The Influence of Geometry and Wall Character of Pores on the Permeation of Ions and Water through Desalination Membranes

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Abstract
The transport of water and ions across mimicked nanotube membranes with pseudo atoms is studied using molecular dynamics simulations under equilibrium conditions and hydrostatic pressure. Different pore surface properties are constructed by assigning partial charges on the sites of specified atoms to explore the influence of charges and polarity. The energetics of water and ion transports through the nanopores was calculated to evaluate their filterability to water. The simulation results show that the free energy barriers to water and ion conduction much depend on the charges at the pore entrance and the dipole within the pore. The membranes with hydrophobic pores and negatively charged entrances would be very efficient in the water transport and ion rejection. The charges and dipoles of the pore wall and the aligned dipoles of water molecules in the pore can create a significant force on ions.

Keywords: pore geometry; chemical character; charge; molecular dynamics

INTRODUCTION
Membranes have long been utilized for the desalination of seawater to produce fresh water suitable for human consumption and irrigation in areas of water scarcity. The nature of the membrane desalination method is high pressure, and thus significant energy consumption, required to force water through the membranes. This is one of the major impediments to influencing the wide application of the seawater desalination method.

The geometry of pores and the chemical character of the pore surface have a great influence on the permeation of ions and water. One mechanism to reduce the energy is thus to develop membranes containing nanopores with unique morphology and surface character that can lead to high-flux water desalination at a lower pressure than existing membranes, such as the semipermeable membranes used for “reverse osmosis” desalination method. This interest is based on the existence of some selective biological pores that admit the flow of water and block ions (Beckstein et al., 2003; Luzhkov and Åqvist, 2001; Sui et al., 2001). It has been demonstrated that the mechanical properties of nanotubes can be changed by altering their electronic structure (O’Connell et al., 2002). Anionic surface charge density of carbon nanotube membranes have been enhanced by covalently attaching carboxylate groups to the nanotube walls through using an electrochemical derivatization method, as a result, the electroosmotic flow (EOF) was in the direction of cation migration across the membrane and the EOF rate increased (Miller and Martin, 2002). A membrane structure consisting of an aligned array of open ended carbon nanotubes with anionic charges at the tips was designed for the diffusive transport of aqueous ionic species (Majumder et al., 2008). Water molecules show different electro tropism near these charged nanotubes. It has been found that water molecules tend to form very ordered structures inside CNTs and at the entrance of charged pores (Hata et al., 2004; Koga et al., 2001). The electric field may lead to fast transport of water and efficient rejection to ions.
In this work, we expect to explore how the water and ion conductions cross a membrane depend upon its geometry, charges and polarity. The comprehension of these dependences was explored with MD simulations of salt solution passing across a radically simplified nanotube membrane model. The behaviours of water and ions conducting through membranes were captured from the simulations to address how the physical and chemical properties of pores affect the permeation of ions and water.

**MOLECULAR DYNAMICS**

The complexity of pores in realistic membranes makes them difficult to disentangle the contributions of various pore properties. To reduce the number of geometrical and chemical parameters, a simplified pore model was designed to capture the pore characteristics of the membranes currently used for water desalination.

A hexagonal periodic system containing a nanotube membrane sandwiched by bulk water was constructed, as shown in Figure 1. The membrane was created by pseudo atoms. The embedded nanotube has a diameter of 0.72 nm and a thickness of 3.5 nm. As the present work focuses on the influence of pore geometry and pore surface properties, different pores were created by assigning charges in the membrane, where the pseudo atoms are held in their equilibrium position by harmonic constraints. The Lennard-Jones parameters for the interaction between a pseudo atom and a water oxygen are $\varepsilon=0.16971$ kcal/mol and $\sigma=3.355\text{Å}$. The initial system configuration was created by solvating the membrane model with water and, then, by replacing some water molecules with $\text{Na}^+$ and $\text{Cl}^-$ ions to reach a target salt concentration. In the simulation, high salt concentration of 120g/kg was used. The total thickness of the salt water reservoir was 6.0 nm.

