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Understanding water and ion transport behaviour and permeability through poly(amide) thin film composite membrane

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ABSTRACT

Molecular dynamics (MD) together with the adaptive biasing force (ABF) and metadynamics free energy calculation methods was used to investigate the permeation properties of salt water through poly(amide) thin film composite reverse osmosis membranes. The thin films were generated by annealing an amorphous cell of poly(amide) chains through an MD method. The MD results showed they have typical structural properties of the active layer of thin film composite membranes and comparable water diffusivity ($2.13 \times 10^{-5} \text{ cm}^2/\text{s}$ for the film with a density of 1.06 g/cm^3) and permeability ($9.27 \times 10^{-15} \text{ cm}^3 \text{ cm/cm}^2 \text{ s Pa}$) to experimental data. The simulations of water permeation through the films under different transmembrane pressures revealed the behaviours of water molecules in the thin films and the dynamic regimes of water permeation, including Brownian diffusion, flush and jump diffusion regimes. The intermolecular interactions of water and ions with poly(amide) chains showed a strong dependence on the local structure of films. The attraction between water and poly(amide) molecules can be up to 8.5 kcal/mol in dense polymer regions and 5 kcal/mol in the pores of about 3 nm. The ABF and metadynamics simulations produced the profiles of free energy potential of water and ions along the depth of the thin films, which provided important information for quantitatively determining the barrier energy required for water permeation and rejection of ions. The thin film with a density of 1.06 g/cm^3 and a thickness of 6 nm offers a rejection to Na^+ but a slight absorption of Cl^- (0.25 kcal/mol) at 0.3–0.4 nm distance to its surface. Water molecules must overcome 63 kcal/mol energy to move to the centre of the film. The dependences of the barrier energy and the water–polymer interaction energy on the local free volume size in the thin film were analysed. The simulations of water permeation under high transmembrane pressures showed a nonlinear response of the concentration and distribution of water molecules in the film to the imposed pressure. Compaction of the film segments close to the porous substrate and water congestion in dense regions significantly influenced the water permeation when the membrane was operated under pressures of more than 3.0 MPa.

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1. Introduction

Thin film composite membranes [1–3] are currently applied in commercial water treatment and water pollution control worldwide. They offer advantages over single-material asymmetric cellulose acetate membranes in high flux, high rejection to salt and some low molecular weight organics, and stability at higher temperature and over a larger pH range [4,5], as the top-barrier layer formed in situ and the bottom porous substrate can be easily controlled both in chemistry and structure to maximise the overall membrane performance. The top-active layers are often a thin layer of poly(amide) polymer made by interfacial polymerisation of an aromatic polyamine, such as

m-phenylenediamine (MPD), with aromatic poly(acyl)-halides, such as trimesoyl chloride (TMC) [4,6]. The layer is essential for the performance of the membranes as it predominantly determines the separation properties, while the substrate as a support layer gives the necessary mechanical properties. The water permeation and ion rejection properties of the thin film poly(amide) membranes are strongly affected by a considerable number of parameters. The most important are the properties of the skin layer, including polymer composition [7–10], molecular structure [11–13], free volume and its distribution [14], morphology [15–17] and electric potential on surface [18].

Extensive experimental investigations have been performed with significant interest in developing high water flux and energy efficiency, high contaminant selectivity, and high chemical-stable thin-film composite membranes. The theoretical interpretation

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based on the available experiments [18–21] has provided useful qualitative information in understanding water and ion transport through poly(amide) membranes. Nonetheless, many aspects of the molecular mechanism governing the membrane performance are still unclear, such as the dependence of water and ion diffusions on polymer structure and dynamics and salt and water transport in the active layer of poly(amide) TFC membranes.

Molecular dynamics (MD) is an effective tool to probe molecular interaction in polymer penetrant systems. MD simulations of the structures and diffusions of water, Na^+ , and Cl^- in poly(amide) membranes have suggested that H_2O transport occurs by a jump-diffusion process with each jump $\sim 3 \text{ \AA}$ in length [22,23]. Equilibrium MD simulations of a hydrated poly(amide) membrane were performed to determine the density and diffusivity of water within the membrane [24]. MD simulation technique was incorporated with positron annihilation lifetime spectroscopy (PALS) to understand the fine-structure of polyamide active layers of thin-film composite membranes in a dry and a wet condition [13] and the structural properties of a polydimethylsiloxane (PDMS) membrane and the feed transport behaviours of ethanol and water during a pervaporation process [25–27]. The effects of residual solvent in a 6FDA-mPDA PI membrane on the gas sorption and permeation of the poly(amide) membrane and on the flexibility of the polymer segments were analysed based on the energy data from MD simulations [28]. Two atomistic models were proposed for ODPA-ODA amorphous phase to study the effects of skin layer of a glassy polyimide on gas permeation [29] and to investigate the gas permeation in bulk models of the glassy oxydipthalic anhydride and oxydianiline (ODPA-ODA) polyimide [30].

