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Correlation of the Swelling and Permeability of Polyelectrolyte Multilayer Films

Matthew D. Miller and Merlin L. Bruening*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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Alternating adsorption of polycations and polyanions on porous supports yields a variety of size-selective membranes whose swelling and transport properties depend on constituent polyelectrolytes, capping layer choice (polycation or polyanion), and deposition conditions. This report shows that in aqueous experiments, ellipsometrically determined swelling percentages correlate well with nanofiltration (NF) rejections and diffusion dialysis fluxes. For example, hyaluronic acid (HA)/chitosan films swell 4 times more than poly(styrene sulfonate) (PSS)/poly(allylamine hydrochloride) coatings, and in NF experiments, the HA/chitosan membranes permit a 250-fold greater fractional passage of sucrose. In general, films prepared from polyelectrolytes with a high charge density show low swelling and slow solute transport, presumably because of a high degree of ionic cross-linking. In the case of PSS/poly(diallyldimethylammonium chloride) (PDADMAC), PDADMAC-capped films can swell 4-fold more than their PSS-terminated counterparts, and as would be expected, glucose and sucrose transport rates in diffusion dialysis are about 1.7- and 17-fold more, respectively, when these films end in PDADMAC. Polyelectrolyte multilayers also exhibit wide-ranging swelling properties in ethanol, but transport rates do not correlate with ethanol uptake. In this solvent, the density of ionic cross-links and film hydrophobicity likely exert opposite effects on swelling, which could complicate the correlation between swelling and transport.

Introduction

Polyelectrolyte multilayers (PEMs) are attractive as selective films in applications such as pervaporation,[1−6] nanofiltration (NF),[7−11] and encapsulation.[12−21] Their synthesis, which simply involves alternating adsorption of polycations and polyanions,[22] yields ultrathin (<50 nm) coatings capable of allowing high fluxes.[9,11,23] Additionally, many materials can be used to form PEMs,[2,24−26] and judicious selection of component polyelectrolytes and deposition conditions results in films with a wide range of permeation properties.[2,8,9,11,25,27,28] In an effort to better understand the permeability of polyelectrolyte films, this report aims at correlating transport through PEMs with their swelling in both aqueous and ethanolic solutions.

Several groups have already examined the swelling of individual PEMs in solvents. Neutron reflectometry studies suggest that poly(styrene sulfonate) (PSS)/protonated poly(allylamine) (PAH) film swelling is a function of the capping layer, as films capped with PAH swell 25% less than those capped with PSS (40% versus 30% D_2O as a function of capping layer).[29] Wong et al. observed the same outer-layer dependence for PSS/PAH films when they performed ellipsometric swelling experiments in 99% relative humidity.[30] Harris and Bruening found that immersion of $[\text{PSS/PAH}]_{10}$

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* To whom correspondence should be addressed. E-mail: bruening@chemistry.msu.edu. Phone: (517) 355-9715 ext. 237. Fax: (517) 353-1793.

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films in pH 3.2- and 6.3-buffered water solutions results in a thickness increase of 40% relative to ambient humidity conditions, while exposure of these films to pH 10 buffers yields even greater swelling followed by film delamination.[31] Other studies showed that PSS/PAH swelling is affected by deposition pH and ionic strength as well as swellant pH.[32,33] Though most swelling research has been performed on PSS/PAH films,[29−36] Schlenoff and Dubas demonstrated that water uptake in poly(acrylic acid) (PAA)/poly(diallyldimethylammonium chloride) (PDADMAC), PSS/PDADAMC, and PSS/PAH films is a strong function of the swellant ionic strength and that PAA/PDADMAC and PSS/PDADMAC films swell more in water than PSS/PAH coatings.[37] Two recent papers showed that the swelling of PAA/PAH films depends on both deposition conditions and pretreatments.[38,39] Burke and Barrett also found that, in some cases, PAH/hyaluronic acid (HA) films are capable of 800% swelling.[40] Excepting Schlenoff and Dubas' work,[37] however, there have been no systematic studies of how "dry" versus water-swollen PEM thicknesses differ with variables such as constituent polyelectrolytes and capping-layer choice.

In contrast, several studies show that the permeability of PEMs varies dramatically with their composition. Tieke and co-workers found that transport rates in pervaporation and diffusion dialysis (DD) through PEMs generally decrease as the charge density in the film increases.[2] Presumably, greater charge density on the polyelectrolytes results in more ionic cross-linking, less swelling, and lower permeabilities.[2,8,9,11] As not all prospective applications of PEMs are in water, swelling in other solvents is important as well. PEM swelling should depend on both the solvent and the hydrophobicity of the polyelectrolytes. Poptoshev et al. demonstrated that exposure of poly(ethyleneimine) (PEI)/PSS/PAH films to a solution of >40% ethanol in water collapses these films to essentially their dry thickness,[36] but another study suggests that thicker PSS/PAH films undergo only a 5% thickness reduction when immersed in ethanol rather than water.[41] Regardless, the permeability of solutes through PEMs will likely be significantly different in ethanol than in water.

