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Water transport and ion rejection investigation for application of cyclic peptide nanotubes to forward osmosis process: A simulation study

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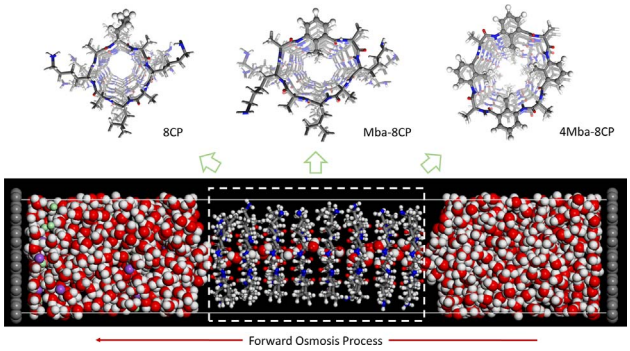
GRAPHIC ABSTRACT



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ABSTRACT

In this study, the transport performance of water molecules and the ion-rejection ability of cyclic peptide nanotubes (CPNTs) were examined on a molecular level via a simulation of forward osmosis (FO) filtration phenomena. A FO filtration model and three types of CPNTs, 8CP, Mba-8CP, and 4Mba-8CP (with different levels of modification by hydrophobic functional groups), were constructed via molecular dynamics (MD). MD simulation was adopted to explain the diversity transport mechanism between different types of CPNTs, and to analyze how hydrophobic modified functional groups affect the FO filtration process. The hydration structures of cations and anions were validated via radial distribution function (RDF) and hydration analysis. The interaction energy of van der Waals (vdW) and coulombic energies at the interface between water molecules and the first cyclic peptide cage suggested that hydrophobic modified functional groups reduced the interior affinity between water molecules and nanotubes, which made it difficult for water molecules to enter a nanotube. During FO filtration calculation, the alteration in the number of water molecules in each region of saltwater, pure water and membrane was traced and recorded. The osmotic pressure was considered as the driving force for concentration-driven FO process which was calculated via the Van't Hoff equation in this work. By combining the above results, water permeabilities of the three types of CPNTs could be directly calculated and compared. The results of the water permeabilities agreed well with the interaction energy analysis. Finally, the hydration structure of cations within a nanotube was used to directly study the ion rejection mechanism of CPNTs. Three types of CPNTs showed high selectively between water molecules and ions. The partial charge distribution of a cyclic peptide

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cage illustrated how cations are trapped within nanotubes. A microscopic view of this information was informative in the analysis of nanotube properties and in the application of CPNTs to the filtration process.

1. Introduction

As populations grow and climates change, water resources have escalated in importance. To meet the ever-increasing demand, desalination processes via membrane filtration technologies are being widely applied. Nevertheless, the requirements for drinking water have increased, which means the development of novel membranes that combine high levels of flux and solvents/particulate rejection is required in energy-saving processes. Aquaporin was isolated from the human kidney [1]. Aquaporin is a type of protein channel that simultaneously transports water rapidly while completely rejecting ions [2]. This excellent transport performance has obviously attracted the interest of scientists working in related fields, and attempts to embed "water channel" properties into membranes are now being developed. Kumar et al. successfully revealed Aquaporin-embedded lipid bilayer membranes that have outstanding water permeability [3]; other pioneering studies have shown these types of membranes to have water permeability that is as much as 100-fold that of common polymeric RO membranes [2,4]. Even so, Aquaporin has drawbacks that include expensive acquisition and a complex molecular structure, which makes it difficult to produce on an industrial scale. On the other hand, Gramicidin A (GA) is considered another candidate because of a relatively simple peptide structure that can form a nano-scale porous membrane with a lipid bilayer. Although GA has shown performance similar to Aquaporin in RO application [5,6], GA is toxic, and must be treated cautiously, which limits the applications. Therefore, ways to develop inexpensive, stable and safe water channels with high levels of water flux remains an interesting theme.

