

UNDERSTANDING AND CONTROLLING WATER-ORGANIC CO- TRANSPORT IN CARBON MOLECULAR SIEVE MEMBRANES

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UNDERSTANDING AND CONTROLLING WATER-ORGANIC CO-TRANSPORT IN CARBON MOLECULAR SIEVE MEMBRANES

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To my loving parents Dr. Jeyong Yoon and Dr. Hyenmi Chung

and my brother Youngchul Yoon for their lifelong supports,

To my dearest Advisor, Dr. Ryan P. Lively,

And to my loving husband, Jinhee Lee

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LIST OF SYMBOLS AND ABBREVIATIONS

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
TSS	Total suspended solids
BTEX	Benzene, toluene, ethylbenzene, xylenes
ATSDR	The Agency for Toxic Substances and Disease Registry
WHO	World Health Organization
USEPA	The United State Environmental Protection Agency
VOC	Volatile organic compounds
MF	Microfiltration
UF	Ultrafiltration
PSf	Polysulfone
PES	Polyethersulfone
PVDF	Polyvinylidene fluoride
PAN	Polyacrylonitrile
CA	Cellulose acetate
MOF	Metal-organic frameworks
CMS	Carbon molecular sieve
SD	Sorption-diffusion
PIM	Polymer of intrinsic microporosity
VP	Vapor permeation
RO	Reverse osmosis
PV	Pervaporation

NF	Nanofiltration
PF	Pore-flow
μ_i	Chemical potential of species i
p	Pressure
γ_i	Activity coefficient of species i
c_i	Concentration of component i
P_i	Permeability of i
α_{ij}	Permselectivity of fast component i over slow component j
N	Flux
ℓ	Membrane thickness
Δf_i	Fugacity difference of component i across the membrane
D_i	Transport (Fickian) diffusivity of component i
S_i	Sorption coefficient of component i
$\bar{D}_i$	Maxwell-Stefan diffusivity
M-S	Maxwell-Stefan
ρ	Membrane density
Γ	Thermodynamic correction factor
q^{sat}	Saturation loading
θ	Fractional occupancy
ΔH_{S}	Integral heats of sorption
R	Gas constant
T	Temperature
S_o	Pre-exponential factor for sorption coefficient
E_D	Activation energy of M-S diffusion

$D_{o,A}$	Pre-exponential factor for M-S diffusion
E_P	Activation energy of permeation
$P_{o,A}$	Pre-exponential factor for permeation
k	Permeability coefficient
η	Dynamic viscosity
n	Total number of guest species
D_{ij}	Multicomponent diffusion coefficient
x^f	Mole fraction in feed
x^p	Mole fraction in permeate
φ_i^{sat}	Saturation fugacity coefficient
p^{sat}	Saturation pressure
$\hat{V}_l$	Molar volume
P_R	Reduced pressure
T_R	Reduced temperature
B_{ii}	Second virial coefficient
Z_i	Compressibility factor
ω	Acentric factor
$\beta_{i/j}$	Separation factor of i over j
TDS	Total dissolved solids
TOC	Total organic carbon
CAB	Cellulose acetate butyrate
TFTPN	Tetrafluoroterephthalonitrile
TTSBI	5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane
DCM	Dichloromethane

DMF	Dimethylformamide
THF	Tetrahydrofuran
DMAc	N,N-Dimethylacetamide
DI	Deionized water
UHP	Ultra high purity
WK	Wicke-Kallenbach
HPLC	High performance liquid chromatography
GPC	Gel permeation chromatography
M_w	Average weight molecular mass
PDI	Polydispersity Index
wt	weight
HK	Horvath-Kawazoe
STP	Standard temperature pressure
XPS	X-ray photoelectron spectroscopy
SEM	Scanning electron microscopy
ϕ	Dimensionless diffusion coefficient
M_t	Sample mass with adsorbed vapor at time t
M_∞	Sample mass with adsorbed vapor at equilibrium
GC	Gas chromatography
$\dot{n}_i$	Molar flow rate of i
TCD	Thermal conductivity detector
A	Permeation area of the membrane
OD	Outer diameter
nPDF	Neutron pair distribution function
MMM	Mixed matrix membrane

T_g	Glass transition temperature
NLDFT	Non-local density functional theory
PSD	Pore size distribution
R_g	Radius of gyration
SAXS	Small angle X-ray scattering
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
T_p	Pyrolysis temperature
IAST	Ideal adsorption solution theory
VLE	Vapor liquid equilibrium
HF	Hollow fiber
a	Activity
$\bar{\theta}^m$	Average guest loading in membrane
J	Diffusive flux
k_{dilution}	Dilution factor

SUMMARY

Addressing water scarcity and pollution is important for global sustainability and environmental conservation. Industrial wastewater management plays a critical role in mitigating water pollution and ensuring safe water supplies. Membrane separation has emerged as a cost-efficient and highly effective approach for separating water from dissolved organic solvent contaminants. This dissertation focused on exploring the potential of a scalable rigid microporous material as a membrane for achieving desired separation performance in water and organic solvent separation. Carbon molecular sieve (CMS) is investigated as an advanced membrane material known for its impressive separation performance in gas and organic solvent separation. This study focused on p-xylene as an organic contaminant, which is a common aromatic organic solvent encountered in industrial wastewater. Overall, the study sought to understand a structure-transport relationship of water-organic solvent mixture in CMS membranes to optimize the utilization of CMS membranes for the water-organic separation.

The research examined the structure of amorphous CMS membranes derived from the PIM-1 (polymer of intrinsic microporosity-1) precursor. Experimental findings provided valuable insights into the microporous structures of CMS. Then, the transport studies on water and p-xylene vapors in CMS membrane derived from polyvinylidene fluoride (PVDF) were performed using a sorption-diffusion (SD) model. The investigation extends further to PIM-1 (polymer of intrinsic microporosity-1) derived CMS membranes fabricated under various conditions to achieve different micropores structures and surface chemistries. We were able to confirm that the separation performance of water and p-

xylene can be controlled via adjusting the properties CMS membranes. The study further investigated the transport of water and the dilute concentration of p-xylene in the liquid phase, in PIM-1 derived CMS hollow fiber membrane using the SD model.

Overall, this research may provide valuable insights for the engineering and optimization of CMS membranes for water-organic separation challenges by understanding the relationship between membrane structure, transport regime, and separation modality. What we learned here may be useful in understanding and developing CMS membranes as effective tools in addressing the complex separation of water and organic solvents in industrial wastewater treatment.

CHAPTER 1. INTRODUCTION

1.1 The Demand for Water and Organic Solvent Separation

Approximately 97.5 % of the total water supply on earth is comprised of salty water and only ~1 % of the remaining fresh water is available for human consumption [1]. Unfortunately, the global water withdrawal has expanded by a factor of six over the previous century (Figure 1. 1) [2]. Such a drastic increase can be attributed to the rapid development of the global economy, increase in population growth, and the worsening effects of climate change. Therefore, it is becoming more important to explore alternative ways to supply water to meet the demands of the emerging society.

Water reuse (or water reclamation) is one method for maintaining a reliable water supply, provided that it undergoes a proper treatment. Wastewater is an important aspect of the water management cycle that is often overlooked compared to water supply challenges. Effective wastewater management is essential for improving human health outcomes and equity, the environment, and the sustainability of global water supplies.

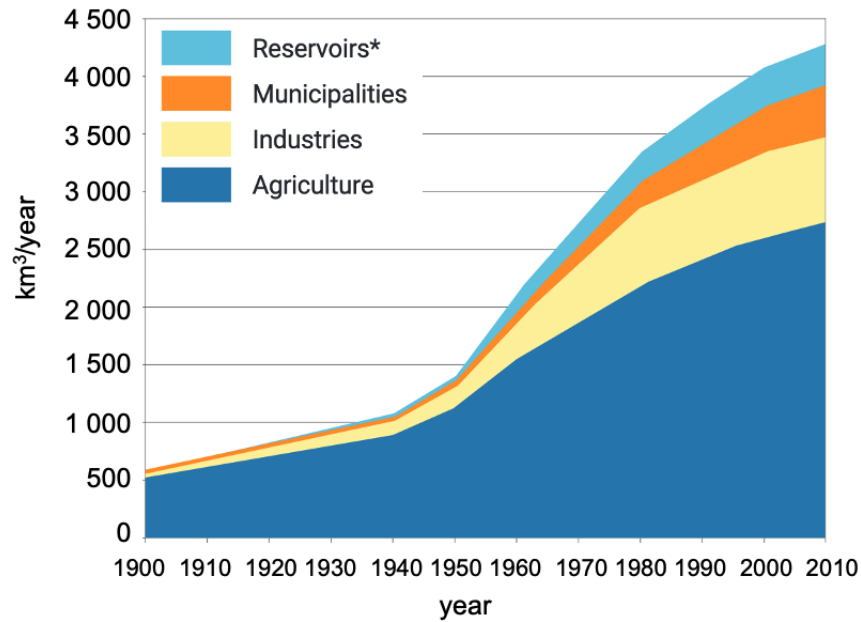


Figure 1. 1. Global water withdrawals over the previous century. Note: The * indicates evaporation from artificial lakes.

Remarkably, a significant amount of the world's wastewater is discharged into waterbodies without proper treatment (Figure 1. 2) [3]. The United Nations (UN) has set a Sustainable Development Goal (SDG) in wastewater management to address this issue, which is to reduce the untreated wastewater discharge by half by 2030. In fact, wastewater can be a valuable resource for obtaining water, energy, nutrients, and other beneficial byproducts. Effective use of wastewater reclamation can help alleviate pressure on freshwater resources, especially in the areas experiencing water scarcity.

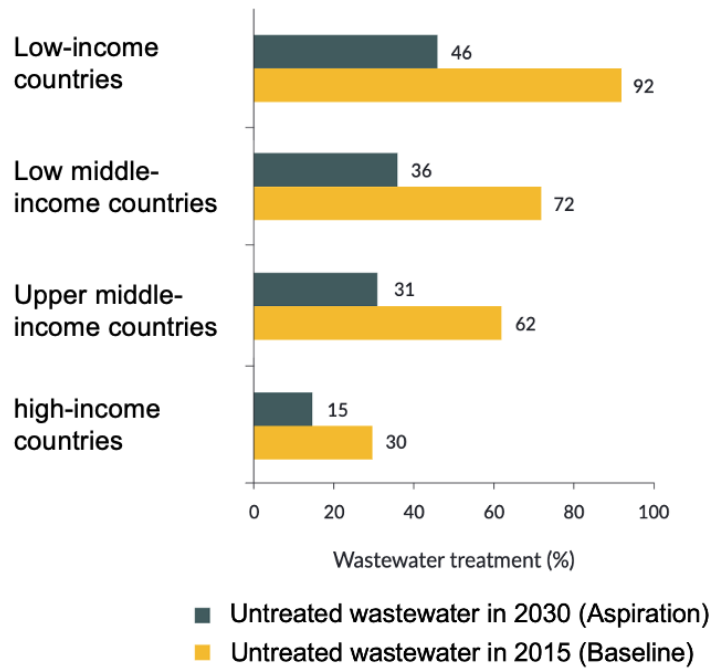


Figure 1. 2 Percentage of untreated wastewater in 2015 (yellow) and goal for 2030 to reduce by half (green)

The industrial sector accounts for approximately 22 % of global water consumption [4], relying on surface/groundwater, seawater, and recycled water from industrial wastewater and urban sewage sources. Water serves an essential role across a variety of industries, while the majority of water used ends up as wastewater discharge [1]. However, discharging the wastewater into the environment carries a significant environmental impact and other potential hazards. Therefore, minimizing industrial water usage and treating wastewater for reuse or safe disposal is crucial.

