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# Molecular dynamics simulation of transport of water/DMSO and water/acetone mixtures through boron nitride nanotube

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ABSTRACT

The transport properties of fluids are significant quantities needed in engineering application. In this research, transport of water/dimethyl sulfoxide (DMSO) and water/acetone mixtures through armchair boron nitride nanotubes (BNNTs) was investigated using molecular dynamics simulations technique. The studied systems were composed of (6,6) BNNTs, water/DMSO or water/acetone mixtures. External pressures were applied in these systems along the x axis of the simulation cell. These simulations allow us to explore the mechanisms of transport and separation of solvents as organic contaminants. Without an applied pressure, DMSO or acetone molecules enter and occupy inside the BNNT, but their passing was not significant. For complete analysis of the systems, we calculated the density profiles of species, the radial distribution function of molecules, the retention time of solvents and their hydrogen bonds. The results showed that the transport of solvents through the BNNT was dependent on the amount of applied pressure.



## 1. Introduction

Aqueous binary mixtures are extensively investigated due to their applications in various fields of science. In some cases, these binary mixtures have different properties from the pure substance which are made of them [1–3]. For example, a few materials are dissolved in some mixture, but they do not dissolve in their pure substance. Among the binary mixtures, the water/dimethyl sulfoxide (DMSO) and water/acetone are the most important solvents. We have DMSO with the formula $(CH_3)_2SO$ that is a colorless organosulfur solvent, water-soluble, and hygroscopic which freezes at 19 °C and boils at 189 °C. DMSO as an organosulfur compound has great affinity with water and form the greatest probability potential toxic in water. This solvent has got increasing importance as an intermediate solvent in synthetic processes [4]. DMSO is a water miscible solvent [5] consisting of a polar SO group and two hydrophobic $CH_3$ groups. A major property of DMSO is its ability to interact with water molecules through dipole-dipole and hydrogen bonding interactions that are stronger than those formed between water molecules themselves. DMSO can affect the hydrogen bonding network of water molecules. Due to the negative charge on the oxygen atom of the DMSO, it gives hydrogen bonds (H-bonds) with water molecules. In the formation of H-bonds in water/DMSO mixture, water acts as both H-bond donor and acceptor, but DMSO is only acts as H-bond acceptor. Due to this phenomenon, aqueous solution of DMSO display a non-ideal behavior which is reflected in a number of physical properties such as the freezing temperature, excess mixing volume, rotational diffusion constants and viscosity [6,7]. Some studies on MD simulations of the water/DMSO mixture were done in scientific lectures to study dynamics [8], hydrogen bond distribution [9] and the structure [10] of the water/DMSO mixtures. These studies are based on investigations to reveal the spatial solvation structure and topological features in the mixture of DMSO and water. A mixed solvent showed a nonideal behavior and low freezing point [11,12]. Also simulation studies were reported to show the place where large organic solutes are dissolved in DMSO or in aqueous mixture of DMSO [13,14].

On the other hand, acetone ($(CH_3)_2CO$) is one of the industrial organic solvents having a wide range of applications and industrial uses and is a good solvent for many plastics and some synthetic fibers [15,16]. Acetone is a colorless, volatile, highly flammable liquid and it dissolves a great number of organic molecules and also is an important solvent for cleaning purposes in the laboratory. Since the acetone is miscible with water in any ratio, as the percentage of acetone in the water/acetone mixture increases, it increases the solubility of non-water-soluble molecules in this new

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solution. For acetone aqueous solution, C=O group interacts with water forming hydrogen bond. Although being highly flammable, it is used extensively as a solvent for the safe transportation and storage of acetylene which cannot be safely pressurized as a pure compound. About a third of the world's produced acetone is used as a solvent and a quarter is consumed as acetone cyanohydrin.

Transport of fluids through nanotubes is currently a subject of great interest with many applications, such as solvent separation. Separation of mixed fluids cannot be done without cost and energy. The easiest method for separating mixed fluids is use of their boiling point. But this technique has limitations such as azeotropic points and large amount of energy consumption to reach boiling points of liquids. Today, scientists are trying to find new ways to enable them to carry out separate solvents without spending more energy [17–19]. Accordingly, in this research molecular dynamics (MD) simulations of transport of water/DMSO and water/acetone mixtures through boron nitride nanotube (BNNT) were investigated. Molecular dynamics is a technique for computer simulation of complex systems. It has been modeled at the atomic level and computes atomic trajectories by solving equations of motion numerically, with using force fields. Actually in MD simulations, the time evolution of a set of interacting particles is followed via the solution of Newton's equations of motion as follows [20]:

$$F_i = m_i \frac{dr_i^2}{dt^2} \tag{1}$$

where $r_i$ is the position vector of $i$th particle and $F_i$ is the force acting upon $i$th particle at time $t$ and $m_i$ is the mass of the particle.

