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### A MOLECULAR DYNAMICS STUDY ON THE ABSORPTION OF IONS INTO CARBON NANOTUBES

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#### ABSTRACT

*The ability of ions to be selectively absorbed into nanopores is important for a wide range of industrial and biological processes. To make practical use of such ionic selectivity, a molecular-level understanding of the dynamics is required, so that conditions can be tailored and optimised as required. This is especially the case when the ions being separated are very similar. We have therefore conducted molecular dynamics simulations in order to study the selective absorption of sodium and potassium ions into a nano-scale pore. We show how ion hydration and the presence of a negative ion lead to alternative selectivity depending on the size of the pore.*

#### NOMENCLATURE

RDF Radial Distribution Function

#### INTRODUCTION

The ability of ions to selectively enter nano-scale pores is a fundamental process that has application in a wide range of processes. This occurs naturally, for example, as a fundamental process of cell life within living organisms, and can also be applied artificially for separation technologies. As a result, the absorption of ions into and through nano-scale pores, on both

an equilibrium and non-equilibrium basis, has been extensively studied (eg, [1–5]). Based on these results it is clear that the absorption of ions into nano-scale pores is very sensitive to small changes in pore properties, such as changes in pore width or polarity.

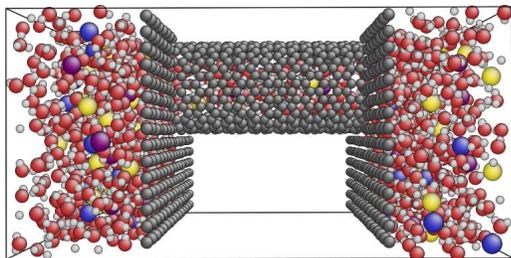
In the design of nano-scale devices which make use of selective ion absorption, it is important to consider the details of the dynamics which lead to the absorption, so that it may be tailored to be as efficient and effective as possible. This is especially challenging when the desire is to selectively absorb two very similar ions such as  $\text{Na}^+$  and  $\text{K}^+$  which both carry a  $+1e$  charge and are of similar sizes. We have therefore considered the question of the selective absorption of these two ions into a model nano-scale pore.

#### SIMULATION DESIGN

In considering the entry of these ions into a nano-pore, it is important to consider the nature of the pore. Since it is the dynamics of the entrance of these ions which is of interest, the dependence on the details of the pore-model should be minimised. Meanwhile though, it is prudent to choose a model pore which is somewhat representative of potential future applications of differential absorption technology. Carbon nanotubes therefore seem ideal candidates for such a study. By treating the nanotube as a simple, fixed, uncharged structure, the dynamics and inter-

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**FIGURE 1.** SYSTEM DESIGN.

actions of the solution atoms can be considered without dependence on the precise nature of the wall, allowing the results to be extended to other situations. Furthermore, carbon nanotubes have been shown to be highly promising for use in tailor-made artificial absorption and filtration devices [6–10], and as such, simulations concerning their application in this field are of particular relevance. Therefore, we choose carbon nanotubes to represent our model pores.

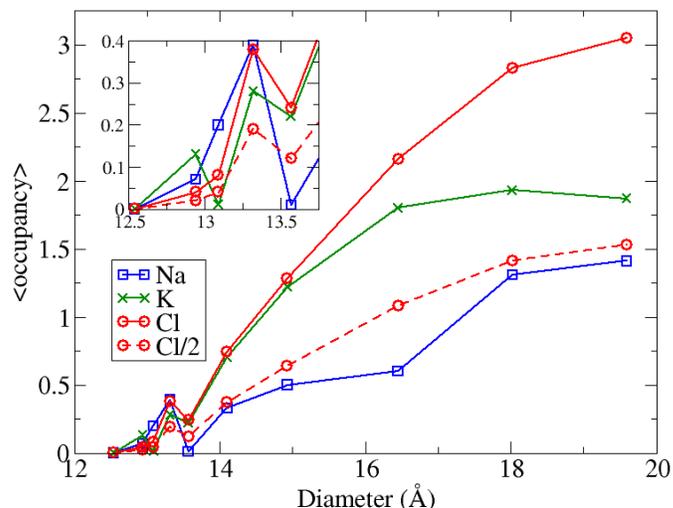
In order to maintain neutrality, the  $\text{Na}^+$  and  $\text{K}^+$  are mixed with another common ion,  $\text{Cl}^-$ , to form a neutral  $\text{Na}^+\text{K}^+2\text{Cl}^-$  solution at about 1M concentration. A bath of this solution of  $30\text{\AA}^3$  is attached to the nanotube (figure 1) which is also approximately  $30\text{\AA}$  in length, and the occupancy of the ions inside the nanotubes are measured for typically 10-18ns. While the nanotube in figure 1 seems off-centre, it can be noted that periodic boundary conditions are employed in the simulation, so that the system can be considered as an infinite lattice of nanotube pores. This removes any undesired size-effects of the simulation.

