

Competitive Entry of Sodium and Potassium into Nanoscale Pores

James J. Cannon,^{†,‡} Dai Tang,[†] Nahmkeon Hur,^{†,‡} and Daejoong Kim^{*,†,‡}

Department of Mechanical Engineering, Sogang University, 1 Shinsu-dong, Mapo-gu, Seoul, 121-742, Republic of Korea, and Multi-Phenomena CFD ERC, Sogang University, 1 Shinsu-dong, Mapo-gu, Seoul, 121-742, Republic of Korea

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We have studied the competitive entry of potassium and sodium into carbon nanotubes using molecular dynamics simulations. Our results demonstrate how a combination of strong sodium hydration coupled with strong potassium–chlorine interaction leads to enhanced potassium selectivity at certain diameters. We detail the reasons behind this, and show how variation of nanotube diameter can cause a switch to sodium selectivity, or even cause a decrease in overall ion entry despite an increase in diameter. These results demonstrate the importance of considering inter-ion dependence in the theoretical study of pore selectivity and show that, with careful design, the practical separation of sodium and potassium is possible using diameter variation alone.

Introduction

Filtration using nanoscale pores is a fundamental process that has application in a wide range of situations. In biology, for example, ion-selective channels form an important part of the function of cells.^{1,2} There is also interest in using artificial membranes for filtration applications, and as our ability to manipulate structures on the nanoscale improves, membranes such as those made from carbon nanotubes are becoming increasingly precise and tuned.^{3,4}

The potential applications of artificial membranes are wide-ranging. For example, it has been shown that there is exciting potential for use of such membranes in desalination applications,^{5,6} or for ion filtration. The importance of the latter in biology and industry has led it to be extensively studied in recent times, with a view to actively controlling the ion selectivity. In an attempt to reproduce the remarkable selectivity that nature gives us, much research has been done regarding the attachment of hydrophilic groups to otherwise hydrophobic carbon nanotubes in order to achieve desired selectivity. The placement of such groups has been explored both at the ends^{7,8} and in the interior of nanotubes.⁹

While the attaching of groups to the walls of carbon nanotubes can offer an effective method of filtration, it adds an extra layer of complexity in the preparation of such nanotubes, with the associated risks of creating defects and a nonuniform distribution of groups. A simpler method is perhaps the application of a charge to a nanotube array,^{10,11} although this is most effective in the separation of ions which carry different charges.

Reducing the complexity of preparation further, the separation of ions based simply on the diameter of the pore is an attractive option. The effect of diameter on the energy of the ions, and particularly their hydration shell, has been studied,^{12,13} revealing important information about the ability of ions to fit inside carbon nanotubes, as well as information about the deformation of the ion hydration shells.

When considering ion separation utilizing pore diameter, the challenges in separating ions such as sodium (Na^+) and potassium (K^+) are particularly acute, since they carry the same $+1e$ charge and are of similar sizes. As well as considering novel methods of separating these two ions using charged groups,¹⁴ some recent works have also considered simple diameter-based separation. Liu et al.¹⁵ recently highlighted how the weaker hydration shell of K^+ compared to Na^+ can lead to K^+ selectivity in a small nanopore. Song and Corry¹⁶ also recently highlighted the influence of hydration on Na^+ and K^+ selectivity, showing Na^+ ions could be favored over K^+ ions when absorbed into small nanopores under high pressure.

While these recent studies offer important information about the effect of diameter on ion hydration and the subsequent ability for selective absorption, in many situations, the direct competition for entry between ions, including interaction between the ions themselves, may play an important role in the selectivity, and it is therefore important to take this into account.

It is for these reasons that we report here a molecular dynamics simulation study of the competitive entry of Na^+ and K^+ into carbon nanotubes, with the aim of achieving their separation utilizing only a variation in diameter of the nanotubes, while taking into account ionic interaction as well as entrance effects. Our results show that ionic interaction can play a central role in selectivity at concentrations that may typically be observed in the natural environment.