Few publications link polyelectrolyte swelling and transport,[31,41−44] and many specialize in PEM capsules[41] or materials formed by precipitation of polyanion/polycation complexes,[42,44] rather than layer-by-layer adsorption. In this work, we attempt to directly correlate swelling with permeability data for three PEM systems: PSS/PAH, PSS/PDADMAC, and hyaluronic acid (HA)/chitosan. These systems were selected in part because they exhibit a wide range of transport properties, as reported previously.[9,11] For example HA/chitosan membranes have a molecular weight cutoff (MWCO, solute molecular weight required to achieve 90% rejection in NF) of >17000, while PSS/PAH films have a MWCO of 200.[9,11] Consistent with these transport data, this work shows that the percent swelling of HA/chitosan films in water is 4-fold greater than that for PSS/PAH. Remarkably, similarly striking differences in swelling and transport properties occur on going from a PSS-capped to a PDADMAC-capped PSS/PDADMAC film. Below, we examine swelling and transport as a function of deposition ionic strength, capping layer composition, and swelling solvent.

Experimental Section

Materials. Poly(styrene sulfonic acid) sodium salt (M_W 125000, Alfa Aesar), poly(diallyldimethylammonium chloride) (M_W 100000−200000, 20 wt % in water, Aldrich), poly(allylamine hydrochloride) (M_W 70000, Aldrich), chitosan (medium molecular weight, 75−85% deacetylated, Aldrich), hyaluronic acid (M_W 1500000−1800000, sodium salt, Fluka), polyethyleneimine (M_W 25000, Aldrich), NaCl (CCI), glycerol (anhydrous, CCI), glucose (Aldrich), sucrose (Aldrich), raffinose (Aldrich), hydrogen peroxide (30%, Jade Scientific), sulfuric acid (concentrated, CCI), and ethanol (Pharmco) were used as received. Deionized water (Milli-Q, 18.2 MΩ cm) was used for membrane rinsing, preparation of polyelectrolyte solutions, and aqueous swelling experiments.

Film Deposition. For swelling experiments, films were prepared on pieces of silicon wafers (Si(100), Silicon Quest International) that were first cleaned in a 3:1 solution of concentrated sulfuric acid and hydrogen peroxide. (Caution! This solution reacts violently with organic compounds and should be stored in slightly open containers!) Following copious rinsing with water, the wafers were dried in a stream of N_2 and then cleaned with UV/O_3 (Boekel UV-Clean model 135500) for 15 min. The cleaned silicon was immersed in 1 mg/mL PEI at pH 9 for 15 min to establish a dense, positively charged layer,[45] and films were then built on this precursor layer. For NF and DD experiments, porous alumina supports (0.02 μm Whatman Anodisc filters) were also UV/O_3 cleaned for 15 min, but because these supports are positively charged below pH 9,[46] no precursor PEI layer was necessary. The cleaned alumina membranes were subsequently placed in an O-ring holder so that the concentrate side of the alumina membrane contacted the deposition solution.

Synthesis of PSS/PDADMAC films began with a 3-min immersion of the substrate in an aqueous solution containing 0.02 M PSS (concentrations of polyelectrolytes are given with respect to the repeat unit) and 0.1 or 0.5 M NaCl. The substrate was then rinsed with deionized water for 1 min and dipped in a 0.02 M solution of PDADMAC in 0.1 or 0.5 M NaCl for 3 min. The sample was then rinsed again with deionized water for 1 min, and this entire process was repeated until the desired number of bilayers was deposited.

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PSS/PAH films were deposited using the same polyelectrolyte concentrations (no pH adjustment) and deposition times, except that films were only deposited from 0.5 M NaCl. HA/chitosan films were deposited using 5 min immersions of the PEI-coated silicon slides or bare alumina supports in pH 5 solutions containing 0.15 M NaCl and 1 mg/mL polyelectrolyte, with 1 min rinses with 0.15 M NaCl at pH 5 after polycation and polyanion adsorption. Films were rinsed with pure water and dried with N_2 only after all layers were deposited.

