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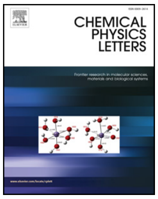

Research paper

Ion transport through single-walled carbon nanotubes: Effects of electric field and fixed surface charge

Michelle P. Aranha, Brian J. Edwards*

Materials Research and Innovation Laboratory (MRAIL), Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996, USA

HIGHLIGHTS

- Molecular Dynamics simulations illustrate the transport of ions in carbon nanotubes.
- Two-stage cation transport: stage 1 – migration-driven, stage 2 – diffusion-driven.
- Charge imbalance results in a reversal potential, inducing diffusional transport.
- Electrolyte transport rate depends on co-ion concentration within the nanotube.
- Electrolyte transport rate can be tuned using fixed charges on the nanotube.

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ABSTRACT

We investigate the ion permeation trends for an aqueous sodium chloride solution through negatively charged carbon nanotubes under the simultaneous effects of a concentration gradient and an electric field using Molecular Dynamics simulations. A two-stage ion transport process was observed that resulted in a tunable effective ion flux toward the low concentration reservoir wherein the first stage resembled an electric-field assisted counter-ion (sodium) migration to the downstream reservoir for a short period of time followed by a second stage consisting of diffusion-driven electrolyte transport governed by the strength of the Donnan potential formed by the fixed charge on the nanotube.

1. Introduction

In spite of their narrow diameters and hydrophobicity, carbon nanotubes (CNTs) are readily wetted by water and, in the case of pressure-driven flow, the flux of water observed can be many orders of magnitude higher than that expected from continuum theory; these points have been observed both via experiment and computer simulation [1–4]. Furthermore, CNT diameter can be tuned and its surface can be chemically functionalized to allow a degree of control over ion selectivity and ion transport through the tube [5–8]. Consequently, these materials have attracted a large amount of attention since large water flow rates with low energy consumption and a high degree of control over ion selectivity are desirable qualities for ultra-efficient nanofiltration membranes, such as for possible use in novel desalination applications. At the same time, CNTs also bear structural and functional similarity to biological channels and can thus serve as simplified biomimetic devices to study water and ion transport in these systems [9–11].

Flow of water and ions through nanotubes can be achieved by application of an electric field [12], pressure differential [13], concentration gradient, uneven charge distribution [14], and/or osmotic pressure [4]. The desired rate and selectivity of ion transport can be controlled by various means, such as varying the tube diameter, the ion concentration, the charge distribution, the density of charges, and via chemical functionalization. Simple ion exclusion can be achieved via steric hindrance or the sieving mechanism when the diameter of the tube is smaller than that of the hydrated ion but still large enough to allow water molecules to translocate [15]. However, if one wishes to construct membranes of practical interest where appreciable flow rates are desired, the diameter of the CNT must exceed the size of the ion. In such cases, ion transport is usually tuned by a combination of sieving, application of charges onto the CNT surface, and application of external electric fields [7,12]. The various contributions to ion exclusion arise from a combination of sieving, electrostatic interaction of ions with charges and other ions that may be present in the system, the modification of the hydration shell of the ions, and the anisotropic dielectric

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* Corresponding author.
E-mail address: bje@utk.edu (B.J. Edwards).

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environment within the CNT (which is quite different from the bulk phase). In the absence of well-known theories at the nanoscale and very limited experimental studies, it is quite a challenge to quantify the exact contributions and significance of each of these exclusion mechanisms to the total ion exclusion as a function of CNT diameter, ion type, concentration of fixed charges, external electric field strength, and external solution concentration. Without the ability to predict physical properties and the extent of ion exclusion within carbon nanotubes, progress is impeded towards the rational design of nanofluidic devices which employ them.

Molecular Dynamics (MD) simulation is a computational method that allows water and ion transport to be resolved at the nanoscopic level. Molecular Dynamics, in which the positions and momenta of all atoms within the system are explicitly tracked by solution of Newton's equations of motion, has long been a standard computational method of study to understand water and ion transport under confinement. In the past 15 years, various studies have reported on structural and dynamical features relating to ion transport, and in some cases ion translocation events have been resolved through uncharged and charged CNTs under a variety of scenarios; these include systems at equilibrium and under hydrostatic pressure, under the influence of large electric fields caused internally by ion concentration gradients, or by external electrical fields [13,16–23]. Along with the direct observation of translocation events, potential of mean force calculations employing umbrella sampling have been used to ascertain the energy barriers to single-ion transport [24,25]. A review of these studies concludes that large energetic barriers to ion translocation at the sub-nanometer level are correlated with a significant loss of the outer hydration shell of the ions. This occurs because of a significant reduction to the energetic barrier within tubes larger than a nanometer in diameter, resulting in a significant coupling between water/ion structure and dynamics [12,15].

