Study of ionic transport through metalized nanoporous membranes functionalized with self-assembled monolayers

Damena D. Agonafer, a,*, Muhammed E. Oruc, c Edward Chainani, d, Ki Sung Lee, b, Huan Hu, e, Mark A. Shannon b,c,1

a Department of Mechanical Engineering, Stanford University, Stanford, CA 94305-3030, USA
b Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
c Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
d Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
e Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

A R T I C L E I N F O

Article history:
Received 22 January 2014
Received in revised form 27 February 2014
Accepted 5 March 2014
Available online 15 March 2014

Keywords:
Permeability
Interfacial transport
Self-assembled-monolayers
Metalized nanoporous membranes

A B S T R A C T

Ionic transport through synthetic nanoporous membranes has received great attention in applications related to biosensing, fuel cell, and desalination. Past work has demonstrated that charge selectivity can be achieved by applying a potential across a metalized conductive membrane. However, challenges arise for improving charge selectivity as a result of irreversibility of the system from the anion adsorption at the membrane surface. This study demonstrates how charge selectivity can be improved with the presence of a well grown self-assembled monolayer (SAM), which can aid in applications that use chemical separation processes based on the surface charge of the nanopore.

In this work, the transport and selectivity properties of gold-coated conductive nano-capillary-array-membranes (NCAMs) are studied using charged species methyl viologen paraquat, (MV2+) and naphthalenedisulfonate disodium salt (NDS2–). The selectivity coefficients for MV2+ and NDS2– increased with the functionalization of undecanethiol on the gold-coated NCAM surface. With the presence of a SAM, the selectivity coefficients increased by 44% for MV2+ and 200% for NDS2–. The influence of ionic transport from the diffuse layer potential at the walls and surface of the nanopore is also discussed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nanoporous membranes have received great attention in the fields of water desalination, biosensing, and chemical separations [1–17]. There have been numerous studies for the separation of biomolecules and analytes based on charge selectivity [18–23]. It has been demonstrated that proteins can be separated by applying potentials across conductive alumina membranes [24]. Cheow et al. developed a platinum coated nanoporous alumina membrane to demonstrate the permeeselectivity of proteins by applying different potentials across the membrane [25]. Several studies have also been done demonstrating charge selectivity through nanoporous membranes [26–31]. Studies have included fabrication of ion-tracked polyethylene terephthalate membranes, with the membrane surface terminated with carboxylate terminal groups [3]. The membrane’s selectively transported cations and prevented migration of anions. Attaching amino moieties on the membranes surface and pore wall proved to reverse the selective properties of the membrane. It has also been demonstrated that functionalizing gold nanotubule membranes with self-assembled monolayers (SAMs) could alter the pH responsiveness of the membrane [32]. Selective transport through nanopores has also been found to be dependent on the hydrophobic interaction between the analyte and membrane surface. Zenglian et al. used an electroless gold-deposited PCTE membrane modified with a hydrophobic terminated thiol surface. The competing effects between the interactions of the entrance and surface of the nanopore were compared. It was concluded that the entrance effect had the most influence on the transport of analyte across the nanopores [33].

Several studies have shown that anion adsorption on a conductive NCAM surface can affect the exclusion enrichment effect of coions and counterions. Mun et al. demonstrated charge selectivity using electroless gold coated polycarbonate track etched membranes (PCTE) [34]. The PCTE membranes are fabricated by bombarding a polycarbonate film with a collimation of high-energy nuclear fission fragments, which results in damaged
tracks through the film. The damaged tracks are then etched by an aqueous base solution to create cylindrical pores within the polycarbonate film [35]. The PCTE gold-coated surface was functionalized with propanethiol for the prevention of anion adsorption (e.g., chloride ions) on the surface of the membrane. However, it was observed that the permeability of the membrane was inhibited when positive potentials (anodic) were applied at the membrane surface. It was concluded that the poor quality of SAM layer led to irreversibilities on the charge selective system as a result of adsorption of anions. Although the membrane was immersed in thiol solution for 24 h, studies have shown that more allocated time is necessary to grow a well-ordered SAM [36–38]. The authors have shown that detection of analytes can be achieved by interactions with the membrane surface/pore wall [39–41]. Schmuhl et al. investigated electric field-driven transport of ions through supported mesoporous γ-alumina membranes, with surfaces metalized with gold [42]. The studies showed that the electrolyte composition could affect the flux of copper ions through a permselective membrane. It was demonstrated that the flux of copper ions (Cu²⁺) was enhanced by the presence of adsorbed chloride ions on the gold-coated alumina surface. The same experiments were done with solutions containing fluoride (F⁻) and nitrate (NO₃⁻) ions. Flux enhancement of Cu²⁺ was not present when electrolyte solutions containing F⁻ and NO₃⁻ were used. As a result from XPS analysis, it was found that chemisorption of chloride on to the gold-coated membrane surface occurred, resulting in a negatively charged surface. It was concluded that the negatively charged membrane surface led to a local accumulation of counter ions, which enhanced the flux of Cu²⁺ ions.