Ellipsometry. Ellipsometric thicknesses of the SiO_2 layers on Si wafers were first determined assuming literature values for the refractive indices of Si and SiO_2 at the 44 wavelengths of the ellipsometer (J.A. Woollam model M-44 rotating analyzer ellipsometer, 75° angle of incidence) between 414.0 and 736.1 nm. After coating of these wafers, film thicknesses under nitrogen ($<5\%$ relative humidity (RH)), water, or ethanol were obtained using a home-built cell with glass windows. The ellipsometric thicknesses and refractive indices of each type of film were determined at three different points per wafer on three different wafers, and the reported results are the averages and standard deviations of these values. Film thicknesses were also obtained in 55% RH (ambient) for comparison to AFM data. Optical constants of water as a function of wavelength were calculated using the Cauchy equation in coordination with constants in the literature.[47,48] For ethanol, literature optical constants were interpolated to obtain data at the ellipsometer wavelengths, but due to limited ethanol literature data, fitting of ellipsometric measurements in this solvent was performed only between 476.5 and 632.8 nm.[49] Swelling percentages were subsequently determined using eq 1.

$$\text{percent swelling} = \frac{\text{swollen thickness} - \text{dry thickness}}{\text{dry thickness}} \times 100\% \qquad (1)$$

Atomic Force Microscopy. AFM experiments (Digital Instruments Dimension 3100, Nanoscope III controller in Tapping Mode, TappingMode etched silicon probe tip, spring constant 20−100 N/m) were performed to validate the “dry” ellipsometric PEM thicknesses. Thicknesses were determined by scratching a film-coated Si wafer with Techni-Tool tweezers and scanning a 3×25 μm area over the scratch to produce an average line scan. A “step height” measurement subtracted the average height of the bare silicon wafer from the average height of the film on top of the wafer. Three PEM-coated wafers were each scanned three times (in different places) for every type of film examined in this study. The RMS roughness values were equal to or less than the standard deviation of the thickness measurements for all coatings except 4.5-bilayer PSS/PDADMAC films deposited from 0.5 M NaCl, which had an RMS roughness of 11% of the film thickness. Due to experimental constraints, the AFM thicknesses were measured at 54% RH and are compared to ellipsometric thicknesses measured at 55% RH.

Transport Experiments. Film permeation properties were investigated by DD and cross-flow NF experiments, some of which were reported previously.[9] New data reported here include all DD in ethanol, aqueous dialysis with the PSS/PAH and HA/chitosan systems, and NF data for PSS/PAH. Diffusion dialysis was performed using a glass apparatus in which the membrane separated a source phase from a receiving phase that was initially deionized water or pure ethanol.[9,11] In water, source-phase solutions for all PSS/PAH films, PDADMAC-capped PSS/PDADMAC films deposited from 0.5 M NaCl, and HA/chitosan films contained 5 mM glycerol, glucose, sucrose, and raffinose, while DD solutions for PSS/PDADMAC films deposited from 0.1 M NaCl and PSS-capped PSS/PDADMAC films deposited from 0.5 M NaCl contained 5 mM glycerol, glucose, and sucrose and 15 mM raffinose. For ethanol-based diffusion dialysis, the feed contained only 140 μM glucose, sucrose, and raffinose because of the low solubility of these compounds. Because glycerol was not present in all solutions (it coelutes with ethanol during analysis), its transport rates are not reported. When present, glycerol was always the fastest transporting solute. Samples were collected every 10−30 min and subsequently analyzed by liquid chromatography (Dionex, DX-600, CarboPac PA-10 column, 100 mM NaOH mobile phase) with integrated amperometric detection (Dionex, ED-50).

Nanofiltration experiments occurred at a pressure of 4.8 bar (70 psi), and feed solutions were flowed across the membrane at a rate of 18 mL/min.[8,9,11] NF rejection is defined by eq 2, where R is the percent solute rejection and C_{perm} and C_{feed} are the concentrations of the solute in the permeate and the feed, respectively. The NF feed solutions contained 1 mM glycerol, glucose, sucrose, and raffinose for PSS/PDADMAC as well as HA/chitosan films, and 1 mM glycerol and glucose with 5 mM sucrose and raffinose for PSS/PAH films. The system was equilibrated for 18 h before permeate samples were acquired.

$$R = \left(1 - \frac{C_{\text{perm}}}{C_{\text{feed}}}\right) \times 100\% \qquad (2)$$

Results and Discussion

Swelling. Ellipsometry, which involves the measurement of the ratios of the complex reflection coefficients for p- and s-polarized light, served as the primary tool for ascertaining the extent of film swelling. From the phase difference, Δ, and the ratio of amplitudes, tan Ψ, of the two reflection coefficients, one can calculate film thickness and refractive index using a model that sums the many individual reflections in the system (see Figure SI-1 in Supporting Information). In the particular case of coatings on Si wafers, this model includes both film and SiO_2 layers on the substrate, so oxide layer thicknesses were determined prior to deposition of films. To examine the reliability of ellipsometric data, we calculated how the ellipsometric parameters Δ and Ψ vary with coating refractive index and thickness in nitrogen, water, and ethanol. Figure 1 and Figures SI-2 and SI-3 of Supporting Information show examples of simulations where the film is immersed in water, nitrogen ($<5\%$ relative humidity), and ethanol. With a possible error of 0.3° in Δ and Ψ due to both window effects and measurement uncertainty, the simulations show that film thicknesses and refractive indices can be determined to at least $\pm 5\%$ and ± 0.01, respectively, in both water and ethanol. For “dry” films, thicknesses and refractive indices can be determined to $\pm 5\%$ and ± 0.04, respectively.