The nature of contaminants, contaminant composition, and volume of industrial wastewater widely varies, and thus a portfolio of treatment processes is necessary. Wastewater treatment typically involves primary, secondary, and tertiary operations [1]. Primary processes focus on pre-processing the complex wastewater to protect the

subsequent secondary and tertiary processes and prevent process failures. Primary treatment commonly involves pH modification, filtration, and clarification. Secondary treatment involves physiochemical and/or biological processes to remove ~85-95 % of BOD (biochemical oxygen demand), COD (chemical oxygen demand), and TSS (total suspended solids) from wastewater. Tertiary treatment typically achieves over 99 % removal of toxic pollutants, providing the final effluent with desired purity.

The separation of miscible water and organic solvent mixture is a common separation challenge in the tertiary treatment of industrial wastewater. Applications include purification of produced water, recovery of homogeneous catalysts from water-organic reaction systems, and water removal from black liquor. Benzene, toluene, ethyl-benzene, and xylenes (BTEX) are common contaminants in these situations. The BTEX group are small aromatic hydrocarbons and are volatile and toxic, making them one of the most significant contributors to hazardous pollution from produced water [5]. In this dissertation, p-xylene was investigated as an exemplar for a small aromatic organic solvent contaminant commonly found in industrial wastewater.

Common sources of BTEX pollution are industrial discharge, accidental spills, and pipeline leakages [6]. The Agency for Toxic Substances and Disease Registry (ATSDR) recognizes benzene and ethylbenzene as potential carcinogens and has reported the neurotoxic effects of BTEX compounds [7]. BTEX exhibits high concentrations in the aqueous phase due to their high water solubility relative to other hydrocarbons. The permissible limits of BTEX from the World Health Organization (WHO)'s drinking water guidelines are 100, 700, 300, and 500 $\mu\text{g/L}$, respectively [8], and the US Environmental Protection Agency (USEPA) limits to 3, 1000, 700, 10,000 $\mu\text{g/L}$, respectively [9].

However, various sources of water systems have reported higher concentration of BTEX detected [10]. For instance, the BTEX concentrations of 27,000, 37,000, 19,000, and 611 $\mu\text{g/L}$, respectively, have been detected in Weld County, Colorado, an area with intensive hydraulic fracturing activities [6]. Therefore, exposure to BTEX exceeding the permissible limits can be a significant health risks and an efficient treatment process is essential.

1.2 Current State of the Art for Water and Organic Solvent Separation

Conventional separation methods for BTEX removal from wastewater include technologies such as adsorbents, catalytic oxidation, air stripping, and membrane separation [11,12]. Activated carbon adsorption is an economical approach that also provides high sorption capacity for BTEX removal from an aqueous solution. However, the use of activated carbon exhibits an operational disadvantage in requiring frequent regeneration of adsorbents [13,14]. The catalytic oxidation of dissolved organics is effective in pollutant removal [14]. However, it requires careful implementation and analysis of the fate of harmful chemicals, post-treatment of the treated solution, and the operational challenge of deactivating the catalyst during oxidation due to the deposition of carbon or leaching of active metals [15–17]. Air stripping is simple and effective for removing volatile organic solvents thus has been used as a conventional separation method for decades [18]. However, air stripping requires post-separation air purification [19] and the technique is only effective for the removal of volatile organic compounds (VOC).

Membrane separation can operate at a steady-state, which results in easier process control and increased productivity [20]. Moreover, the minimal usage of chemicals and negligible thermal energy requirements improve process safety, potentially enabling cost-

effective separation of water and organic mixture. Additionally, there is the possibility of obtaining high purity organic products.

1.2.1 Membrane materials for water and organic solvent separation

The development of membrane separation technologies for oily wastewater treatment has gained attention from industry and the academy [12]. Membrane technologies have been tested on a small scale and shown potential for commercial use. Membranes with microfiltration (MF) and ultrafiltration (UF) are already in use for this two-phase oil-water separations as the average size of the oil particles in oily wastewater are quite large, and these membranes are thus able to reject the oil particles while allowing water to pass through effectively.

Membrane materials are deployed in various form factors such as hollow fiber, spiral, and tubular modules. Commonly used materials include polysulfone (PSf), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) and cellulose acetate (CA) [12,21]. Polymeric materials can be fabricated into reverse osmosis membranes, which have shown great performance in removing organic contaminants with low manufacturing cost compared to that of ceramic and other inorganic membranes. However, the polymer membranes have drawbacks in its poor performance in removing small organic compounds such as BTEX and high fouling activity on the surface of the membrane that results in reduced flux.

On the other hand, ceramic and inorganic membranes are able to achieve a high degree of productivity and selectivity based on a narrow and well-defined pore size distribution. Also, the thermal and chemical stability of ceramic membranes enables a

broad window of membrane operation as well as membrane cleaning in harsh conditions. However, ceramic membranes have the critical disadvantage of high manufacturing cost, and they cannot exhibit small pore size distribution that can remove small organic molecules. Other inorganic materials such as zeolites and metal-organic frameworks (MOFs) possess a uniform distribution of micropores, enabling molecular separation with minimal differences in molecular size in 0.1 Å scale. While these materials offer promising potential, their practical application is limited due to the costly supports required and the challenges in scaling up their production. Therefore, an inorganic membrane like carbon molecular sieve (CMS), which possesses rigid micropores and offers an easy scalable fabrication process, would be advantageous for separating the dissolved small organic compounds from wastewater at scale.

1.3 Research Objectives

The overarching goal of this thesis is to understand and control the transport of water and p-xylene in carbon molecular sieve (CMS) membranes. The four primary objectives of the thesis are the following:

Objective 1. Gaining a deeper understanding of the formation of the ultramicropores in CMS

Objective 2. Investigating the transport mechanism of water and p-xylene in PVDF-derived CMS membrane using a sorption-diffusion (SD) model

Objective 3. Understanding the relationship between membrane structure and transport characteristics of water and p-xylene separation in CMS membranes

Objective 4. Modeling of the liquid separation of water and p-xylene in PIM-1 derived CMS membrane

1.4 Dissertation Organization

This thesis work encompasses an exploration of CMS membranes for water-organic separation, including membrane fabrication, characterization, and fundamental transport mechanism studies in various membrane operation modalities.

Chapter 1 includes an introduction to the research. Chapter 2 provides the background, theory, and context for the dissertation by providing an overview of the different types of membrane separation, their transport mechanisms, and the membrane material of interest. Chapter 3 includes the experimental methods and materials employed throughout the dissertation. Chapter 4 discusses the structural studies of PIM-1 (polymer of intrinsic microporosity-1)-derived CMS. The amorphous structure of CMS is investigated via techniques such as neutron total scattering, small angle X-ray scattering, and gas physisorption. The aim is to gain direct evidence of the structural modifications that enhance the membrane performance observed in previous studies, specifically for xylene isomer separation [22]. Chapter 5 explores the potential of CMS membranes as an organic-selective membrane for water/organic separation. The transport mechanism of water and p-xylene is investigated using the SD model, with an experimental investigation of sorption and diffusion behavior using gravimetric sorption experiments to model permeability. Vapor permeation (VP) experiments are conducted to verify the SD transport mechanism of water and p-xylene in PVDF-derived CMS. Chapter 6 focuses on the study of the structure-transport relationship of water and organic solvent in CMS. PIM-1-derived

CMS membranes were fabricated under various pyrolysis conditions, resulting in diverse pore structures. Similar to Chapter 5, the water transport in PIM-1-derived CMS is studied using SD model, which has not been previously investigated. Moreover, the separation of water and p-xylene in various PIM-1-derived CMS membranes is compared with that in PVDF-derived CMS. The effects of varying the polymer precursor and pyrolysis conditions on the separation performance of CMS are investigated. In Chapter 7, the liquid separation of water and p-xylene is examined in a PIM-1-derived CMS hollow fiber membrane. The study explores the application of the CMS membrane in reverse osmosis (RO) and pervaporation (PV) systems for liquid separation. The transport of the liquid mixtures within these systems is examined by utilizing the SD transport model and the transport coefficients obtained from vapor sorption experiments. In Chapter 8, the thesis concludes with a summary, key findings, the remaining knowledge gaps, and future research directions. This thesis aims to contribute to the advancement in the understanding of CMS membranes for water-organic separation, by focusing on the unraveled structure of CMS, the transport mechanism, and the potential applications.

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CHAPTER 2. BACKGROUND AND THEORY

2.1 Overview

This chapter provides background and theory for this dissertation. An overview of membrane separation is shown in Section 2.2. Section 2.3 provides relevant fundamental membrane transport theory. Section 2.4 discusses membrane processes used for water/organic solvent separation. Section 2.5 provides a brief description of carbon molecular sieve materials.

2.2 Membrane Separations

The separation, concentration, and purification of chemical species in mixtures are of major interest in chemical industries [1]. Conventional separation processes such as distillation, drying, and evaporation are highly energy-intensive [2]. Membrane separation processes avoid the utilization of heat energy for phase change and are steady-state processes. Therefore, membrane separation processes have been used to augment or even replace existing separation processes to provide cost- and energy-efficient separation.

The separation process in membranes is straightforward: a membrane functions as a semi-permeable barrier between feed mixtures and controls the transport of the different substances. Membranes let more permeable substances selectively pass through (permeate) while rejecting the less permeable species on the upstream of the membrane (retentate) (Figure 2. 1). The separation in membrane processes is governed by the differences in the transport rates of mixture species through the membrane. The transport in membranes is influenced by the mobility and the concentration of the species in the membrane, as well

as the driving force, which is the chemical potential gradient across the membrane. The mobility of a species in the membrane is determined by the molecular size of the adsorbent and the physical structure of the membrane material, such as the rigidity, pore sizes, crystallinity, etc. The concentration of the adsorbents in the membrane is affected by the chemical interaction of the guest species and the membrane. The chemical potential gradient driving force covered in this work is governed by the pressure, temperature, and concentration gradient.

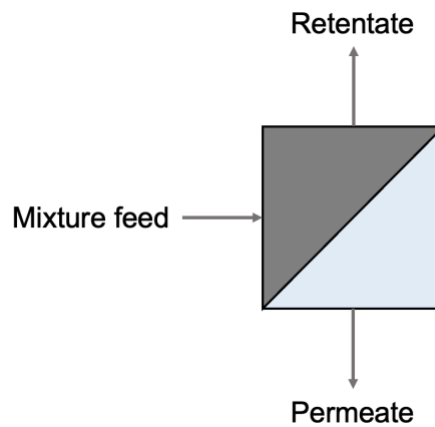


Figure 2. 1. Simplified schematic for membrane separation.

