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Selectivity of Carbon Nanotubes under An Electric Field on Transferring Water – Alcohol Mixtures

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Abstract. Carbon nanotubes (CNTs) have shown a great promise for nanofluidic-based applications such as for separation membranes. Water confined in nanotubes has different properties compared with those in bulk. Therefore, to develop a membrane with CNTs, it is very important to clarify the behavior of water in CNTs. In this study, we show effects of an electric field on water in a CNT by molecular dynamics simulation. An electric field aligns the dipole moment of water molecules and induces formation of an ordered structure in a CNT. As a result, the electrostatic interaction between water molecules within the structure becomes stronger. Strengthening of the electrostatics interaction facilitates water molecules preferring to fill a CNT over alcohol molecules. This indicates a strong separation effect for water-alcohol solutions.

Keywords: selectivity, carbon nanotube, electric field, transfer, water-alcohol

1. Introduction

It is well known that carbon nanotubes (CNTs) have been applied in various fields because of their excellent properties including mechanical, electrical, and heat transfer properties. Furthermore, CNTs show outstanding property for fluid transport. They are able to transport fluid very fast compared with other materials [1,2,3]. More interestingly, CNTs can transfer substances selectively. These properties are promising for separation membranes such as for desalination membranes [4,5], air separation membranes [6], *etc.* Water confined in nanometer space shows different behavior than that in bulk [7]. Moreover, water molecule is easily influenced by an external electric field because it is a polar molecule. With the combination effect of an electric field and confinement of nanotube wall, water shows interesting properties that are potential for nanotechnology applications and also significant for biological science [8,9]. Water in biological cell channels can be affected by strong electric field due to difference of ion concentration [10,11]. It is believed that CNTs can be used to understand water behavior in biological cell channels [12].



In this study, we perform molecular dynamics (MD) simulations to investigate effects of an axial electric field on water molecules in a CNT. An electric field makes molecular orientation of water molecules more uniform and consequently, water molecules form an ordered structure in a CNT. Electrostatic interaction between water molecules becomes stronger with the presence of an electric field. As a result, CNTs can separate of water-alcohol solutions.

2. Simulation Method

The simulation system consisted of a CNT embedded into two graphene sheets and two reservoirs at the both sides as shown in Fig. 1 [13,14]. The CNT length was 2.95 nm and homogeneous electric fields E were introduced in z -direction. The reservoirs were filled with water molecules. In addition, to demonstrate the separation effect, the reservoirs were filled with a mixture of water and ethanol molecules. Mole fraction of water was only 0.19. Models of water and ethanol molecules were SPC and OPLS-UA, respectively. The Lennard-Jones (LJ) parameters for carbon atoms of CNT were $\sigma_C = 0.34$ nm and $\epsilon_C = 0.3612$ kJ/mol. The van der Waals interactions were cut off at 1.5 nm, while the electrostatics were treated using a particle mesh Ewald method with a real-space cut-off at 1.5 nm as well [15]. The MD simulations were carried out using Gromacs 4.5.5 software [16]. We performed simulation with $NL_xL_yP_zT$ where the constant pressure in z -direction was maintained at 0.1 MPa with Parrinello-Rahman scheme [17]. The temperature was kept at 300 K using Nosé-Hoover coupling scheme [18,19].

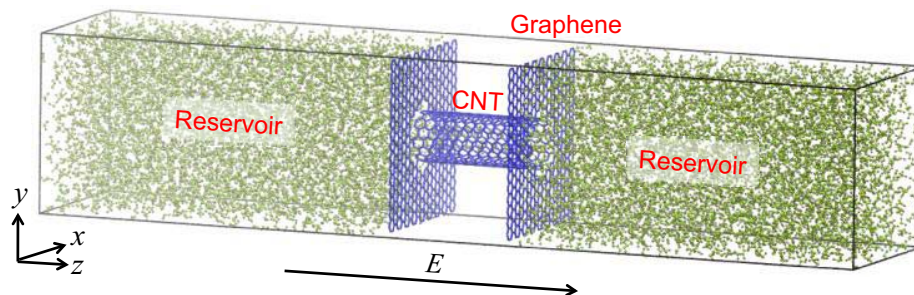


Figure 1 Molecular simulation system consisted of a carbon nanotube (CNT), two graphene sheets, and reservoirs in the both sides. An electric field E was applied in the axial direction.