To further validate the ellipsometric results, we determined PEM thicknesses using atomic force microscopy (AFM) images of intentionally scratched PEM-coated Si wafers. A typical AFM image can be found in Figure SI-4 of Supporting Information. AFM-derived thicknesses for PSS/PDADMAC deposited from 0.1 M NaCl, $[\text{PSS/PDADMAC}]_4$PSS deposited from 0.5 M NaCl, and HA/chitosan films were

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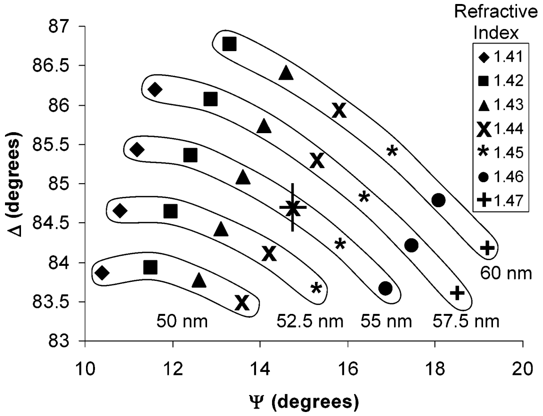

Figure 1. Calculated Ψ and Δ values for a Si/SiO$_2$/film system (water as the ambient medium and a 2.0 nm silicon oxide layer) as a function of the refractive index and thickness of the film. The simulation was performed at a wavelength of 450.5 nm where the optical constants are as follows: water $-$ $n = 1.3395$, silicon oxide $-$ $n = 1.4644$, $k = 0$, and silicon $-$ $n = 4.7108$, and $k = 0.0963$. The point with a thickness of 55 nm and a refractive index of 1.44 represents a 9.5-bilayer PSS/PDADMAC film deposited from 0.1 M NaCl, and the black lines through that point show the ±0.3° uncertainty in Ψ and Δ measurements. Enclosed data points correspond to identical thicknesses at different refractive indices.

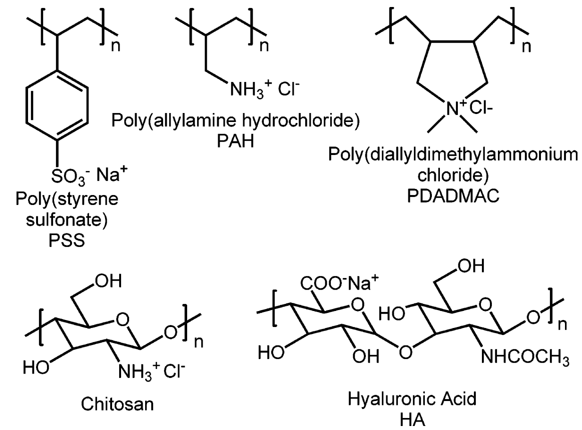

Figure 2. Structures of the polyelectrolytes used in this work.

consistently 10−15% greater than the ellipsometric thicknesses acquired at a similar relative humidity. AFM-derived thicknesses for [PSS/PDADMAC]$_4$ deposited from 0.5 M NaCl and PSS/PAH films were not significantly different from ellipsometrically determined thicknesses. The positive deviation of AFM thicknesses from ellipsometric thicknesses has been reported before[50] and could result from scratching of the underlying SiO$_2$ layer or deposition of the removed material on the nearby film. In any case, the ellipsometric measurements are validated by the reasonable agreement between ellipsometric and AFM methods. One assumption in most ellipsometric thickness determinations is that films are smooth and uniform. The RMS roughness values of PSS/PAH, PSS/PDADMAC, and HA/chitosan films were always less than 15% of film thickness.