Mass transfer through membranes can occur through diffusion or convective flow, depending on the permeating species and the membrane pore structure. Diffusion-based membrane transport shows higher selectivity but low productivity, while the convective flow results in reduced selectivity but faster permeation. Therefore, the selection of the proper membrane process needs to be made for the separation of interest based on various factors, including the mixture properties, the volume scale of the mixture, the degree of separation, and the process cost [3].

Pressure-driven membrane processes can be categorized into four processes, which include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) (Figure 2. 2). These membranes are typically classified by their pore sizes and applied pressure [4], although they can also be defined based on driving forces employed [5]. MF uses porous membranes that have pore sizes > 50 nm and are typically operated at low pressure below 1 bar (gauge). UF systems use membranes with smaller pore sizes (2-50 nm) and are run in the pressure range of 1-6 bars. NF membranes have even smaller pores (< 2 nm) and are run at 5-15 bars. RO membranes are dense or have ultramicropores (< 0.7 nm) and operate at higher pressures, typically up to 60 bars for seawater desalination.

Larger pore-sized membranes (MF or UF) can prevent the passage of non-dissolved solutes that exceed the size of the membrane pores, and such membrane rejection can be operated at low pressure. On the other hand, membranes with smaller pores (NF) or dense structures (RO) can reject dissolved molecules and achieve high rejection. UF membranes employed in pilot trials for removal of BTEX compounds from wastewater demonstrated 54 % rejection of benzene, toluene, and xylene from produced water in the Snorre field in the North Sea [6]. While an impressive feat for a UF membrane, this is likely insufficient rejection to satisfy most discharge or reuse regulations. RO membranes have the potential to achieve separation efficiencies that are sufficiently high to enable sustainable wastewater discharge and reuse. This study focuses on the use of permanently microporous RO membranes instead of the more conventional polymeric RO membranes.

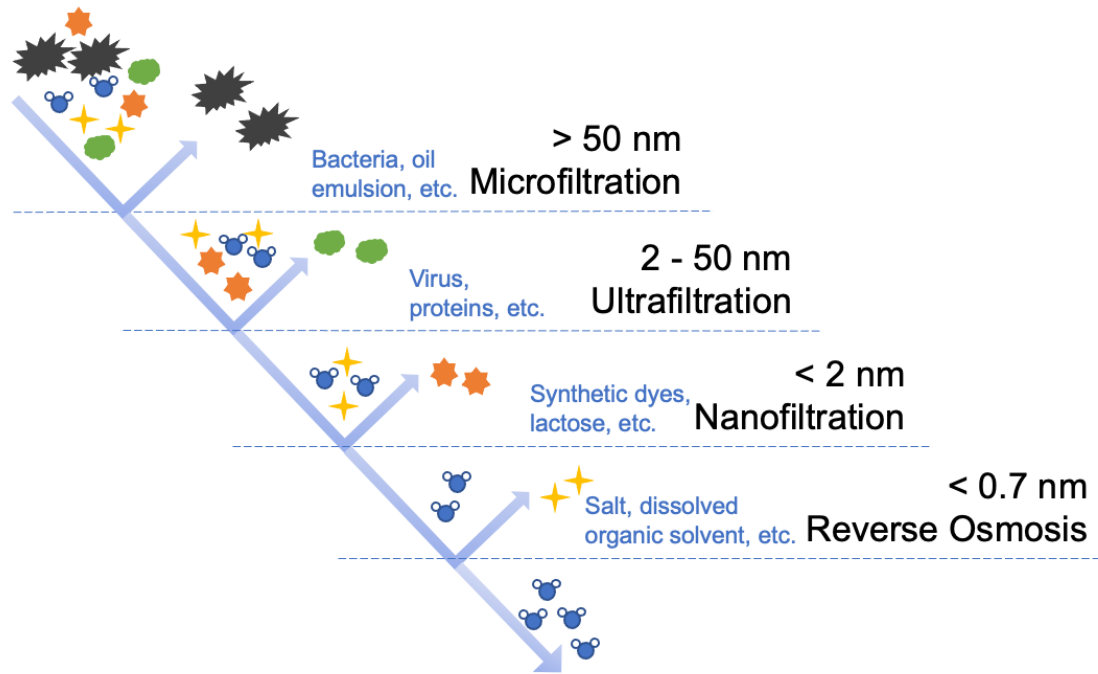


Figure 2. 2 Simplified classification of pressure-driven membrane separation process

2.3 Membrane Transport Theory

Two mathematical models can be used to describe the membrane transport theories for water and p-xylene transport in microporous membranes: (1) sorption-diffusion (SD) and (2) pore flow (PF) (Figure 2. 3). The transport across dense or microporous membranes follows the SD model, and the transport across membranes with permanent and large microporosity (i.e., $> 7 \text{ \AA}$) can often be explained by the PF model [7]. Both models operate with a chemical potential gradient across the membrane as the driving force for membrane transport. The SD model assumes the chemical potential difference based on the concentration gradient within membranes [8], and the pore flow model assumes the chemical potential gradient based on the pressure difference across the membrane.

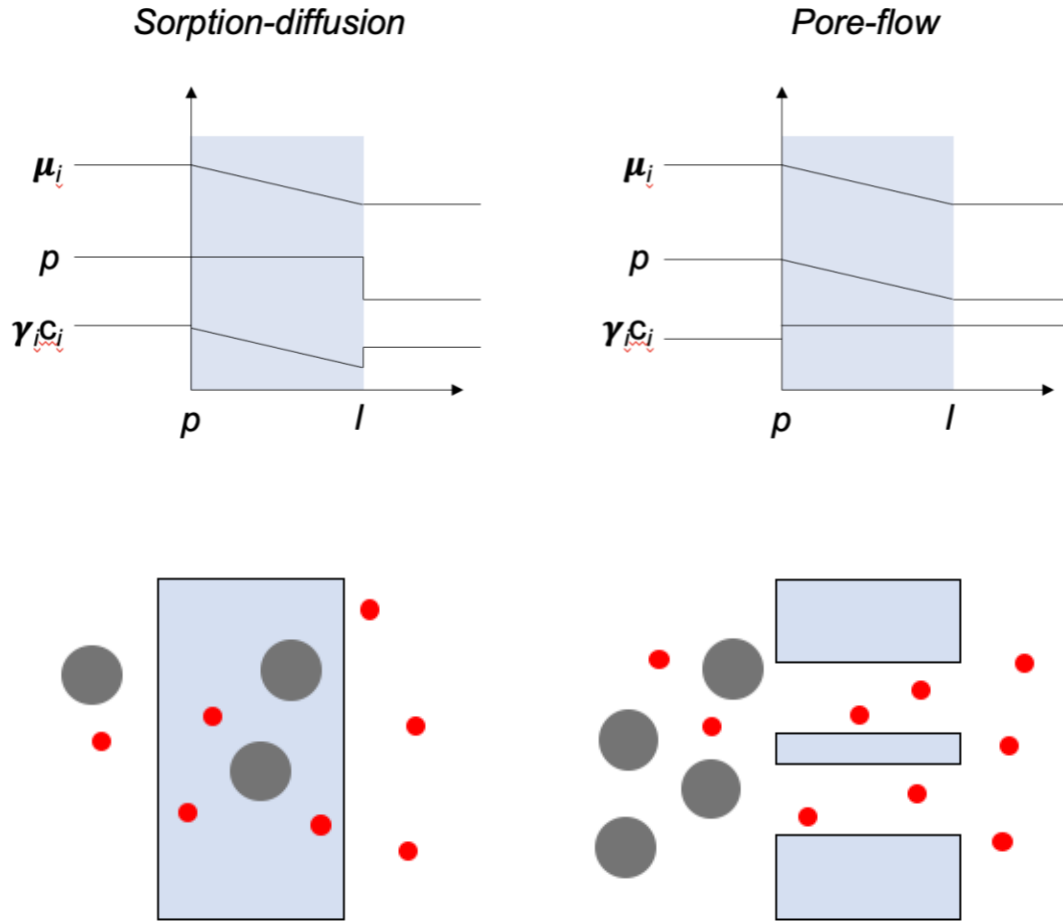


Figure 2. 3. Simplified schematics of chemical potential, pressure, and activity profiles across a membrane in sorption-diffusion and pore flow transport models. μ_i is the chemical potential of species i , p is the pressure, γ_i is an activity coefficient of species i , and c_i is the concentration of component i .

2.3.1 Sorption-diffusion model

The ideal performance of a microporous material such as dense/microporous membranes can be described by two main parameters: permeability ($\mathbb{P}$) and permselectivity (α). Permeability is a measurement of intrinsic productivity, and permselectivity is a measurement of separation efficiency. The permeability of permeate i ($\mathbb{P}_i$) can be measured by normalizing the flux of i (N_i) by the membrane thickness (ℓ) and the chemical potential

gradient driving force, which is easily notated using the fugacity difference across the membrane (Δf_i) for pure component systems (Eq. (2- 1)). The ideal permselectivity for penetrants i and j (α_{ij}) is expressed as the ratio of the permeability of the fast component i to the slow component j (Eq. (2- 2)), when the downstream side of the membrane is a vacuum. The transmembrane fugacity can typically be approximated to the partial pressure difference across the membrane for gas and vapor separation.

$$\mathbb{P}_i = \frac{N_i \ell}{\Delta f_i} \quad (2- 1)$$

$$\alpha_{ij} = \frac{\mathbb{P}_i}{\mathbb{P}_j} \quad (2- 2)$$

Guest molecules in membranes of different diffusion length scales exhibit different transport mechanisms. Reverse osmosis and pervaporation membranes that lack interconnected pores capable of supporting continuum-level fluids typically exhibit a sorption-diffusion (SD) transport mechanism. The SD model explains that the penetrants adsorb onto the membrane on the upstream, diffuse through the membrane, and then desorb on the downstream. In the SD model, the permeability can be expressed in terms of the product of a diffusivity (D_i), a kinetic factor, and a sorption coefficient (S_i), a thermodynamic factor (Eq. (2- 3)). Generally, smaller molecules exhibit a greater diffusion coefficient, whereas molecules that are soluble and have stronger interactions with polymers tend to possess a higher sorption coefficient. The ideal permselectivity in the SD model can be obtained from the ratio of pure permeabilities or the product of diffusion selectivity and sorption selectivity (Eq. (2- 4)).

$$\mathbb{P}_i = D_i \times \mathbb{S}_i \quad (2-3)$$

$$\alpha_{i/j} = \frac{\mathbb{P}_i}{\mathbb{P}_j} = \left(\frac{D_i}{D_j} \right) \times \left(\frac{\mathbb{S}_i}{\mathbb{S}_j} \right) \quad (2-4)$$

The SD model is derived based on Fick's law of diffusion [9], and thus utilizes a Fickian (or “transport”) diffusivity (D_i). However, the transport diffusivity is dependent on the loading of guest molecules. On the other hand, a Maxwell-Stefan (M-S) diffusivity ($\bar{D}_i$) is ideally independent of guest loading and is therefore employed in this dissertation. The expression for the sorption coefficient was derived (Eq. (2- 6)) based on the SD model and the M-S mass transfer formulation for single component transport (Eq. (2- 5)). The permeability, $\mathbb{P}$, can be expressed by the normalized flux (Eq. (2- 1)) and also via the sorption-diffusion model (Eq. (2- 3)), which provides a useful method to experimentally determine the applicability of the sorption-diffusion model via application of several distinct experiments (e.g., sorption isotherms, kinetic uptakes of guest molecules, and steady-state permeation of guests). More specifically, the flux can be expressed using the Maxwell-Stefan (M-S) formulation [10] in terms of the membrane density, ρ , M-S diffusivity, $\bar{D}$, the thermodynamic correction factor, Γ , and the saturation loading, q^{sat} (Eq. (2- 5)). The normalized flux expression for permeability can be viewed as the product of $\bar{D}$ and the rest of the expression, which is then defined to be the sorption coefficient, $\mathbb{S}$ (Eq. (2- 6)).

$$\mathbb{P} = \frac{N \cdot \ell}{\Delta f} = \frac{(-\rho \bar{D} \Gamma q_{sat} \nabla \theta) \cdot \ell}{\Delta f} = \bar{D} \frac{(-\rho \Gamma q_{sat} \nabla \theta) \cdot \ell}{\Delta f} = \bar{D} \cdot \mathbb{S} \quad (2-5)$$

$$S = \frac{(\rho \Gamma q_{sat} \nabla \theta) \cdot \ell}{\Delta f} \quad (2- 6)$$

The permeation and diffusion of adsorbent species in microporous membranes are described as activated processes. The activation energies of permeation and diffusion can be described using Arrhenius relationships, and the heat of sorption can be obtained from Van't Hoff equation [11].

