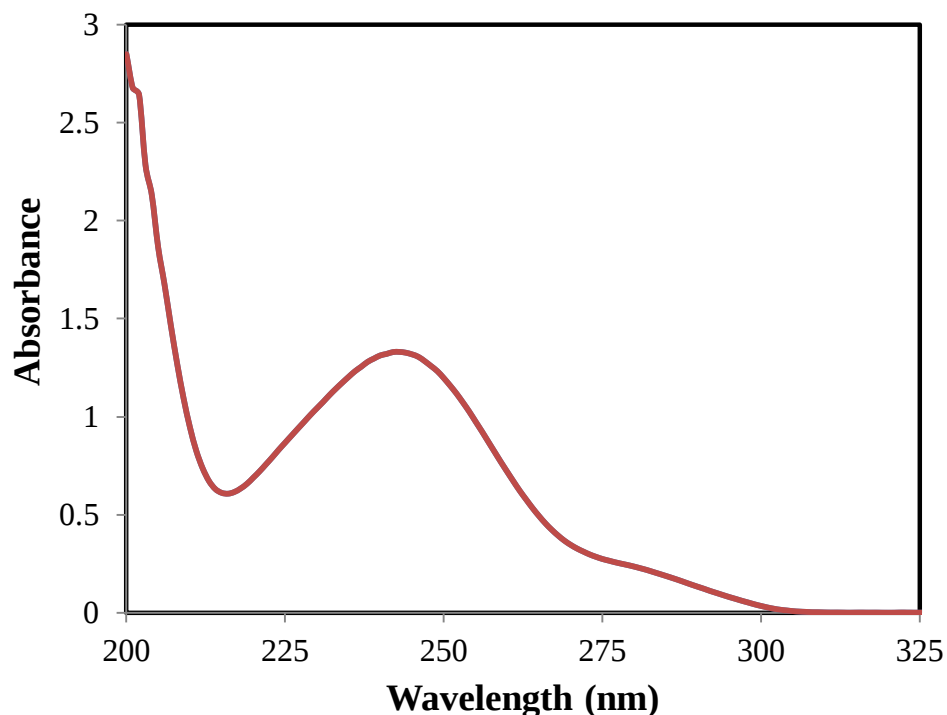


Figure 5.2. UV/Vis spectrum of 20 ppm ACT in water. $\lambda_{\text{max}}=243$ nm.

Table 5.2 shows the rejections of ACT by different membranes. The NF-270 membrane exhibits rejections <20% because of its relatively large pores. In contrast, NF-90 and (PSS/PAH)₇ on porous alumina have similar rejections of around 65%, but the solution flux is 24 to 32% lower than that through NF-270. PSS/PAH films terminated with PSS, (PSS/PAH)₇PSS, exhibit lower rejections than PAH-terminated films. The feed solution has a pH of 6.4, which is lower than the pK_a value of ACT, so this compound should be neutral during filtration and unaffected by the charge on the membrane. The slight decrease in rejection on going from (PSS/PAH)₇ to (PSS/PAH)₇PSS might stem from increased swelling for the PSS-terminated film,^{27, 31, 32} but this explanation is inconsistent with the trends in fluxes. We also

studied NF with (PSS/PAH)₉ membranes and observed a 22% decrease in solution flux and no increase in rejections relative to (PSS/PAH)₇ films (data not shown). Evidently, 7-bilayer films are sufficient to achieve full coverage of the alumina support and addition of more layers only decreases permeability.

Table 5.2. Rejections and solution fluxes from nanofiltration experiments with NF-270 and NF-90 membranes, and PSS/PAH films deposited on porous alumina. The feed solutions contained 100 ppm ACT.

Membrane	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	rejection, %
NF-270	1.85 ± 0.12	15.9 ± 0.6
NF-90	1.26 ± 0.08	64.9 ± 3.4
(PSS/PAH) ₇ on alumina ^a	1.40 ± 0.20	65.6 ± 0.9
(PSS/PAH) ₇ PSS on alumina ^a	1.21 ± 0.03	54.4 ± 3.3

^aDeposition occurred from solutions containing 0.02 M PSS and 0.02 M PAH.