If specific adsorption of a molecule occurs on the surface of a membrane, ion selectivity for separation will be inhibited by the loss of interaction between the membrane surface and analyte as shown in Fig. 1a. If the membrane surface is well covered by the SAM in order to minimize ion adsorption, ion selectivity can be enhanced for a specific molecule of interest (Fig. 1b).

The applications of SAMs are often limited by the immersion time allocated for the growth of the SAM. Past work has focused on studying the properties of a well-ordered SAM by electrochemical impedance spectroscopy (EIS) [37,43]. It was found that a minimum of 48 h is needed to grow a well-ordered SAM [37,38].

Surface functionalization is crucial for bioseparation and biosensing applications. Savariar et al. functionalized the surface of a polymeric membrane with SnCl₂, which led to the separation of analytes by electrostatic and hydrophobic interactions [44]. Additional work has focused on studying the transient current response based on the interaction between proteins and walls of single nanopores [41,45]. Wei et al. were able to immobilize proteins by using an OH⁻-terminated thiolated SAM to act as a protein receptor. The interaction between the protein and nanopore wall can be quantified by the time constant associated with adsorption and desorption events. Without the presence of a SAM on the surface, non-specific protein adsorption can occur on the walls of the nanopore. This can lead to effective blockage within the nanopore with non-targeted proteins, leading to a smaller measurable current (lower S/N ratio) across the nanopore [41]. Moreover, redox currents typically increase the background noise for electrochemical sensors. If detection can be accomplished with lower applied potentials, S/N ratios can be improved for electrochemical sensing of specific analytes [46].

In this work, we study the transport of methyl viologen (paraquat, MV²⁺) and napthalenedisulfonate disodium salt (NDS²⁻) across a conductive NCAM while applying a range of potentials with respect to the membrane surface at the entrance side. A polycarbonate track etched (PCTE) membrane was made conductive by sputter coating gold on the membrane surface. Transport studies were done in a voltage range in which faradaic current was minimized at the surface of the gold-coated nanocapillary-array-membranes (NCAMs). The goal of the transport studies is to demonstrate improved charge selectivity when a well-grown 1-undecanethiol monolayer is assembled at the

---

**Fig. 1.** Schematics (a) and (b) of a gold coated NCAM, which illustrates the improvement when a well-grown SAM is attached to the monolayer.
surface of the NCAM for a wide range of applied potentials (−400 mV < \( V_{\text{appl}} \) < 400 mV). Results show the selectivity of charged analytes through the metallized NCAM can be improved by functionalizing the surface with a self-assembled monolayer (SAM).

2. Experimental

2.1. Preparation of gold-coated NCAMs

PVP coated polycarbonate membranes (PCTE) (Osmonics Inc., MN) were sputter-coated with 50 nm of gold on each side of the membrane surface, with a 6 nm thick titanium adhesion layer. The membrane thickness, nominal pore size, and pore size density were 6 \( \mu \)m, 30 nm, and \( 6 \times 10^{12} \text{ cm}^{-2} \), respectively. The sputtering power was 300 W with a 23 nm/min deposition rate. The chamber pressure during sputtering was 0.67 Pa, and the distance between the gold target and sample was approximately 30 cm. To avoid electrical shorts between each side of the membrane, the edges around the permeation area were not coated. After 2 min of gold sputtering, the inner pore diameter of the NCAM did not exhibit any noticeable decrease in pore size (Fig. 2). 11-Undecanethiol, purchased from Sigma Aldrich, was dissolved in absolute ethanol (Pharmaco-AAPER, Shelbyville, KY) in order to prepare 1 mM thiol solution. The NCAM was placed in a membrane holder and immersed in undecanethiol solution for 48 h.