![Figure 1](image.png)

**Figure 1.** Water and ions pass through a membrane. The membrane with 0.72 nm pore diameter is shown in light gray. $\text{Na}^+$ in gray, $\text{Cl}^-$ in cyan and water molecules in red and white.

MD simulations were performed with NAMD (Phillips et al., 2005) based on TIP3P potential and Lennard-Jones parameters of CHARMM force field. The electrostatic interactions were computed with a particle mesh Ewald method (Essmann et al., 1995). The local interaction distance of 1.2 nm cutoff was used for both electrostatic and van der Waals calculations. All simulations were performed at constant temperature (295 K) and pressure (1 atm) with periodic boundary conditions. The Langevin temperature control scheme was used. The integration time step was 1 fs and
coordinates were saved every 1 ps. Initially, the nanotube was empty and energy minimization was performed to equilibrate the system. The water diffusion into the pores was then simulated under a constant pressure.

Ten types of membranes were created by assigning charges on all or some pseudo atoms within the pore. The osmotically driven transport of water molecules through the hexagonally packed nanotube membranes was also simulated to assess their suitability for desalination. The number of water molecules and ions that pass through the nanotubes during a constant hydrostatic pressure difference of 1160MPa across the membranes was counted and converted to water flux. All simulations were performed for 20 ns with coordinates recorded every 1 ps. The last 19 ns of each trajectory were used for analysis.

RESULTS AND DISCUSSION

Effect of surface charge
The static and dynamic properties of water in a confined geometry are strongly affected by the surface charge on the confined wall. The injection of charges into membrane pores also influences the ion-selective permeation. Thus, a membrane with well-defined pore structures and proper injected charge density may offers possibilities of extremely fast water transport and salt filtration. To study the effect of injected charge at the pore entrance on the dynamic properties of water and ion, six levels of charged pores were created and for each pore the charges are evenly injected into the sites of atoms of the pore entrance. The partial charges are +0.5e, +0.3e, +0.1e, -0.5e, -0.3e and -0.1e. Figure 2 compares the water structure in the membrane pores with and without surface charge.

Figure 2. Snapshots for water structure in the nanotubes with and without injected charges (red for negative charges and blue for positive charges) from MD simulations of 1160MPa driven pressure at 395 K and 1atm. Water molecules in the pore and the bulk are depicted in CPK.
The water molecules adopt a single-file formation with 1D hydrogen banding (HB) in the narrowest nanotube, whereas in the wider nanotubes they appear to be more disordered (Hummer, Rasaiah, and Noworyta, 2001). Figure 2 indicates, however, that a single-file of water only forms at the center of the 0.72-nm-diameter pore, no matter with or without injected charges, even at high axial pressure driven transport. The water molecules are reoriented at the pore entrance and high density is observed there. However, in a carbon nanotube of 0.86 nm diameter, the water molecules form a highly ordered lattice and a multicolumnar water structure was observed (Mashl et al., 2003). The charges on the atoms of the nanopores alter the orientations of water molecules and the density distribution in the pore entrance. In the negatively charged pores, the water molecules in the entrances are highly polarized with all the hydrogen atoms pointing toward the wall of the pores. The oxygen atoms prefer to interact with hydrogen atoms of other water molecular to form HB in the cases of -0.1e and -0.3e charged pore entrances, whereas the number of HB (nHB) was not found close to the 0.5e charged nanopore orifice due to such high surface charge. In the positively charged cases, the dipole moment of water molecules is incident normal to the pore axis as the same as in the negatively charged pores, while the oxygen atoms point toward the wall of pores.

Figure 3. Orientation distributions of water molecules within nanotubes with/without injected charges. The angles between the dipole moment of water molecule and the positive axial direction (ODDM) were averaged from 19,000 frames (1ps/frame). The axial direction is opposite to the transport direction of water.