The Van't Hoff equation for the sorption coefficients is used to study the temperature dependence of sorption coefficients of water and p-xylene. The integral heats of sorption (ΔH_S) can be obtained:

$$S_A = S_{o,A} \exp \left(-\frac{\Delta H_{S,A}}{RT} \right) \quad (2- 7)$$

where R is a gas constant, T is an absolute temperature, S_o is a pre-exponential factor for sorption coefficient, and ΔH_S is an extensive heat of sorption, which is always negative.

The temperature dependence of diffusion follows an Arrhenius relationship for diffusivity. The activation energy of diffusion (E_D) can be obtained:

$$D_A = D_{o,A} \exp \left(\frac{-E_{D,A}}{RT} \right) \quad (2- 8)$$

where $D_{o,A}$ is a pre-exponential factor for diffusion.

Similarly, the temperature dependence of permeation is explained using an Arrhenius relationship. The activation energy of permeation (E_P) can be obtained, where the $P_{o,A}$ is a pre-exponential factor for permeation.

$$P_A = P_{o,A} \exp\left(\frac{-E_{P,A}}{RT}\right) \quad (2-9)$$

Following sorption diffusion model, the activation energy for permeation can be expressed as the summation of activation energy for diffusion and the integral heat of sorption.

$$E_{P,A} = E_{D,A} + \Delta H_{S,A} \quad (2-10)$$

2.3.2 Pore flow model

Transport of guest molecules through membranes with permanent porous structures that are sufficiently larger than the guest molecules ($\sim 3\times$ larger than the kinetic diameters of the mobile species [12]) follows the pore-flow model. Microfiltration, ultrafiltration, and nanofiltration are typically well-described by the pore flow model. In this model, the transport of molecules is driven by the pressure gradient across the membrane, and the membrane does not exhibit a concentration gradient of the guest loading.

Darcy's law is used to mathematically demonstrate the pore flow model, viz.,

$$J = \frac{k\Delta p}{\eta\ell} \quad (2- 11)$$

where k is the permeability coefficient, Δp is the transmembrane pressure difference, and η is the dynamic viscosity. The permeability coefficient is dependent on the pore size, porosity, and tortuosity of the membrane.

2.3.3 Maxwell-Stefan transport model

The transport of dilute mixtures in reverse osmosis involves the simplified sorption-diffusion model, which utilizes Fick's law that can easily be applied. The multicomponent transport can be written in terms of Fick's law (Eq. (2- 12)) [13,14]:

$$J_i = - \sum_{j=1}^{n-1} D_{ij} \nabla C_j \quad (2- 12)$$

where n is the total number of guest species, D_{ij} are multicomponent diffusion coefficients, and C_j is the molar concentration of j .

Fick's law possesses simplifications that are not applicable to some mixture systems. First of all, Fick's law dictates that the flux is directly proportional to the concentration driving force, which would result in an infinite increase in flux at an infinite driving force. While this applies to pore-flow models, the SD model displays an upper bound to flux due to the existence of a maximum transmembrane concentration gradient (Figure 2. 4). Moreover, the D_{ij} has a complex dependence on concentration. However, the

classical Fickian theory assumes that diffusion coefficients are independent of concentration.

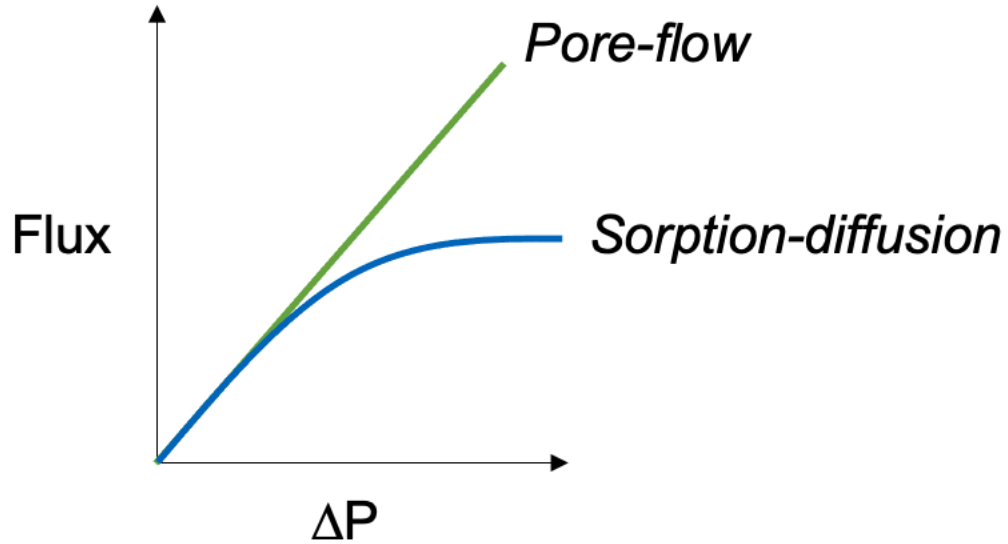


Figure 2. 4. Flux and pressure driving force relationship in pore flow and SD model [9].

The Maxwell-Stefan equation can be applied to describe the multicomponent transport of gas and liquid in porous materials [15]. The Maxwell-Stefan (M-S) description (Eq. (2- 13)) is derived from a force balance between the motion of species, and the friction experienced between the multicomponent species and the membrane surface. ρ is the density of membrane material, θ_i is the fractional occupancy of species i , μ_i is the chemical potential of the sorbed species i , q_i is the sorbate loading on the membrane, q^{sat} is the saturated loading, N_i is the molar flux of i , D_{ij} is the Maxwell-Stefan diffusivity describing interchange between i and j , and D_i is the Maxwell-Stefan diffusivity of species i in the membrane. The M-S transport approach is based on the idea that the diffusion coefficients are reciprocal to molecular drag coefficients between different molecules and membranes.

In the case of a pure component mass transport, the M-S diffusivity ($\bar{D}$) can be obtained by using a thermodynamic correction factor (Γ) on the transport diffusion coefficient (D) (Eq. (2- 14)) at infinite dilution for the guest loading.

$$-\rho \frac{\theta_i}{RT} \nabla \mu_i = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{q_j N_i - q_i N_j}{q_{\text{sat}} \bar{D}_{ij}} + \frac{N_i}{q_{\text{sat}} \bar{D}_i} \quad (2- 13)$$

$$\bar{D} = \frac{D}{\Gamma} = D \frac{d \ln q}{d \ln f} \quad (2- 14)$$

2.3.4 Liquid separation in membranes

The separation performance in a liquid system can be described by permeance ($\mathbb{P}/\ell$) and rejection. Permeance is used to show the productivity of membranes that are difficult to measure its effective separation layer thickness (ℓ). For dense membranes, the membrane thickness can be directly measured. While dense membranes are advantageous for fundamental membrane transport studies, they often exhibit slow transport, which is not optimal for scale-up processes. Since membranes with higher productivity can lead to lower capital costs, the membrane processes are optimized to show high separation performance and high productivity to provide an economic separation.

Asymmetric membranes consist of a thin dense layer that acts as a separation layer and a thicker, highly porous sublayer that acts as a mechanical support. The mass transfer resistance in the thin selective layer is the controlling resistance of the transport across the entire membrane. Therefore, high productivity can be achieved from the asymmetric

membranes, which is especially beneficial for the sorption-diffusion mechanism of permeation, of which the permeation is relatively slower. While the thin selective layer provides higher flux, it is also significant for the thin selective layer to be defect-free to achieve high separation performance in asymmetric membranes.

In liquid separation, asymmetric membranes are often used to withstand high transmembrane pressure and to achieve high flux. In these systems, the selective layer thickness of the membrane may be difficult to determine, as noted earlier. Therefore, permeance, which is a thickness-normalized permeability, is used to show the productivity of the membrane.

$$\frac{\mathbb{P}}{\ell} = \frac{J}{\Delta f} \quad (2- 15)$$

Rejection is used to define the separation performance in liquid separation (Eq. (2- 16)).

$$\text{Rejection (\%)} = \left(\frac{x^f - x^p}{x^f} \right) \times 100 \quad (2- 16)$$

where x^f and x^p are mole fractions of rejected species in feed and permeate, respectively.

Fugacity is employed as a measure of the chemical potential of a component that drives the transport across a membrane. Unlike the chemical potential, which tends towards negative infinity at vacuum, fugacity is more conveniently used, as its value approaches zero at vacuum. The fugacity of liquid guest molecules is calculated using (Eq. (2- 17)):

$$f_i = x_i \gamma_i p^{\text{sat}} \varphi_i^{\text{sat}} \exp\left(\frac{\widehat{V}_i(p - p^{\text{sat}})}{RT}\right) \quad (2-17)$$

where γ_i is the activity coefficient of the species i , p^{sat} is the saturation pressure, φ_i^{sat} is the saturation fugacity coefficient, $\widehat{V}_i$ is the molar volume, and p is the applied hydraulic pressure. The fugacity coefficient for each species is obtained using (Eq. (2-18)) where the Z value was calculated from Abbott equation (Eq. (2-19)) [16]:

$$\varphi_i^{\text{sat}} = \exp\left(\frac{B_{ii}p_i^{\text{sat}}}{RT}\right) = \exp(Z_i^{\text{sat}} - 1) \quad (2-18)$$

$$Z = 1 + \left(0.083 - \frac{0.422}{T_R^{1.6}}\right) \frac{P_R}{T_R} + \omega \left(0.139 - \frac{0.172}{T_R^{4.2}}\right) \frac{P_R}{T_R} \quad (2-19)$$

The separation factor can also be used to show the separation performance, and is especially useful for complex separations that exhibit ‘negative rejections.’

$$\beta_{i/j} = \frac{x_i^{\text{permeate}} / x_j^{\text{permeate}}}{x_i^{\text{feed}} / x_j^{\text{feed}}} \quad (2-20)$$

2.4 Membrane processes for water organic solvent separation

Membranes have performed effectively water purification from a variety of sources including producing water from groundwater, surface water, and wastewater. As a result, membrane separations have become a widely-used method for effective water purification. Recently, membrane technology has emerged as an efficient separation method to separate

mixtures of water and organics, with its capability of effective elimination of organic species that surpasses conventional methods [17]. So far, three types of membrane separation methods for separating mixtures of water and organic solvents have been investigated: reverse osmosis, pervaporation, and vapor permeation (Figure 2. 5).

