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Temperature dependence and the effect of charge configuration on water permeation through modified carbon nanotubes: A simulation study

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ABSTRACT

We have investigated the water permeation through carbon nanotube (CNT) membranes as a model of peptide nanotube channels (PNCs). The effect of different charge configured CNTs which tailored based on some artificial ion channels on the water permeation through the channels have been studied. In addition, the temperature dependence of the permeation has been investigated. We have found that there is a jump in the permeation which is somehow related to the characteristics of each channel and the temperature of this permeation jump changes according to the channel configuration. Our investigation on the channels shows that the temperature at which the permeation jump occurs is related to the height of energy barrier, in such a way that the jump for the larger barrier happens at high temperature. So, in this regard, we could find the fundamental aspects for classifications of any channels using some order parameters such as permeation jump, energy barrier of the channel and hopping rate of water molecules into the channels.

1. Introduction

The promotion and prosperity of nanotechnology frameworks to solve some key problems make it as a master key in the field of science and technology. The permeation of fluids through nanopores have wide applications from medical treatment to industrial applications. The efficient transport of water through the cell membrane requires special pathways to cross the lipidic low dielectric medium that surrounds cells and organelles with special charge groups [1].

Water permeation through channels of molecular dimensions is therefore of great interest in biology [2–4], but also in technological applications. Combined with the transport of ions, nanometer size channels are used as sensitive detectors embedded in supported bilayers, with multiple applications such as detection of protein–ligand interaction [5,6] and pH sensors [7]. Popular choices for biology inspired pore-based sensing devices are gramicidin A(gA) derivatives [8] and a-hemolysin [9].

Carbon Nanotubes have attracted much scientific and industrial interest regarding their characteristic structure [10], mechanical and electric properties [11]. Since the discovery of CNT [12], extensive studies have been carried out on these novel materials. Due to their special characteristic, CNTs can be used as best alternatives to conventional materials in many applications [13–15].

The CNTs can be manufactured with diameters ranging from less than 1 nm to more than 100 nm. They can be attached to each other [16], protonated or functionalized with variety of substances [17] that each gives a special character to CNTs. The functionalized CNTs make it possible to design different nanotubes with desired characteristics.

On the other hand, simulations can provide the ultimate details, concerning individual particle motion as a function of time. This can be used to address specific questions about the properties of a model system often more easily than experiment on the actual system [18]. This method could help us to investigate the properties of the model system such as CNTs – with their special characteristics – in more detail.

Despite the hydrophobic nature of CNTs [19], Hummer et al. [20] first demonstrated that a short and narrow CNT can be filled with a single line of water molecules and therefore acts as a possible model system for biological system. However, biological water channels are much more complex than CNTs, with irregular surfaces and highly inhomogeneous charge distribution.

In living cells, there exist analogous water channels that the most notable ones are aquaporins (AQPs), a family of membrane channel proteins, which are abundantly present in nearly all live systems [21]. They have been found in multiple tissues, such as kidney, eye and brain. The CNTs can serve as prototypes for these

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Nomenclature

J_w	net molar water flux (mol/L/s)
J_{tr}	tracer molar flux (mol/L/s)
p_o	osmotic permeation (1/s)
p_d	diffusion permeation (1/s)
Δc_s	concentration difference for specie s (mol/L)
$\Delta\mu$	chemical potential difference (kJ/mol)
ΔP	pressure gradient (Pa)
R	gas constant (J/mol/K)
T	temperature (K)
k	hopping rate (1/s)
A	frequency factor (1/s)
E_a	activation energy (kJ/mol)

biological channels, which can be investigated more easily by molecular dynamics (MD) simulations due to their simplicity, stability, and their small size.

Peptide nanotubes are artificial tubular materials which constitute a new class of synthetically readily accessible peptide-based biomaterials having unique structural and functional properties. The properties of the outer surface and the internal diameter of the peptide nanotubes can be simply adjusted by the choice of the amino acid side chain and the ring size of the employed peptide subunit. Such modified peptide nanotubes, which are unique, have been already enabled their application for design of biologically-relevant transmembrane water and ion channels and pore structures, as well [22].