Simulation Method

Many of the works highlighted in the Introduction make use of the molecular dynamics simulation method, and this is with good reason. Molecular dynamics simulations consider the individual motions of constituent atoms of the system, and can therefore realize the atomic-level resolution required for the study of such nanoscale systems. The molecular dynamics method has therefore been applied for the study of a wide range of nanofluidic phenomena and applications, such as osmosis,^{6,17,18} nanopumping,¹⁹ electro-osmosis,^{20,21} and not least for the study of biological systems.^{22–25}

In order to discern the selectivity of various diameters of carbon nanotubes, we consider the absorption of ions into the

* To whom correspondence should be addressed. E-mail: Daejoong@sogang.ac.kr.

[†] Department of Mechanical Engineering.

[‡] Multi-Phenomena CFD ERC.

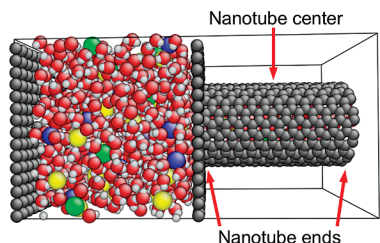


Figure 1. Schematic of the simulation system. Periodic boundary conditions mean that the wall on the far left is reproduced on the right of the simulation cell, around the right end of the nanotube.

nanotubes in an equilibrium setting. By considering the relative occupancies of the ions within the nanotubes, an indication of the ability for ions to flow into (and hence through) the nanotubes can be obtained.

In order to ensure a neutral system, chlorine (Cl^-) ions are added to the solution, resulting in a 0.95 M solution which will henceforth be referred to as NaKCl_2 . The solution is held initially in a pool of 30 \AA^3 (Figure 1) attached to a nanotube of 30 \AA in length. The size of the pool is chosen in order to be larger than the length of the van der Waals cutoff radius of 10 \AA , to ensure that bulk properties can be properly obtained. Similarly, the length of the nanotube is deliberately chosen so that atoms in the center may be fairly independent of the dynamics at the ends, and enough ions can fit inside the nanotube so that reliable statistics can be obtained. Since we are concerned with interpreting the occupancy of the nanotube by the ions in terms of the ability for selective flow and filtration, the last 2.5 \AA at each end are excluded from measurement of ion occupancy, to ensure that ions have penetrated a reasonable distance inside.

In total, 15 nanotube diameters are considered, ranging from 12.54 to 20.35 \AA . This range is sufficient to explore from bulk-like properties in the largest nanotube down to no entry at all in the smallest nanotube. The system has complete periodic boundary conditions, and the nanotube is open at both ends. Two walls consisting of a square array of carbon atoms are placed around the ends of the nanotube (i.e., without blocking the apertures), to mimic a simple membrane, allowing flow into, but not around, the nanotube. Due to the periodic nature of the system, atoms can enter the nanotube from both sides.

Prior to making measurements, the system must be equilibrated. To this end, all solution particles are initially placed in the pool at random positions and with velocities appropriate for the desired temperature of 300 K . The particles are then allowed to flow into the initially empty nanotube, with careful velocity scaling to avoid a change in temperature. It was observed that the un-natural forces involved in the initial filling of the nanotube could result in artificially high ion occupancies if measurements were made too soon, and an equilibration time of 6 ns was found to be sufficient to ensure the occupancy measurements were unaffected by the initial conditions. Since the larger nanotubes present a greater volume to be filled, the number of atoms in the pool needed to be adjusted slightly after initial filling, to ensure that the force pushing the ions and water into the nanotubes during measurements of ion occupancy was constant across all diameters. Adjustment of the number of water molecules and ions was done while maintaining the ion concentration for the system as a whole. Alternatively, the position of the left-side wall in Figure 1, along with the box length, could be adjusted slightly in order to increase or decrease the volume of the pool. Thus, these adjustments were made so that the average force on each carbon atom of each wall was 700 J/mol/\AA .

