Elucidation of liquid phase permeation phenomena in nanoporous membranes by non-equilibrium molecular dynamics

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Abstract

The objective of this work is to explain the phenomenon of liquid phase permeation in nanopores separation membranes, which have applications in fields such as water treatment. The results of investigations using the non-equilibrium molecular dynamics method, a molecular simulation technique, are summarized here. Molecular simulation enables the analysis of diffusion phenomena at the molecular level in nanostructures. However, the adaptation of this approach to non-equilibrium systems, such as membrane permeation, has been limited by methodological challenges and computational burdens, which have restricted previous research. This thesis focuses on the Fluctuating-Wall Molecular Dynamics (FW-MD) approach, which is capable of handling non-equilibrium systems. It applies molecular simulations to liquid-phase membrane separation systems, where no previous reports have been available. After demonstrating the quantitative aspects of simulating liquid phase permeation phenomena, the study applies this methodology to organic solvent separation and the evaluation of novel water-permeable membranes, revealing the permeation phenomena within nanopores at the molecular level. The thesis comprises chapters 1 through 7. Chapter 1 serves as an introduction, elucidating the background, objectives, and research approach of the study. This text discusses the importance of membrane separation technology in addressing the global water scarcity issue. It highlights the role of molecular simulation in membrane engineering and outlines the principles of molecular dynamics and the methodological characteristics of FW-MD.

Chapter 2 discusses the application of FW-MD to predict the permeation flux of isotropic membranes with nanopores. The osmotic pressure difference drives the osmotic process and knowledge of the osmotic pressure of the solution allows the prediction of the permeation flux. The permeation flux obtained through FW-MD closely matches the theoretical values. In addition, this chapter proposes a method to determine the concentration dependence of osmotic pressure from the solvation structure around the solute. This method has been validated using simulation results from FW-MD. Although the membrane model used in this chapter is relatively simple, it effectively demonstrates the applicability of FW-MD to isotropic membrane research. This demonstration considers more complex membrane structures and operating conditions.

Chapter 3 discusses the application of FW-MD to organic solvent reverse osmosis (OSRO). This is a separation technique that is gaining attention as an alternative to distillation. The study predicts the permeability and separation performance of organic solvents in Y-type zeolite membranes with nanoporous, visualizing the permeation phenomenon within membrane pores at the molecular level. The results reveal differences in permeation characteristics compared to vapor-permeation separation. Selecting suitable membrane materials and separation systems is considered essential for effective

OSRO based on the discussion of results. Therefore, FW-MD is used to separate low-molecular-weight alcohol mixtures, demonstrating the usefulness of Y-type zeolite membranes.

Chapter 4 proposes methods for enhancing permeation flux in OSRO and verifies them using FW-MD. The pressure dependence of permeation flux in OSRO is lower than in aqueous systems, so increasing operating pressure does not yield sufficient permeation flux. Therefore, a less polar high silica FAU zeolite is selected to increase permeation flux, which is verified using FW-MD. The results demonstrate improvements in permeation flux and selectivity in ethanol/cyclohexane mixtures compared to Y-type zeolite membranes. Moreover, it has been demonstrated that modifying the adsorption characteristics on the permeate side membrane surface can enhance permeation flux. Additionally, the modification of the permeate side membrane surface has been shown to improve permeation flux. The study finds that membrane materials suitable for OSRO are different from those used for vapor permeation separation and that modifying the permeate side membrane surface improves permeation flux.

Chapter 5 evaluates the permeability of water in carbon nanotube with charged pore walls as an example of a novel membrane structural design using FW-MD. Changing the charge distribution on the pore walls can change the orientation of the permeating water molecules, thereby affecting the permeation flux. Molecular-level analysis shows that the ease of hydrogen bond formation between pore wall charges and permeating water molecules influences this phenomenon. Thus, designing the charge distribution on the walls of nanoporous can enable the creation of highly permeable water-permeable membranes.

Chapter 6 proposes a novel membrane material based on self-assembled supramolecular to achieve high water permeability. The permeability is predicted using FW-MD. The study focuses on the pillar-shaped structure of cyclic tetramers of 2-phenyl-1,3,4-oxadiazole and analyzes water permeation within membranes stacked with these supramolecular in detail. The study reveals that a single-file diffusion of molecules within the pores leads to high water permeability. By altering the supramolecular structure, multiple membrane models with varying pore sizes were created to identify the optimal pore size for maximizing permeability. The proposed mechanism of supramolecular membrane permeation is unique and suggests a novel water permeation mechanism for achieving high permeability.

Chapter 7 serves as a summary of chapters 1 through 6. Throughout the thesis, simulations of liquid phase membrane permeation phenomena using FW-MD have been consistently conducted. Using FW-MD has allowed analyzing membrane permeation phenomena under a constant pressure gradient. The knowledge gained provides theoretical design guidelines for the development and improvement of nanoporous separation membranes for water treatment systems. Selective water-permeable membranes are crucial for effectively addressing water scarcity issues, making the findings of this doctoral thesis industrially significant.