2.2. Preparation of monolayer surfaces

Fig. 3 shows a summary of steps involved for the preparation of a gold-coated NCAM functionalized with a SAM. The steps include sputter-coating gold on the membrane surface followed by functionalizing the gold-coated NCAM with undecanethiol. The monolayer-coated membrane surface is then rinsed with absolute ethanol and DI water, followed by blow-drying the NCAM surface with \( \text{N}_2 \). Prior to experiments, the NCAM was subjected to the channel outgas technique \[47\] in order to saturate the membrane pores with electrolyte solution. The NCAM was placed in a membrane holder and immersed in undecanethiol solution for 48 h.

2.3. Preparation of Kapton electrodes

To establish an electrical connection to the conductive membrane surface, two pieces of gold-coated Kapton (Du Pont 500 HN, 127 \( \mu \)m) were used as electrodes to apply a potential at each surface of the membrane. Kapton films were scored in a long rectangular shape with a 5 mm diameter punched permeation hole for ionic transport. The Kapton film was cleaned with solvents followed by 1 min of oxygen plasma treatment at 100 W, which removed organic matter from the surface in order to improve bonding between the adhesion and gold layers. A 5 nm titanium layer was deposited as an adhesion layer, followed by a 100 nm deposited gold layer. Wires were soldered to the electrodes for electrical connection to the bipotentiostat.

2.4. Transport experiments

Fig. 4 shows a schematic of the membrane permeate flow cell (MPFC). The membrane was sandwiched between two gold-coated Kapton electrodes. The Kapton electrodes were then clamped between the feed and MPFC. Ag/AgCl reference and gold counter electrodes were placed in the feed cell. A CBP Pine Instruments bipotentiostat (Pine Instrument Co., Grove City, PA) was used to apply a potential at each side of the gold-coated NCAM. 1 mM phosphate buffer solution (PBS) was prepared as a ratio of mono- and dihydrogen potassium phosphate salts (Sigma-Aldrich, St. Louis, MO) in DI water, serving as an electrolyte. The permeate cell initially had 1 mM potassium phosphate buffer solution (PBS) with pH of 7. The total dead volume of the circulating solution was 1 mL. A peristaltic pump (Masterflex L/S 7520-47) was used to circulate PBS solution from the MPFC through a Z-cell (FIAlab Instruments, Bellevue, WA) for the UV detection of molecules.

The two molecules being investigated for transport experiments were methyl viologen dichloride (MV\(^2+\)) and naphthalene 1,5 naphthalenedisulfonic acid disodium salt (NDS\(^2-\)), each purchased...
and without the presence of an alkane-terminated SAM on the surface. The fluxes for NDS$^{2-}$ are higher for applied potentials of $-0.4$ V, 0 V, and $+0.4$ V (vs. Ag/AgCl) when the NCAM is functionalized with undecanethiol. The increase in flux for NDS$^{2-}$ with the presence of a SAM layer on the membrane surface can be attributed to the reduction of anion adsorption (e.g., phosphate, NDS$^{2-}$). Several studies have confirmed that adsorption of anions on a bare gold surface, which functions as a working electrode, occur over a range of applied electrochemical potentials [48–52]. In those studies, phosphate buffer solutions (PBS) were used as a background electrolyte. While rarely used as supporting electrolyte in electrochemical studies, phosphate buffer solutions are prevalent in physiological and biochemical studies. There are few studies of phosphate anion adsorption on gold [53–57], and even fewer done at close to neutral pH [55]. Those studies suggest that phosphate adsorption is higher than sulfate adsorption, but is considerably weaker than halide (Cl$^-$, Br$^-$) ion adsorption [57].

Fig. 7 illustrates the entrance length of the gold-coated membrane layer is approximately 1.5 times greater than the characteristic pore diameter, which means the surface interaction at the membrane surface can have a strong influence on the transport of charged species. The ratio between the thickness of the gold layer and pore diameter can be thought as an access resistance in terms of electrostatic interaction of ions at the wall entrance of the pore [58,59]. As the ratio increases, the interaction of ions at the gold layer can become significant; whereas a smaller gold thickness–pore diameter ratio will lead to a less effective entrance effect as a result of a smaller effective surface area for ions to interact with the charged gold layer. As a result, the functionalization of the gold-coated NCAM surface with an alkane-terminated SAM can play a crucial role for influencing the wall interaction with analytes (e.g., Cl$^-$, NDS$^{2-}$, phosphate ions) present in the electrolyte solution. The effect of adding SAMs on the NCAM surface is significant at positive applied potentials (Fig. 6). This suggests that there is specific adsorption of NDS$^{2-}$ as observed in previous work [34]. Although the adsorption of phosphate ions and NDS$^{2-}$ is weaker for neutral and negative applied potentials, there is still a slight increase in flux of NDS$^{2-}$ when functionalized with a SAM. The thickness of the Au coated layer is only a small fraction of the total thickness of the NCAM (50 nm=6 µm). It can be concluded that the thickness of the gold layer does not have any significant impact on the flux of ionic species related to the total thickness of the membrane.