BNNTs are of importance for researchers due to their unique and prominent properties [21–25]. A BNNT can be imagined as a rolled up hexagonal BN layer. These nanotubes were firstly predicted theoretically in 1994 [26] and then experimentally synthesized in 1995 [27] by arc-discharge. BNNTs have explicit advantages confronted to systems, such as they have supreme oxidation resistance and distinct chemical stability and are ineffective against most acids and alkalis [28,29]. Also they are noncytotoxic [30,31]. In recent years, BNNTs have shown promise as separation membranes for desalination, gas/water, gas, and organics/water separation [32–37]. Also in the case of water transport through the BNNTs some researches have been done [38–41]. Moreover, the study of the transport and separation of DMSO and acetone through BNNTs has attracted considerable attention.

Very few data on the properties of the water/DMSO and water/acetone mixtures were accessible in the scientific reports; therefore, it was considered worthwhile to report these results. Pure solvents such as DMSO and acetone have many applications in various industries including pharmaceutical industry, production of plastic, synthetic fibers and many others [42–45]. In these processes, these solvents are mixed with water. Hence, it is very important to isolate them from the water for reusing. Hence, we examined the transport of DMSO and acetone solvents through BNNT at the presence of applied pressures. In this work we designed a system including four BNNTs and show that they can effectively separate solvent from water. The main focus of this study is the trend of selective transport of water/DMSO and water/acetone mixtures through BNNT with different applied pressures.

## 2. Computational methods

We examined an open ended armchair BNNT with (6,6) chirality index with a length of 23 Å and diameter of 8.3 Å. The geometry optimization of this nanotube was performed at the B3LYP level of theory using the 6–31G (2d, 2p) basis set carried out in the GAMESS-US [46]. The initial boron-nitrogen bond length was obtained 1.44 Å which is consistent with previous studies [47]. A periodic system containing four side by side cubic-packed identical BNNTs sandwiched by solvent/water per unit cell were simulated.

Before introducing the simulation process, it is necessary to explain how to prepare the initial configurations of system. The initial simulations were built as follows (see Figs. S1 and S2 in Supporting Information): First, pure solvent molecules including pure DMSO and pure acetone were filled into two ($30 \times 30 \times 30$ Å$^3$) boxes separately. Then these solvent boxes went through 10 ns NPT simulations to equilibrium at 300 K. Secondly, these solvents boxes individually were mixed with water bulk; consequently, two boxes of water/DMSO and water/acetone were created. Mixed solvents boxes went again through 10 ns NPT simulations to equilibrium at 300 K. A Langevin thermostat and a hybrid Nose-Hoover Langevin piston were used to maintain the temperature and pressure of the system at 300 K and 1 bar, respectively [48]. In this step, our solvents box were prepared to be added in main simulation box including BNNT so that this nanotube were used as a membrane.

The final MD box consisted of four (6,6) BNNT, 348 water molecules, and solvents (42 DMSO molecules or 69 acetone molecules) reservoirs on both sides of simulation box (see Fig. 1). The dimensions of the simulation boxes were $84 \times 19 \times 18$ Å$^3$. MD simulations were performed with the NAMD2.9 software [49] with a 1 fs time step using a 10 Å cutoff for vdW (van der Waals) interactions and a particle mesh Ewald scheme [50] for electrostatic calculations. Also, all analysis were carry out using VMD1.9.2 [51] same as in previous works [52–57]. The energy variations of systems during transportation were added to the Supporting Information as Fig. S3. The MD simulations were performed with periodic boundary condition (PBC) in all three directions to imitate a system with an infinitely large area. The potential energy of intermolecular interactions was given by the sum of coulomb potentials and Lennard-Jones for long range and short range interactions, respectively. Lennard-Jones parameters for different interactions were calculated through the combining rules to compute the cross interaction parameters [58]. The TIP3P model [59] was used to represent water molecules. The force field parameters for the BNNT and solvents were gained from Refs. [60–62]. During the simulations the BNNTs were held fixed while DMSO, acetone and water molecules were allowed to move freely. The system was subject to a zero temperature energy minimization for 1 n, and then MD simulations were performed for 5 ns at 300 K. The temperature of the systems was maintained at 300 K using a Langevin thermostat.

For the separation of solvents through nanotube, an external force was utilized to oxygen atoms of water molecules so as to create a pressure drop in the x direction to the system. This technique was extended by Zhu et al. to apply a hydrostatic pressure [63,64]. The applied force on water molecules is given by:

$$\mathrm{F} = \frac{\Delta P \cdot A}{n} \tag{2}$$

where F (pN) is a force along the x direction of the simulation box, ΔP (pa) is the pressure, A (m$^2$) is the area of the system, and n is the number of water molecules in the selected area. This method was used in many studies on pressure-driven flow [65–68]. The used pressures were in the range of 10–200 MPa.

## 3. Results and discussion

### 3.1. Permeation phenomenon in the absence and presence of pressure

DMSO or acetone and water molecules permeate through BNNTs under the influence of applied pressures. The arrangement