The orientational distribution of water in the nanopores can be better described by the direction of the dipole moment of water molecular as shown in Figure 3. The angle between the dipole moment of water and the positive axial direction (ODDM) is only provided here to show the reorientation and orientational distribution of water in different pores, although the angle between water OH-bond and the positive axial direction (ODOH) was also computed. Due to the surface charge, the water molecules in the exterior of the pore become more ordered as a result of the electrostatic interaction when compared to the case without charge. When the water molecules leave the charged surface and continuously move into the pore, the hydrogen atoms tend toward the atoms with negative charges, whereas the oxygen atoms like toward the positive charged atoms. The angles of less than 90° and more than 90° are observed in the positively charged pores and in the negatively charged pores, respectively. Water molecules tend to form ordered single-file water within narrow tubes. With the increase in pore diameter, the flipping of the water dipole becomes more frequent (Sinnott, Aluru, and Liming, 2006). In -0.1e, -0.3e, -0.5e, +0.1e and +0.3e charged pores, the
flipping of water molecules is found in the centre of the nanopores. When hydrogen bonds between water molecules in the centre of the nanotubes break, they quickly reform and the water molecules move in the rest half of nanopores by a new single file.

It was found that an exterior force is required to drive the water molecules into the nanotube without any charge. Once the water molecules are in the tube, they will be easily transferred within the confined space before escaping from another end of the tube. Figure 4 shows the potential of mean force (PMF) (Luzhkov, 2008) for water, which indicates the free energy barrier as water molecular is brought from bulk into the pore and exiting the pore from another side. As how much of the influence of injected charges on the water molecules in the bulk is unclear before calculation, the comparison was performed with respect to the PMF of water at the exit of pore (z= -17.5 nm). It was found that the PMF of water drops within the hydrophobic tube close to the exit.

In contrast to the case of the nanotube without charge, water molecules were found to be sucked into the negatively charged nanotubes very quickly. However, the electrostatic and the van der Waals interactions confine the entered water molecules in the entrance of the nanotubes. The further motion of the water molecules into the centre of the nanotubes is also restricted (Figure 4). For the case of -0.1e charged pore, the water molecules can easily release the restriction and move into the centre of pore. As a result, faster water molecule flow through the -0.1e charged nanopore than the pore without charge was found in the simulation (Figure 5). This suggests that the water flow can be enhanced by injecting an optimum negative charge level. For the -0.3e charged nanopore, the restriction is much higher than in the -0.1e charged pore (Figure 4) and results in lower transport rate (Figure 5). It was also found the -0.5e charged nanopore entrance strongly confined the sucked water molecules close to the charges and resisted the water flow. The positive charges have more considerable influence on the motion of water molecules. The restriction to the water molecules is stronger compared to the negative charged pores with the same number of charges. The approximate same PMF was found at the entrances of the -0.1e charged and +0.1e charged pores. Once the water molecules enter the pore the positive charges push them into the centre of the pore, but, surprisingly, there appears to be more force required for water to move further.
It is also found that, once inside the pore without charge, when the water molecules move to certain position in the pores of -0.1e, -0.3e, +0.1e and +0.3e charged entrances, the PMFs of them are almost flat (Figure 4). This indicates that the sections of nanopores corresponding to the flat PMFs are almost frictionless and no additional energy barriers are required for water to move longer. Therefore, the conduction of water through these nanopores is largely independent of their length.

