Temperature effect on ion selectivity of potassium and sodium ions in solution

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ABSTRACT

The effect of temperature on ion selectivity of various-diameter nanopores in an NaCl and KCl solution has been studied with molecular dynamics simulation. Our results indicate that ion selectivity is absent at high temperature, while pores become increasingly selective as the system temperature decreases, but that depends on the nano-pore diameter. By investigating how the hydration shell of ions and cation–anion interactions affect the ability of ions to access the nanopore, we reveal the mechanism behind this dependence of selectivity on temperature. The implication that ion selectivity is vulnerable to higher temperature may provide a useful selectivity-control mechanism, and may help improve the performance of permeable membranes.

1. Introduction

Ion selective transport is widely applied in many separation processes. The ions of salt solution can be separated by distinguishing the physical properties of particles [1] such as in the case of drug delivery in biological ion channels [2–5] and protein channels [6–8]. Ion selective transport also occurs in chemical purification using micro/nano scale pores [9] where external electric fields are applied, as well as in the changing of concentration or pressure across membranes, such as in the case of desalination of seawater and brackish groundwater [10,11]. The mass transport [12,13] through a sieve-like porous component is affected by various properties, such as the pH of the solution [14], ligand chemical components [15], size of pores [16–19], the bonding between particles [20–23], and pressure and temperature [24–27], however the basic efficiency of ion selective transport relies on the size of pores being ideal for the molecule dimensions [28,29]. Water is the most common solvent for salt solution, and its physical properties [30] are altered from the bulk solution when confined in nano-scale channels [31]. Single file water conduction was observed in simulation through a small hydrophobic carbon nanotube [32], and when water confined in nanotubes experiences a first order phase transition, it can form an ice-nanotube. The inter-dependence of temperature and pore diameter is highlighted by dependence of phase-transition temperature on the pore diameter [33].

A wide range of separation phenomena have been observed to have a dependence on temperature. For example, temperature-dependent selectivity was found to occur for copper separation from zinc in iminodiacetic acid at 60 °C [26,34], while in osmosis, higher temperature was proved to afford higher initial fluxes in forward osmosis experiments but caused adverse effects on membrane scaling and cleaning [35]. A thermally-driven [36] desalination process has also been studied recently [37,38], which has proved to be useful at high temperatures and have low energy consumption. In order to optimize the aforementioned temperature-dependent separation technologies and take advantage of nano-fabrication technology, it is important to have a fundamental understanding of the nano-scale processes involved. This is where Molecular Dynamics (MD) simulation can play a highly important role. This simulation method is well-established for the study of solvated ions [39,40], and has been successfully used to carry out simulations of water conduction through ion channels, osmosis on the nanoscale [41], etc. over several nanoseconds and nanometers. The MD integration method has an advantage of providing the dynamics of system with significant statistical accuracy.

We have therefore applied MD simulation to the important topic of thermal influence on separation technology, in order to gain a fundamental picture of how temperature effects ion separation processes. The results suggest that careful selection of an appropriate temperature and pore-diameter combination can effectively strengthen the functionality of a permeable membrane.

2. Simulation details

We have considered a 1:1 NaCl and KCl solution mixture at various temperatures and interacting with pores of various diameters. A schematic figure is shown in Fig. 1. The guiding principle behind
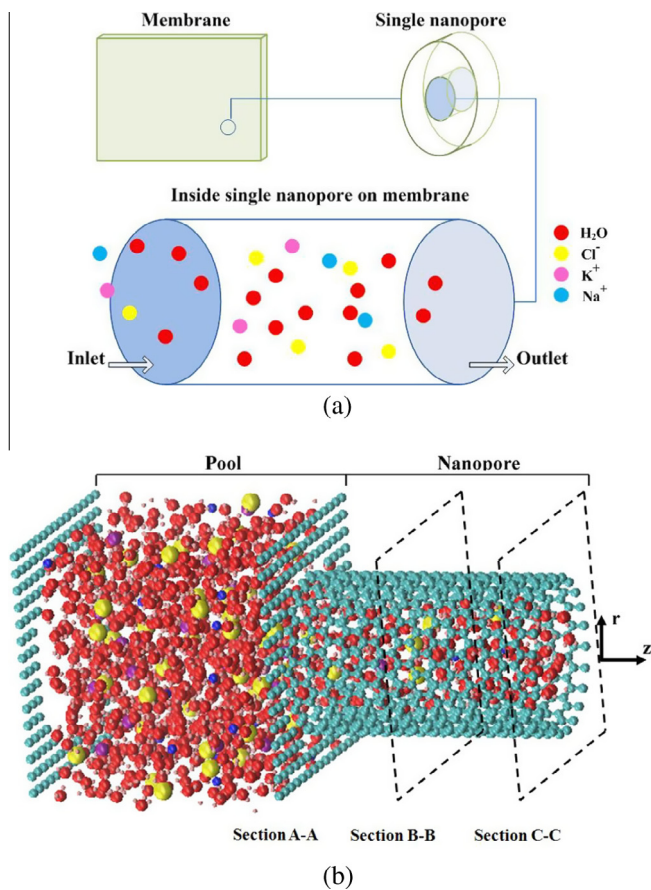
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Fig. 1. (a) Schematic diagram of permeable membrane; (b) Schematic of simulation model. A 1:1 solution mixture of NaCl and KCl was used to establish the environment surrounding the nanopores. Different color dots represents different type of particles. The cyan dots are structure particles (carbon); the blue, purple and yellow dots are sodium ions, potassium ions and chlorine ions respectively; and the red and pink dots represent the oxygen and hydrogen atoms of water molecules.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

