

다층 고분자 전해질 막의 나노여과 특성에 미치는 지지체의 영향

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Effects of Substrates on Nanofiltration Characteristics of Multilayer Polyelectrolyte Membranes

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요약: 선행 연구에서 poly(styrene sulfonate) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC) 나노 여과막을 사용하여 불소 이온을 포함한 1가 이온 혼합물을 분리하는 것이 가능함을 보였다. 예를 들면, 다공성 알루미나 지지체에 (PSS/PDADMAC)₄PSS 필름을 코팅한 경우 염소/불소 이온의 선택도가 3 이상이었으며, 4.8 bar에서 용액의 플럭스가 3.5 m³/m²-day이었다. 그러나, PSS/PDADMAC 이층의 수가 4.5에서 5.5로 증가하면 염소/불소 이온의 선택도가 1.9로 떨어졌으며, (PSS/PDADMAC)₆PSS 필름의 경우에는 염소 이온의 배제율이 급속히 증가하면서 선택도가 1에 가까웠다. 이러한 선택도의 감소 현상은 예상치 못한 것으로서 다른 지지체를 사용하여도 같은 경향을 보이는지 여부는 불분명하였다. 따라서, 본 연구에서는 다공성 알루미나 대신에 분획 분자량이 50 kDa인 다공성 polyethersulfone (PES)에 PSS/PDADMAC을 적층하고 불소/염소 이온 혼합물의 나노 여과 특성을 살펴보았다. 그 결과 다공성 알루미나의 경우와 비록 적층 수는 달랐으나 불소 이온의 배제율이 최대가 되는 최적 적층수가 존재하였으며 이로부터 이러한 현상이 지지체에 무관한 일반적인 사실임을 알 수 있었다.

Abstract: In a previous study, we probed the potential of poly(styrene sulfonate) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC) nanofiltration (NF) membranes for the separation of monovalent anions, with an emphasis on the selective rejection of F⁻. Remarkably, deposition of (PSS/PDADMAC)₄PSS films on porous alumina supports yielded membranes that exhibited Cl⁻/F⁻ selectivity > 3 with minimal Cl⁻ rejection, and a solution flux of 3.5 m³/m²-day at 4.8 bar. When the number of PSS/PDADMAC bilayers was increased from 4.5 to 5.5, however, F⁻ rejection decreased from 73% to 50% and Cl⁻/F⁻ selectivity dropped to 1.9. Addition of another bilayer to form (PSS/PDADMAC)₆PSS films resulted in a significant increase in Cl⁻ rejection to give essentially no Cl⁻/F⁻ selectivity. The decrease of selectivity with deposition of more than 4.5 bilayers was not expected and it was unclear whether this characteristic was substrate independent. In this study, to investigate the effect of substrates on NF performance of multilayer polyelectrolyte membranes, PSS/PDADMAC films were deposited on 50 kDa polyethersulfone (PES) ultrafiltration supports instead of porous alumina supports. The results indicate that, although fluoride rejection and the number of bilayers at which a maximum F⁻ rejection occurs are different, the trend is similar for both types of substrates. Therefore, we can conclude that the NF characteristics of multilayer polyelectrolyte membranes may be substrate independent.

Keywords: nanofiltration, membranes, polyelectrolytes, anions, substrates

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1. Introduction

For many years, nanofiltration (NF) has received much attention in the separation process area [1-3]. This technique is similar to reverse osmosis (RO) in that pressure drives a solvent (usually water) across a membrane against a concentration gradient. However, NF membranes allow higher salt passage than RO membranes, which decreases osmotic pressure and avoids the need for remineralization. Moreover, the high permeability of NF membranes also lowers the pressure needed for water purification. Hence in applications such as water softening, where high rejections of NaCl are not required, NF is preferable to RO.