As discussed earlier, anions adsorb on the gold-coated NCAM surface without the presence of an alkane-terminated monolayer. This can lead to specific adsorption of anions (e.g., NDS$^{2-}$ and Cl$^-$) [42,57]. As a result, the charge from an external applied potential on the membrane surface can be countered by more than an equivalent charge of anion adsorption [60]. The adsorption of anions creates a negative surface charge density, which creates a diffuse layer potential at the membrane–electrolyte interface. This in turn distorts the local concentration of ions at the surface around the pore entrance. Although the bulk concentration of NDS$^{2-}$ is believed to not change over the time of the experiment, the local concentration of anionic species at the entrance of the membrane pore can decrease, leading to a smaller local concentration gradient across the nanopore. This in turn can reduce the driving mechanism for diffusion of NDS$^{2-}$ across the NCAM. As a result of the absence of a SAM on the membrane surface, NDS$^{2-}$ molecules are screened due to a negatively charged membrane surface. With the functionalization of a SAM on the NCAM surface, the negative surface charge density is reduced, lowering the driving mechanism for enrichment and screening of counter and coions, in order to preserve electroneutrality. This enables NDS$^{2-}$ molecules to transport across the NCAM with less electrostatic interaction ascribed from the surface charge at the membrane surface; which in turn enables NDS$^{2-}$ to permeate with a higher
transport of NDS$_2^-$ in contrast to the presence of a SAM layer on the NCAM. The results are in contrast to previous work that demonstrated the enrichment effect of NDS$_2^-$ at the nanoscale. This enrichment effect is attributed to the presence of a SAM layer on the membrane surface, which leads to a decrease in the accumulation of NDS$_2^-$ at the membrane surface. This in turn, increases the local concentration of MV$^2+_{\text{+}}$ at the entrance of the membrane, resulting in an increase of diffusional flux of MV$^2+_{\text{+}}$ across the nanopore. As mentioned earlier, the net negative surface charge on the membrane surface is significantly reduced when undecanethiol is functionalized at the NCAM surface. This leads to a reduction of a negative surface charge attributed from the specific adsorption of anions. Reduction of anion adsorption subsequently acts to reduce the accumulation of MV$^2+_{\text{+}}$ at the membrane surface. The decrease in accumulation of MV$^2+_{\text{+}}$ leads to a smaller flux across the membrane compared to the condition when the gold-coated NCAM surface is not functionalized with a SAM. Although the variation of diffusional flux varies at all applied potentials, the effect of surface functionalization with SAMs is significant for potentials at 0 V and +0.4 V. In contrast, the addition of a SAM layer has minimal contribution for diffusional flux experiments for NDS$_2^-$ at an applied potential of 0 V. As previously discussed, the different mechanisms for ion selectivity between NDS$_2^-$ and MV$^2+_{\text{+}}$ can be attributed to the difference in electrolyte composition. Chloride ions are present in the buffer solution of MV$^2+_{\text{+}}$, but absent in the electrolyte solution containing NDS$_2^-$ and MV$^2+_{\text{+}}$. As also discussed earlier, Cl$^-_{\text{−}}$ ions have a higher affinity to adsorb as NDS$_2^-$ or phosphate ions. This can lead to a higher impact on minimization of the ion exclusion–enrichment-effect over a wider range of potentials due to the reduction of adsorption with the presence of a SAM.