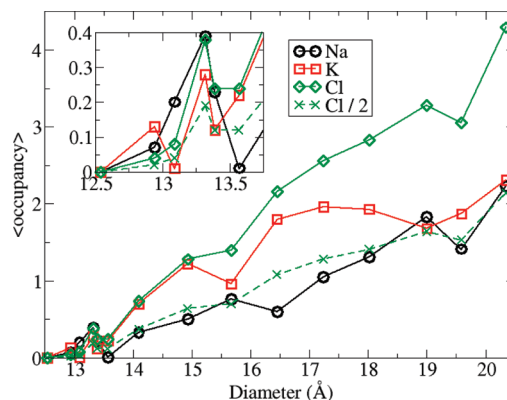


Figure 2. Average occupancy (average number of ions per observation) of each nanotube diameter.

It is well-understood that the precise dynamics of flow into and out of the nanotube can be very sensitive to the model used, and so it is important to choose the parameters carefully to ensure reasonable accuracy. In this work, the SPC/E model²⁶ for water is utilized, and the parameters for ions are chosen to ensure accurate hydration characteristics.^{27,28} Interaction parameters for carbon are meanwhile derived from water interactions with graphite,²⁹ and the carbon atoms of the walls and nanotubes are frozen in the desired position to allow a 2 fs time step to be implemented and hence allow relatively long simulation times (10 – 18 ns of measurement time per simulation). The Nosé–Hoover thermostat³⁰ is meanwhile employed to maintain constant temperature among the moving atoms in this NVT (constant number of atoms, volume, and temperature) ensemble, with a relaxation constant of 1 ps . Long-range Coulomb interactions are treated using the Ewald method,³¹ while short-range van der Waals interactions are truncated with a simple cutoff at 10 \AA . All simulations described here are conducted using DL_POLY 2.20.^{32,33}

Results and Discussion

During measurement, snapshots of the number of ions inside the nanotube were taken at 1 ps intervals, giving 1000 data points per nanosecond of simulation time. The total number of ions observed in the nanotube over the course of the simulation was then divided by the number of observations, giving an average ion occupancy in the nanotube. The results for all diameters are shown in Figure 2. Since there are twice as many Cl^- ions as Na^+ and K^+ , the occupancy of ($\text{Cl}^-/2$) is also shown in the graph, in order to help make the relative occupancies clearer. The results can be categorized into three main stages.

At the largest diameters, beyond about 18.5 \AA , the bulk ratio of $1:1:2$ for $\text{Na}^+:\text{K}^+:\text{Cl}^-$, respectively, can be observed, suggesting that the confinement of the nanotube at such large diameters is no longer significantly restricting the ability of the ions to enter, and as such no purpose would be served by considering larger diameters.

Below these largest diameters, however, clear ion selectivity is observed. Remarkably, the potassium ion is selective over the sodium ion over a wide range of diameters, down to about 13.5 \AA . The detailed reasons for this are discussed in the following section. Meanwhile, at the very smallest diameters, sodium selectivity can be observed, suggesting a change in dynamics compared to larger diameters, and the reasons for this are also reported.

Potassium Selectivity. The K^+ selectivity that persists over a wide range of diameters is quite clear, and it is important to

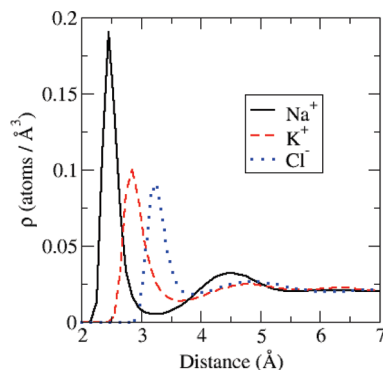


Figure 3. Average density of water as a function of radial distance from each of the ion types, in the pool.

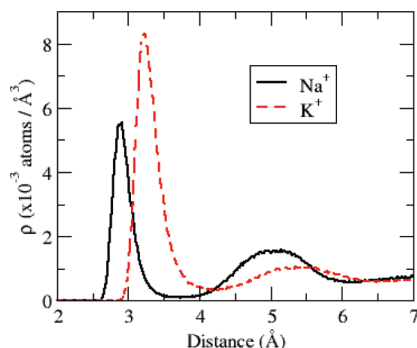


Figure 4. Average density of the positive ions as a function of radial distance from Cl^- ions, in the pool.

consider the reasons behind this. Figure 3 shows the radial density of the water surrounding each ion. The figure shows that water bonds to the Na^+ ion very strongly; far more so than to the other ions. This is somewhat expected, since the Na^+ ion is smaller than the K^+ ion and water can therefore approach more closely. Since the strength of any interaction between a positive and negative charge rapidly becomes stronger as the distance decreases, the density of the water at the peak (in the first hydration shell) of the Na^+ is much stronger than that for K^+ and Cl^- and decays with distance.

