Vision and Objectives

Reverse osmosis (RO) membrane filtration has become an important technology for drinking water purification in several US cities, as well as in regions with limited fresh water resources around the world. However, the lack of a predictive theoretical framework that links molecular level material structure to flux and selectivity has limited advances in RO membrane performance to incremental improvements over the past decade. Most notably, while the rejection capability for charged species (ions such as Na⁺ and Cl⁻) have been optimized in pursuit of desalination applications, removal of organic compounds, which often can be carcinogenic or otherwise harmful, from a broader range of water sources including contaminated ground and surface water, brackish water, recycled water, industrial process water, and fracking fluids remains a challenge. To consider organic compounds and further improve the performance of RO systems beyond the current plateau requires new approaches and tools to address the problem at the nanoscale—understanding the molecular level interactions between polymeric membranes and water or contaminant molecules.

The objective of the ISEN-funded work was open a new approach to the modeling the transport of water and the rejection of contaminants through polymeric RO and NF membranes by utilizing molecular dynamics (MD) simulations with the ultimate goal of leveraging the results seek further funding from the NSF, EPA, DOE, DOD, or private corporations (e.g. GE Water & Process Technologies). In pursuit of this objective, we carried out preliminary MD simulations to investigate at the molecular level the effects of membrane structure and solute properties on the permeation of water and organic/inorganic solutes.

Background

Despite their huge success, technological advances in conventional polymeric RO membranes plateaued in the late 1990s, and recent incremental improvements have primarily focused on increasing membrane area per module or costly and time-consuming trial-and-error experimental approaches to modifying membrane chemistry and structure. Surprisingly, little is known about the molecular scale transport in polymeric RO membranes that are used commercially around the world—the nanoscale transport mechanisms in the tortuous pores of RO membranes remain obscure, and a direct link between the membrane structure and chemistry and transport metrics remains to be established in a predictive way, hampering further improvements in performance metrics such as water flux and contaminant rejection. Current RO membranes readily reject a very high percentage of charged contaminants such as sodium chloride (typically 98% or more), but a much lower percentage of uncharged organic contaminants. For desalination of seawater, sodium chloride rejection by current RO membranes is adequate (though improved effectiveness in terms of water flux and salt rejection would be highly desirable). The bigger and increasingly important challenge is the removal of organic compounds, which often can be carcinogenic or otherwise harmful, from a broader range of water sources including contaminated ground water, brackish water, recycled water, and industrial wastewater such as fracking fluids.

Here we study RO membranes at the molecular level using molecular dynamics (MD) simulations. MD simulation is a powerful computational method to bridge the gap between what actually occurs at the nanoscale and macroscale experimental observations or continuum models for membrane filtration. We use a substantially different approach than previous researchers for the study of RO membranes that is based on Non-Equilibrium Molecular Dynamics (NEMD), which provides direct transport metrics in a similar fashion to experiments. In order to understand and effectively predict the two key performance measures (water flux and contaminant rejection) for RO membranes, several questions need to be addressed. What is the pore size distribution in a polymeric RO membrane? How are the pores connected...
to each other? How do pore size distribution and pore connectivity affect water flux and contaminant rejection? How do the membrane and solute chemistry impact water flux and solute rejection?

Results
Over the last 12 months, we have made substantial progress on a preliminary study of the transport and rejection of small ionic and organic solutes in water. The process begins with algorithms to efficiently construct polymeric membranes, in this case the cross-linked polyamide commonly known as FT-30. The approach we took involved annealing and cooling hundreds of m-phenylenediamine (MPD) and trimesoyl chloride (TMC, or benzene-1,3,5-tricarboxylic acid chloride) monomers to create a mixture. Then the monomers are artificially polymerized by creating amide bonds when a carboxyl carbon of TMC is within 3.5 Å of a free amine nitrogen of MPD. The structure arising from virtual crosslinking simulations is shown in Fig. 1, where the colors represent different fragments (chains). The density of the resulting dry membrane was approximately 1.1 g cm\(^{-3}\), close to the experimental value of 1.06 g cm\(^{-3}\). The surface structure is quite loose, consistent with experimental results.

The virtual membranes are then placed between a 5 M solution on the left and pure water on the right, as shown in Fig. 2. Graphene sheets are oriented to constrain the liquid on either side of the membrane. Forces can be applied to the graphene sheets to generate a trans-membrane pressure (\(\Delta P = P_1 - P_2\)) normal to the plane of the membrane. Periodic boundary conditions are used in the transverse directions to emulate a larger continuous membrane that is roughly 4 nm thick. This is only about 2% of the thickness of the thin film layer of a commercial membrane, but it is adequate to provide a relatively homogeneous polymeric membrane structure for this initial study. Several atoms of the membrane were fixed, so that the majority of the membrane atoms could vibrate, but the entire membrane could not translate or rotate. Forces corresponding to 1 atm pressure were added to the graphene planes on both sides of the membrane for about 10 ns to hydrate the membrane before the reverse osmosis pressure difference was applied. Then trans-membrane pressures up to 150 MPa were applied to simulate the RO process. In this preliminary study, four organic solutes (urea, methanol, ethanol, and 2-propanol) were considered along with sodium chloride. Simulations were performed using NAMD with the generalized AMBER force field.