Several recent papers examined the abilities of different multilayer polyelectrolyte membranes to separate monovalent and divalent ions such as Cl^- and SO_4^{2-} [4-13]. The layer-by-layer deposition of these coatings affords control over film thickness through variation of the number of adsorbed layers and allows the formation of defect-free skins with thicknesses less than 50 nm [4]. In a previous study, we probed the potential of poly(styrene sulfonate) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC) nanofiltration (NF) membranes for the separation of monovalent anions, with an emphasis on the selective rejection of F^- [12]. Remarkably, deposition of (PSS/PDADMAC)₄PSS films on porous alumina supports yielded membranes that exhibit Cl^-/F^- selectivity > 3 with minimal Cl^- rejection, and a solution flux of $3.5 \text{ m}^3/\text{m}^2\text{-day}$ at 4.8 bar. When the number of PSS/PDADMAC bilayers was increased from 4.5 to 5.5, F^- rejection decreased from 73% to 50% and Cl^-/F^- selectivity dropped to 1.9. Addition of another bilayer to form (PSS/PDADMAC)₆PSS films resulted in a significant increase in Cl^- rejection to give essentially no Cl^-/F^- selectivity. Moreover, flux decreased monotonically with an increasing number of bilayers because of increasing film thickness, so 4.5-bilayer membranes will obviously be preferred for F^- removal.

Although decreases in flux with increasing film thickness were expected, the decreasing selectivity with

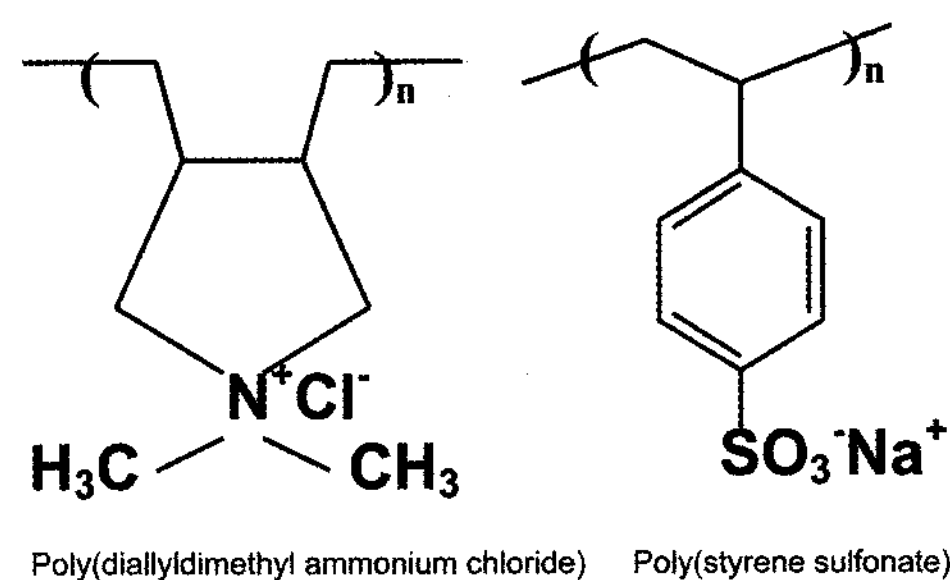


Fig. 1. Structures of the polyelectrolytes used in this study.

deposition of more than 4.5 bilayers was not. Several studies indicate that polyelectrolyte films are not homogeneous and that the first few bilayers have properties different from those in the bulk, including lower hydration [14-17]. Moreover, in thick films, the film-solution interface is more strongly hydrated than the bulk [14,17]. However, it was not clear whether this characteristic was substrate dependent or general behavior. This work examined the effect of substrates on NF performance of multilayer polyelectrolyte membranes. PSS and PDADMAC films were deposited alternatively on 50 kDa polyethersulfone (PES) ultrafiltration supports instead of porous alumina supports.

