MOLECULAR UNDERSTANDING OF OSMOSIS USING MOLECULAR DYNAMICS SIMULATION: EFFECTS BY SIZES OF IONS AND NANPORES AND OCCURRENCE OF OSMOSIS

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삼투압 현상의 분자적 이해를 위한 분자동역학 시뮬레이션: 이온의 크기와 나노포어의 상관관계 및 삼투 현상 발생에 관한 연구

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The report summarizes research activities in the Multiscale Energy System Laboratory at Sogang University during September 2009 and February 2010. They are mostly about molecular dynamics simulation of osmotic flows at nanoscale.

Key Words : Osmosis, Molecular Dynamics Simulation, Ion Size

1. OVERVIEW

Having recently started exploring nano-fluidic phenomena from a simulation perspective, progress has been made both in terms of the preparation of the simulation hardware and systems, as well as the subject of the research itself. Using this developing computational ability, we have made good initial progress in the research of ion transport and prepared systems for osmosis studies. Initial results are highly promising, and we are continuing to develop these studies further.

Initial systems of study have been two-fold: firstly, the transport and separation of ions using nano-scale pores, as well as osmotic phenomena. In each case, the aim is to obtain a molecular-scale understanding of the respective phenomena, and then apply this knowledge in order to manipulate and control the properties of the system as desired.

The ability to filter and separate ions is important for a wide range of biological and industrial processes, however this can often be very challenging. This is especially the case for Potassium (K+) and Sodium (Na+) which carry the same charge and are of similar sizes. Therefore, in order to investigate their separation, molecular dynamics simulations of NaK2Cl solution are being conducted, and their preferential absorption into carbon nanotubes is being studied. By making this study we hope to identify the key mechanisms of filtration, which will be of interest for practical separation applications.

2. SYSTEM DESIGN

Carbon nanotubes are used in order to provide simple model pores which ensures results are not due to any unusual pore characteristics. The simulations consist of a nanotube which is 30Å in length, surrounded by a cubic box which extends for a further 30Å. The system is periodic in all three Cartesian directions, as shown in figure 1. A wall is placed around each end of the

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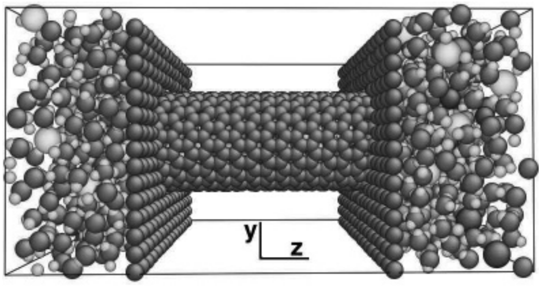

Fig. 1 Simulation snapshot

nanotube to restrict flow to inside the nanotube.

Simulations consider a charge-neutral 0.95M solution of NaK2Cl. The diameter of the nanotube, as calculated from the centre of the carbon atoms, ranges from 13.32Å to 14.93Å. At each diameter the average occupancy of each ion species inside the nanotube is calculated. Since we are concerned with interpreting these results in terms of ionic transport, only ions that have entered more than 2.5Å from the ends of the nanotube are counted as having occupancy.

3. RESULTS AND DISCUSSION

The initial results demonstrate a clear variation in the average ion occupancy of the nanotube with diameter (figure 2), and show how the selectivity of the system varies, with Na+ and K+ being strongly favoured at diameters of 13.32Å and 14.93Å respectively.

Generally, as the diameter of the nanotube becomes smaller, the occupancy of all the ions also reduces. As the diameter decreases, the extent of reduction of the occupancy is unequal between the ions. For both Cl- and K+, the magnitude of occupancy in the largest diameter is significantly greater compared to that at smaller diameters. In contrast, entry by Na+ is dominant at the smallest diameter.

The reasons behind this can be deduced by considering the relative hydration of the ions. Fig. 3 shows the radial distribution functions for the Cl--Na+ and Cl--K+ interactions. K+ and Na+ have the same positive charge, however the smaller size of Na+ allows it, on average, to approach closer to Cl-, reflected in the closer peak in figure 3. Despite this closer binding to the Cl-, the density of K+ a little further from Cl- is more than double that of Na+, highlighting a stronger Cl--K+ binding. In contrast, water interaction is much stronger with Na+ than with K+ (not shown here) resulting in entry of Na+ observed at smaller diameters which is independent of the other ions, while KCl tandem entry occurs where the larger diameters allow it.

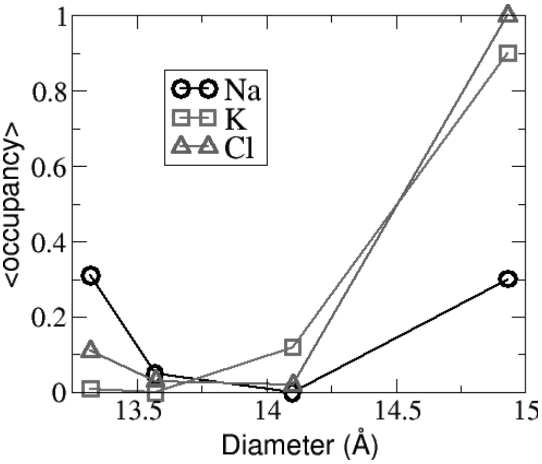

Fig. 2 Ion occupancy in nanotube

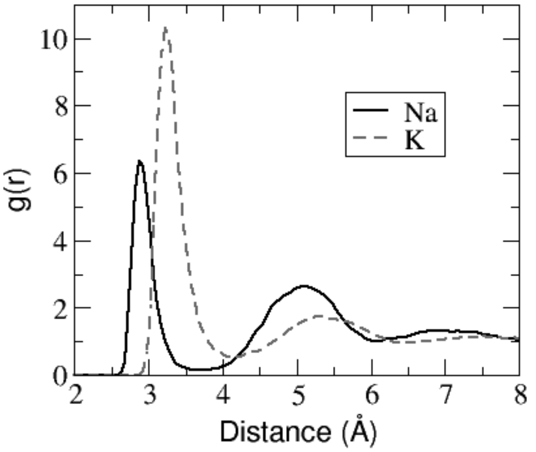

Fig. 3 Cl-ion radial distribution function

In the middle diameter of 14.10Å, all three kinds of ions are excluded from entering nanotube, attributed to the increased competition for entry during the transition from Na+ entry to KCl entry. During this time, KCl is, on average, closer to the entrance of the nanotube, hindering entrance of Na+, whilst itself being unable to enter.

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