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Facilitated ion transport through polyelectrolyte multilayer films containing metal-binding ligands



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ABSTRACT

Alternating layer-by-layer adsorption of poly[(*N,N'*-dicarboxymethyl) allylamine] (PDCMAA) and protonated poly(allylamine) (PAH) at low pH yields thin films with abundant Cu^{2+} -binding sites. When deposited on porous alumina substrates, (PDCMAA/PAH)₃PDCMAA or (PDCMAA/PAH)₄ films show average $\text{Cu}^{2+}/\text{Mg}^{2+}$ diffusion dialysis selectivities around 50. PDCMAA/PAH membranes also exhibit $\text{Cu}^{2+}/\text{Ni}^{2+}$ and $\text{Cu}^{2+}/\text{Ca}^{2+}$ selectivities > 10. The high $\text{Cu}^{2+}/\text{Mg}^{2+}$ selectivity despite similar aqueous diffusion coefficients and equal charges for the two ions suggests a facilitated transport mechanism. For comparison, poly(styrene sulfonate)/PAH films with 7 bilayers show $\text{Cu}^{2+}/\text{Mg}^{2+}$ selectivities around 10, perhaps also due to facilitated transport via PAH. With PDCMAA/PAH membranes, Cu^{2+} flux increases nonlinearly with increasing CuCl_2 concentrations in the feed. Sorption isotherms show that PDCMAA/PAH films contain both strong and weak binding sites, and the nonlinear increase in flux with increasing CuCl_2 feed concentration likely represents hopping between weak binding sites, probably the amine groups of PAH. Strong binding of Cu^{2+} to PDCMAA may displace ionic cross-links in the film and create free amine groups for facilitated transport. Additionally, Cu^{2+} binding to the film suppresses Mg^{2+} transport, either through electrostatic exclusion or occupation of hopping sites.

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1. Introduction

Layer-by-layer adsorption of oppositely charged polyelectrolytes [1,2] offers a simple and versatile way to form functional thin films on porous membrane supports. Moreover, variation of the polyelectrolyte composition [3], deposition conditions [4] and post-deposition treatments [5] affords control over the thickness, permeability and charge density of the polyelectrolyte multilayers (PEMs). Several research groups investigated the permeability of PEM-coated membranes in pervaporation [6,7], gas separations [8,9] and various separations with dissolved ions [10–17]. In particular, in nanofiltration [18–20] PEMs allow selective passage of monovalent ions over multivalent ions, which is important in water softening, and the minimal PEM thickness affords high water permeabilities [20,21]. The monovalent/divalent ion selectivity may stem from differences in either ion hydration or electrostatic exclusion for the two types of ions [22]. However, for ions with the same charge and similar hydrated radii, e.g. Cu^{2+} and Mg^{2+} , PEMs will likely show minimal

selectivity. Thus, typical PEM membranes would likely not prove useful in applications such as selective metal recycling and removal of specific transition metal ions from waste streams.

Facilitated transport through membranes can address the challenge of obtaining selectivity when separating ions with the same charge and comparable hydrated radii. This type of transport relies on ion complexation in the membrane along with either ligand diffusion across the membrane or ion hopping between immobile binding sites [23–26]. The development of facilitated transport has progressed from liquid membranes [27] to supported liquid membranes [28,29] to polymer inclusion membranes [30] and molecularly imprinted membranes [31]. Nevertheless, most facilitated transport systems still suffer from limited stability, selectivity or permeability. PEM membranes may overcome some of the stability issues that plague liquid membranes, and the low thickness of these films will enhance permeance relative to thicker solid membranes.

Development of facilitated transport through PEMs requires polyelectrolytes that bind metal ions and allow hopping between binding sites. Additionally, the rate of diffusion of uncomplexed ions through these films must be much lower than the rate of facilitated transport. Schlenoff et al. suggest that ions pass through PEMs via hopping between ion-exchange sites created by dissociation of polymeric ion pairs at high ionic strength [32]. Unfortunately, such a mechanism will not likely provide high selectivities among ions with the same charge unless complexation occurs.

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¹ Professor Baker passed away unexpectedly on October 17, 2012. We dedicate this work as a memorial to him.

Tieke et al. described the formation of membranes through alternating adsorption of charged macrocyclic compounds, i.e. calixarenes, azacrowns and cyclodextrins, and oppositely charged polyelectrolytes [3,11,33–35]. However ions that specifically interact with the macrocycles, especially calixarenes, pass through these membranes more slowly than through the macrocycle-free PEM membranes. Additionally, the selectivities among ions with the same charge, either monovalent or divalent, are < 5 .

This paper reports the formation of membranes through layer-by-layer adsorption of poly[(*N,N'*-dicarboxymethyl) allylamine] (PDCMAA) and protonated poly(allylamine) (PAH). Fig. 1 shows the structures of these polymers. PDCMAA contains iminodiacetic acid (IDA) groups that strongly bind Cu^{2+} , and at high concentrations Cu^{2+} may also interact with the amine groups of PAH. In prior work we found that PDCMAA/PAH films bind Cu^{2+} at levels as high as 2.5 mmol per cm^3 of film [36]. Remarkably, this study shows that PDCMAA/PAH membranes exhibit $\text{Cu}^{2+}/\text{Mg}^{2+}$ diffusion dialysis selectivities around 50. For comparison, poly(styrene sulfonate) (PSS)/PAH multilayer films show typical selectivities around 10. Sorption isotherms for Cu^{2+} and measurements of transport rates as a function of feed concentration suggest that facilitated transport may proceed via the amine sites in PDCMAA/PAH films.