In order to investigate the variation of absorption of the two positive ions, the diameter of the nanotube is varied and the average occupancy (ie, average number of ions in the nanotube) is measured in each case. This variation of diameter ranges from  $12.5\text{\AA}$  to  $19.6\text{\AA}$ .

The SPC/E model [11] for water is used, and the parameters for ions are chosen to ensure accurate hydration characteristics [12,13]. Interaction parameters for carbon are meanwhile derived from water interactions with graphite [14] which are widely applied in nanotube simulation studies (eg [15–18]). The simulation step size is 2fs, and long-range coulomb interactions are treated using the Ewald method [19]. All simulations described here are conducted using DLPoly 2.20 [20,21].

## RESULTS

The occupancy by the nanotubes of the ions at different diameters are shown in figure 2. Since there are twice as many  $\text{Cl}^-$  ions as  $\text{Na}^+$  and  $\text{K}^+$ , the occupancy of  $(\text{Cl}^-/2)$  is also shown on the graph (dashed line with circles), in order to help make the relative occupancies clearer. The selectivity of the diameters can be seen to go through a number of distinct stages.



**FIGURE 2.** AVERAGE OCCUPANCY BY IONS IN NANOTUBES OF VARYING DIAMETER.

At the largest diameters the occupancies can be seen to be tending towards the bulk ratios of 1:1:2 for  $\text{Na}^+ : \text{K}^+ : \text{Cl}^-$  respectively. Meanwhile,  $\text{K}^+$  selectivity is observed at the medium diameters, while  $\text{Na}^+$  selectivity can be observed at a few of the smallest diameters.

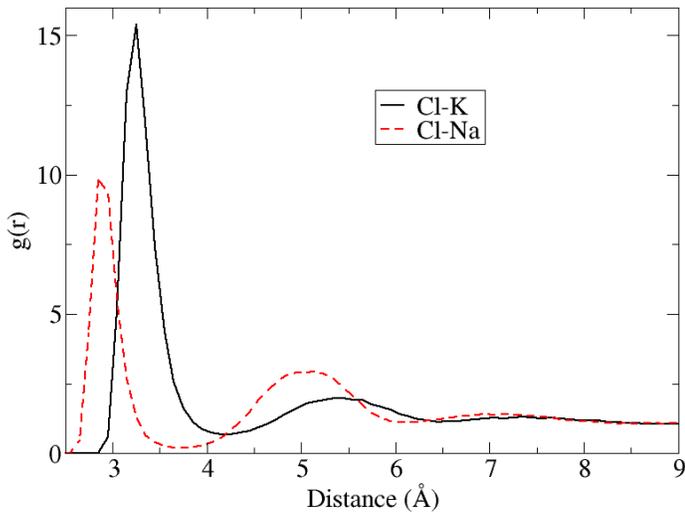
### Potassium selectivity

The strong  $\text{K}^+$  selectivity observed in the medium diameters is quite clear, and it is interesting to consider the physical reasons behind this. Figure 3 shows the radial distribution function (RDF) between the  $\text{Cl}^-$  ion and both the  $\text{K}^+$  and  $\text{Na}^+$  ions. It can be seen that while the smaller  $\text{Na}^+$  ion is able to approach the  $\text{Cl}^-$  ion more closely than  $\text{K}^+$ , the density of the  $\text{Na}^+$  shell around  $\text{Cl}^-$  is far smaller than that of  $\text{K}^+$ . Indeed, if absolute numbers are considered (in contrast to the relative density shown by the RDF), potassium is seen to have twice as many ions at its peak density compared to sodium.