In the present study, we applied an external electric field and a fixed charge to the CNT surface to examine the rate of electrolyte transport, which at the same time is also under the influence of a concentration gradient. Our interest lies in ultimately finding an optimal means of tuning ion transport through carbon nanotubes via the application of electric fields and charges on the nanotube wall. To do this, we have performed a large suite of MD simulations by varying the magnitude of the applied charge on the surface of a 3 nm diameter (22,22) CNT as well as the strength of the electric field. Previous studies have used electric fields that are significantly greater than those encountered under physiological conditions and, in fact, possibly greater than the dielectric breakdown voltage of water (65 mV/nm); i.e. the field strength at which water itself becomes a conductor [12]. In the present study, we utilized electric field strengths in the range of 0–100 mV/nm, which is more similar to biological conditions. As discussed in detail below, a two-stage permeation behavior through the 3 nm CNT was observed: an initial transient migration of cations induced by the electric field, followed by a diffusion-driven transfer of the ions after the establishment of a reversal potential that counterbalanced the applied electric field. The diffusion-driven permeation was dependent on the co-ion concentration/occupancy in the nanotube, which in turn depended on the strength of the electric field and the charge on the CNT surface. For a fixed concentration gradient, the steady-state diffusion-driven electrolyte transport through the CNT turned out to decrease with increasing magnitude of the fixed charge on the nanotube.

2. Computational methods

The simulation setup consisted of a carbon nanotube that connected two bulk reservoirs, one containing a sodium-chloride solution and the other containing pure water—see Fig. 1. The single-walled armchair (22,22) CNT used in this study was 3 nm in diameter and 5 nm in length. The water-filled CNT that was used as the starting structure in the simulation system was obtained from a separate NPT simulation wherein the CNT was first solvated in a pre-equilibrated (300 K, 1 bar) water bath in which the water molecules inside the tube were initially removed such as to permit water to reenter the tube naturally during the course of the simulation. This allowed the simulation to attain the natural density of water inside the nanotube, which is lower than the bulk density of water. The water-filled CNT thus obtained was then used to connect the two reservoirs, extending 0.5 nm into each of the bulk reservoirs to eliminate possible boundary effects. The two reservoirs contained pre-equilibrated TIP4P/2005 (rigid body) water molecules at 300 K and 1 bar, where the LINCS algorithm was employed to keep the bonds rigid. The concentration of the electrolyte in Reservoir 1 was specified as 1 M by removing water molecules and adding the requisite number of ions (~ 280 pairs of sodium-chloride ions in about 15,000 water molecules) while Reservoir 2 contained pure TIP4P/2005 water. The concentration of 1 M was chosen so that the concentration within Reservoir 1 would remain essentially constant over the duration of the simulation while ensuring a significant number of ion transfer events. The reservoirs were bounded by rigid graphene walls perpendicular to the axial direction of the CNT, with periodic boundary conditions applied in the other directions. No solute (Na^+ or Cl^-) was present in the nanotube at the beginning of the simulation. Ions could pass from one reservoir to the other only via the CNT.

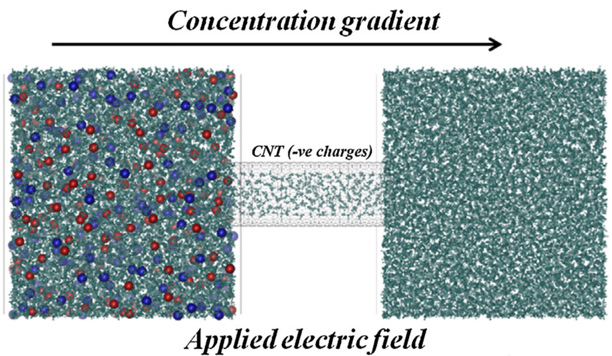

Fig. 1. Schematic representation of the simulated CNT/reservoir system. The simulated particles are colored according to species: water molecules (cyan), sodium ions (red), chloride ions (blue), and carbon atoms (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Three cases of negative fixed surface charges on the tube were simulated (≈ 0.3 M, 1 M, and 2 M) corresponding to charge values of 5e-, 15e-, 30e-. The case of a neutral CNT with no surface charge (0 M) was also examined as a control. The fixed charges were calculated based on the aqueous solution volume inside the nanotube and were uniformly distributed as partial charges on the individual CNT atoms. Given the total volume of the CNT and the known volume that the water molecules occupy within it, the number of ions required to attain a certain molarity was calculated. Once this number was known, the total net charge was distributed evenly over all carbon atoms comprising the CNT by dividing the total net charge by the number of atoms, and then assigning that partial charge to each atom of the CNT. To maintain overall electroneutrality, a set number of random chloride ions equal to the total fixed charge on the CNT was removed from Reservoir 1. On top of this, an electric field was applied in the same direction as the concentration gradient. The electric field strengths applied for each of the fixed-charge cases were 0, 20 mV/nm, 40 mV/nm, 60 mV/nm, 80 mV/nm, and 100 mV/nm. The total number of simulation scenarios thus generated was 24.

The parameters used in the simulations were those of the OPLS-AA forcefield; they are summarized in Table 1. The carbon atoms and the graphene sheets were held fixed during the simulation using a harmonic restraining potential with a force constant of 10,000 $kJ/mol/nm^2$. The LINCS algorithm was used to keep the water molecules rigid, and the Lennard-Jones parameters of cross interactions were calculated based