2.4.1.1 Reverse Osmosis

Reverse osmosis (RO) enables liquid separation without requiring a phase change across the membrane. RO separation of water and organic solvents employs stable, scalable, and molecular selective membranes. While polymeric materials are commercially used and effective for many water purification applications, microporous materials with rigid and tunable pores may have promise for the separation of water-organic mixtures.

For instance, zeolites and polyamide membranes have been tested for produced water treatment [18]. α -Alumina-supported, MFI-type zeolite membranes were utilized to decrease the salt content of produced water in the upstream process of oil production [19,20]. The zeolite membranes showed an organic rejection of 99.5 % for 100 ppm toluene and 17 % for 100 ppm ethanol at water flux of $0.03 \text{ kg m}^{-2} \text{ h}^{-1}$ and $0.31 \text{ kg m}^{-2} \text{ h}^{-1}$, operated at 400 psi. Also, Mondal and Wickramasinghe [21] have tested a commercial thin film composite RO membrane, BW30 (FilmTech Corporation, Dow Chemical), on produced water from Colorado. BW30 demonstrated TDS rejection of 47.8 % and TOC rejection of 66.9 % from produced water feed with 2090 mg/L TDS and 136.4 mg/L TOC, operated at 5.5 bar [5].

While inorganic zeolite membranes exhibit excellent separation performance, they encounter challenges when it comes to scale-up. On the other hand, commercial polyamide

RO membranes demonstrate poor organic compound rejection. Composite membranes that combine the advantages of both inorganic and polymer materials have been developed to address the challenges of separating small organic molecules from water. Carbon nanotube/polyvinylidene fluoride (PVDF) nanocomposite membranes have achieved BTEX rejection above 90 % when operating at pressures below 10 psi. The flux reached $\sim 10 \text{ kg m}^{-2} \text{ h}^{-1}$, with a feed concentration of 80 mg/L [22]. Moreover, polyethersulfone (PES)/cellulose acetate butyrate (CAB) composite hollow fiber membranes have been developed to enhance the hydrophilicity of the dense PES membrane and achieve high flux and rejection. These membranes have demonstrated BTEX rejection of 82-84.6 % from feed solution with 150-500 ppm BTEX when operated at 100 psi with $\sim 16.5 \text{ kg/m}^2/\text{h}$ flux [23]. This advancement shows the effectiveness of RO membranes in separating BTEX from water and highlights the potential of scalable inorganic RO membranes to achieve effective BTEX separation.

2.4.1.2 Pervaporation

Pervaporation is a membrane separation process for liquid mixtures that involves a phase change of the liquid phase on the feed into the vapor phase on the permeate side [24]. Separation of mixture species is due to the guest molecules having different chemical affinities to the membrane and/or having different diffusivity in the membrane. Therefore, the more permeable components are collected in the permeate in the vapor phase, and the less permeable components are retained in the retentate side in the liquid phase (Figure 2. 5b).

Pervaporation utilizes large fugacity gradients across the membrane by maintaining a low fugacity on the membrane downstream. The low chemical potential on the permeate side can be enabled by flowing a sweep inert gas (Figure 2. 5b-1) or by applying a vacuum (Figure 2. 5b-2).

Common applications for pervaporation in industry are (1) organic solvent dehydration, (2) dilute organic impurity removal from aqueous solutions, (3) organic mixture separation [25,26]. Although pervaporation involves phase change, the process is less energy intensive than distillation, especially when applied to selectively transport the minor components in the mixture. A common example is the production of anhydrous ethanol in the pharmaceutical industry. Pervaporation enables an effective purification from the azeotropic distillation mixture without risking ethanol contamination by harmful substances [27].

Pervaporation separation for dissolved organic molecules from water has been investigated in polymer membranes and has demonstrated an excellent separation performance. PVDF hollow fiber membranes have been used in pervaporation to purify 120 ppm benzene feed aqueous solution and showed an organic/water separation factor of 1834 with a total flux of $0.046 \text{ kg m}^{-2} \text{ h}^{-1}$ under 19 mmHg. The pervaporation separation of BTEX from water was also investigated in a composite membrane of hydrophobic polypropylene hollow fiber membrane coated with polydimethylsiloxane (PDMS). The separation factor of BTEX/water higher than 6000 and a total flux of $0.01 \text{ kg m}^{-2} \text{ h}^{-1}$ was achieved at permeate pressure of 160 mmHg from 100 ppm BTEX feed solution [28].

The permeance in pervaporation experiments can be calculated using (Eq. (2- 21)). p_i^{permeate} can be approximated as 0 in most applications. N_i is the flux of species i through the membrane, x_i^{feed} is the concentration in the feed, γ_i is an activity coefficient, and p_i^{sat} is the saturation pressure.

$$\frac{P_i}{\ell} = \frac{N_i}{x_i^{\text{feed}} \gamma_i p_i^{\text{sat}} - p_i^{\text{permeate}}} \quad (2- 21)$$

2.4.1.3 Vapor permeation

Vapor permeation involves the feed mixture and permeates to be in the vapor state (Figure 2. 5c). Unlike pervaporation, vapor permeation avoids the use of vaporization energy in the guest molecules transport, and the system does not involve phase change or a significant temperature difference across the membrane. A common application for vapor permeation is to remove organic compounds from an aqueous or gaseous system for pollution control or valorization of recycled materials [27]. Moreover, the dehydration of natural gas and various organic solvents, such as biofuel, is often employed using hydrophilic membranes [29]. Vapor permeation is also driven by the fugacity gradient across the semi-permeable membranes.

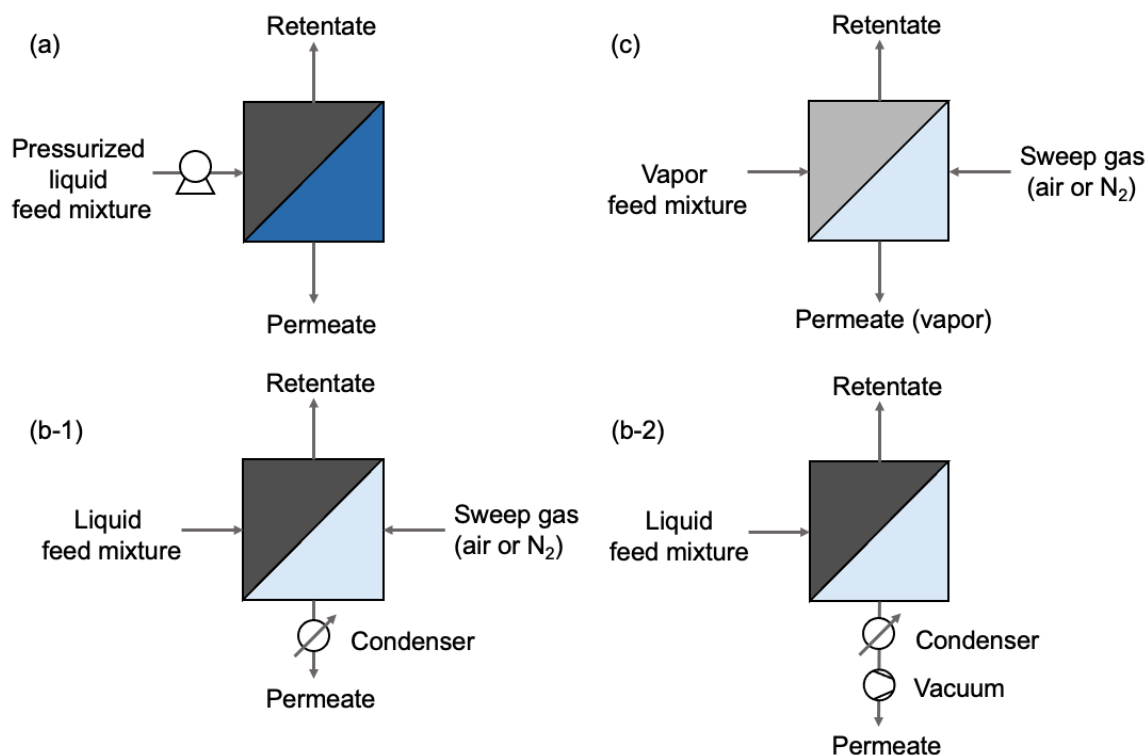


Figure 2. 5. Simplified scheme of (a) reverse osmosis, (b) pervaporation, and (c) vapor permeation. (b-1) uses sweep gas, and (b-2) uses vacuum downstream to create chemical potential gradient across the membrane

2.5 Carbon molecular sieve (CMS) membranes

Carbon molecular sieve (CMS) materials are rigid and carbonaceous inorganic materials that have an amorphous structure while possessing precisely controlled bimodal pore size distribution. CMS materials are typically derived from polymer precursors and are fabricated through pyrolysis reaction, which involves a controlled temperature ramping to a high temperature under a controlled atmosphere environment. CMS materials are different from activated carbon as CMS has a micropore structure that enables size- and shape-selective separation. Moreover, CMS membranes are derived from high glass transition temperature polymers that enable the prevention of morphological collapse during the high-temperature reaction.

CMS membranes have shown great separation performances in the gas and organic liquid separation. These membranes exhibit exceptional selectivity for gases with similar sizes due to entropic contributions. Moreover, CMS membranes have shown promising separation performance for a challenging organic solvent separation of xylene isomers [30,31]. After carbonization, CMS shows reduced swelling and plasticization from gas and organic solvents compared to its polymeric precursors. Moreover, the membrane transport properties can be precisely controlled by adjusting the pore size by modifying the polymer precursor and the pyrolysis conditions.

Flat sheet CMS membranes have low resistance to pressure, similar to MOF or zeolite membranes. However, CMS membranes, which are derived from polymer precursors, can be processed into various membrane form factors, allowing resistance to high transmembrane pressure. For instance, PVDF-derived CMS hollow fiber membranes have shown to endure transmembrane pressures up to 100 bar without breaking in liquid xylene isomer separation [30]. Therefore, CMS membranes are potential advanced membrane material that has high separation performance and material stability, comparable to most inorganic materials, but can also be scaled up, as demonstrated in the literature [32].

Research has been conducted on understanding the structure of carbon materials. However, there is still limited understanding of the formation process and structure of CMS due to the disordered nature of the material. It is crucial to gain a thorough understanding of the formation process and structure of CMS to fully optimize the performance CMS membranes for water-organic solvent separations.