**Effect of dipole-electric field**

As polar molecules, water molecules well align in a narrow nanotube. The average dipole moment per water molecule has been found to be 2.7D for water wires in the absence of the nanotube (Mann and Halls, 2003). High polarizability of pores would significantly alter the behavior of confined polar substances. The flow of water and ions through membranes is largely limited by chemical interactions of functional molecules at the pore entrances (Majumder et al., 2008). In the present study, the pore was modified to be incomplete hydrophobic by injecting partial charges of ±0.26e on two entrance atoms 0.29 apart. This will lead to a dipole moment of 3.74D be parallel to the pore axis and has the opposite direction to water transport. Two dipoles (2D) and four dipoles (4D) were injected into two pores, respectively. The dipoles were evenly distributed around the entrance to produce a dipole moment along the pore axis (2D and 4D in Figure 6). All the atoms in the pore were also charged to produce a hydrophilic nanotube with total dipole moment of zero (full charged in Figure 6).

The water molecules reoriented in all polarized-entrance pores. Such behavior can be attributed to the partial breakdown of the tetrahedral HB network. As the dipole moment is +Z, the reorientation of water molecules at the entrance of the pores is the same as the positively charged pores (Figure 3 and Figure 7). The difference in the reorientational motion is that the flipping of water molecules occurs when they move away from the polarized pore surface. The reorientational motion of water molecules can be characterized by the dipole moment reorientation time. It has been found that the reorientation of water molecules confined in carbon nanotubes is a function of the temperature and the nanotube size and the reorientation ability of water inside a nanotube was characterized by using an autocorrelation function of water dipoles (Sinnott, Aluru, and Liming, 2006). In the present simulation, the deviation of the dipole moment direction was analyzed to assess local orientation rate of water molecules. It was found that the introduction of either two or four dipoles did not observably reduce the reorientational rate of the water molecules. The water molecules inside the pores with dipoles spend a longer time in their dipole moment reorientation compared to the no-
charged pore. However, in the case of -0.3e charged-entrance pore, the reorientation of the water molecules confined in the pore entrance is speeded by the injected charges.

![Figure 6. Snapshots for water structure in nanotubes with and without dipole (red/blue) from MD simulations of 1160MPa pressure driven at 395 K and 1atm. Water molecules in the pore and the bulk are depicted in CPK.](image)

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In the complete or incomplete hydrophobic pores of 0.73nm in diameter, the water adopts a single-file arrangement even though the pores are wide enough to admit three water molecules (Figure 2). However, in the hydrophilic pore (full charged in Figure 7), the water spontaneously orders into a regular array (Figure 8). On average, about 4 water molecules can simultaneously move through a cross section of the pore. The highly ordered structures of water have been found in carbon nanotubes and suggested to arise from the best match of the oxygen and carbon van der Waals interactions and the formation of optimal hydrogen bonding networks (Corry, 2008; Peter and Hummer, 2005). The hydrogen bonds for the water molecules confined in the nanotubes are counted when the oxygen distance of two water molecules is smaller than 0.3nm and the angle between the O-O axis and one of O-H bond is less than 30°. It was found that the water column is much compacted. The average HB number from 9999 frames was found to be 31 for 55 water molecules confined in the pore, which is much higher than about 6 HBs for about 17 water molecules in hydrophobic or incomplete hydrophobic pores. Because it is energetically costly to rupture the tight HB network inside the nanotube, high PMF was found for the water in the case of...
full charged pore (Figure 4). The higher resistance to the water molecules moving through the pore is also due to the interaction of hydrogen of water and the atoms of pore wall. This also results no significant increase in the flux of water through the hydrophilic pore even though the density of water molecules is much higher compared to other cases (Figure 5).

Figure 8. Snapshots from MD simulations of 0.7256 nm diameter pore at 295 K and 1 atm. Water are in red and white. The negative and positive charges are coloured by cooper and blue, respectively.

