



Insights on the mechanism of water-alcohol separation in multilayer graphene oxide membranes: Entropic versus enthalpic factors



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ARTICLE INFO

Article history:

Received 4 July 2017

Received in revised form

1 November 2017

Accepted 6 November 2017

Available online 7 November 2017

ABSTRACT

Experimental evidence has shown that graphene oxide (GO) can be impermeable to liquids, vapors and gases, while it allows a fast permeation of water molecules. Theoretical studies to understand the filtration mechanisms come mostly from water desalination, while very few works have been dedicated to alcohol dehydration. In this work, we have investigated the molecular level mechanism underlying the alcohol/water separation inside GO membranes. A series of Molecular Dynamics and Grand-Canonical Monte Carlo simulations were carried out to probe the ethanol/water and methanol/water separation through GO membranes composed of multiple layered graphene-based films with different interlayer distance values and number of oxygen-containing functional groups. Our results show that the size exclusion and membrane affinities are not sufficient to explain the selectivity. Besides that, the favorable water molecular arrangement inside GO 2D-channels forming a robust H-bond network and the fast water permeation are crucial for an effective separation mechanism. In other words, the separation phenomenon is not only governed by membrane affinities (enthalpic mechanisms) but mainly by the geometry and size factors (entropic mechanisms). Our findings are consistent with the available experimental data and contribute to clarify important aspects of the separation behavior of confined alcohol/water in GO membranes.

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1. Introduction

Graphene oxide (GO) membranes have been investigated as very promising candidates for water filtration and/or separation membranes [1,2]. Recently, experimental evidence has shown that in the aqueous phase, water molecules can permeate through GO membranes while blocking the passage of ions [3,4] and molecules such as alcohols [5–8], gases [9,10] and others [11]. GO membranes composed of stacking GO sheets can exhibit complex topologies depending on the experimental techniques used to fabricate them. They can lead to distinct micro- and nano-morphologies and transport pathways that directly affect their selectivity properties [12]. The molecules inside the membrane are supposed to be transported through the percolating two-dimensional channels

formed between GO sheets. A typical single GO sheet structure contains a high percentage of functionalized regions (~82%), pristine regions (~16%) and structural holes (~2%) [13]. The pristine regions have the same local structure as pristine graphene and they are responsible for water fast slip inside the channels [14]. On the other hands, the functionalized regions have a large amount of hydroxyl, epoxy and carboxyl groups that are attractive sites for water and other polar molecules [15]. The number of functional groups can be tunable through some chemical post-treatments [16,17]. The typical interlayer distance between GO sheets is ~6–7 Å under dry conditions and about 12–13 Å under humidification, and it can be also controlled by physical confinement, as recently shown by experimentalists [4,18].

The promising application of GO membranes for water removal from alcohols, such as ethanol and methanol, would have important relevance in biofuels production processes. Ethanol is the most commercialized biofuel that might help world energy supply demands with minor negative environmental impacts [19]. However, to improve sustainability and cost gain of this renewable resource,

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efficient membrane separation is still needed to reduce energy cost during the process of ethanol dehydration [20,21]. The first experimental evidence that GO membranes are permselective for water rather than ethanol was reported by Nair et al. [5]. In their experiment, a GO membrane sealed the open aperture of a container with vapor water-ethanol (50:50) mixture. After several days, only water was evaporated until the concentration of ethanol in the feed side reaches ~80%. To cite another example, Yeh et al. obtained high water permeability and excellent selectivity for ethanol dehydration through pervaporation by using nanofibrous membranes containing multilayered graphene oxide barrier layers [22]. In both experiments, the separation mechanism has been attributed to the formation of a network of nano-capillaries that allow nearly frictionless water flow, while blocking the alcohol. However, the origin of GO membranes selectivity is not evident since water and alcohol molecules are neutral and have similar affinities to the polar oxygen-containing functional groups of GO. Thus far, the role of GO membrane in the water-alcohol separation remains unclear, limiting further improvements on their selectivity performance.

Theoretical studies devoted to understand the water filtration mechanisms inside GO membranes came mostly from those dedicated to water desalination [23–25]. Some works on alcohol-water separation have focused on the performance of adsorbents such as metal-organic framework and zeolites [26–28], and some in 2D materials. For example, Gravelle et al. have performed MD simulation in multilayer pure graphene-membrane to probe permselectivity of ethanol [29] and Kommu et al. investigated the separation in stacked hexagonal boron nitride [30] membranes. To the best of our knowledge, this is the first time that a computational investigation of multilayer GO membranes for water-ethanol and water-methanol separations is performed. In this work, we propose a structural model that simulates a fluid flowing from an infinite reservoir through a multilayer GO-based membrane by molecular dynamics (MD) simulations. This method allows the investigation of the capillary effects considering only the different pressure between both reservoirs as the driven force. In addition, we have also carried out Grand-Canonical Monte Carlo (GCMC) simulations to probe ethanol/water and methanol/water vapor mixtures adsorptive separation. To obtain a deep understanding of these mechanisms at the molecular scale, a careful inspection on the structural aspects (how the molecules are spatially arranged) of the molecules inside the membranes, as well as membrane/molecule affinities and molecular permeation were analyzed.