Furthermore, considering the binding of the Na^+ and K^+ ions to the Cl^- ion outside the nanotube in a similar fashion, the binding is remarkably different (Figure 4). Although positive charges cause both the K^+ and Na^+ to be attracted to the negative Cl^- , the density of the K^+ ion peak is significantly higher, indicating a much stronger binding. This is despite the fact that the smaller Na^+ ion can bind more closely to the Cl^- . In fact, in terms of absolute numbers, there are twice as many K^+ ions at the peak density, compared to Na^+ .

Furthermore, we observe that, while Na^+ sees a significant reduction in its peak density around Cl^- inside the nanotube compared to outside, the K^+ ion in contrast experiences no change in its peak density around Cl^- . This suggests that entry into the nanotubes by a KCl ion pair can be performed without any cost associated with a reduction in the strong binding between the two ions. The Na^+ ion on the other hand does experience a reduction in the interaction with Cl^- as it enters the nanotube, and thus, pairwise NaCl entry is less common.

It is therefore clear that the binding between the potassium and chlorine is much stronger than that between the sodium and chlorine, and Figure 3 suggests that this comes about due to the strong hydration of the sodium ions, with weaker potassium hydration. This then feeds into the pairwise entry of the ions with the chlorine, with the potassium maintaining the

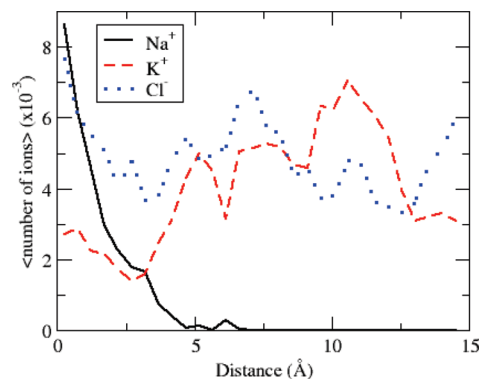


Figure 5. Average number of ions within 0.5 Å intervals, inside the 13.57 Å diameter nanotube as a function of distance from the entrance (thus the right side of the graph represents the center of the nanotube).

interaction, while sodium favors more independent hydrated entry. As it is apparent in Figure 2, the fact that there are twice as many Cl^- ions as the other ions leads to greater occupancy of the nanotubes by Cl^- . The strong binding with K^+ then in turn results in enhanced K^+ occupancy of the nanotubes at these medium diameters.

The Smallest Diameters. While the medium diameters have been shown to favor K^+ selectivity, very different dynamics are revealed at the smallest diameters. In fact, as it can be observed in the inset of Figure 2, some of the diameters actually promote Na^+ selectivity, and K^+ selectivity occurs at a diameter smaller than that of the Na^+ selectivity. This can all be explained by the confinement of these very small pores.

In the previous section, it was highlighted how Cl^- played a central role in the selectivity. By contrast, here, the nanotube diameter is small and the ability of Cl^- , or indeed a KCl pair, to fit inside is restricted for the very smallest diameters. Therefore, the first diameters which display K^+ selectivity (12.94 Å) and Na^+ selectivity (13.09 Å) can only be a product of independent entry. This is reflected in the low occupancy by Cl^- , and analysis of the ionic binding inside the nanotubes corroborates this further. The reason that K^+ selectivity is observed before Na^+ selectivity is a result of the hydration, and has been discussed before, perhaps most comprehensively by Carrillo-Tripp et al.^{12,34} The greater flexibility of the more weakly bound hydration shell permits earlier entry of the K^+ compared to Na^+ . The studies of Carrillo-Tripp et al. considered only lone ions inside a nanopore, and thus correspond well with our interpretation of independent entry at these diameters.