In an effort to achieve higher rejections, we modified commercial membranes with polyelectrolyte films (Table 5.3). Adsorption of (PSS/PAH)₃ on NF-270 increases rejection to only 27%, perhaps because of the relatively large pores in the base membrane. However, adsorption of a single PSS/PAH bilayer on NF-90 membranes increases rejection to 81% while maintaining a solution flux $1.09 \text{ m}^3/(\text{m}^2\text{day})$. Even adsorption of a single PSS layer enhances ACT rejection from 65 to 73%. On NF-90 membranes, rejection of ACT reaches a maximum of 81% with adsorption of 1 or 2 PSS/PAH layers and then decreases after deposition of a third bilayer. Prior studies showed that the structure of PDADMAC/PSS^{33, 34} films on alumina substrates varies dramatically with the number of layers in the film, which leads to an optimal

number of bilayers for salt rejection and selectivity. Nevertheless, such behavior is unusual for PSS/PAH films.

Table 5.3. Rejections and solution fluxes from nanofiltration experiments with NF-270 and NF-90 membranes modified with polyelectrolyte coatings. The feed solutions contained 100 ppm ACT.

Membrane	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	rejection, %
PSS on NF-90	1.11 ± 0.01	73.7 ± 1.9
$(\text{PSS/PAH})_1$ on NF-90	1.09 ± 0.03	80.7 ± 1.0
$(\text{PSS/PAH})_2$ on NF-90	1.07 ± 0.07	80.7 ± 1.5
$(\text{PSS/PAH})_3$ on NF-90	1.02 ± 0.01	73.8 ± 2.4
$(\text{PSS/PAH})_3$ on NF-270	1.41 ± 0.04	26.8 ± 3.8

5.3.1.1. Effect of polyelectrolyte type and concentration on the rejection of ACT

The thickness of PEM films often increases with the concentration of polyelectrolytes in deposition solutions. Instead of increasing the thickness through adsorption of additional layers, we varied the polyelectrolyte concentrations in deposition solutions from 0.01 to 0.02 M. Such concentration changes can lead to a 10 - 20% increase in PEM thickness.³⁵ However, on both NF-270 and NF-90 membranes (Table 5.4), the use of the higher polyelectrolyte concentrations led to decreases in flux and no significant change in rejection.

Table 5.4. Rejections and solution fluxes from nanofiltration experiments with NF-270 and NF-90 membranes modified with PSS/PAH films deposited from solutions containing different polyelectrolyte concentrations. The feed solutions contained 100 ppm of ACT.

Membrane	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	rejection, %
(PSS/PAH) ₂ (0.01 M deposition) on NF-90	1.07±0.07	80.7±1.5
(PSS/PAH) ₂ (0.02 M deposition) on NF-90	1.00±0.04	78.4±1.4
(PSS/PAH) ₃ (0.01 M deposition) on NF-270	1.41±0.04	26.1±3.8
(PSS/PAH) ₃ (0.02 M deposition) on NF-270	1.34±0.03	26.2±1.5

We also investigated whether varying the type of polyelectrolyte could increase the rejection by modified membranes and found that deposition of (PAA/PAH)₁ on NF-90 leads to an ACT rejection of 85% (Table 5.5). This small increase in rejection relative to modification with (PSS/PAH)_n may occur because the higher charge density in PAA than PSS leads to a more cross-linked film.^{27, 28}

Table 5.5. Rejections and solution fluxes from NF experiments with PSS/PAH and PAA/PAH films deposited on NF-90 membranes. The feed solutions contained 100 ppm of ACT, and the transmembrane pressure was 4.8 bar.

Membrane	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	rejection, %
(PSS/PAH) ₁ on NF-90	1.09±0.03	80.7±1.0
(PAA/PAH) ₁ on NF-90	1.08±0.01	84.8±1.3

