

# Molecular simulation on the separation of water/ethanol azeotropic mixture by poly(vinyl alcohol) membrane

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## ABSTRACT

Grand canonical Monte Carlo (GCMC) simulation is used to investigate the performance of poly(vinyl alcohol) (PVA) membrane in separating the azeotropic water/ethanol mixture (95.57 wt% ethanol) over a wide range of pressures (10–1000 kPa), temperatures (298–338 K) and PVA polymerization degrees (100–1000). By calculating the sorption isotherms and the ethanol-to-water separation factors, we observe that the water/ethanol adsorption amount and separation factor decline slowly with the increase of temperature; as the polymerization degree rises, both of adsorption amounts first increase and then decrease, while the separation factor changes adversely. Concepts such as fractional free volume (FFV) and hydrogen bonding interactions are analyzed to explain the observation. As the polymerization degree increases, the FFV changing trend is similar to the one mentioned in the discussion of adsorption amount, but their inflexions are different. Hydrogen bonding interaction successfully explains this variation. We further deduce that the fact that the change of adsorption amount results from a transition from cooperation to competition between FFV and hydrogen bonding interactions. The optimal operating conditions for separation are 298 K and 101.325 kPa. Under this condition, the PVA membrane (polymerization degree 1000) has a separation factor of ~80 for the water/ethanol azeotropic mixture, which means that the concentration of ethanol can be refined to 99.96 wt% and anhydrous ethanol is possible to be obtained by PVA membrane separation.

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## 1. Introduction

Anhydrous ethanol, as a green fuel, is of increasing practical significance in alleviating current energy shortage and reducing air pollution. Membrane separation techniques have attracted considerable attention owing to its potential applications in medication, energy, food and environmental protection. In particular, pervaporation separation technology is hopefully to be developed more widely in industry, especially in producing anhydrous ethanol; because it has lots of advantages within the separation process, such as requiring no introduction of a third component, simple equipments, high single-stage separation efficiency, no pollution and low energy consumption [1–9]. Tusel et al. [10] shows that the employment of a ethanol-producing technique, distillation–pervaporation membrane preparation method, in dehydrating ethanol from 95.57 wt% to 99.85 wt%, can bring a 28% and 40% decrease in investment and operating costs respectively, compared to the traditional azeotropic distillation method.

In particular, poly(vinyl alcohol) (PVA) is a very important material for the separation of water/ethanol solutions by pervaporation [11], because the PVA membrane shows excellent selectivity toward water and also has remarkable film-forming characteristics as well as good resistance to organic mixtures, despite of its poor stability in aqueous mixtures [12]. In addition, PVA membrane has many attractive advantages such as air-tightness property, biodegradability, nontoxicity, and good tensile, tear and impact properties, which make it a new generation of environment-benign materials. In recent years, studies concerning separation of water/ethanol mixture using other membranes abound. Uragami et al. [13] studied the separation factors and permeation rate of water/ethanol by organic–inorganic hybrid membranes composed of PVA and tetraethoxysilane with different tetraethoxysilane content. Yeom et al. [14] studied the performance of sodium alginate and PVA blend membranes on the pervaporation separation of the ethanol–water mixtures with the temperature range of 323–353 K. Rhim et al. [15] investigated the effect of the crosslinking density of PVA membrane on the separation of water/ethanol mixtures. All these experimental studies have shown their interesting separation characteristics, but the separation mechanism of PVA membranes is still obscure due to the difficulties in identifying their microscopic structure by experiments. Whereas, molecular simulation

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can provide better understanding of the relationship between material structure and property and guide experiments to develop in a safer, more efficient and more economical way. Therefore, there are strong incentives for simulating at the molecular level. Zhang et al. [16] investigated the characteristics of swollen PVA and analyzed the intrinsic relationship between the microstructure of the swollen PVA and the diffusion of water and ethanol in PVA matrix using molecular dynamics (MD) simulations. However, the composition and density of water and ethanol mixtures in membrane systems of some previous works was arbitrarily set, not determined from GCMC simulations, so the diffusion properties obtained from some previous works may not be reasonable, since the diffusion of small molecules in confined system is strongly dependent on concentration and composition. For mixture separation simulations [17–21], inorganic zeolites and carbon nanotubes are mostly adopted, while less attention is paid on polymeric systems. In addition, the effect of polymerization degree on the separation performance and the structure–property relationship of polymer membranes with different polymerization degrees are seldom investigated.

We perform grand canonical Monte Carlo (GCMC) simulations to investigate the performance of PVA membrane in separating the azeotropic water/ethanol mixture (95.57 wt% ethanol). In order to find the optimal operating conditions for producing anhydrous ethanol, we discuss the influence of different factors such as temperature, pressure and polymerization degree of PVA. Our discussion and explanation are mainly at the microscopic level, using not only the traditional FFV method but also the new hydrogen bond analysis. Our findings may also provide guidance to related experiments, and help to understand more profoundly the feasibility of industrially applying polymeric membrane to the separation of water/ethanol mixture.