2. Experimental

2.1. Materials

Poly(styrene sulfonate) (PSS, $M_w = 70,000 \text{ Da}$), poly(diallyldimethylammonium chloride) (PDADMAC, $M_w = 100,000 \sim 200,000 \text{ Da}$, 20 wt% in water), and NaF (99 + %) were obtained from Sigma-Aldrich and used as received. The structures of the polyelectrolytes are shown in Fig. 1. NaCl (Jade Scientific, ACS reagent grade) was also used as received. Polyethersulfone (PES) membrane with molecular weight cutoff of 50 kDa (PBQK 02510) was purchased from Millipore, Bedford, MA. Deionized water (Milli-Q, $18.2 \text{ M}\Omega\text{cm}$) was used for membrane rinsing and preparation of the polyelectrolyte solutions.

2.2. Film Deposition and Characterization

SEM images showed that PES ultrafiltration mem-

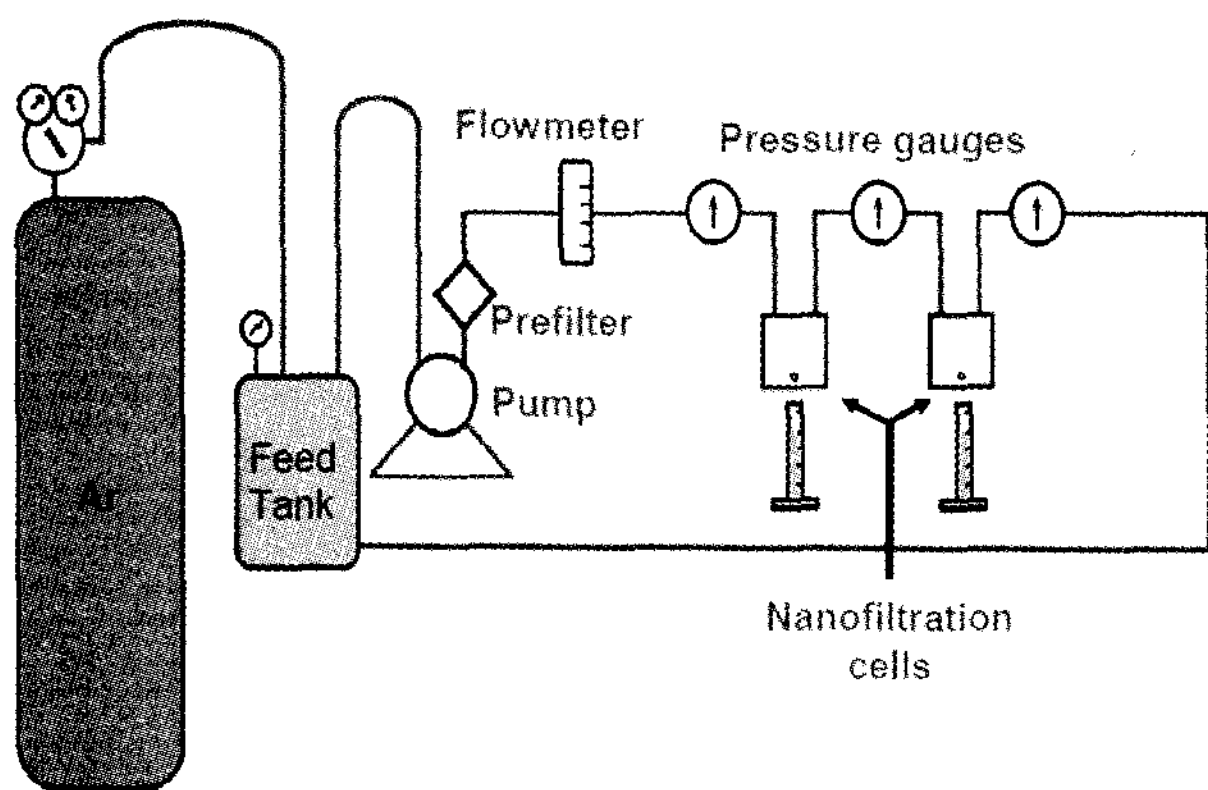


Fig. 2. A schematic diagram of nanofiltration set up.

branes with a molecular weight cut off (MWCO) of 50 kDa have essentially continuous surfaces, while the surfaces of 500 and 300 kDa membranes have a sponge structure with pore sizes as high as 0.4 and 0.2 μm , respectively [13]. Transport studies with neutral molecules (glycerol, glucose, sucrose, and raffinose) also suggested that complete coverage by polyelectrolyte films did not occur with 500 and 300 kDa supports [13]. Therefore, in this study, PES ultrafiltration membranes with a MWCO of 50 kDa were used as supports.