3.2. Effects of ion selectivity when monolayer formation is present

Table 1 summarizes the flux and selectivity coefficients for transport experiments for NDS$_2^-$ and MV$^2+_{\text{+}}$. For NDS$_2^-$, the percentages of increase in flux with the presence of a SAM are approximately 20%, 12%, and 73% for potentials of −0.4 V, 0 V, and 0.4 V respectively. The results show that with the addition of an alkane-terminated monolayer, the enrichment effect of NDS$_2^-$ at positive applied potentials is increased, due to a reduction of irreversibilities on the membrane surface. The addition of the monolayer increases the ability to enhance flux of anions when the contributions of a negative surface charge density are reduced. The percent decrease of flux of MV$^2+_{\text{+}}$ when a monolayer is added is 0.5%, 26%, and 52% for applied potentials of −0.4 V, 0 V, and 0.4 V respectively.

![Fig. 6. Diffusional flux measurements of NDS$_2^-$ through a conductive NCAM when the gold surface of the NCAM is not functionalized with a SAM (a), and when functionalized with undecanethiol (b).](image1)

![Fig. 7. Schematic representation of a 50 nm sputtered-gold layer at the surface of the NCAM. The thickness of the gold layer is the same order of magnitude of the NCAM pore diameter, indicating the relevance of the interaction of analytes at the gold-electrolyte interface.](image2)
The selectivity coefficient for anions is defined as

$$\alpha_{+0.4/-0.4} = \frac{\text{flux of anion at } 0.4 \text{ V}}{\text{flux of anion at } -0.4 \text{ V}}$$ (1)

The selectivity coefficient for cations is defined as

$$\alpha_{-0.4/+0.4} = \frac{\text{flux of cation at } -0.4 \text{ V}}{\text{flux of cation at } 0.4 \text{ V}}$$ (2)

The selectivity coefficient increases from 4.3 to 6.2 when undecanethiol is attached to the gold-coated NCAM. This supports the argument that irreversibilities on the surface of a gold-coated NCAM can be reduced when a monolayer is grown on the surface. This can be attributed to the surface charge density formed on the bare gold surface, which aids in screening the NDS$^{2-}$ molecules from transport across the NCAM. When the alkane-terminated monolayer is added, the electrostatic repulsion between anions is reduced, leading to a higher flux of NDS$^{2-}$. With the reduction of specific ionic adsorption, the contributions of ionic transport are mainly from the externally applied potential at the membrane surface and surface charge density at the PVP coated walls, which will be discussed later in the next section. Similarly, MV$^{2+}$ displays a distinct improvement for selectivity when undecanethiol is functionalized at the surface. As mentioned earlier, the selectivity of methyl viologen is improved with the addition of a monolayer, due to an increased ability of the membrane to selectively screen MV$^{2+}$ at positive applied potentials.

### 3.3. Effects of a charged nanopore and EDL thickness on the transport of NDS$^{2-}$ and MV$^{2+}$

The mechanism for ionic transport across the NCAM is by passive transport. At low ionic strength, the exclusion enrichment effect of ionic species can occur as a result of the surface charge at the walls of the nanopore. This can reduce the effective permeability and cross sectional area of the nanopore for transport of coionic species due to the electrostatic forces at the walls of the nanopore. Although there is no electric double layer (EDL) overlap, it has been postulated that EDL overlap is not required in order to distort the local equilibrium concentration within a nanopore [3,22,62].

At an ionic strength of 7 mM, the EDL covers about 27% of the diameter of the nanopore.

<table>
<thead>
<tr>
<th>Applied voltage (V)</th>
<th>Flux of NDS$^{2-}$ (nmol min$^{-1}$ cm$^{-2}$)</th>
<th>Flux of MV$^{2+}$ (nmol min$^{-1}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unmodified</td>
<td>Modified</td>
</tr>
<tr>
<td>0</td>
<td>1.44 x 10$^{-2}$ ± 5.71 x 10$^{-4}$</td>
<td>1.61 x 10$^{-2}$ ± 1.30 x 10$^{-3}$</td>
</tr>
<tr>
<td>+0.4</td>
<td>4.75 x 10$^{-2}$ ± 3.23 x 10$^{-3}$</td>
<td>8.24 x 10$^{-2}$ ± 1.38 x 10$^{-3}$</td>
</tr>
<tr>
<td>-0.4</td>
<td>1.11 x 10$^{-2}$ ± 5.71 x 10$^{-4}$</td>
<td>1.33 x 10$^{-2}$ ± 8.33 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Selectivity coefficient for NDS$^{2-}$</th>
<th>Selectivity coefficient for MV$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>Modified</td>
</tr>
<tr>
<td>α$^{+0.4/-0.4}$</td>
<td>4.3</td>
</tr>
<tr>
<td>α$^{-0.4/+0.4}$</td>
<td>7.81</td>
</tr>
</tbody>
</table>

The selectivity coefficient is calculated as:

$$\alpha = \left( \frac{E_2 C_1}{E_1 C_2} \right)^{1/2}$$

where $\kappa$ and $a$ are defined as the inverse Debye length and diameter of the nanopore.