Beyond 13.09 Å, our analysis of the Na^+ binding to other ions and water inside the nanotubes shows that it continues to enter the nanotubes independently, with its first hydration shell intact. At the point of transition from Na^+ selectivity to K^+ selectivity, however, a marked drop is observed in the ability of any of the ions to enter. This can be attributed to the competition for entry during the transition between the two positive ions, with the hydrated Na^+ ion fitting easily into the nanotube on one hand and the Cl^- ion encouraging K^+ entry on the other. Since both the Na^+ and K^+ ions repel each other, the ability for both ions to enter is impaired.

This is particularly well highlighted when considering the average position of the atoms inside the 13.57 Å diameter nanotube which is in the middle of this transition. Figure 5 demonstrates the competition for entry quite clearly, with the Na^+ ion able to penetrate less than 5 Å into the nanotube and the K^+ ion restricted to the center of the nanotube. Where the

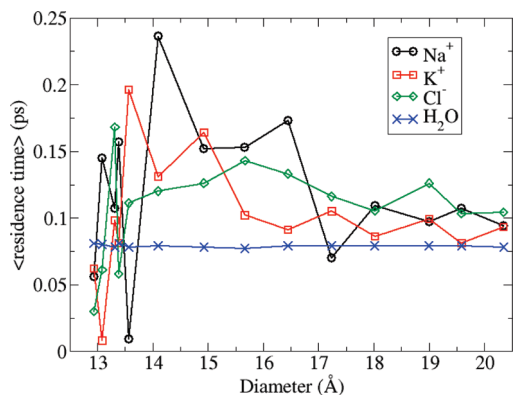


Figure 6. Average residence time of the ions and water as a function of nanotube diameter.

K^+ ion is present, it follows with roughly the same occupancy as the Cl^- ion, which would correspond with correlation in their entrance ability. The fact that the Cl^- ion has no restriction on its position highlights that rather than any geometric considerations, which would affect all ions, it is the Na^+ and K^+ repulsion which keeps the positive ions in their separate positions.

While Figure 5 offers a qualitative insight into the distribution of ions inside the nanotube at the point of transition, a more quantitative method may be to look at the residence time of the individual ions inside the nanotubes. Ions which are restricted to the ends of a nanotube will have a relatively short residence time per entry event, while ions which tend to be more in the center of a nanotube will have a longer residence time. This is reflected well in Figure 6.

For the case of the 13.57 Å nanotube highlighted earlier with the K^+ ion tending to be in the center and the Na^+ ion tending to be toward the ends, the average occupancy time can be seen to be at its peak for the K^+ ion and at its lowest recorded value for Na^+ . The Na^+ ion also experiences a peak in the residence time during these transition diameters, highlighting how the overall flow rate of both types of ions is being impaired at the transition. Although we do not directly consider nonequilibrium flow in the current study, it is clear that separation of the positive ions to the center and edges of the nanotubes can result in a blocking effect, causing one type of ion to have an unusually long residence time while the other is unusually short and unable to pass through the nanotube. This, in combination with the drop in the overall ion occupancies, suggests the rather counterintuitive effect that the number of ions that can be filtered during a given time period at these transition diameters is lower than at smaller diameters, despite a larger cross-sectional area. Further studies of a nonequilibrium nature are required to shed additional light on such a phenomenon.

Substantial variation in the residence times can be observed at the smallest diameters, a result of the high confinement and competition for entry, while at the largest diameters the residence time is seen to tend to that for the water in the nanotubes, consistent with a return to the bulk-fluid-like nature in the largest nanotubes studied here.