PES ultrafiltration membranes were initially soaked in deionized water about 1 h, during which the water was replaced two or three times. The washed support was first placed in an O-ring holder so that only the feed side of the alumina support was exposed to the polyelectrolyte solutions. Film deposition started with exposure of the top of the PES support to an aqueous solution containing 0.02 M PSS in 0.5 M NaCl for 3 min (concentrations of polyelectrolytes are always given with respect to the repeating unit). The PES support was then rinsed with deionized water for 1 min before exposure to 0.02 M PDADMAC in 0.5 M NaCl for 3 min, followed by a second 1-min water rinse. (PSS was always deposited first because hydrophobic interactions of PSS with neutral PES are probably important for commencing adsorption.) After deposition of the desired number of polyelectrolyte layers, membranes were stored in water until use. Deposition times were selected based on previous studies [12,13]. Additional bilayers were deposited similarly until the target

number of bilayers was produced. ATR-IR spectra from a previous study confirmed the layer by layer deposition of PES/PDADMAC films on PES ultrafiltration supports with MWCO of 50 kDa [13].

2.3. Transport Studies

NF experiments were performed with a home built cross-flow apparatus and a schematic diagram is shown in Fig. 2. This system was pressurized with Ar, and a centrifugal pump circulated the analyte solution through the apparatus and across the membrane, which had an exposed area of 1.5 cm^2 . The flow rate across the membrane was controlled by a flowmeter located between the pump and membrane cells. After 18-h of filtration, four permeate samples were collected using a graduated cylinder for time periods ranging from 10 to 30 min each, depending on the flux of the membrane, and the feed was analyzed at the end of the experiment. The flux measurements reported are the steady-state solution flux after the initial 18 h of filtration. Anion concentrations were determined using ion chromatography (Dionex 600 Ion Chromatograph with an Ionpac (AS14A) column) with conductivity detection, and all reported transport results are the averages of experiments with at least two different membranes.

3. Results and Discussion

Table 1 contains percent rejection values, selectivities, and solution fluxes from NF experiments with several PSS/PDADMAC membranes. NF experimental results using porous alumina supports are also provided for comparison [12]. Percent rejection, R , is defined by Eq. (1) where C_{perm} and C_{feed} are the solute concentrations in the permeate and feed, respectively. The selectivity, S , for solute A over solute B is defined by Eq. (2), which can be conveniently expressed in terms of rejections as shown. Percent rejection and selectivity were determined after allowing 18 h for the system to achieve steady-state permeate concentrations, and the feed volume was sufficient that its concentration varied

Table 1. Rejections, Solution fluxes, and Selectivities from NF Experiments with (PSS/PDADMAC)_n-Coated Membranes and Solutions Containing NaF (1 mM) and NaCl (1 mM). NF was Performed at 4.8 bar with a cross-flow rate of 18 mL/min

Number of bilayers, n	Solution flux, m ³ /m ² -day	Chloride rejection, %	Fluoride rejection, %	Chloride/fluoride selectivity
3.5 ^a	2.6 ± 0.1	17.2 ± 1.5	61.0 ± 1.0	2.1 ± 0.0
4.5 ^a	2.4 ± 0.1	13.9 ± 0.6	50.2 ± 0.5	1.8 ± 0.1
5.5 ^a	2.3 ± 0.1	38.8 ± 1.2	51.0 ± 0.5	1.2 ± 0.1
4.5 ^b	3.5 ± 0.2	9.5 ± 1.1	73.1 ± 0.9	3.4 ± 0.2
5.5 ^b	2.6 ± 0.1	7.3 ± 1.2	50.2 ± 0.5	1.9 ± 0.0
6.5 ^b	2.0 ± 0.1	52.1 ± 1.2	57.5 ± 1.1	1.1 ± 0.1

^a PES supports with MWCO of 50 kDa were used.