3. Results and Discussion

The direct effect of an electric field on a water molecule is a change in molecular orientation by the electrostatic forces on the negative charge of oxygen atom and the positive charge of hydrogen atoms. That causes molecular orientation of water more uniform *i.e.* direction of the dipole moment is parallel to that of the electric field [13]. Furthermore, the uniformity of molecular orientation induces formation of an ordered structure in a CNT. Figure 2(a), (b), and (c) show structures of water molecules in (8, 8) CNT at 0, 1, and 2 V/nm, respectively [13]. An electric field changes the structure of water molecules in the CNT. With 1 and 2 V/nm, structure of water molecules in (8, 8) CNT becomes helical. An electric field induces phase transition in the CNT [13,14]. Water structures in CNTs depend on the CNT diameter and strength of the electric field. The structure can be helical or other ordered structures [13].

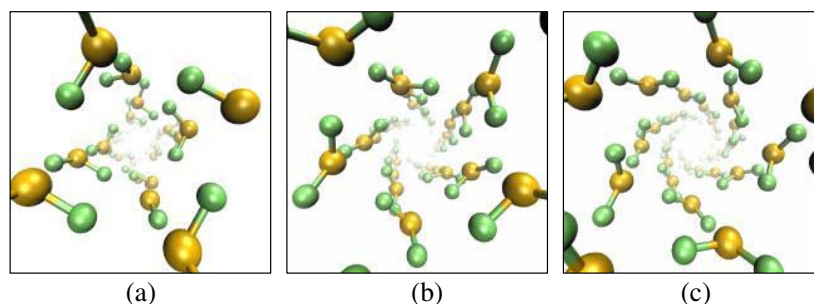


Figure 2 Structures of water molecules in (8, 8) CNT with an electric field of (a) 0 V/nm, (b) 1 V/nm, and (c) 2 V/nm. With the presence of an electric field, water molecules form helical structures in the CNT. Reprinted with permission from [13]. Copyright 2015, AIP Publishing LLC.

Figure 3 represents distribution of coulomb potential energy of water in (8, 8) CNT. The coulomb potential energy of water molecules in the CNT decreases significantly with an electric field. This implies that formation of the ordered structure strengthens the electrostatic interaction between water molecules. Moreover, energy of the electrostatics interaction within water structure in a CNT causes water favor to fill CNTs. Occupancy of water molecules in CNTs increases with an electric field [13].

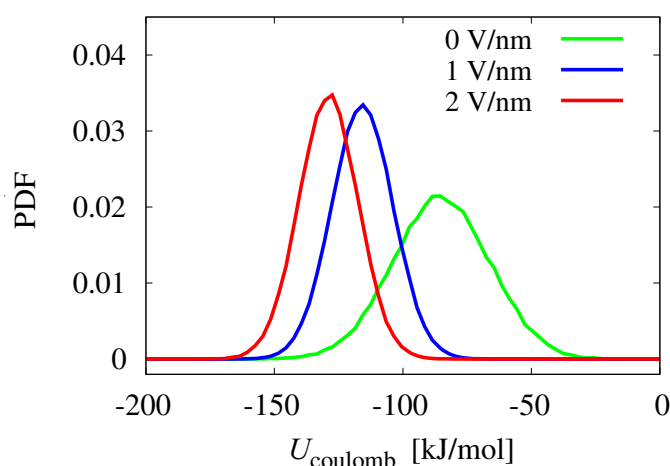


Figure 3 Distribution of coulomb potential energy of water molecules in (8, 8) CNT with 0, 1, and 2 V/nm. The vertical axis represents probability distribution function (PDF). With an electric field, the potential energy of water molecules in the CNT decreases. That indicates strengthening of the electrostatic interaction. Reprinted from [20] – Published by The Royal Society of Chemistry.