There are a large number of computational as well as experimental investigations which use CNTs as a biological channel [23,24]. The simulations reveal that a CNT with 8.1 Å in diameter is spontaneously filled with a single file of water molecules and that water diffusion through the nanotube can concertedly move with a fast rate. The key characteristics which account for the transport of water through water channels are the osmotic permeability (p_o) and diffusion permeability (p_d) both of which are experimentally measurable [25].

The osmotic permeability of a channel, p_o, is defined through

$$J_w = p_o \Delta c_s \tag{1}$$

where Δc_s is the concentration difference of an impermeant solute between the two reservoirs connected by a channel, and J_w is the net molar water flux through the channel. Water flows from the reservoir with the lower solute concentration to the other reservoir, because the two reservoirs have different chemical potential (denote as $\Delta\mu$) for water. But it is of interest to find the nature of water diffusion when there is no concentration difference. For this type of exploration, experiments have been designed in which a fraction of water molecules is labeled such as using an isotopic replacement.

When the reservoirs on both sides of a membrane have different concentrations of tracer, in which its interactions with membrane and other water molecules are assumed to be identical, a diffusional tracer flux will be established into the low concentration side along the concentration gradient. Then, a tracer flux J_{tr} through a single channel can be shown as:

$$J_{tr} = p_d \Delta c_{tr} \tag{2}$$

where Δc_{tr} is the tracer concentration difference and p_d is defined as the diffusion permeability of the channel which quantifies the exchange of individual water molecules between two reservoirs at the equilibrium.

In 2002, a Continues Time Random Walk (CTRW) model [26] was proposed to describe the transport of single-file water in the channels. This model assumes that each channel is always occupied by N water molecules and the whole water row moves in hops, i.e., a translocation that shifts all water molecules by the distance separating two neighboring water molecules, simultaneously and concertedly. So, the obtained parameters using CTRW model is based on the hopping rate calculations [27,28]. For further details of the method, please see Ref. [28].

In the present work, we have chosen a method which is provided by our simulation package, NAMD [29], for applying a pressure gradient which is proportional to a chemical potential difference [30] in our simulation rather than other conventional methods in MD simulations [31].

We have prepared three systems, each composed of four identical CNT channels; one has neutral CNTs and others have charge distributed CNTs according to some proposed biological channels to investigate the mechanism of water transfer in any on demand channels [32]. We have prepared two possible charge distributions on the CNTs which are in accordance to the D and L cyclic peptide nanotubes [33].

We have investigated the permeation in systems with induced pressure difference (p_o) to find the effect of different charge configurations as well as temperature dependence on water permeation under these situations. These models can also be used to find out the way to prevent water molecules to transport or reduce the rate of water permeation, i.e., controlling the water permeation due to the charge distribution. On the other hand, it can be used to find the properties of the channel using permeation investigation through it; such as temperature dependence as well as net water flux of the channel.

In our systems, there is a pressure gradient which is corresponding to a concentration gradient based on the van't Hoff law:

$$\Delta P = RT\Delta c_s \tag{3}$$

The details of the pressure gradient applied in the system could be found in Ref. [28].

Regardless of our interest in the material science or biological applications, we should understand the thermodynamic and transport properties of fluids through CNTs. Our results which are even reliable for higher and lower temperatures than the body temperature can be used for designing the channels which can be used for water transport [31] as well as water treatment in industry. It was found that there is a sharp increase in the number of permeation for the channels via temperature [28]. We found that for the systems with different charge configurations, this jump in permeation will be varied based on the properties of the channel and could be used as a characteristic parameter for evaluating the other properties of the channels.

2. Methods

We consider a system composed of four ordered parallel structure of CNTs each with 144 carbon atoms. These CNTs (144 atm) are of (6.6) armchair type each with a diameter of 8.1 Å and the length of 13.4 Å. Using the CHARMM force field parameters, the $R_{min}/2$ was set to 2 Å, So, in this scale, with the force field parameter of water molecules, the water movement into the channel will be as a single file. It means that only one water molecule can cross the vertical length of the CNT at a time. This type of CNTs and the way that they are arranged in the unit cell is comparable to those measured in the biological channels [34]. Fig. 1 shows the arrangement of the CNTs in a unit cell. The reason that we have used these kinds of CNTs as a model for the biological channels is that such a tetramer arrangement of CNTs is well consistent with some biological membrane channels such as aquaporins and peptide nanotube channels