Table 1 shows the ellipsometric thicknesses of PSS/PAH, PSS/PDADMAC, and HA/chitosan films under nitrogen (<5% RH), water, and ethanol (see Supporting Information Figures SI-5, SI-6, and SI-7 for some typical experimental and fitting data for "dry," water-submerged, and ethanol-submerged films). The numbers of bilayers in these films were chosen such that all coatings would have similar thicknesses. There are clear variations in percent swelling as a function of both the constituent polyelectrolytes and the swelling solvent. Figure 2, which presents the structures of the constituent polyelectrolytes, shows that chitosan, PDADMAC, and PAH contain one positive charge per 11, 9, and 4 non-hydrogen atoms, respectively. In the case of the polyanions, PSS contains one negative charge per 12 non-hydrogen atoms, while HA has only one charge per 26 non-hydrogen atoms. Thus, if swelling increases with decreasing charge density on the polyelectrolytes (due to a lower density of ionic cross-links), HA/chitosan should swell much more than PSS/PDADMAC, which should swell more than PSS/PAH, and this is generally the case in water, though swelling in ethanol is complicated by other factors. The especially low charge density on HA and chitosan results in films that are nearly 80% water. In accord with such a high water content, refractive indices at 603.1 nm for swollen [HA/chitosan]$_7$HA films are only 1.382. (At the same wavelength, dry [HA/chitosan]$_7$HA films have a refractive index of 1.53, while the refractive index of water is 1.333.) For all types of water-swollen or ethanol-swollen films, the refractive index is essentially a linear combination of the refractive indices of water and the dry film, as described by eq 3 where T_{sf} and T_{df} are the thickness of the swollen film and the dry film, respectively, and n_{sf}, n_{df}, and n_{s} are the refractive indices of the swollen film, the dry film, and the swelling solvent (ethanol or water), respectively. Estimations of n_{sf} calculated with eq 3 vary from ellipsometrically determined n_{sf} values by less than 1.5% in water and less than 3% in ethanol.

$$T_{\mathrm{sf}}n_{\mathrm{sf}} = (T_{\mathrm{sf}} - T_{\mathrm{df}})n_{\mathrm{s}} + T_{\mathrm{df}}n_{\mathrm{df}} \tag{3}$$

In most cases, the difference in swelling between films terminated with a polycation and a polyanion is not statistically significant. This is consistent with previous studies that suggest that although water uptake can depend on the composition of the terminating layer in PSS/PAH films,[29,30,51]

Table 1. Ellipsometric Thicknesses of PEMs under Nitrogen (<5% RH), Water, or Ethanol, and Percent Swelling in the Two Solvents

film type	dry film thickness (nm)	film thickness in H$_2$O (nm)	percent swelling in H$_2$O	film thickness in ethanol (nm)	percent swelling in ethanol
[HA/chitosan]$_8$	24 ± 4	118 ± 9	390 ± 50	55 ± 1	130 ± 20
[HA/chitosan]$_7$HA	24 ± 3	118 ± 6	390 ± 40	55 ± 3	130 ± 20
[PSS/PDADMAC]$_4$ from 0.5 M NaCl	20 ± 1	95 ± 9	380 ± 60	30 ± 1	54 ± 10
[PSS/PDADMAC]$_4$PSS from 0.5 M NaCl	24.4 ± 0.4	50 ± 2	106 ± 9	33 ± 2	37 ± 8
[PSS/PDADMAC]$_{10}$ from 0.1 M NaCl	24.7 ± 0.9	57 ± 1	129 ± 7	52 ± 1	110 ± 7
[PSS/PDADMAC]$_9$PSS from 0.1 M NaCl	24 ± 1	54 ± 1	124 ± 8	51.2 ± 0.5	112 ± 5
[PSS/PAH]$_{10}$	25.2 ± 0.7	51 ± 1	101 ± 6	49 ± 2	94 ± 8
[PSS/PAH]$_9$PSS	25.1 ± 0.5	49 ± 2	95 ± 9	49 ± 3	96 ± 13

Table 2. Percent Rejection in Nanofiltration of Glucose, Sucrose, and Raffinose Dissolved in Water[a]

film type	percent swelling in water	percent rejection		
		glucose	sucrose	raffinose
[HA/chitosan]$_8$HA	390 ± 40	<12%	<12%	<12%
[PSS/PDADMAC]$_4$ from 0.5 M NaCl	380 ± 60	17 ± 4	28 ± 9	36 ± 8
[PSS/PDADMAC]$_4$PSS from 0.5 M NaCl	106 ± 9	64 ± 6	97.2 ± 0.9	98.9 ± 0.7
[PSS/PDADMAC]$_5$ from 0.1 M NaCl	129 ± 7	44 ± 5	85 ± 2	91.3 ± 0.8
[PSS/PDADMAC]$_5$PSS from 0.1 M NaCl	124 ± 8	58 ± 6	96 ± 2	98.8 ± 0.6
[PSS/PAH]$_5$	101 ± 6	91.3 ± 0.6	99.6 ± 0.1	99.8 ± 0.1
[PSS/PAH]$_5$PSS	95 ± 9	88 ± 1	99.70 ± 0.09	99.90 ± 0.07