The relation between membrane structure and water transport in a 2 Å thick slice midway across the thickness of the membrane is shown in Fig. 3. Traces of water molecules can be compared to the percolated free volume, as calculated by a geometrical method with a 2.8 Å diameter spherical probe (the size of a water molecule). Clearly, the water molecules find their way through the free volume of the membrane structure.
One of the most intriguing finding from the simulations is that the membrane itself is in constant motion due to thermal fluctuations and collisions with water and contaminants, resulting in vibrations across the entire membrane’s molecular structure, leading to dynamic pore dimensions.\textsuperscript{27} In fact, the free volume calculated without considering this membrane mobility at the monomer scale is much smaller than the water-accessible space shown in Fig. 3. This result, which would not be possible except from these MD simulations, reveals the role of the local fluctuations of the monomers and the dynamics of the polymer chains are important factors facilitating water transport.

Our preliminary work also demonstrates how the relation between membrane structure and solute transport can be investigated for specific solutes. For example, Fig. 4 shows the path of an individual 2-propanol molecule over time with 30 ps corresponding to each line segment between pairs of dots. The molecule initially exhibits Brownian motion in the water between the left graphene sheet and the membrane surface. It enters the membrane at A, but, in spite of the applied pressure gradient, the molecule actually comes back out of the membrane. It eventually makes its way to the top of the membrane, where it finally makes its way through the membrane to the other side. Videos of the particle motion and the trajectories shown in Fig. 4 indicate that once within the membrane, the molecule travels relatively quickly through certain portions of the membrane (where the dots and interconnecting line are sparse), while it remains temporarily trapped, presumably in a void, or “pore,” in other locations (B and C near the top of the membrane). The molecule spends about 5 ns in pore B, but requires less than 1 ns to travel from pore B to pore C.

**Recent Publications and Ongoing Funding:**

In June 2014, we presented a paper at the annual meeting of the North American Membrane Society (NAMS) that was well received. In October 2014, as a follow up to the NAMS Presentation, we
described our research to date to an interested researcher at the Dow Chemical Company. This has potential to lead to future research funding from Dow. We are currently finishing up a paper that will be submitted to the Journal of Membrane Science on the results to date. In addition, we have submitted a proposal to NSF in which we propose to use the advantages of MD over experiments to control the degree of polymerization to obtain structures with diverse characteristics to probe the water flux and solute selectivity. Two major thrusts are included in the proposed NSF work:

I. Understand the link between membrane nanostructure and water flux/solute rejection:

The idea is that the membrane thickness, porosity, pore structure, and surface structure can be computationally varied to create multi-dimensional property maps that explain factors governing flux and selectivity. We will also directly explore the membrane structure with molecular probes having the size of water or a variety of ionic and organic solutes to precisely assess the connections between open volumes in the membrane nanostructure. MD simulations of RO membranes also open up numerous opportunities for creating “designer membranes” computationally. We can change the degree of cross-linking in the membrane by simply controlling the time during which we allow the artificial polymerization to proceed during computational “fabrication” of the membrane. Relatively loose or tight membrane structures could be developed in this way or the tightness of the structure could be varied in the membrane, perhaps with more small pores near the surface and larger pores deeper in the membrane. It is further possible to consider other polyamide polymeric structures, including hypothetical molecular structures or to simulate membranes specifically designed to be chlorine-resistant.

II. Correlate membrane/solute chemistry with the rejection of ionic and organic contaminants

Commercial RO membranes reject more than 98% of monovalent ions, but the rejection of small neutral organic compounds (2-propanol, urea, formaldehyde) is very low. Since ions can often be rejected more readily than neutral organic molecules of the same size, it is clear that the chemistry of the interaction between the contaminant and the membrane plays an important role. Several questions arise. How does the membrane chemistry (hydrophilic/hydrophobic, charged/uncharged, etc.) affect water flux? How does the solute rejection depend on the membrane chemistry, the solute properties (hydrated size, hydration energy, overall charge, charge distribution that affects solute orientations), and the membrane/solute interaction (or membrane chemistry)? Of course, the membrane chemistry is much easier to change and analyze in MD simulations than in conventional experiments. Furthermore, forces between molecules (for instance, hydrogen bonds) can be arbitrarily turned on or off to probe the effect on solute transport and rejection.

Personnel

ISEN funding was used to support approximately 9 months of salary for a post-doc, Dr. Meng Shen. An additional 3 months of support was provided by the PI's from discretionary funds. Dr. Shen is currently interviewing for a position at Argonne National Laboratory, but if that does not work out she will continue her work on the project for another 6 months, funded by the PI's discretionary funds.

References

21. Sougrat, R.; Pinnau, I. In Characterization of the Nanostructure of Polyamide Thin Films in RO Membranes Using TEM Tomography, the Conference of North American Membrane Society (NAMS), Houston, TX, May 31 - June 4; Houston, TX, 2014.