this structure is to mimic mass transport and selectivity through nanopore of a permeable membrane. The simulation system was prepared as a cubic cell with side length 30 Å, connected with a fixed 30 Å-length nanopore along the z-axis. The nanopore was composed of frozen carbon atoms and given the convenient generic inert structure of a carbon nanotube. The geometry parameters were the same for all trials except for the diameter of the nanopore which was altered according to the desired system of study. In order to gather sufficient representative data within computational limits, we chose 14.10 Å and 14.93 Å diameters to represent small diameter pores, 17.24 Å and 18.02 Å for middle diameter pores, and 19.59 Å and 20.35 Å for large diameter pores. For the purpose of maintaining constant concentration of NaCl and KCl, 873 water molecules are included in all tested cases. Each system contains 21 Na^+ ions, 21 K^+ ions, and 42 Cl^- ions with a constant bulk concentration (~ 1.34 M). In total there were 18 controlled trials under different conditions of nanopore diameter and system temperature (300 K, 450 K, and 600 K).

The molecular dynamics simulations were carried out using the DL_Poly 2.20 [44] software in the NVT ensemble. Many membrane processes are done in geometrically fixed structures, e.g. in reverse osmosis systems with a spirally-wound module and electrodialysis systems with a plate-and-frame module. We thus chose the NVT ensemble to have the system comparable to experiments. In all simulations, the periodic boundary conditions were applied in all

three Cartesian directions. The liquid water is characterized by the Extended Simple Charge Point (SPC/E) water model [45], employing the SETTLE algorithm [46]. The salt solution is modeled using charged Lennard–Jones potentials [47], expressed as

$$U(r_i r_j) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{r_{ij}}, \tag{1}$$

here is the atomic hard-sphere distance and is the depth of the potential well, while is the atomic charge. Heterogeneous Lennard–Jones parameters [48] are obtained through the Lorentz–Berthelot mixing rules [49] for ions–water, carbon–water and ions–carbon.

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}, \quad \sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{2}$$

The length of the van der Waals cutoff radius is 10 Å, which is shorter than the half-width of cubic box (pool region) outside the nanopore. The Nosé–Hoover thermostat [50] is employed to maintain constant system temperature.

Ions and water molecules are initially randomly placed in the cubic box outside the nanopore. In order to obtain proper bulk properties, a 2 fs time step is used, which is small enough to achieve sufficient accuracy whilst maintaining reasonable computational cost. In each equilibration simulation, ions and water molecules spontaneously access the nanopore for 6 ns until an equilibration state is achieved and the whole system is filled. The thermal motion of the salt solution during the production simulations was recorded every 1 ps configuration in terms of position, velocity and force on each particle. After the 6 ns equilibration, all data such as the trajectory of particles, was collected from another 24 ns production simulation on average. We performed the block averaging method [51] in order to insure that the equilibration time was sufficient, and as a consequence we obtained a reliable measurement of the variance. Generally, a 24 ns production simulation is sufficiently long to observe statistically-significant mass transport into the nanopores. Here we rechecked simulation output data with the block averaging method to confirm the accuracy of various diameter and temperature controlled trials.

3. Results and discussion

In this study, we investigate the effect of temperature on the ion selectivity of different pore-diameter nanopores. Although the net charge within the nanopores will fluctuate slightly depending on the number of ions within the pore, such fluctuations are only temporary and minor in this equilibrium system. In order to quantitatively describe the ion selectivity, we calculated the average number of ions inside the nanopores.

Fig. 2 shows the average number of Na^+, K^+, and Cl^- in various diameter nanopores at different temperatures. When the average number of Na^+ is equal to that of K^+, we can assume that the nanopore environment is similar to that inside the pool. In the case of non-zero difference between Na^+ and K^+, there is some degree of ion selectivity. We observe distinct ion selectivity at 300 K and the diameter range to exhibit this selectivity is the same as we found in our previous paper [43]. On the contrary, at elevated temperatures of 600 K and 450 K, it is clear that no ion selectivity occurs for all the tested nanopores. We calculated the axial density distribution of ions inside the nanopore, also shown in Fig. 2. Because the axial density distribution of ions is symmetric about the center of the nanopore, the figures show the results for one half pore for the diameter of 18.02 Å and the other half for the diameter of 19.59 Å. It shows that spontaneous ions transport occurs within small diameter hydrophobic nanopore even in the absence of external pressure [32,57–59].