5.3.2. Nanofiltration of CFN with NF-270, NF-90 and PSS/PAH films

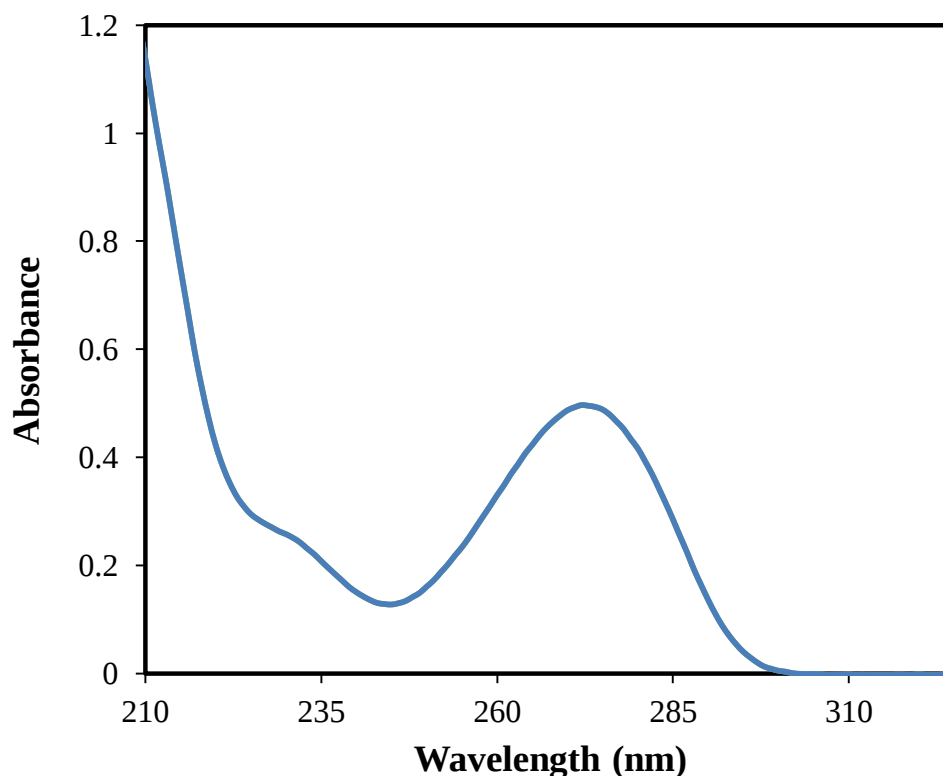


Figure 5.3. UV/Vis spectrum of 10 ppm CFN in water. $\lambda_{\max}$ =272 nm.

Figure 5.3 shows the UV/Vis spectrum of CFN, and the clear $\lambda_{\max}$ at 272 nm readily allows determination of CFN concentrations using a calibration curve. Table 5.6 shows the rejections of CFN using different membranes. NF-270 shows a relatively low 49% rejection of CFN because of the large pores in this membrane. In contrast, NF-90 shows a CFN rejection of 78%, whereas (PSS/PAH)₄ films show a similar rejection but a flux that is twice that through NF-90. Upon addition of a terminating layer of PSS to create (PSS/PAH)₄PSS films, rejection of CFN decreases to 52% and flux increases. Both of these changes are consistent with the trends in ACT rejections in Table 5.2, and an increase in film swelling when terminating films

with PSS.^{27, 32} Remarkably, (PSS/PAH)₇ films exhibit a CFN rejection of 94% along with a solution flux greater than that through NF90. Thus, the polyelectrolyte membranes show significantly higher rejections or fluxes than the commercial NF membranes. The higher rejections of CFN than ACT most likely stem from the slightly higher molecular weight (Table 5.1) or size of CFN.

Table 5.6. Rejections and solution fluxes from nanofiltration experiments with NF-270 and NF-90 membranes and PSS/PAH films deposited on porous alumina. The feed solutions contained 100 ppm CFN.

Membrane	solution flux, $\text{m}^3/\text{m}^2\text{-day}$	rejection, %
NF-270	1.76±0.22	48.5±4.8
NF-90	0.94±0.02	77.7±4.6
(PSS/PAH) ₄ on alumina	2.14±0.02	79.2±1.4
(PSS/PAH) ₄ PSS on alumina	2.95±0.04	52±6
(PSS/PAH) ₇ on alumina	1.33±0.02	93.6±0.6

5.4. Conclusions

(PSS/PAH)₇ membranes show ACT rejections similar to commercial NF-90 membranes, but the CFN rejection by (PSS/PAH)₇ films is 94% whereas that for NF-90 membrane is only 78%. Thus, caffeine passage is 3.5-fold greater through the NF-90 membrane than through (PSS/PAH)₇. Moreover, the solution permeabilities of (PSS/PAH)₇ and NF-270 membranes are almost the same. Modification of NF-90 membranes with 1 bilayer of PAA/PAH increases the

ACT rejection from 65% to 85% with only a 14% decrease in flux. PSS/PAH adsorption on NF-90 also increases ACT rejection, but not to the same extent as addition of PAA/PAH. The high rejections and permeabilities of PSS/PAH films on porous alumina and on NF-90 membranes make polyelectrolyte adsorption an attractive option for creating nanofiltration membranes that reject PhACs.