This favourable binding of  $\text{K}^+ \text{Cl}^-$  over  $\text{Na}^+ \text{Cl}^-$  is fundamental to the potassium selectivity observed, and comes about because the hydration of the  $\text{Na}^+$  (not shown here) is far tighter and stronger than the other ions, leading the  $\text{Na}^+$  to favour interaction with water and the  $\text{K}^+$  to favour interaction with  $\text{Cl}^-$ . The net result is that when the more-numerous  $\text{Cl}^-$  enters the nanotubes, it helps to pull  $\text{K}^+$  in with it, giving rise to the enhanced  $\text{K}^+$  occupancy of the nanotubes.

### The smallest diameters

While the medium diameters have been shown to favour  $\text{K}^+$  selectivity, the smallest diameters in this study reveal very differ-



**FIGURE 3.** RDF OF  $Cl^- - K^+$  AND  $Cl^- - Na^+$  INTERACTION.

ent dynamics. Indeed, it can be seen from the inset in figure 2 that some of the diameters studied actually reveal  $Na^+$  selectivity instead of the normal  $K^+$  selectivity. Again, it is interesting to consider the dynamics of this change in selectivity, as the reasons behind the change help to confirm and extend understanding about the  $K^+$  selectivity already described.

No entry is observed in the smallest diameter, despite the fact that the nanotube is still large enough to admit entrance by the ions. When it is considered that the ions are hydrated and interact with each other, then this lack of entry could be expected. At the second diameter studied here however,  $K^+$  selectivity is observed, before  $Na^+$  selectivity at slightly larger diameters, despite the fact that the  $Na^+$  ion is smaller in size. While this may initially seem counter-intuitive, this is consistent with previous studies of individual ions inside small pores [2] which highlight how potassium can often fit more easily into nano-scale pores due to its more-flexible hydration shell, while the tight binding of water to sodium only allows entry when the hydration shell does not need to be deformed.

The correspondence of this observed selectivity at smaller diameters with previous reports which considered only single ions, highlights how the dynamics have changed from assisted entry (be it binding with chlorine or water-hydration) to individual entry dynamics, where only one ion can enter the nanotube at a time. Thus an important part of the transition from the  $K^+$  selectivity to  $Na^+$  selectivity is the restriction of the number of atoms able to enter the nanotubes at these smaller diameters.

Finally, it can be observed that following the preferential sodium absorption into the nanotubes, and prior to the establishment of clear potassium selectivity, a reduction in the overall ability of ions to enter the nanotube is observed around  $13.5\text{\AA}$ .

This can in turn be attributed to the competition for entry during the transition, resulting in a reduced occupancy for both types of ion.

## CONCLUSION

We have shown that potassium and sodium can be selectively absorbed into carbon nanotube pores based on small changes in the diameter of these pores. These results have increased our understanding of the role of ion-interaction and hydration in the ability of ions to be selectively absorbed into nano-scale pores, which may find application in future nano-fluidic technologies. Our results have demonstrated how the hydration of sodium coupled with strong chlorine-potassium interaction leads to strong preferential potassium absorption into the medium diameters of nanotubes studied here.

Meanwhile, at the smaller diameters studied here we have observed a change in the selectivity of potassium and sodium, attributed to the respective hydration shells and consistent with previous studies of individual ion absorption into nano-pores.

Finally, it is worth highlighting that although our results detail the potential for careful selective ion absorption into nano-scale pores, one of the great challenges still to be addressed is the ability to manufacture on scales of fractions of an Angstrom. If this can eventually be achieved, these simulation results show significant promise for such technologies.

## ACKNOWLEDGMENT

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