^b Porous Alumina supports were used. Data from reference 12.

Table 2. Molecular Weights (*M_w*), Stokes' Radii (*r_s*), and Aqueous Diffusion Coefficients (*D*)[18] of the Anions Used in Transport Studies

Anions	<i>M_w</i> (g mol ⁻¹)	<i>r_s</i> (nm)	<i>D</i> (m ² /s)
Fluoride	19.0	0.166	1.48 × 10 ⁻⁹
Chloride	35.5	0.121	2.03 × 10 ⁻⁹

only slightly during the experiment.

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

$$S = \frac{C_{A,perm} C_{B,feed}}{C_{A,feed} C_{B,perm}} = \frac{100 - R_A}{100 - R_B} \quad (2)$$

All the membranes were terminated with a PSS layer because the negative charge of the polyanionic surface should enhance Cl⁻/F⁻ selectivity [4]. In the case of (PSS/PDADMAC)₃PSS films deposited on PES supports, F⁻ rejection was 61%, whereas Cl⁻ rejection was 17%, and Cl⁻/F⁻ selectivity was 2.1. When the number of PSS/PDADMAC bilayers was increased from 3.5 to 4.5, however, F⁻ rejection decreased from 61% to 50% and Cl⁻/F⁻ selectivity dropped to 1.8. Compared to (PSS/PDADMAC)₄PSS membranes with alumina supports, solution flux, fluoride rejection, and Cl⁻/F⁻ selectivity are larger for membranes with alumina supports, while chloride rejections for both types of membranes are similar. A previous study showed that the PES support might provide a small contribution to mass transport resistance. Although the PES support

was initially very permeable, it probably undergoes compaction that reduces solution flux [13]. Addition of another bilayer to form (PSS/PDADMAC)₅PSS films resulted in a significant increase in Cl⁻ rejection to give essentially no Cl⁻/F⁻ selectivity, which is similar to (PSS/PDADMAC)₆PSS membranes using alumina supports. Moreover, flux decreased monotonically with an increasing number of bilayers because of increasing film thickness.

Assuming that the separation of F⁻ and Cl⁻ is due to sieving of F⁻, which has the larger Stokes' radius (Table 2), trends in F⁻ rejection with the number of PSS/PDADMAC bilayers suggest that the effective pore size of PSS/PDADMAC films increases upon going from 3.5 to 4.5 bilayers. Zeta potential measurements also suggest that the zeta potentials of films on porous PES supports decrease with an increase in the number of bilayers. On going from (PSS/PDADMAC)₃PSS to (PSS/PDADMAC)₄PSS films on a 100 kDa polyethersulfone membrane, zeta potential decreased from -8.0 to -0.6 mV. (In this case, deposition solutions contained 1 M NaCl) [19].

The NF experimental results indicate that, although the fluoride rejection and the number of bilayers at which a maximum F⁻ rejection occurs are different, the trend is similar for alumina and polymer supports. Therefore, we can conclude that the NF characteristics of multilayer polyelectrolyte membranes may not be substrate dependent but a kind of general behavior.

4. Conclusions

The simple layer-by-layer deposition of PSS/PDADMAC films on polyethersulfone (PES) substrates results in high-flux membranes capable of selective removal of F^- in the presence of Cl^- . Similar to the previous study using porous alumina supports, Cl^-/F^- selectivity varies with the number of layers in the film. The results indicate that, although the fluoride rejection and the number of bilayers at which a maximum F^- rejection occurs are different, the trend is similar for both types of supports. Therefore, we can conclude that the NF characteristic of multilayer polyelectrolyte membranes may be substrate independent.

Acknowledgements

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