[a] PSS/PDADMAC and HA/chitosan data are from a previous publication.[9] The swelling values are from analogous films (Table 1).

the solvent fraction in PAH-capped films is only 25% less than that in PSS-capped films (40% versus 30% water as a function of capping layer).[29,30] PSS/PDADMAC films deposited from 0.5 M NaCl are a notable exception to the phenomenon of capping layer choice not affecting swelling. The water uptake in [PSS/PDADMAC]$_4$ films prepared in 0.5 M NaCl is almost 4-fold greater than that in the corresponding [PSS/PDADMAC]$_4$PSS films. We speculate that this occurs because the PDADMAC penetrates the entire film and disrupts ionic cross-linking. This is similar to the explanation for the rapid, exponential (as a function of the number of adsorption steps) growth of some PEMs.[52,53] Indeed, PSS/PDADMAC films grown in >0.3 M NaCl do show exponential growth, while films grown in 0.1 M NaCl do not.[54] Consistent with PDADMAC penetrating the entire film, Smith et al. used ^{13}C solid-state NMR to show that PDADMAC is more mobile than PSS in PSS/PDADMAC films.[55] This high mobility was attributed to the low glass transition temperature of PDADMAC, which is below room temperature when there is >20% water content.[55,56] McCormick et al. also reported an increase in both water and PDADMAC mobility in PSS/PDADMAC films when PDADMAC is the top layer.[57]

Interestingly, in ethanol, there is only a small difference between the swelling of [PSS/PDADMAC]$_4$ and [PSS/PDADMAC]$_4$PSS prepared in 0.5 M NaCl (54 versus 37%), and the swelling of both of these films is only one-third to one-half of that for corresponding coatings prepared in 0.1 M NaCl. Films deposited from 0.1 M NaCl likely swell more in ethanol because they contain fewer ion-exchange sites and are less hydrophilic than films deposited from 0.5 M NaCl. The hydrophilic, nonpolyelectrolyte-paired (ion-exchange) charged groups in PSS/PDADMAC films deposited from 0.5 M NaCl likely make them less susceptible to swelling in ethanol.[37] Moreover, ethanol may not lower the glass transition temperature of PDADMAC the same way that water does, which could decrease chain mobility and reduce swelling. NMR studies of PEMs in ethanol could reveal if the lack of swelling in PSS/PDADMAC deposited from 0.5 M NaCl correlates with a lack of PDADMAC mobility.[57] HA/chitosan films also swell less in ethanol than in water, and this likely reflects the fact that ethanol is a poorer solvent for these hydrophilic polymers. Additionally, increased ion pairing (cross-linking) may occur in the presence of ethanol. In the case of films that are already heavily cross-linked in water (PSS/PAH and PSS/PDADMAC deposited from 0.1 M NaCl), swelling is similar in ethanol and water.

Below, we compare swelling and transport results. For HA/chitosan and PSS/PDADMAC deposited from 0.5 M NaCl, films used in transport and swelling experiments had essentially the same number of bilayers, but in the case of PSS/PDADMAC deposited from 0.1 M NaCl and PSS/PAH, more bilayers were used in ellipsometric than in transport studies. This was necessary because ellipsometric measurements require relatively thick films for accurate refractive index and thickness determinations, but overly thick films severely retard flux in transport experiments. PSS/PDADMAC deposited from 0.1 M NaCl and PSS/PAH are less permeable than the other systems, so the minimal thickness required for accurate transport experiments with these films was not sufficient for ellipsometric thickness determinations in solvents. A previous study showed that the permeability of PSS/PDADMAC is constant after the deposition of 5 to 6 bilayers,[58] so we expect that the swelling of 9.5- and 10-bilayer films should still be relevant to transport through 5- and 5.5-bilayer systems. Our previous NF studies also indicated that solute rejections by PSS/PDADMAC films deposited from 0.1 M NaCl did not change on going from 5.5 to 6.5 bilayer films.[9]

Transport Experiments in Water. Large changes in swelling by water correlate well with both NF and DD data. Table 2 shows that the rejections of glucose, sucrose, and raffinose in NF generally increase as film swelling decreases, as would be expected. Highly swollen [HA/chitosan]$_8$HA films show essentially no rejection of any of the sugars, while the least swelling system, PSS/PAH, rejects 99.6−99.7% of sucrose. DD data (Table 3) confirm the trends seen in NF. With the possible exception of the comparison of PSS/PAH films with PSS-capped PSS/PDADMAC deposited from 0.5 M NaCl (the swelling is similar between the films), fluxes of glucose, sucrose, and raffinose all increase with increasing film swelling, even though the more swollen HA/chitosan and PSS/PDADAMC films prepared in 0.5 M NaCl are about 1.5 to 2-fold thicker than the other films. DD fluxes through