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CHAPTER 3. MATERIALS AND EXPERIMENTAL METHODS

3.1 Overview and Collaborator Acknowledgements

This chapter provides a detailed list of materials used and the experiments designed to investigate the structural and transport properties of water and p-xylene in carbon molecular sieve membranes. Parts of this chapter are adapted from ‘Y.H. Yoon, R.P. Lively, Co-transport of water and p-xylene through carbon molecular sieve membranes. *Journal of Membrane Science* **654**, 120495 (2022)’ and ‘Y.H. Yoon, D. O’Nolan, M.L. Beauvais, K.W. Chapman, R.P. Lively, Direct evidence of the ultramicroporous structure of carbon molecular sieves. *Carbon* 118002 (2023).’ ‘Direct evidence of the ultramicroporous structure of carbon molecular sieves’ was performed in a highly collaborative approach. The key contributions from the coauthors are highlighted as the following: Conceptualization of the study and the analysis of neutron total scattering and small angle X-ray scattering were conducted by Daniel O’Nolan (Georgia Institute of Technology). Analysis of neutron total scattering was assisted by Michelle L. Beauvais (Stony Brook University), and Karena W. Chapman (Stony Brook University).

3.2 Materials

3.2.1 Materials for PIM-1 derived CMS Fabrication and Characterization

Tetrafluoroterephthalonitrile (TFTPN) (Sung-Young Chemical Limited, China) and 5,5’6,6’-tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-spirobisindane (TTSBI) (Alfa Aesar) were purified before use. TFTPN was recrystallized using a vacuum sublimation at 140 °C, and TTSBI was purified via reprecipitation from hot methanol with dichloromethane.

Methanol (CH₃OH, 99%), potassium carbonate (K₂CO₃, anhydrous, 99%), chloroform (CHCl₃, >99.8%), dichloromethane (DCM, >99.5%), dimethylformamide (DMF, >99.8%), tetrahydrofuran (THF, >99.5%) were purchased from Alfa Aesar and used as received.

Moreover, argon (UHP 5.0 Grade), 4 vol% hydrogen balanced with argon liquid nitrogen, carbon dioxide (bone dry), and neon (99.996% purity) were purchased from Airgas.

3.2.2 Materials for PVDF derived CMS Fabrication and Characterization

Poly(vinylidene fluoride) (PVDF) was purchased from Alfa Aesar and dried in a vacuum oven overnight at 60 °C. N,N-Dimethylacetamide (DMAc, anhydrous 98%, Sigma-Aldrich), methanol (MeOH, anhydrous, 99.8%, Sigma-Aldrich), p-xylylenediamine (99.5%, TCI America), sodium hydroxide (NaOH, ACS reagent, ≥ 97.0%, pellets, Sigma-Aldrich), and p-xylene (99%, Alfa Aesar) were used as received.

3.2.3 Materials for CMS Membranes Permeation Characterization

DI water was provided in lab via an Elga DV35 Purelab Option water purification system. p-Xylene (99 %) was purchased from Alfa Aesar and was used as received. Helium (UHP grade) was purchased from Airgas and used as the feed carrier gas and sweep gas in Wicke-Kallenbach (WK) permeation experiments.

3.3 Experimental – Material Fabrication

3.3.1 Synthesis of PIM-1

PIM-1 was synthesized using the low-temperature polycondensation method reported by Budd et al. [1]. The two monomers were purified in advance to the polymerization reaction. The TTSBI was first dissolved in MeOH, which dissolves both oxidized and non-oxidized monomers. Then DCM was then added to the solution and vitrified only the non-oxidized TTSBI, while dissolving the oxidized TTSBI. The solution was vacuum filtered, and the solid purified TTSBI was collected. The TFTPn was recrystallized via vacuum sublimation at 140 °C.

The two purified monomers, TFTPn and TTSBI, were dissolved in an anhydrous DMF at an equimolar ratio. Finely ground anhydrous K_2CO_3 (2.5 mol eq. times to TFTPn) was added to the solution to initiate the polymerization, and the reaction was continuously stirred under nitrogen at 65 °C for 72 hours. After the reaction, the solution was allowed to cool to room temperature then the deionized water was used to quench the reaction and precipitate the PIM-1 polymer. The crude product was collected by vacuum filtration, washed excess salts with additional deionized water. The PIM-1 crude polymer was purified by dissolving in chloroform and reprecipitated in MeOH. Additional purification was conducted via dissolving in DMF and reprecipitating in MeOH. Finally, the fluorescent yellow PIM-1 polymer was dried at 70 °C under a vacuum. The molecular weight was determined by gel permeation chromatography (GPC) in HPLC grade chloroform. The PIM-1 used for film membrane fabrication was determined to be $M_w = 157k$ with a PDI = 5.8, and the PIM-1 for hollow fiber membrane fabrication is determined to be $M_w = 39k$ with a PDI = 3.4 when compared against polystyrene standards.

3.3.2 Dense Film Membrane Preparation

The dried PVDF was mixed with an anhydrous DMAc at 25 wt% loadings. The PVDF polymer solution was mixed in a roller at room temperature for 2 days to form a homogeneous solution. The clear and colorless homogeneous polymer solution was used to cast a dense film membrane in a solvent-saturated glove bag (Glas-Col). The polymer solution, a casting blade, a glass plate, and an open container with DMAc was put inside the leveled support in the glove bag. The glove bag was purged with argon 5 times and was sealed. The glove bag was saturated with DMAc for 3 days to ensure sufficient time for the high boiling point solvent to saturate inside the glove bag. Then the polymer solution was transferred to the glass plate. The casting blade was drawn to cast the polymer dope into a membrane film with uniform thickness, as in Figure 3.1. The polymer film was dried in the solvent saturated bag for 3 days. Then the sealed bag was opened, the membrane was carefully harvested from the glass plate, and dried in a vacuum oven at 60 °C.

A similar procedure was used for a dense PIM-1 film membrane fabrication (Figure 3.1). 2 wt% PIM-1 was homogenously dissolved in an anhydrous THF for 2 days to make a 7 ml polymer solution. PIM-1 film membranes were cast in a THF solvent-saturated bag. The glove bag was purged with argon 3 times and sealed. The bag was saturated with THF for > 6 hours before transferring the polymer solution to a Teflon petri dish (diameter = 79 mm). The polymer film was dried in the Teflon petri dish for 2 days. Once the membranes were dried, the membranes were harvested from the casting bag. The film membranes were dried in a vacuum at 80 °C overnight before use.

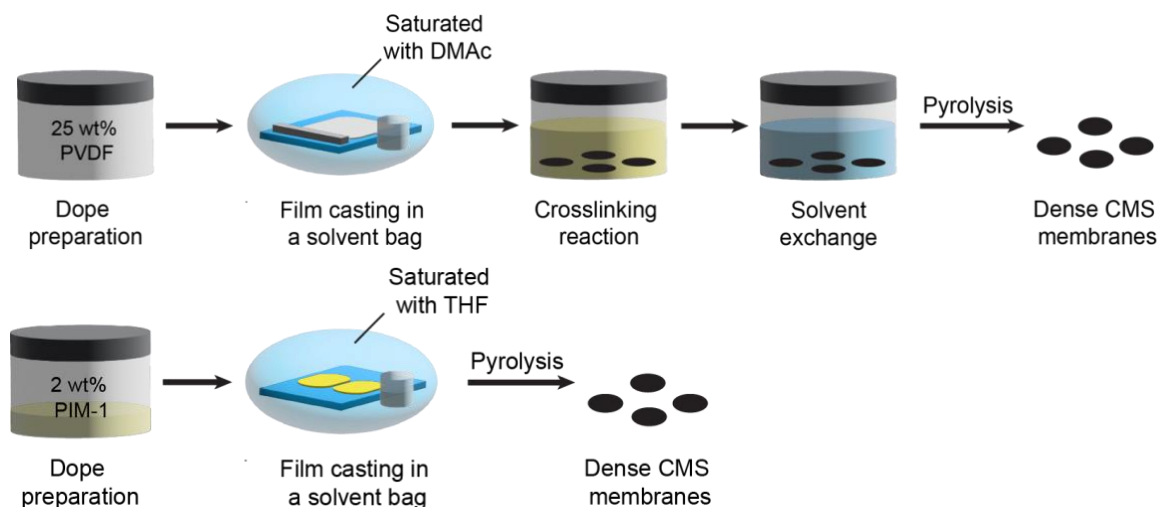


Figure 3.1. Schematic diagram of dense PVDF-CMS membrane fabrication procedure

3.3.3 Crosslinking PVDF as a pre-treatment of CMS fabrication

Commonly used precursor polymers such as polyimides do not require pre-treatment as they can withstand the high pyrolysis temperature without melting and preserve the macroscopic morphology of polymer precursors. However, PVDF has a melting point of 165 °C at which point the polymer undergoes liquefaction during pyrolysis and loses its macroscopic morphology. The one-pot crosslinking technique developed for PVDF by Koh et al.[2] was used to protect the morphology of the membranes from high-temperature pyrolysis. The crosslinked PVDF in which the precursor polymer backbones are covalently bonded to p-xylylenediamine (Figure 3.2) showed retention of storage modulus above 300 °C and preserved the membrane morphology during pyrolysis. The resulting CMS from cross-linked PVDF exhibits bimodal pore size distribution.

The one-pot crosslinking of PVDF using p-xylylenediamine involves NaOH, MeOH, p-xylylenediamine, and MgO nanopowder. NaOH is ground from pellets and was

dried in a vacuum oven at 60 °C for 2 hours to remove moisture. The 0.5 g of dried NaOH was dissolved in a 15 g of anhydrous MeOH. Then 2 g of p-xylylenediamine and 1 g of MgO nanopowders were added to the solution and mixed into a dispersion. Methanol saturates hydrophobic PVDF pores and lets the crosslinking agents diffuse into the membrane. The NaOH-defluorinated (-HF) PVDF creates carbon-carbon double bonds that are more susceptible to the amine chemical attack. Then the amine reacts with the olefinic group in the polymer backbone via the Michael addition, crosslinking between the vinylidene fluoride chains. Simultaneously, the solution is neutralized by MgO, which reacts with HF and creates MgF and H₂O.

The vacuum-dried PVDF membranes are aligned in parallel and installed in a vial with chemical-resistant stainless steel mesh spacers in between. Then the crosslinking reaction solution was added to the vial with PVDF membranes. The crosslinking reaction occurred on a roller for 44 hours at room temperature. The crosslinking reaction was ended by solvent exchange with 1 M nitric acid for 1 hour, which was followed by solvent exchange with DI-water for 6 hours 3 times, methanol for 2 hours 3 times, and hexanes for 2 hours 3 times to remove any residual crosslinking reagents and byproducts. The crosslinked PVDF membranes were vacuum dried at 60 °C before use.