**Ion conduction**

In order to calculate the effect of the electric decoration of nanopore entrance on the control of the ions entering to the nanopore, the potential of mean force (PMF) is also calculated for ions (Figure 9). Compared to the PMF for water (Figure 4), there is a very large free energy barrier to ions to prevent their conduction arising predominantly at the entrance of the nanotubes of no-charge, -0.1e charged, +0.1e charged, 2D and 4D. For the nanotube of -0.3e charged entrance the free energy barrier to ion is about 10 times higher than that to water and the sharp increase was found after the ion enters into the nanotube. This suggests that the ion could block the water conduction in a narrow pore. The simulation of water and salt diffusion into a membrane with 0.42 nm pores shows that the water diffusion is blocked by a Na\(^+\) at the pore gate. The full-charged neutral nanotube shows the lowest free energy barrier to ions (Figure 9) and, however, the highest barrier to water (Figure 4), compared to other nanopores but the +0.3e charged one.

The modeling on ionic flux through the membrane structure indicated that the overall ionic flux is largely limited by chemical interactions of ions, the surrounding molecules at the entrance of the membrane pores, the bulk water, and the van der Waals and coulombic interactions with the atoms forming the nanotubes. When an ion enters the pore it has to shed its hydration shell and has energy cost to move the ion from the bulk of water to the nanopore membrane. However, these costs are reduced by coulombic attraction. It was found that the energy difference when the ion is in the month of the pore compared to when it is in the bulk is reduced by about 20 kcal/mol due to the -0.1e charge injection and full-charge injection. The anionically charged pore entrances as gatekeepers dramatically improved cationic transport into the nanotubes but restricted cationic penetrate through the membrane due to coulombic attraction. The highest PMFs in the -0.1e and -0.3e charged entrance pores are 16 kcal/mol and 84 kcal/mol higher than that in the complete hydrophobic nanotube, respectively. The polarized pore improved not only the entrance of cationic into the month of the pore but also the further motion into the pore core. The highest free energy barrier to cationic is reduced by the polarization of the pore entrance.
For narrower nanotubes, stripping the surrounding water occurs as the ion is entering the pore and comes with energy cost as the tubes are not large enough to an ion to enter with its hydration shell. The simulation results show that the 0.72 nm nanopore is roomy enough for an Na\(^+\) enter with its first surrounding shell. An Na\(^+\) has a coordination water molecule number of about 6 in the bulk. It was found that in the hydrophilic pore an Na\(^+\) is also in contact with 6 water molecules. Whereas, the entered Na\(^+\) in the hydrophobic pore replaces one of the water molecules in the single file chain, so that it is in contact with one water molecule on either side. Thus the lowest free energy barrier for the hydrophilic pore was found in the simulation compared to all nanotubes but +0.3e charged. For the +0.3e charged pore the data are ambiguous. The low flat PMF in the hydrophilic pore suggests that the energy cost to move a cationic into the pore mainly relays the interaction in the pore entrance.

**CONCLUSIONS**

The membranes for water desalination can be modulated by attaching functional ‘gate-keeper’ molecules of different size, charge, hydrophilicity and hydrophobicity at the pore entrances. Molecular dynamics simulations showed that the dynamic properties of water and ionic transports through the membranes can be significantly altered by the introduction of charges and dipole. The positive charge injection will impede the water enters to the nanopores, whereas the injection of low-level negative charge can improve the water conduction and make the membrane more efficient to reject salt ions and there is an optimum charged level for a nanotube. The water conduction can also be enhanced by the introduction of certain amount of dipoles, however, the barrier to ions is also reduced. The hydrophobic nanopore showed much lower free energy barrier to water and higher impedance to cationic than the hydrophilic nanopore. The water conduction in single file chain was found in the 0.72 nm hydrophobic nanotube, even though it is such wide that four water molecules can be admitted. The simulation also shows that the energy barriers to water in the hydrophilic nanotube arise predominantly at its entrance and the water conduction in the rest region is almost frictionless. However, in other nanotubes, the frictionless region much depends on the level of the charge or dipole injected. Meanwhile, high energy cost to ion transport was found at...
the entrance of all nanotubes. These results suggest that very efficient transport of water and well rejection to ion is possible in hydrophobic pores with negatively charged entrances.

References