2. Experimental

2.1. Materials

Poly(allylamine hydrochloride) ($M_w = 120,000\text{--}200,000$ Da) was purchased from Polysciences, and PDCMAA was synthesized as described previously [36]. Poly(sodium 4-styrene sulfonate) ($M_w = 70,000$ Da), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NiCl_2 and 3-mercaptopropionic acid (MPA) were obtained from Sigma-Aldrich or Spectrum, and all reagents were used without further purification. Ethylenediaminetetraacetic acid disodium salt (EDTA-Na_2) was purchased from Jade Scientific, and aqueous solutions were prepared with deionized water (18 M Ω cm, Milli-Q). Alumina membrane supports (Anodisc, pore diameter = 0.02 μm) were purchased from Whatman, and colloidal silica nanoparticles (70–100 nm, SNOWTEX-ZL) were obtained from Nissan Chemical Industries.

2.2. Film preparation and characterization

PEMs were first deposited on Au-coated wafers (200 nm of Au sputtered on 20 nm of Cr on Si(100)) for determination of ellipsometric film thicknesses. The Au-coated wafers were cleaned with UV/ozone for 15 min before a 30 min immersion in 5 mM MPA in ethanol, followed by rinsing with ethanol and then water for 1 min each, and drying under a N_2 stream. The MPA-modified wafer was immersed in a PAH solution for 5 min, rinsed with water from a squirt bottle for 1 min, immersed in a polyanion solution (PSS or PDCMAA) for 5 min, and rinsed again. The dip-and-rinse process was continued to deposit the desired number of polyelectrolyte bilayers. Adsorption of PEMs on porous alumina membranes followed essentially the same procedure starting with polyanion adsorption. The alumina membrane was placed in a holder that exposed only the top of the membrane to the solutions. All polyelectrolyte solutions contained 0.01 M polymer repeating units and 0.5 M NaCl. The pH of these solutions was adjusted to 3 with 0.1 M HCl or 0.1 M NaOH. The addition of NaCl to deposition solutions results in differences in IR spectra and ellipsometric thicknesses compared to our previous work that employed adsorption from solutions containing no added salt [36]. The 0.5 M NaCl in deposition solutions may also lead to more IDA sites that do not form electrostatic complexes with PAH [37]. In one

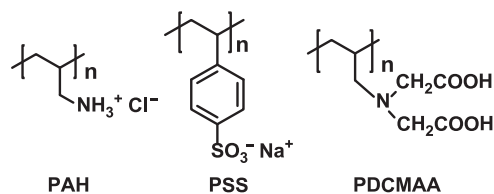


Fig. 1. Structures of the polymers employed to prepare PEMs.

case, we used the same membrane in more than 8 consecutive dialysis experiments without losing high selectivity. Previous work showed that in cross-flow nanofiltration PEMs are stable for several days [13].

In modification of silica nanoparticles, 50 mL of a 0.01 M PAH, 0.5 M NaCl solution (pH = 3) was added to 0.1 g of silica colloids in a centrifuge tube. This mixture was sonicated for 5 min, and the adsorption solution was left to stand for 10 min with continuous stirring. The solution was then centrifuged for 10 min at 3000 rpm. After the supernatant was removed, 20 mL of water was added to the sample, and the solution was sonicated for 5 min and again centrifuged prior to removal of the supernatant. Subsequently, 50 mL of a 0.01 M PDCMAA, 0.5 M NaCl solution (pH = 3) was added to the remaining colloidal solution, and adsorption and rinsing proceeded as with PAH deposition. Similar adsorption and washing steps were performed to prepare PAH/PDCMAA coatings with 10 bilayers. The procedure was performed with 12 centrifuge tubes to obtain the required quantity of modified particles.

Thicknesses of films deposited on Au-coated wafers were determined using a rotating analyzer ellipsometer (J.A. Woollam model M-44), assuming a refractive index of 1.5 for the dry films. Reflectance Fourier transform infrared spectra of these films were obtained with a Thermo Scientific Nicolet 6700 FT-IR spectrometer (80° incident angle, Pike grazing angle apparatus) with a MCT detector. A UV/ozone-cleaned Au-coated wafer served as a background. UV–vis spectra of Cu^{2+} -containing solutions were acquired with a PerkinElmer UV/VIS spectrophotometer (Lambda 25).

2.3. Diffusion dialysis

Diffusion dialysis studies were carried out in a home-made apparatus that consists of feed and permeate chambers separated by a membrane with the PEM facing the feed solution [38]. Initially, 90 mL of salt solution and 90 mL of deionized water were added to the feed and permeate chambers, respectively, and the two solutions were stirred vigorously throughout the experiment. The specific compositions and pH values of the feed solutions are provided for each experiment in the results and discussion section. An aqueous 0.1 M MgCl_2 solution has a pH of 6.4, whereas 0.1 M CuCl_2 has a pH of 3.6 due to water hydrolysis by Cu^{2+} . A solution containing both 0.1 M MgCl_2 and 0.1 M CuCl_2 also has a pH of 3.6. For analysis, 1-mL aliquots were removed from the permeate chamber approximately every 5 min for 40–60 min. To balance the water level in the two chambers, 1 mL of solution was simultaneously removed from the feed. The permeate aliquots were diluted 10-fold with 2% nitric acid and analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (Axial ICP-OES, Varian 710-ES). Over the course of these experiments, the salt concentration in the permeate was always small compared to that in the feed so the concentration gradient and the flux across the membrane were essentially constant. Thus when normalized to the exposed membrane area (2.1 cm^2), the slopes in plots of moles of ion passed through the membrane versus time gave values for ion fluxes. Between diffusion dialysis with different solutions, the membrane and cells were rinsed with deionized water. Unless

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