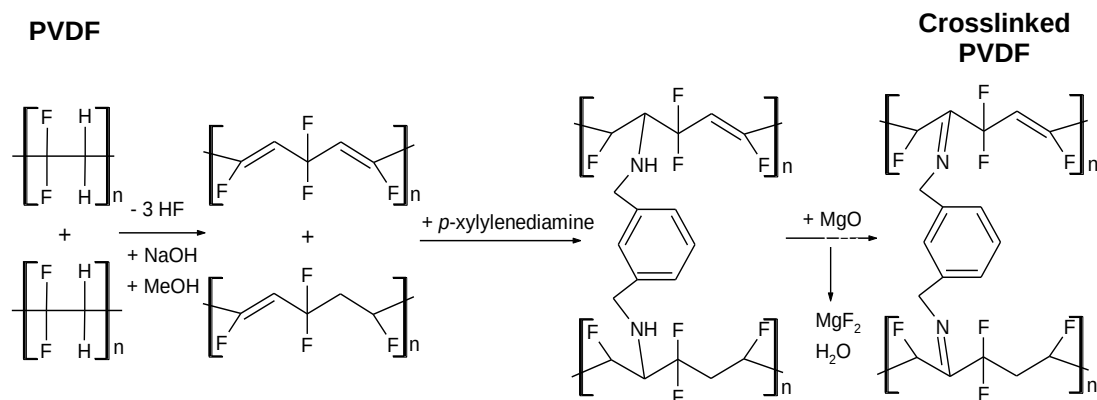


Figure 3.2. Crosslinking of PVDF with p-xylylenediamine. The NaOH defluorinates (-HF) PVDF creating carbon-carbon double bonds. Then the amine reacts with the olefinic group in the polymer backbone via the Michael addition, crosslinking between the vinylidene fluoride chains. The solution is simultaneously neutralized by MgO, which reacts with HF and creates MgF and H_2O .

3.3.4 PIM-1 Hollow Fiber Membrane Fabrication

The defect-free, integrally skinned, asymmetric PIM-1 hollow fiber membranes were fabricated using a dual-bath method in dry-wet spinning. Spinning PIM-1 hollow fibers is challenging due to the lack of suitable nonvolatile solvents. PIM-1 only dissolves in THF or chloroform, which are volatile solvents with boiling points of 66 and 61.2 °C, respectively. However, the PIM-1 spinning was enabled by using a triple orifice spinneret [3]. The PIM-1 hollow fiber membranes were fabricated by co-extruding three solution layers, bore fluid, polymer dope, and sheath solution. The outermost sheath layer was co-extruded as a water-immiscible layer that protects the polymer solution layer from exposure to air and reduces the evaporation of the THF, and enables the formation of thin but defect-free selective PIM-1 layer. The polymer dope comprises PIM-1, solvent, and non-solvents (15 wt% PIM-1, 69.5 wt% THF, 13.25 wt% DMAc, and 2.25 wt% ethanol). The bore fluid is composed of solvent and non-solvents (45 wt% THF, 46.75 wt% DMAc,

and 8.25 wt% ethanol) to keep the center of the fibers hollow. The sheath solution (82.5 wt% 1-butanol and 17.5 wt% THF) protects against too-fast evaporation of the volatile solvent THF and creates a defect-free skin layer. The spinning was conducted under the lab temperature of 20.5 °C and the relative humidity of 10 %. The bore, core, and sheath solutions are pumped through the spinneret using mechanical syringe pumps (1000D for sheath and core, 500D for bore fluid, Teledyne Isco) at a flow rate of 90, 105, and 65 ml/hour. The three-layer extrusion through the triple orifice spinneret is sent to the DI-water quench bath after an air gap of 1.5 cm. The extrusion goes through phase inversion in the quench bath with a bath temperature of 50 °C. The phase-inverted polymer fiber was guided through the quench bath and collected on a take-up drum at a 1.5 m/min speed. The fibers were rotated on the take-up drum for 1 hour to ensure sufficient phase inversion. The fibers were then collected on a separate DI water bath for complete phase inversion. The fibers were solvent exchanged in DI water for 3 days and were repeated 3 times. The fibers were solvent exchanged with less surface tension solvents such as methanol for 2 days for 3 times and then hexane for 2 days for 3 times, to protect the porous structure of the fiber. Then the fibers were air-dried and were activated in a vacuum oven at 80 °C before use.

3.3.5 *Pyrolysis of polymer membrane precursors*

The pyrolysis experiments took place in a three-zone furnace (MTI Corporation) with a quartz tube (Figure 3.3). The flat film membranes were supported on flat chemical-resistant stainless-steel meshes covering the top and bottom to avoid curling during pyrolysis. The hollow fiber membranes were also supported on a chemical-resistant stainless-steel mesh to prevent the fibers from curling and mending to each other during the pyrolysis.

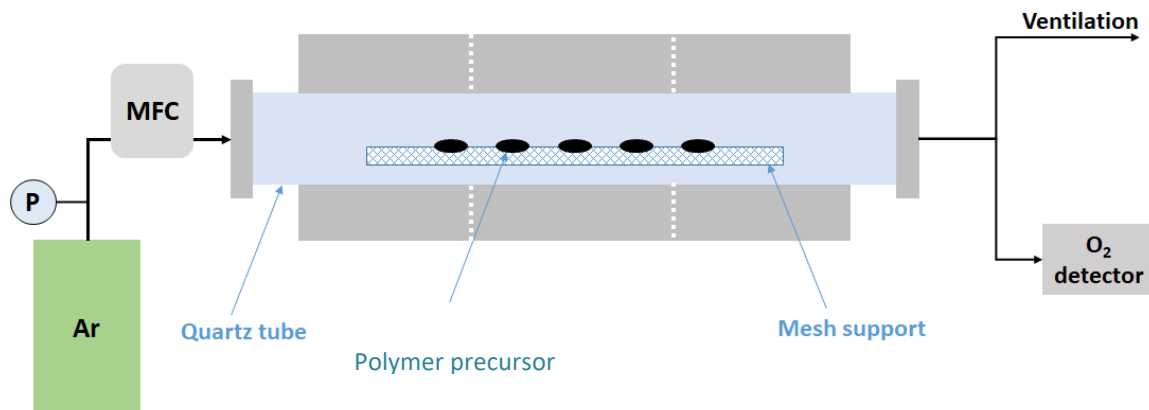


Figure 3.3. Schematic diagram of pyrolysis furnace set-up for CMS fabrication.

Once the polymer precursor samples were placed inside the quartz tube, the tube was sealed on both sides using flanges, and a pyrolysis gas was fed into the tube at a set rate. The pyrolysis gas and flow rate are specified for each study. The samples in the pyrolysis tube were purged for > 6 hours. Once the oxygen level in the tube was measured below 2 ppm by the oxygen analyzer, the pyrolysis protocol was initiated. The ramping protocols for PVDF- and PIM-1-derived CMS membranes are provided in Table 3.1. After every pyrolysis, the quartz tube was wiped down with acetone and baked in the air at 800 °C for 2 hours to remove contamination from prior pyrolysis experiments.

Table 3.1. Pyrolysis temperature ramping profile for PVDF [2] and PIM-1 derived CMS.

	PVDF-CMS		PIM-1 CMS		
Phase	Heating rate (°C/min)	Final pyrolysis temperature	Heating rate (°C/min)	Final pyrolysis temperature	
		500 °C		500 °C	800 °C
Ramp	10	50-250 °C	10	18-100 °C	18-100 °C
Activate	-*	-	0	at 2 hours at 100 °C	
Ramp	3.8	250-485 °C	10	100-200 °C	100-500 °C
	0.25	485-500 °C	3	200-485 °C	500-785 °C
	-	-	0.25	485-500 °C	785-800 °C
Soak	0	at 2 hours at 500 °C	0	at 2 hours at 500 °C	at 2 hours at 800 °C
Cool	-	Natural cooling back to room temperature under pyrolysis environment	-	Natural cooling back to room temperature under pyrolysis environment	

*ex-situ activation before pyrolysis

3.4 Experimental – Characterization

3.4.1 Gas physisorption

The pore size distribution of carbon molecular sieve materials was investigated via gas physisorption using nitrogen, carbon dioxide, and neon as probe molecules.

Nitrogen isotherm was measured at 77 K using an Accelerated Surface Area and Porosimetry system (ASAP 2020, Micromeritics, USA). Analysis temperature was controlled using a liquid nitrogen dewar, which is assumed to control the temperature for 2 days. Prior to isotherm measurements, the CMS samples were degassed overnight at 110 °C under vacuum (10^{-2} kPa). HS-2D-NLDFT (heterogeneous surface two-dimensional non-local density functional theory) calculation for carbon materials with infinite slit pore model (MicroActive software package, Micromeritics, USA) was used to estimate the pore size distributions.

Carbon dioxide physisorption at 273 K was measured in the ASAP 2020HD (Micromeritics, USA) and Belsorp Max II (Microtrac, USA) in the 0.1-760 torr range. Analysis temperature was controlled using an ice water bath. HS-2D-NLDFT (heterogeneous surface two-dimensional non-local density functional theory) modeled pore-size distribution calculations were obtained from the CO₂ isotherm using the MicroActive software package (Micromeritics, USA) [4].

Neon physisorption was used to study the microporous structures of PIM-1 derived CMS at 40.15K using a cryostat (CH-104, ColdEdge, USA) equipped with a He compressor (CH-4A, ColdEdge, USA) using a High-Pressure Volumetric Analyzer (HPVA II, Micromeritics, USA). Free space was measured using helium at ambient and analysis temperatures, followed by the neon adsorption experiment. The quasi-Gemini free space correction calculation using MicroActive software (Micromeritics, USA) obtained the neon isotherms exhibiting excess surface adsorption. The CMS samples were degassed at 383.15 K overnight under vacuum. The equilibrium criteria of 0.03 mbar in 10 minutes or 600 min maximum was used. The temperature was controlled at 40.15 ± 0.05 K. The neon isotherm is measured in the range of 0.08 - 3000 torr. The pore size distribution from the neon isotherm was calculated using Horvath and Kawazoe (HK) method [5]. The HK method was implemented on the neon isotherms using an in-house HK Matlab code (the code is provided in Appendix A).

The in-house HK Matlab code in this work was modified from the code developed by Thompson [6] via three major changes: 1) neon molecular parameters were introduced to incorporate neon as an adsorbate (Table 3.2.), 2) the isotherm modeling of Ne and N₂ used a logarithmic isotherm instead of a Langmuir isotherm, and 3) the kinetic diameter of

neon was used for the molecular diameter in HK calculation. A logarithmic fitting used an equation of

$$\theta = \frac{q}{q^{\text{sat}}} = a \cdot \ln\left(\frac{p}{p^{\text{sat}}}\right) + b \quad (3-1)$$

where q is the calculated volume of adsorbates (cm^3 STP/g). q^{sat} is the saturated volume of adsorbates (cm^3/g) in the micropore region that shows significant uptake and plateaus. a and b are unitless fitting parameters that are empirically derived. Langmuir fitting used an equation of

$$\theta = \frac{q}{q^{\text{sat}}} = \frac{b \cdot p}{1 + b \cdot p} \quad (3-2)$$

where q is the calculated volume of adsorbates (cm^3 STP/g). q^{sat} is the saturated volume of adsorbates (cm^3/g) in the micropore region that shows significant uptake and plateaus. b is a fitted affinity parameter (bar^{-1}).

Table 3.2. Parameters used in HK PSD analysis

	Liq. density (at Temp.)	Molecular diameter	Polarizability [7,8]	Magnetic susceptibility [7,8]	Surface density
unit	g/cm^3 (K)	Å	10^{-24} cm^3	10^{-29} cm^3	10^{14} molecule/ cm^2
Ne	1.043 (40.15) [9]	2.75*	0.39	1.17	2.35
N ₂	0.810 (77) [10]	3.64*	1.46	2	6.7
C	-	3.4	1.02	13.5	38.5

* Kinetic diameters are used for adsorbent molecules.

