

Predicting Transport in Lyotropic Liquid Crystal Membranes with Molecular Dynamics Simulations – Outline

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February 10, 2017

1 Introduction

Nanostructured membrane materials have become increasingly popular in desalination and wastewater treatment applications because they offer the ability to control membrane architecture at the atomic scale.

- Current state-of-the-art reverse osmosis membranes are dense and unstructured with tortuous and polydisperse pores which lead to inconsistent performance
- Tortuosity and polydispersity drive up energy requirements which strain developing regions and contribute strongly to CO₂ emissions
- With nanostructured materials, solute rejecting pores can be tuned uniformly – drives down energy requirements

Development of nanostructured materials has been limited by the ability to synthesize and scale various fundamentally sound technologies.

- Leading technologies and their limitations:
 - Graphene sheets -atomically thick which gives excellent permeability but defects during manufacturing severely impact performance
 - Carbon Nanotubes - MD studies are promising but synthetic techniques unable to achieve necessary alignment and pore monodispersity
 - Zeolites - Good rejections/selectivities, but low flux and high cost of manufacturing. Generally limited to applications needing thermal/chemical resistance

Lyotropic Liquid Crystals (LLCs) share the characteristic ability of nanostructured membrane materials to create highly ordered structures with the benefits of low cost and synthetic techniques which are feasible for large scale production.

- Forms lamellar, bicontinuous cubic and hexagonal phase based on solution composition
- My monomer forms HII phase consisting of vertically aligned, monodisperse, straight pores in a hexagonal array
- Hydrophilic regions point towards pore centers
- Until recently, they could not be aligned - hindered progress
- Talk about Yale alignment techniques
- LLC HII phase membranes offer potential for high permeability and selectivity which equals low energy consumption

Constructing a molecular model may give a clearer picture of the microscopic structure of LLC membranes which will change how we think about their design.

- The arrangement of sodium ions in the channels is thought to be confined to the pore walls. It is possible they are arranged more randomly
 - This could change how one thinks about molecules diffusing through membrane
 - Could also be a difference between lyotropic and thermotropic phases
- How many monomers are in a layer?
 - There is no clear answer to this question in literature. I'd like to confirm or deny past predictions
- What is the equilibrium water content in lyotropic phase?

A molecular level understanding of solute transport in LLC membranes will accelerate development efforts by providing guidelines for monomer design.

- HII phase studies currently limited mostly to one monomer with minor variations
- Current optimization efforts performed through trial and error
- Macroscopic models are the only source of predictive modeling
- An atomistic understanding of the mechanism of solute transport can identify performance bottle necks and direct design of future monomers/membranes
- Will we observe Donnan exclusion or some variation on it at the pore entrance
- What are the relative weights of steric and electrical effects that determine selectivity – is there an optimal balance
 - Look at Coulombic vs. Lennard Jones interactions

- Do ions or water have trouble getting through because of interactions with other things in the pores (e.g. ions, water, carbonyl groups, benzene rings)
- Does concentration of ions in the pore repel incoming ions?

A physically accurate molecular model with easily modified structural features will launch a new phase of research into directing design of an optimal LLC membrane.

- The paper will illustrate the development of a predictive molecular model
- Measurements made to validate model
- Observations of transport mechanism
- The model is consistent with experiments and ready to extend to other systems

2 System Setup

HII monomers were parameterized using the Generalized Amber Forcefield with the Antechamber package provided with AmberTools16. All molecular dynamics simulations were run using Gromacs version 5.1.2.

The most suitable monomer structural configuration was decided by applying a simulated annealing process to the parameterized monomer.

- Initially parameterized monomer gives unfavorable structure
- Structure cooled from 1000 to 50 K over 10 nanoseconds
- Result not global minimum but close enough for structure building
- Multiple configurations saved from annealing trajectory to prove independence of starting config

The timescale for self assembly of monomers into the hexagonal phase is unknown and likely outside of a reasonable simulation length.

- Work done that shows coarse grain model self assembly in 1000 ns
- Attempts with HII system not fruitful
- Wrote own code to assemble monomers into HII configuration (described in intro) close to what is expected – equilibration simulations allow structure to relax into expected configuration
- Code has adjustable parameters: Pore-to-Pore distance, pore radius, number of monomer layers (justification for parameters chosen in following paragraphs)

- This is the thermotropic phase, information used depends on thermotropic experimental data

After some experimentation, it was found that twenty monomer layers per pore provided a balance of structural accuracy and computational efficiency.

- Space between membrane layers in z direction - semi-isotropic sims fix z box dimension
- Small number of layers create micellar structure
- Beyond 20 layers is unnecessary to get expected configuration

The starting distance between layers was chosen so that energy minimization occurred with no errors due to overlaps.

- Layers collapse to favorable layer-to-layer distance within first few picoseconds of equilibration

The remaining parameters were chosen based on experimental data.

- SAXS to get Pore-to-Pore
- TEM images estimate pore size

NPT simulations were run at 300 K and 1 bar for system equilibration.

- Monitored 'hexagonality'
- Pores don't show perfect hexagonal character for short sims (20 ns)
- We see a smaller average pore-to-pore distance than reported
- Varied initial pore-to-pore distance and ran very long simulations
- Starting pore-to-pore distances of 4.0 and 4.5 converge to same average with longer sims

After an equilibrated structure was created, a crosslinking procedure was performed in order to better parallel synthetic procedures.