The knowledge of the intermolecular interactions of water and ion with molecules constituted a thin film and the free energies of water and ions during permeation are essential prerequisite to understand the performance of the barrier layer. Most of MD studies [22–24,28], however, were based on equilibrium MD simulations at a constant pressure and no data for free energy of water and ion through poly(amide) thin film have been provided. Reverse osmosis membrane desalination is operated under a pressure gradient, and the membrane structure and water concentration in the membrane will be different from that at a constant pressure. To the best of our knowledge, there are few reports on the water and ion permeations across poly(amide) membrane under pressure gradient at the nanoscale. The current work aims to provide the basic information of water and ions through poly(amide) membranes for understanding the permeation or rejection mechanisms, by investigating the behaviours of water molecules and ions through different poly(amide) membranes and the intermolecular interaction with MD simulation. The free energies were calculated by both metadynamics [31] and adaptive biasing force (ABF) [32,33] methods. The motion features of water molecules in the membrane under a transmembrane pressure were studied. Diffusivity and permeability of water were determined and critically compared with experimental values.

2. Materials and models

2.1. Materials and structure of thin films

Unsupported poly(amide) thin films were created for the MD simulations. As this work focuses on the properties of the active skin layer of polymer membranes, the porous substrate is excluded in the system. Each molecule chain of the thin films is composed of 39 *m*phenylenediamine (MPD) monomers and 19 benzene 1,3,5-tricarboxylic acid chloride (TMC) monomers. The polymerisation of poly(amide) membranes has been described in the literature [22,34,35]. TMC and MPD monomers and the repeat unit of the

poly(amide) were built using PRODRG [36]. Their chemical topologies were created based on the information from PRODRG and the parameters were generated from CHARMM27 [37] and PCFF [38,39]. The atomic charges were determined by the Density Functional Theory (DFT) calculation at B3LYP level using the 6–31G(d, p) basis set and the CHelpG electrostatic potential fitting method [40]. A poly(amide) molecule model composed of two repeat units (2 MPD and 2 TMC) and a methyl at each end was used for the QM calculation and the atomic charges were determined from the middle MPD and TMC. The QM calculation was implemented by using Gaussian 09 [41].

It is challenging to create an atomistic model to exactly represent the array of polymer molecules in a membrane, as there is insufficient information about the chemical and network structures of poly(amide) thin films, where the molecules are cross-linked and overlapped. The experimental measurement of the network structure of the thin film is still a big challenge, although the 3D nanostructure of membranes has been identified by incorporating transmission electronic micro-tomography, image processing, and 3-D reconstruction technologies [16,42]. The realistic modelling of the polymerisation process forming poly(amide) membrane may produce an atomistic model for MD simulations, however, the polymerisation process generally takes place over seconds, which is prohibitively slow on the time scale of MD simulations [24].

In the present work, the atomistic models were generated by annealing an amorphous cell created by randomly placing 40 poly(amide) chains into a supercell with a confined thickness of 6.0 nm in *z* direction and periodic boundary conditions in both *x* and *y* directions. The molecules were placed by also taking into account nonbonded interactions with the already constructed chains, including their periodic images. The sizes of the amorphous cells in *x* and *y* directions were determined by the expected cell density of the thin film ($0.7\text{--}1.5 \text{ g/cm}^3$). A thin film with a comparable density to experiments, 1.06 g/cm^3 , was also built. The density is a calculated value [43,44] based on the experimental density of hydrated FT30 membrane (1.38 g/cm^3) containing 23 wt% water [22] and the assumption that dehydration would not result in layer shrinkage, and it has been used in MD simulation works [24,43–45]. To reconfigure the position and orientation of the poly(amide) molecule chains, each of the initially constructed amorphous cells was then subjected to an energy minimisation of 1.0 ps and a simulated annealing procedure in vacuum. The annealing scheme consists of heating up to 600 K at a heating rate 50 K/ps, holding at 600 K for 50 ns and cooling to 300 K in 6 ps under a pressure of 0.1 MPa using the NPT ensembles, with harmonically constraints placed upon the top and bottom sides (in *z* direction) of the cell. Finally, a dynamic MD simulation of 20 ps was performed to release the residual energy and relax the annealed amorphous cell.

The poly(amide) film was immersed in an orthogonal box of aqueous solution containing 0.017 wt% NaCl to generate a salt-water-film model. The model contains 7998 water molecules and 38 $\text{Na}^+\text{--Cl}^-$ pairs. Before the MD simulations of water and ion conductions through the membrane, energy minimisation and 3 ns equilibrium MD in the constant temperature and pressure (NPT) ensemble (300 K and 1 atm) were performed, successively. The system boundary in *z*-direction was adjusted by using the Langevin piston Nose-Hoover pressure control method with a damping coefficient of 5 ps^{-1} and a constant area in *x*-*y* plane.

2.2. Simulation details

The thin film construction, the salt-water-film model assembly and the MD simulations were performed with the programme VMD and NAMD [46]. The structure file was created for all segments of the poly(amide) membrane and the water molecules,

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