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Table 3. Fluxes in Diffusion Dialysis of Glucose, Sucrose, and Raffinose (Dissolved in Water) through Porous Alumina Coated with Various Polyelectrolyte Films[a]

film type	film thickness (nm)	percent swelling in H_2O[c]	normalized flux[b] (nmol cm^{-2} s^{-1} M^{-1}) glucose	sucrose	raffinose
bare alumina	N/A	N/A	180 ± 20	140 ± 20	120 ± 10
[HA/chitosan]$_8$HA	~25	390 ± 40	180 ± 30	140 ± 20	110 ± 20
[HA/chitosan]$_8$	24 ± 4	390 ± 50	180 ± 20	131 ± 9	110 ± 10
[PSS/PDADMAC]$_4$ from 0.5 M NaCl	20 ± 1	380 ± 60	150 ± 10	120 ± 10	95 ± 9
[PSS/PDADMAC]$_4$PSS from 0.5 M NaCl	24.4 ± 0.4	106 ± 9	90 ± 10	7 ± 2	0.3 ± 0.1
[PSS/PDADMAC]$_6$ from 0.1 M NaCl	15 ± 1	129 ± 7	90 ± 10	24 ± 2	1.9 ± 0.1
[PSS/PDADMAC]$_5$PSS from 0.1 M NaCl	12 ± 1	124 ± 8	90 ± 4	11 ± 2	0.5 ± 0.3
[PSS/PAH]$_5$	12.5 ± 0.6	101 ± 6	43 ± 3	1.2 ± 0.4	0.6 ± 0.4
[PSS/PAH]$_5$PSS	13.1 ± 0.4	95 ± 9	56 ± 9	1.1 ± 0.7	0.5 ± 0.5

[a] The bare alumina and PSS/PDADMAC data are from a previous publication.[9] All film thicknesses were measured in a <5% RH nitrogen atmosphere except for that of [HA/chitosan]$_8$HA, which is an estimate based upon the thickness of 8-bilayer HA/chitosan films. [b] Fluxes were normalized by dividing by the source-phase concentration at the end of the experiment. [c] Values are taken from Table 1 and were measured with films that in some cases had different thicknesses than those used here.

Table 4. Fluxes in Diffusion Dialysis of 140 μM Glucose, Sucrose, and Raffinose in Ethanol through Porous Alumina Coated with Various Polyelectrolyte Films[a]

film type	film thickness (nm)	percent swelling in ethanol[c]	normalized flux[b] (nmol cm^{-2} s^{-1} M^{-1}) glucose	sucrose	raffinose
bare alumina	N/A	N/A	210 ± 20	180 ± 40	190 ± 20
[HA/chitosan]$_8$HA	~25	130 ± 20	100 ± 30	40 ± 20	30 ± 10
[HA/chitosan]$_8$	24 ± 4	130 ± 20	40 ± 20	30 ± 20	30 ± 20
[PSS/PDADMAC]$_5$ from 0.5 M NaCl	27.3 ± 0.9	54 ± 10	150 ± 10	110 ± 10	100 ± 20
[PSS/PDADMAC]$_5$PSS from 0.5 M NaCl	31.8 ± 0.6	37 ± 8	74 ± 6	19 ± 2	28 ± 2
[PSS/PDADMAC]$_6$ from 0.1 M NaCl	15 ± 1	110 ± 7	50 ± 10	<4[d]	<4[d]
[PSS/PDADMAC]$_5$PSS from 0.1 M NaCl	12 ± 1	112 ± 5	40 ± 10	<4[d]	<4[d]
[PSS/PAH]$_5$	12.5 ± 0.6	94 ± 8	13.1 ± 0.1	<4[d]	<4[d]
[PSS/PAH]$_5$PSS	13.1 ± 0.4	96 ± 13	10.4 ± 0.1	<4[d]	<4[d]

[a] All film thicknesses were measured in a <5% RH nitrogen atmosphere except for that of [HA/chitosan]$_8$HA, which is an estimate based upon the thickness of 8-bilayer HA/chitosan films. [b] Fluxes were normalized by dividing by the source-phase concentration at the end of the experiment. [c] Values are taken from Table 1 and were measured with films that in some cases had different thicknesses than those used here. [d] Lower limits of measurable, normalized flux are higher in ethanol than in water because of limited sugar solubility in ethanol.

both HA-terminated and chitosan-terminated HA/chitosan films are essentially the same as those through bare alumina. This is not surprising considering the low (<12%) rejection of sugars in NF and the rapid passage of molecules as large as myoglobin through HA/chitosan films.[9]