The surface charge of PVP-coated PCTE membranes contain a negative surface charge density at a pH level of 7 [63]. As previously discussed, the ionic mobilities of NDS$^{2-}$ and MV$^{2+}$:

Fig. 8. Diffusional flux measurements of MV$^{2+}$ through a conductive NCAM when the gold surface of the NCAM is not functionalized with a SAM (a), and when functionalized with undecanethiol (b).
are comparable due to similar molecular volumes (0.637 nm$^3$ for NDS$^{2-}$ and 0.680 nm$^3$ for MV$^{2+}$), hydrophobic properties (each contain two benzyl rings), and same valencies ($z=2$) with opposite charge. However, as shown in Fig. 9, the flux of MV$^{2+}$ at a potential of 0 V (vs. Ag/AgCl) is 8 and 12 times larger for NCAMs with and without the presence of a SAM layer. It should also be pointed out that the ratio of flux between NDS$^{2-}$ and MV$^{2+}$ decreases as the irreversibilities from anion adsorption at the membrane surface is reduced. Although the EDL only covers approximately 27% of the pore area, screening effects of coions still occur. Fig. 10 shows a schematic of diffusion transport of anionic species through a gold-coated NCAM. Fig. 10a shows that at high ionic strength, the electrostatic interactions at the pore wall are negligible due to a small Debye length. Fig. 10b shows that at low ionic strength, the EDL extension across the nanopore creates a non-homogenous concentration of coionic species. It can be concluded that the flux of NDS$^{2-}$ is significantly less than MV$^{2+}$ due to electrostatic screening from the walls of the PVP-coated PCTE membrane. Although the surface charge density from the surface of the membrane affects ionic transport, the electrostatic effects from the walls of the nanopore prove to be significant. More studies are needed to conclude the relative significance of each electrostatic interaction.

4. Conclusion

It has been demonstrated that functionalizing a metalized NCAM surface with undecanethiol can enhance charge selectivity. For a well-grown alkane-terminated SAM, ionic species can be electrostatically separated from the diffuse layer potential at the monolayer/electrolyte interface (neglecting charge on the head group) at the membrane surface. It was demonstrated that entrance effects at low ionic strengths are not negligible and can dictate the transport of analytes across a nanopore. This work opens up the possibility of utilizing SAMs with different charged head groups to manipulate ionic species based on the diffuse layer potential at the surface of the membrane. EIS experiments in previous work have demonstrated monolayers grown for several days can significantly enhance the quality of a SAM [38], which opens the possibility of improving when incubation times for monolayer growth occur longer than 48 h. Future work should investigate transport mechanisms at lower and higher ionic strengths to find the critical concentration in which entrance effects become negligible. More studies are needed to study the influence of surface charge from the walls and surface of the NCAM effect ionic transport. This may give more insight in how to improve charge selectivity at both anodic and cathodic potentials.

Acknowledgments

This work was supported by the NSF Center WaterCAMPWS (The Center of Advanced Materials for the Purification of Water with Systems). The authors would like to thank Professor Alex Scheeline (Chemistry Department at the University of Illinois, Urbana-Champaign) and Kathleen Motsegood (Beckman Institute at the University of Illinois, Urbana-Champaign) for use of materials and facilities, and are grateful to professors Andrzej Wieckowski and Jacek Lipkowski for the helpful discussions. We would also like to thank Francis Limpoco, Scott Maclaren, and William Wilson for support in using facilities in Frederick Seitz Materials.

Fig. 9. Diffusional flux measurements of NDS$^{2-}$ and MV$^{2+}$ through a conductive NCAM at 0 V. Figures (a) and (b) show permeability measurements performed when the NCAM was not functionalized (a) and functionalized with undecanethiol (b).

Fig. 10. Schematic of the EDL effect on anionic transport. At high ionic strength (a), the Debye length is small, therefore anions can diffuse easily through the nanochannel. At low high ionic strength (b), the Debye length is relatively higher then it reduces the flux of counterions through the nanopore.
Research Laboratory (MRL), University of Illinois at Urbana-Champaign.

References