The preference of water for filling CNT results in the following separation effect. The separation effect was investigated by filling the reservoirs in Fig. 1 with a mixture of water-ethanol molecules. Figure 4 shows occupancy of molecules in (8, 8) CNT with an electric field of 0 and 1 V/nm. Without an electric field, the number of ethanol molecules in the CNT is higher than that of water molecules. However, water molecules are still able to permeate into CNT. In contrast, with an electric field, only water molecules flow into the CNT even though the concentration of water in the reservoirs is very low *i.e.* 0.19. Ethanol molecules are rejected to permeate into the CNT. This indicates a preference of water to flow through a CNT over ethanol as presented before [21]. Similar result is shown when the reservoirs were filled with water-methanol solutions [20]. With an electric field, only water flow into CNT while methanol molecules are rejected. Therefore, under the influence of an electric field, a CNT membrane is able to separate alcohol

from aqueous solution. Interestingly, the separation effect with an electric field does not decrease with an increase of CNT diameter [20,21].

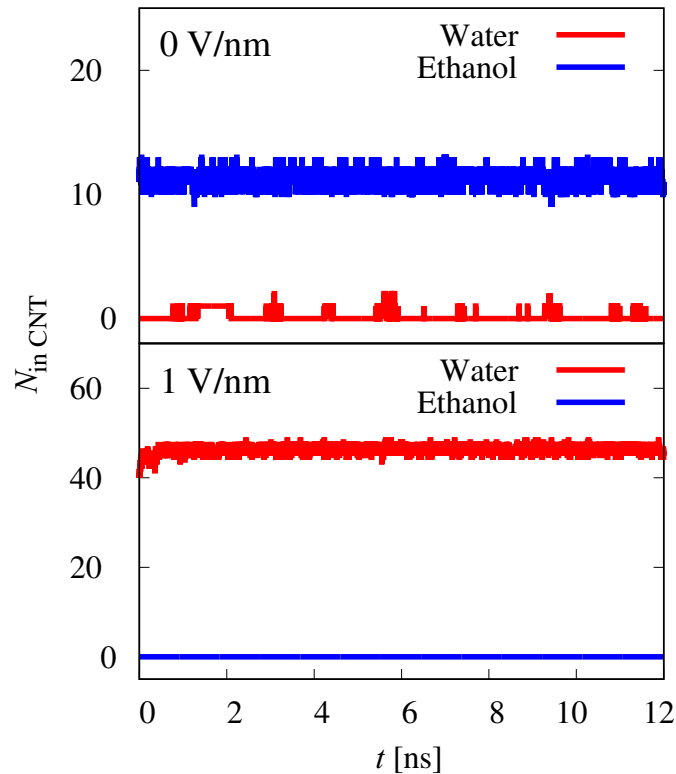


Figure 4 The number of molecules in (8, 8) CNT ($N_{in\ CNT}$) with electric fields of 0 and 1 V/nm. Reservoirs in the simulation system were filled with a mixture of water and ethanol molecules. The mole fraction of water in the reservoirs is 0.19, which is much lower than that of ethanol. With 1 V/nm, only water fills CNT indicating a strong separation effect.

4. Conclusions

We investigate the effects of an axial electric field on water molecules in a CNT with molecular dynamics simulation. The electric field aligns the dipole moment of water molecules and thus they have more uniform molecular orientation. As a result, the water molecules form an ordered structure in the CNT. Formation of the ordered structure strengthens the electrostatic interaction and consequently, water prefers to fill CNT. More importantly, the preference of water to fill CNT results in a strong separation effect for water-alcohol solutions.

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