Ideas for artificial water channels have been developed using carbon nanotubes [7–10], an I-quartet [11–13], and a macrocycle 4 [14–16]. These form nano-scale porous materials with a lipid bilayer, and show properties similar to Aquaporin that are less expensive. With the successes of these pioneer studies, artificial water channels are expected to herald a new generation in desalination membranes. In this study, cyclic peptide nanotubes (CPNTs) were studied as another candidate for an artificial water channel. CPNTs are a type of organic nanotube that is formed through self-assembly of hydrophobic side chains that can be placed into a lipid bilayer to form a specific nanoporous structure that forms a biological membrane with high biocompatibility [17–19]. Therefore, CPNTs are a candidate for the biomimetic material that is used in artificial water channels. In addition, membranes with these types of water channel properties are expected to be applicable to forward osmosis (FO) filtration [20–24]. A biomimetic water channel with high levels of water flux, high levels of solvent rejection, and energy savings, would be a novel membrane material.

In the development of novel materials, it is necessary to study the characteristics on a molecular scale. Microscopic information such as interaction energy between materials and water-transport mechanisms is helpful in material development. Many pioneering simulation studies in the construction of water channels are available to assist in this type of experimental work. Water permeability, transport mechanisms, and selectivity of Aquaporin channels have been discussed in the development of natural water channels [25–29]. GA channel simulation has been explored using molecular dynamic simulations and Monte Carlo methods [30–34]. For artificial water channels, carbon nanotubes have been widely investigated via theoretical studies [35–40]. The structural characteristics and predictions for water transport performance based on solution-diffusion models for different types of CPNTs were presented in our previous work [41]. The above studies have provided much useful information that would have been difficult to obtain from actual experimental work, and the results agree well with those from experimental data.

In this study, three types of CPNTs were adopted in FO filtration simulation. First, the performance of water molecular transport with different types of CPNTs was simulated using MD techniques. Second, the interaction energy of water molecules entering CPNTs and water permeabilities were discussed to elucidate the transport mechanisms for different types of CPNTs in the FO process. Finally, an ion with a hydrated structure was placed into a nanotube to study the rejection mechanism. Selectivity was discussed according to the relative mobility between water molecules and ions via mean square displacement (MSD) analysis. The potential charge distribution in cyclic peptide cages was used to illustrate the ion rejection mechanism.

2. Simulation method

This study used a forward osmosis (FO) simulation model to examine the water permeability performance and ion rejection ability of CPNTs. Three types of CPNT molecular models, 8CP, Mba-8CP, and 4Mba-8CP, were created based on the MD simulation procedures that were used to observe the FO calculation process. Furthermore, predictive water permeabilities and ion rejection were examined. All molecular models were constructed using BIOVIA Materials Studio® commercial software. The model construction, simulation parameters, and physical property estimations are discussed in the following sections.

2.1. Cyclic peptide nanotube molecular model

From our previous study [41], shown in Fig. 1, three types of CPNTs were adopted in this FO process simulation work. Common 8CP via the tailoring of cyclo-[L-Lys-D-Ala-L-Leu-D-Ala]$_2$, Mba modified cyclic peptide, and cyclo-[L-Lys-D-Ala-L-Leu-D-Ala-L-Lys-D-Ala-γ-Mba-D-Ala]

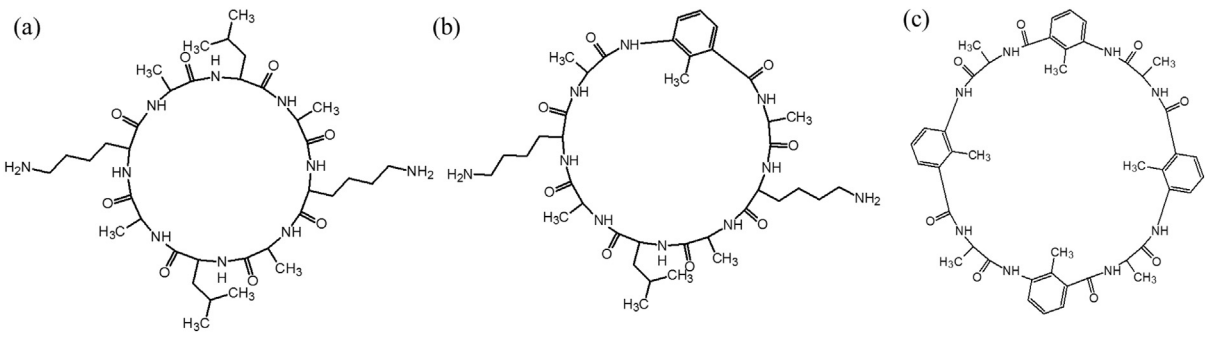

Fig. 1. Chemical structures of (a) 8CP, (b) Mba-8CP, (c) 4Mba-8CP.