Separate Solutions. The previous discussions have focused on the competition for entry into nanotubes by Na^+ and K^+ which feature together in a NaKCl_2 solution, and it has been explained how the reduced hydration of K^+ compared to Na^+ leads to greater $\text{K}^+ - \text{Cl}^-$ interaction and subsequently higher K^+ selectivity. It is not clear though to what extent this represents an enhancement of K^+ selectivity, over the “intrinsic”

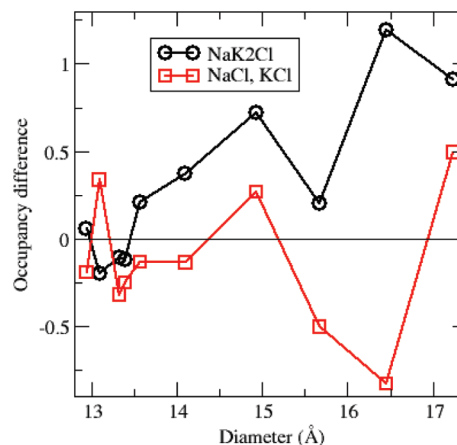


Figure 7. Difference in diameter occupancies ($\text{K}^+ - \text{Na}^+$). A positive value corresponds to K^+ selectivity.

Na^+ and K^+ selectivity of the nanotubes from NaCl and KCl , respectively, and thus, this is considered in the present section.

In order to consider this question, additional simulations of separate NaCl and KCl solutions have been conducted, in order to measure this intrinsic selectivity of the pores for Na^+ and K^+ when paired with Cl^- . In order to ensure identical conditions, simulations were prepared in an identical way to before, except the Na^+ ions of NaKCl_2 were replaced by K^+ ions for the KCl simulations and K^+ replaced by Na^+ for the NaCl simulations.

The difference in the selectivity can be obtained from the two solutions by subtracting the occupancy of Na^+ in an NaCl solution away from that of K^+ in a KCl solution. Thus, a positive value indicates that the nanotube favors K^+ over Na^+ . For comparison, the same difference in occupancy from the combined NaKCl_2 solution was calculated, and both sets of results can be seen in Figure 7. The comparison of separate solutions focuses toward the medium and lower diameters where selectivity is at its most prominent.

The figure shows that the combined solution sees K^+ selectivity being established at a smaller diameter than the separate solutions. This result supports the idea that, in the combined solution, the strong binding of Na^+ to water helps to reduce the hydration of K^+ , resulting in stronger $\text{K}^+ - \text{Cl}^-$ binding and enhanced occupancy. Na^+ is effectively “stealing” the water from K^+ . Furthermore, it can be noted that, even for the two diameters where Na^+ selectivity is observed in both cases, the strength of the Na^+ selectivity is reduced in the combined case. As the diameter increases further, the combined solution continues to have stronger K^+ selectivity, even exhibiting K^+ selectivity when the separate solutions favor Na^+ selectivity, demonstrating importantly how this mixing of the ions can lead to opposite selectivities.

Finally, we note that occupancies of 0.20 and 0.35 were observed for the separate solutions at 12.54 Å diameter for Na^+ and K^+ , respectively. The fact that ions were able to enter in separate solutions but unable to enter in combined solutions serves as a final reminder that the results from study of separate solutions may not always be directly extensible to combined solutions.

Conclusion

Through use of molecular dynamics simulations, we have studied the ability of carbon nanotubes to separate sodium and potassium from a NaKCl_2 solution, using a variation of the nanotube diameter to alter the selectivity. We have deliberately included the effects of ionic interaction and entrance effects in

order to observe the resulting nanotube selectivity. The results have shown that despite carrying the same charge and being of very similar sizes, potassium and sodium separation can be achieved by careful choice of nanotube diameter.

We have described the mechanisms of selectivity in detail. The stronger hydration of sodium has been shown to lead to greater potassium–chlorine interaction, which in turn leads to potassium selectivity as the more numerous chlorine helps to pull potassium into the nanotubes. The selectivity of the nanotubes has been shown to change in favor of sodium at the smaller diameters, with a transition from ion-assisted entry to lone-entry dynamics.

Between these two regions of selectivity, we have demonstrated how the competition for entry between these two positive ions results in an overall reduction in occupancy for both ions, with the somewhat counterintuitive result that some diameters may conduct ions less frequently than smaller diameters, despite having a larger cross section.

From a simulation perspective, this work highlights the important role that ionic interaction can play in the selectivity of nanoscale pores, and suggests that taking this interaction into account, in addition to water hydration, can be important when determining the selectivity.

Overall, these results demonstrate that, if Ångström-scale control of carbon nanotube diameters can be achieved, carbon nanotubes have great potential for application in ion-separation technologies.

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