2. Methods

Molecular dynamics simulations (MD) were performed using the structural model schematically shown in Fig. 1. Typical structural models contain four graphene sheets perforated with nano-slits of width $D \sim 12.7$ Å and parallelly arranged by a distance d . D is the distance between the center of the carbon atoms of the sheet edges without considering the functional groups COOH. We used the reflector wall protocol, where immaterial walls are placed on the extremity of the simulation box and parallel to the membrane to create a molecular flow through a unique path, as schematically shown in the inset of Fig. 1. Two d different values were considered here: 7 and 10 Å. The simulation box dimensions are $76.5 \times 44.2 \times 200$ Å³. Two types of graphene sheets were considered: graphene oxide (GO) with 35% and 14% content of oxygen (from hydroxyl, epoxy and carboxyl groups) atoms, as shown in Fig. 1. To build GO sheets, graphene membranes were functionalized with hydroxyl and epoxy functional groups on the both membrane sides and with carboxyl groups on the sheet edges. In our approach, the interlayer distance and the number of oxygen-

containing functional groups are treated independently. In reality, these two variables are related. The amount of carboxyl and hydroxyl groups and their ionization in aqueous solution would play important roles on the dispersion of GO sheets and, then, on the interlayer distance. However, our simple model allows us to systematically investigate the contribution of each variable on the separation mechanism.

The system configuration was then prepared by placing a water-alcohol liquid reservoir in contact to the fixed membrane. The initial water-ethanol and water-methanol configuration was generated using the Packmol [31] code and equilibrated at ambient pressure (1 atm) and room temperature (300 K) through MD simulations. Once the reservoir is placed in contact to the membrane, the water flow was simulated through controlling the reservoir thermodynamics properties. The reservoir temperature is kept constant at 500 K using a Nosé-Hoover thermostat [32,33] and the pressure is controlled by a movable piston of graphene placed on the bottom of the simulation box. The piston allows the reservoir volume to vary while the water moves into the membrane. The piston position is scaled by the force experienced by the piston as a response of the reaction mixture force. This protocol is very effective to mimic an infinite reservoir by keeping constant the difference of pressure between feed and permeate side.

The positions of the atoms of the membrane are kept fixed, so the bonded interaction description for the membrane is not needed. The Lennard-Jones parameters were extracted from CHARMM [34,35] force field for GO and the Lorentz-Berthelot mixing rules are used to determine the parameters for the cross-interactions [36,37]. Partial charge values were taken from Ref. [38]. The rigid extended simple point charge (SPC/E) model [39] was used to describe water molecules, while the TraPPE force field was used for ethanol and methanol [40]. The van der Waals interactions are truncated at 12 Å, and the long-range Coulomb interactions are computed by utilizing the particle-particle mesh (PPPM) algorithm [41]. Periodic boundary conditions were imposed along the xy -plane containing the membranes, while non-periodic boundaries were used along the z -direction. The MD simulations were carried out using the open source software called large-scale parallel molecular dynamics simulation code (LAMMPS) [42].

Grand-Canonical Monte Carlo simulations were carried out to probe the water/methanol and water/ethanol co-adsorption at 350 K. Three mixtures with mole fraction equal 0.1, 0.3 and 0.5 were considered. The fixed multilayer graphene membrane model and the guest/host interactions using the classical force field formalism were applied as used in the MD simulations. The Ewald summation was also used for calculating the electrostatic interactions while the short-range contributions were computed with a cut-off distance of 12 Å. The GCMC simulations used to estimate the co-adsorption isotherms and adsorption enthalpy were computed using the revised Widom's test particle method [43].

3. Results and discussion

The permeability of alcohols (*i.e.* methanol and ethanol) and water within graphene oxide (GO) membranes were systematically investigated using MD simulations to mimic GO multilayer membranes in contact with a reservoir of water-alcohol mixtures of 0.5 mol fraction. The pure liquid water reservoir was also simulated for comparison purposes. Two types of membranes were built with GO sheets functionalized with hydroxyl and epoxy on both sides and carboxyl groups on the sheet edges, totalizing O/C ratio (number of Oxygen atoms over the number of carbon atoms in the membrane) equal to 35% and 14%, respectively (see Fig. 1). At the

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