For the PSS/PDADMAC systems, the transport data demonstrate that variations in film permeability can occur upon changing the top layer in the film from a polycation to a polyanion. On going from PDADMAC-capped to PSS-capped PSS/PDADMAC films made in 0.5 M NaCl, sucrose rejection in NF increases from 28 to 97% (Table 2), and fluxes in DD decrease by factors of 1.7, 17, and 300 for glucose, sucrose, and raffinose, respectively (Table 3). This correlates well with the almost 4-fold decrease in swelling that occurs upon addition of a PSS capping layer. A similar, though smaller, effect occurs for PSS/PDADMAC films prepared in 0.1 M NaCl, but in this instance the differences in the rejections and fluxes exhibited by PSS-terminated and PDADMAC-terminated films are larger than what one might expect, given the insignificant differences in their water uptake. Other factors such as polymer intermingling and chain mobility probably affect the permeability of these films. As discussed earlier, previous NMR experiments indicate that the PDADMAC portions of PSS/PDADMAC films are more mobile when the entire film is terminated in PDADMAC.[55,57]

The aqueous NF and DD data show that PEMs can exhibit extraordinarily diverse permeability properties ranging from nearly complete rejection to nearly complete passage of sugar molecules, depending on polyelectrolyte type, top-layer choice, and deposition conditions.[9,11] However, many processes are incompatible with water, and aqueous data may not describe PEM behavior in organic solvents.[41] Thus, we investigated diffusion dialysis through PSS/PAH, PSS/PDADAMC, and HA/chitosan films in ethanol.

Diffusion Dialysis in Ethanol. Table 1 shows that there is less swelling of PEMs in ethanol than in water, particularly for the highly water-swollen films [HA/chitosan]$_8$, [HA/chitosan]$_7$HA, and [PSS/PDADMAC]$_4$ prepared in 0.5 M NaCl. Still, there is a significant variation in ethanol swelling among the polyelectrolyte systems, ranging from 37% for [PSS/PDADMAC]$_4$PSS deposited from 0.5 M NaCl to 130% for HA/chitosan films. Nevertheless, DD data in ethanol exhibit minimal correlation between fluxes and film swelling (Table 4). For example, polycation-capped [PSS/PDADMAC]$_4$ films swell slightly more in ethanol than [PSS/PDADMAC]$_4$PSS films (both prepared in 0.5 M NaCl), and glucose, sucrose, and raffinose DD fluxes through [PSS/PDADMAC]$_5$PSS and [PSS/PDADMAC]$_5$ films differ by factors of 2, 6, and 4, respectively. However, the more highly swollen PSS/PAH and PSS/PDADMAC films deposited from 0.1 M NaCl exhibit less sugar flux than either of the less swollen PSS/PDADMAC films deposited from higher ionic strength. Moreover, fluxes through [HA/chitosan]$_8$ films are 70−75% lower than those through [PSS/PDADMAC]$_5$ deposited from 0.5 M NaCl, even though the HA/chitosan swells over twice as much, and the thicknesses of these films differ by only 15%.

In contrast to PSS/PDADMAC prepared in 0.5 M NaCl, HA/chitosan films show significant (2-fold) *decreases* in glucose fluxes in ethanol when the outer layer of the film is a polycation rather than a polyanion (Table 4). Again, however, these trends do not correlate with swelling, as the solvent uptake of these films does not depend significantly on the composition of the top layer. PSS/PAH films show a slightly higher glucose flux when capped by the polycation, but the differences in swelling are negligible. We think that the ethanol swelling reflects a trade-off between ionic cross-linking and film hydrophilicity. Highly cross-linked films may be more hydrophobic and soluble in ethanol, and this may oppose the reduction of swelling due to ionic cross-links, even though cross-linking could slow transport by limiting chain mobility. In contrast, such an effect would amplify decreases in aqueous swelling that result from ionic cross-linking, and in that case, we do see a strong correlation between swelling and flux.

Conclusions

Swelling of PEMs in water increases as the density of charge on constituent polyelectrolytes decreases, and increased water uptake generally leads to decreased sugar rejections in NF and higher solute fluxes in diffusion dialysis. Presumably, higher swelling occurs when fewer ionic cross-links and/or many hydrophilic ion-exchange sites are present in the film. With PSS/PDADMAC films prepared in 0.5 M NaCl, water uptake can vary 4-fold depending on whether the capping layer is a polycation or a polyanion, and the higher water content leads to minimal sugar rejections in NF. Solvent uptake is generally smaller with ethanol than water, and there is no clear correlation between ethanolic DD data and swelling.

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Supporting Information Available: Six additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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