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Chapter 6

Conclusions and Future Work

Layer by layer adsorption of polyelectrolytes from aqueous solutions is an extremely versatile method for fabricating thin films. This technique is attractive for a range of applications due to its fine control over film thickness, applicability to most substrates and substrate geometries, and ability to incorporate a wide range of functional polyelectrolytes. Chapter 1 reviews selected potential applications of PEMs and the factors that influence PEM properties.

Chapter 3 demonstrates that the properties of PDADMAC/PSS coatings vary greatly with the number of adsorbed layers in the film. Streaming potential measurements and ATR-FTIR data suggest the presence of high anion-exchange capacities only in films with more than 7 bilayers, and the presence of these anion-exchange sites dramatically decreases the selectivity of $\text{Cl}^-/\text{SO}_4^{2-}$ separations. The understanding of film chemistry and structure provided by ATR-FTIR spectroscopy and streaming potential measurements is vital for developing PEM membranes to effectively separate anions or cations.

Chapter 4 describes a simple way to introduce fixed positive charges in PEM films by exposing them to 5 mM FeCl_3 for as little as 10 min. Treatment of $(\text{PSS}/\text{PAH})_4$ films (on 50 kDa PES membranes) with FeCl_3 yields a 5-fold increase in the $\text{Na}^+/\text{Mg}^{2+}$ selectivity of the membrane with a minimal decrease in permeability compared to untreated $(\text{PSS}/\text{PAH})_4$ films. Remarkably, the membranes maintain their modification for at least 18 h of nanofiltration with

solutions that do not contain Fe^{3+} . The high $\text{Na}^+/\text{Mg}^{2+}$ selectivities and low operating pressures of these membranes make them attractive for water softening applications.

Chapter 5 examines the rejections of acetaminophen (ACT) and Caffeine (CFN) by PEM films on porous substrates and by the commercial NF membranes, NF-270 and NF-90. Modification of NF-90 with a single PAA/PAH bilayer yields an ACT rejection of 85%, whereas the unmodified NF-90 membrane exhibits a similar flux and an ACT rejection of only 65%. The best membrane in this study shows a CFN rejection of 94% and a solution flux of $1.33 \text{ m}^3/(\text{m}^2 \text{ day})$ at an operating pressure of only 4.8 bar. The ease of preparing these membranes makes them very attractive for removal of pharmaceutically active compounds (PhACs) from water.

This study examined the rejection properties of PEM films using PhACs, but the PEMs may also be effective for removal of endocrine disrupting compounds (EDCs) from water. Conventional NF can isolate EDCs like alkyl phenols (AP) from aqueous solutions, but the removal of lower molecular weight APs is not always effective. López-Muñoz *et al.* found that NF-270 rejected less than 10% of selected phenolic compounds, and NF-90 exhibited rejections ranging from 10-50% depending on the compound studied.¹ Bódalo *et al.* found that a DSS-HR98PP (Dow) membrane could reject up to 80% of phenol.² Jung *et al.* used NF membranes to study the rejections of APs with alkyl groups ranging from C2 to C9 and found that a poly(vinyl alcohol)/polyamide based membrane (NTR-729HF, Nitto Denko Co. Ltd, Japan) rejected 4-n-octylphenol and 4-n-nonylphenol more than 95%, but the rejections of 4-ethylphenol (4-EP) and 4-*tert*-butylphenol (4-BP) were lower than 82%.³ Modification of these membranes with polyelectrolyte multilayers may greatly enhance the rejections of APs.

Future work could also examine the modification of RO membranes with polyelectrolytes. Due to the relatively low permeability of RO membranes, the polyelectrolyte layer would not greatly decrease the flux through this system, and coverage of small defects by the polyelectrolyte film could greatly enhance NaCl rejections. Treatment of the polyelectrolyte layers with Fe^{3+} may further enhance salt rejection. Finally, removal and regeneration of the polyelectrolytes provides a potential way to combat membrane fouling.⁴ Hopefully this work only represents the beginning of efforts to improve membrane properties through polyelectrolyte adsorption.

References

6.1. References

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