University of Colorado Boulder

Department of Chemical and Biological Engineering
596 UCB
Boulder, Colorado 80309

t 303-735-7860
f 303-492-8425
michael.shirts@colorado.edu

May 3rd, 2019

Dear Editors,

We are submitting "Chemically Selective Transport in a Cross-linked H_{II} Phase Lyotropic Liquid Crystal Membrane" by Benjamin J. Coscia and Michael R. Shirts, for consideration for publication as an Article in the Journal of Physical Chemistry B. We expect this work to be of significant interest to researchers who study nanostructured polymer membranes for aqueous separations.

In this article, we use molecular dynamics (MD) simulations in order to observe transport of small solutes in an inverted hexagonal (H_{II}) phase self-assembled lytropic liquid crystal (LLC) polymer membrane. This is one of the first, and by far the most extensive, uses of molecular dynamics to understand the molecular details of solute transport in such chemically complex nanostructured channels. Most importantly, we show how such channels can give rise to selective transport that is not simply size dependent, but also varies according to chemical functionality of the solutes.

Recently, we characterized an atomistic molecular model of an LLC membrane that is maximally consistent with experimental observations (Coscia et al. *J. Phys. Chem. B*, 123, 289–309 (2019)). In this work, we observe and quantify transport of water, sodium and 20 small polar solutes within the pores of our atomistic H_{II} phase LLC membrane model. In general, all solutes exhibit subdiffusive transport behavior characterized by intermittent hops between long periods of entrapment. However, due the pores' inhomogeneous architecture, we observed 3 different mechanisms of entrapment. First, solutes can diffuse out of the pores and become entangled between tails. Second, many of the solutes are capable of donating hydrogen bonds to monomer head groups for extended periods of time. Finally, solutes can associate with monomer head group counter-ions within nanopores. Each solute is influenced by each mechanism to varying degrees dependent on its size and chemical functionality. We begin our discussion with a broad description of these mechanisms in the context of all solutes before restricting the discussion to more detailed analyses of subsets of chemically-similar solutes.

Some suggestions for reviewers are:

1. Menachem Elimelech is a leader in the development of membrane technologies for water desalination and water reuse (Yale University, 203-432-2789, menachem.elimelech@yale.edu).

2. Francisco Hung has used molecular simulations to study nematic liquid crystals and various nanostructured materials (Northeastern University, 617-373-8619 f.hung@northeastern.edu)

3. Mahesh Mahanthappa has experience modeling soft materials using molecular dynamics including work on ion transport in various ordered liquid crystalline phases. (University of Minnesota, 612-625-4599,maheshkm@umn.edu)

Please send correspondence regarding this paper to Michael R. Shirts (contact details in letterhead).

Sincerely,
Michael R. Shirts
Benjamin J. Coscia