- Crosslinking maintains alignment of cylindrical mesophases
- head to tail addition
- Details of crosslinking algorithm (refer to appendix or supplemental info)

The crosslinked system was then solvated with water to mimic a membrane in water.

- x ns sims run to allow full water penetration into pores
- simulated isotropically with enough water in between periodic images

3 Results and Discussion

The final, equilibrated system had pores which were spaced 3.5 nm apart. This is the thermotropic phase though. More to come once system is solvated.

Questions to be answered and experiments to test them:

- Question: How many monomers are in each layer? Do we even see defined layers?
 - **Why this is important:**
 - We can understand how monomer shape/size/length influence pore density
 - Ideally we'd want as many pores as possible per membrane area. More monomers per layer means more material needed and less pores formed.
 - We can see whether the effects of pi stacking are as pronounced as hypothesized in other papers.
 - fixed-charge models may underpredict pi-stacking – searching for a reference to confirm this although that would make sense. How would this limit what we can say about the pore structure?
 - **Experiments to be run:**
 - Use membrane thickness and approximate pore size to define cylindrical disk regions. Measure number of monomers in these regions
 - Visualization will help too
 - **Hypothesis:** There are an average of 7 monomers per layer when defined per unit volume but there are not well-defined layers as pictured in the literature. While long range order is maintained, hexagonal mesophases are disordered within their hydrophilic and hydrophobic domains. Staying completely ordered, stacked on top of each other is not entropically favorable.
- What is the mechanism of sodium transport through the pores?
 - **Why this is important:**
 - Past literature reports ions arranged in a circle about pore walls leaving void space as a pore. Simulations show that they may be arranged gaussian-like
 - Ions may play a different role in transport than previously thought. They might hinder transport by slowing diffusion of other sodiums and molecules.
 - Experimentalists may be over-predicting flux through pores because they view it as a hollow channel.
 - **Experiments to be run and what they can tell us:**

- Measure timescales of counter-ions binding to carbonyl groups. The residence time of a sodium ion – get scripts from Drew.
 - Observe positions of bulk sodium ions over time.
 - Do they go all the way through or do they cause some sort of momentum transfer that pushes a different ion out of the pore on the opposite side? I would expect higher rejections if the sodium ion is required to diffuse all the way through
 - See if we can observe ion diffusion through hydrophobic matrix. Is it negligible? If it's not negligible, there is whole new issue to consider
 - Observe influence of chlorine ion in NaCl? The hydrated NaCl has to fit in the pore. Does it ion exchange with bound sodiums.
 - **Hypothesis:** Sodium ions that are already acting as counterions stay mostly bound to their functional groups. Sodium ions diffusing through from bulk salt water need to diffuse all the way through and drag along a chlorine atom to maintain charge neutrality. Sodium ions tethered to chloride may exchange with sodium ions bound to monomer. There is negligible diffusion of sodium chloride through hydrophobic matrix.
- What is the mechanism of water transport through the pores?
 - textbfWhy this is important:
 - Bottle necks in membrane design which limit water transport will directly affect membrane performance with regard to selectivity and rejection.
 - The configuration/structure of water molecules in confined regions is not well understood
 - **Experiments to be run and what they can tell us:**
 - Observe hydration shell around entering salt. Do waters get stripped from hydration shell?
 - Quantify how much free water goes through vs. how much gets through as a part of hydration shell. More free water would mean higher water flux and higher rejection.
 - Measure water transport down the center of the pore vs. on the pore walls. Do water molecules orient themselves in a specific way at the pore walls? If water primarily passes through the pore center, maybe there is a modification that can be made so the walls are 'slippery-er' and more water can get through.
 - **Hypothesis:** Water molecules will travel with through the pores with a parabolic laminar-like trajectory. Water molecules along the wall will be hindered as they get stuck in the hydrophilic head groups causing slower transport at the walls – This hypothesis will depend on what I see once I solvate and equilibrate the system with water.

I think the arrangement of sodium ions will change when solvated (That could be an interesting conclusion in itself). No water will be transported through hydrophobic regions.

- What are the relative rates of diffusion of water and sodium?
 - **Why this is important:**
 - The relative rates of diffusion are ultimately what characterizes a membrane's performance. These are what must be optimized.
 - **Experiments to be run:**
 - Calculate diffusion of water and sodium.
 - Use these values to calculate selectivity and rejection
- How can we validate the model?
 - Why this is important:
 - Our simulations should mimic the real system as best as we can within the limits imposed by choice of force field
 - **Experiments to Run:**
 - Direct comparison of conductivity measurements to experimental results
 - SAXS structural comparisons

4 Future Work

We can vary the following to make predictions about new systems:

- Liquid crystal used - or a mixture of different liquid crystals
- Minor structural variations (e.g. 7, 8, 9, 10, 11 ... CH₂'s in the tails)
- Counterion – Size/valence of counterion
- Functional head groups
- How does varying these things effect pore separation, pore size, phase stability, and transport and why are these effects observed

5 Conclusion

In this work, a molecular model has been developed which can predict transport in an lyotropic liquid crystal membrane.

- Results presented for HII phase monomer but can be adapted to other LLCs
- Model can be used for prediction of transport properties in new membranes