## 2. Simulation methods and details

### 2.1. Simulation methods

GCMC simulation method is often used to study the adsorption of fluids. It is especially suitable for simulations of mixtures and inhomogeneous systems, such as fluids at interfaces and micropores. In the adsorption process, chemical potential is converted into partial fugacity of each component. Thus, in GCMC simulation, fugacity is also closely related to chemical potential. The equilibrium in GCMC simulation arrives when temperature and chemical potential of the fluids within the system are respectively equal to those of the macro fluids. GCMC deals with open systems where the chemical potential, volume and temperature are fixed (i.e. constant  $\mu$ ,  $V$ ,  $T$  ensemble). It should be noted that these parameters are also constant in the experimental measurements of adsorption process, which facilitates direct comparisons between simulation and experimental results [22].

### 2.2. Simulation details

Molecular simulations were carried out using the Forcite module, Amorphous Cell, and Sorption modules of Materials Studio 4.4 (Accelrys Software Inc). The COMPASS force field was used to simulate the sorption behavior of PVA. Electrostatic interactions were treated with Ewald method [23]; while van der Waals interactions were calculated by the atom-based option [24] with the non-bonded cutoff distance of 1.0 nm. The Metropolis method [25] was employed to accept or reject configurational moves (rotation and translation of the sorbate molecules) as well as for sorbate insertion and deletion, in which the trial configurations were generated without bias and the adsorbate structure was treated as rigid.

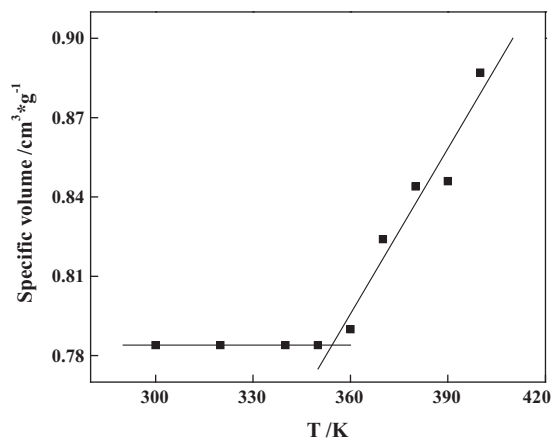


Fig. 1. Specific volume of PVA membrane as a function of temperature.

The initial PVA chain was consisted of 100–1000 repeat units. For PVA control membrane, the packing model with an initial density of 0.9 g/cm<sup>3</sup> was constructed. Periodic boundary conditions were applied to the cubic simulation cells. The initial constructed structures were subsequently optimized by a 5000-step energy minimization to eliminate the unreasonable contact and by an annealing procedure. During the annealing, systems were heated from 298 to 498 K at an interval of 20 K and then cooled back at an interval of 20 K, with temperature being controlled by Andersen [26]. At each temperature interval, 100-ps NPT dynamics was performed. At each desired temperature, a further 5-ns NPT-MD simulation was undertaken. Four configurations at 0, 1, 3 and 5 ns were used for GCMC simulations. Afterwards, GCMC simulations were performed, with  $5 \times 10^6$  steps for equilibration and  $2 \times 10^7$  steps for production. The uncertainty was determined by averaging the results from these four simulations.

In addition, in order to testify the accuracy of the used force field and the reliability of PVA membrane, the specific volume of the PVA membrane with a polymerization degree of 150 was analyzed under 101.325 kPa and 298–410 K. Fig. 1 is the profile showing the relationship between temperature and specific volume of PVA membrane, where an inflexion point exists. Linear fittings are done to both sides of the inflexion point. From the intersection of the two lines, we can read the glass transition temperature ( $T_g$ ) of the PVA. The simulated  $T_g$  is 354.32 K, very close to the experimental value of 349.25 K [27], which demonstrates that the PVA constructed in simulation is adequate to represent the realistic PVA membrane and the used COMPASS force field is suitable.

## 3. Results and discussions

### 3.1. Temperature effect

Temperature is always one of the necessary factors to be considered for an adsorption separation process. Non-crystalline solids, known as “amorphous materials”, do not have their atoms or molecules arranged on a lattice periodically repeated in space. For all amorphous solids, whether glasses, organic polymers or even metals,  $T_g$  is the critical temperature that separates their glassy and rubbery behaviors. “Glassy” in this context means hard and brittle, while “rubbery” means elastic and flexible. A glass is defined as a material that has no long-range atomic or molecular order and that is below the temperature at which a rearrangement of its atoms or molecules can occur. A rubber is a non-crystalline solid whose atoms or molecules can undergo rearrangement. In other words, if a material is at a temperature below its  $T_g$ , large-scale molecular motion is impossible because the material is essentially frozen. If it

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