3.4.2 *X-ray Photoelectron Spectroscopy*

X-ray photoelectron spectroscopy (XPS) was performed using K-Alpha XPS (Thermo Fisher Scientific, West Palm Beach, FL). The X-ray source was a monochromatic Al-K α source. Spectra calibration was conducted with an internal standard, silver oxide. The XPS analysis chamber was evacuated to 2×10^{-8} mbar or lower, before each operation. CMS samples were prepared by crushing the dense film membranes into powders. The powder samples were dried in a vacuum oven at 80 °C overnight prior to the XPS analysis. The XPS survey scans were measured to conduct an elemental analysis. Although the XPS characterization is limited to the material surface, the finely powdered samples were analyzed, which enables the analysis of the average elemental composition of the entire membrane.

3.4.3 *X-ray Diffraction Analyses*

Structural characterization on the PVDF-CMS was performed using X'Pert PRO Alpha-1 X-ray diffractometer (PANalytical) with X'celerator detector. Cu K α radiation with $\lambda=1.5406$ Å was used at a voltage of 45 kV and current of 40 mA. The scanning angle was conducted from $5^\circ < 2\theta < 80^\circ$, with a step size of 0.016° and a scan time of 20 s/step.

3.4.4 *Scanning Electron Microscopy*

Field emission scanning electron microscopy (FE-SEM) images were recorded by a Hitachi SU8010 at a beam energy of 5 – 10 kV. Cross-sectional images of the polymer membranes were obtained by cryo-fracturing the sample in liquid nitrogen.

3.4.5 *Gravimetric Vapor Sorption*

The gravimetric vapor sorption experiments were used to investigate the sorption and diffusion behaviors of pure water and p-xylene in CMS. The vapor sorption measurements were obtained using an automated gravimetric vapor sorption instrument VTI-SA+ (TA instruments, New Castle, DE) operated at ambient pressure. The transient weight change in CMS over time was measured to obtain the kinetic diffusion coefficients. The equilibrated weights at set pressure points were acquired for vapor sorption isotherms. The water relative humidity varied between 5 and 80 %, while the p-xylene relative pressure ranged between 5 and 75 % due to instrument limitations. Water relative humidity was determined by the two-stage chilled-mirror dew point analyzer. p-Xylene relative pressure is calculated by the Wagner vapor pressure equation. Before the vapor sorption measurements, the samples were dried in situ at 110 °C for > 12 hours under a nitrogen flow. The isotherms were obtained at 35, 45, and 55 °C, of which the temperatures are controlled by the instrument.

The transient change in CMS sample mass was measured at set relative humidity/pressure. Thick and dense film samples (average thickness of PVDF derived CMS: $\sim 17.5\ \mu\text{m}$ and PIM-1 derived CMS: $\sim 25\ \mu\text{m}$) were used to assist the guest transport inside the membrane to be the controlling resistance. The thickness of the membrane was obtained by measuring the cross-section in SEM. Multiple cross-sections of the membranes were measured on SEM, and 30 measurements were averaged to get the membrane thickness. Two more criteria were assessed to ensure that the measured kinetic uptake curves represent the isothermal internal diffusion resistance. First, the vapor sorption was confirmed to be isothermal based on Ruthven-Lee's criteria [11,12]. Moreover, each kinetic uptake experiment was evaluated to determine if the exponential boundary

condition or the guest diffusion within the membrane was the controlling resistance. The relative humidity/pressure change in the gravimetric uptake experiment setup is not an instantaneous step change, as experimentally investigated by Pimentel et al. [13]. The exponential boundary condition in the concentration change is considered using the external time constant β (s^{-1}). The length-normalized ratio of the external time constant β (s^{-1}) and the diffusion coefficient $\phi = \frac{\ell^2 \beta}{D}$ were calculated, and only measurements that exhibited $\phi > 5$ were used in the diffusion coefficient calculation to measure the diffusion within the membrane with a minimal margin of error.

The normalized transient weight data were fitted to the Fickian mass transfer equation (Eq. (3- 3)) derived by Crank [14] to obtain the Fickian diffusivity in sheet (film) membranes with an exponential boundary condition. M_t is the amount of vapor adsorbed in the membranes at time t , and M_∞ is the equilibrium amount of vapor adsorbed at given relative humidity/pressure. β is a time constant from the exponential boundary conditions. D is the Fickian diffusion coefficient, and ℓ is half the membrane thickness. The Fickian diffusivity and the time constant were fitted to the experimentally measured kinetic uptake curves.

$$\begin{aligned} \frac{M_t}{M_\infty} = 1 - \exp(-\beta t) \left(\frac{D}{\beta \ell^2} \right)^{\frac{1}{2}} \tan \left(\frac{\beta \ell^2}{D} \right)^{\frac{1}{2}} \\ - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp \left(-\frac{(2n+1)^2 \pi^2 D t}{4 \ell^2} \right)}{(2n+1)^2 \left[1 - (2n+1)^2 \left\{ \frac{D \pi^2}{(4 \beta \ell^2)} \right\} \right]} \end{aligned} \quad (3- 3)$$

3.4.6 Liquid soaking experiment

The sorption uptake at a unit activity, q_i^{sat} , was determined through a liquid water-soaking experiment. Prior to soaking the CMS films, they were dried in a vacuum oven overnight at 80 °C at 25 mmHg. The initial mass of the activated films was recorded, then the films were placed in DI water under 35 °C in a water bath and left to soak. The film mass was measured every 7 days until a steady state was reached. The films were carefully tabbed to remove any residual liquid DI water on the surface to measure the film mass with liquid water uptake accurately. The sorption uptake at a unit activity was determined by calculating the difference between the sample mass at equilibrium uptake and the initial dry sample mass.

3.4.7 Wicke-Kallenbach Vapor Permeation

The pure and mixture component permeation rates were experimentally measured in a Wicke-Kallenbach (WK) vapor permeation setup (Figure 3.4). WK is a well-controlled experiment that avoids many nonidealities in real separation systems and thus provides a useful testbed for evaluating fundamental transport mechanisms. Helium gas is fed to two solvent glass bubblers (7538-27, Ace Glass, USA) installed in series and filled with pure water or pure p-xylene for pure component permeation and water/p-xylene mixtures for mixture component permeation experiments under a controlled mass flow. The outlets of the bubblers were equipped with glass wool demisters to avoid condensed particles entering the membrane feed stream. The bubblers were contained in a stainless steel box wrapped with heating tapes on the inner wall. The saturator temperature was controlled by these heating tapes. For the mixed vapor WK permeation experiments, approximately 50 ml of p-xylene and 50 ml of water were mixed in each bubbler, where the two solvents

form distinct layers in the bubbler. The near-saturated vapor mixture stream is directly fed to GC to measure the vapor concentrations.

The CMS membranes were masked using aluminum tape, sealed with J-B Weld 8272 MarineWeld epoxy, and backed with filter paper to avoid breakage of membranes during the installation and permeation. The downstream was swept with helium gas at 5 - 10 sccm to approximate a zero-activity environment. The upstream helium flow was kept at higher than 20 sccm to avoid the backflow of the downstream helium sweep flow. The guest vapor permeability was calculated using (Eq. (3- 4)) where $\dot{n}_i$ is the downstream molar flow rate, ℓ is the thickness of the CMS membrane, A is the permeation area of the CMS membrane, and p_i^{upstream} and $p_i^{\text{downstream}}$ are the partial pressure of water or p-xylene upstream and downstream. The thickness of the membrane was obtained by measuring the cross-section in SEM. The permeation area of the membrane was obtained using Image J[®] software. The permeate stream composition was detected using gas chromatography (GC, Agilent, Santa Clara, CA) with a TCD detector, and the flow rate was obtained from a bubble flowmeter attached to the membrane downstream. The feed stream composition is also measured using the GC. The permselectivity of p-xylene/water was calculated using the experimental permeability (Eq. (3- 5)). The permeation experiment at each temperature was tested in three different membranes from different pyrolysis.

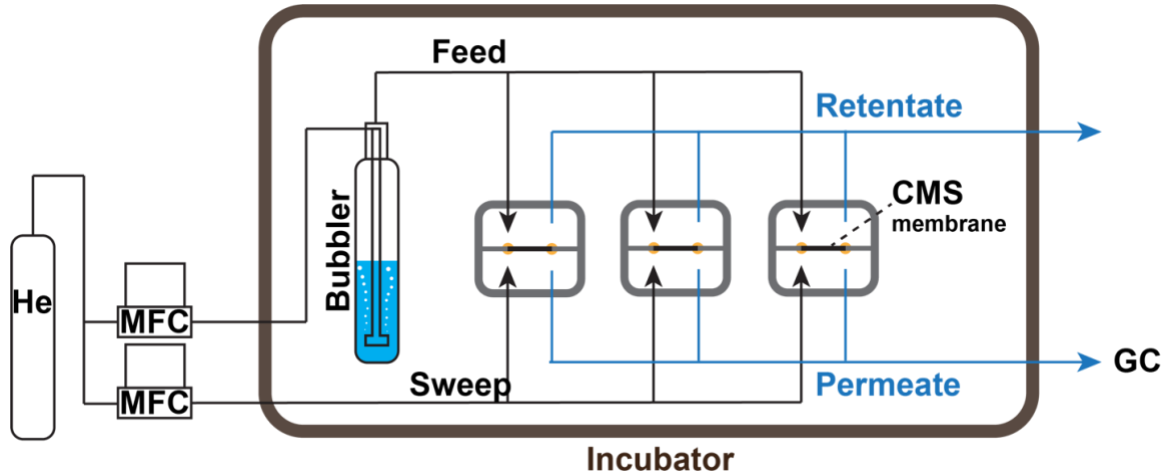


Figure 3.4. Wicke-Kallenbach vapor permeation apparatus for measuring permeation over CMS membranes where the membrane upstream has an activity of 1 and downstream has an activity of 0. Temperature is controlled in the insulation box including the bubbler and the three membrane cells.

$$\mathbb{P}_i = \frac{\dot{n}_i \times \ell}{A \times [p_i^{\text{upstream}} - p_i^{\text{downstream}}]} \quad (3-4)$$

$$\alpha_{\text{p-xylene/water}} = \frac{\mathbb{P}_{\text{p-xylene}}}{\mathbb{P}_{\text{water}}} \quad (3-5)$$

3.4.8 Crossflow Liquid Permeation

Liquid water-p-xylene mixture separation using CMS hollow fiber membranes was conducted in a custom-built crossflow system pressurized by a high-pressure HPLC pump (Azura P 4.1S, Knauer) (Figure 3.5a). The liquid permeation experiments were conducted at room temperature.

Deionized (DI) water saturated with p-xylene (~ 200 ppm) liquid was used as a feed mixture. Prior to running high-pressure liquid permeation experiments on the membranes, the carbon membranes were wetted with the DI/p-xylene mixture liquid on the shell and

the bore side to condition the module overnight. The feed mixture was fed to the shell side of the membranes (Figure 3.5b), and the retentate was cycled back to the feed reservoir to maintain the feed mixture concentration. Once the membrane modules were installed on the crossflow systems, the feed solution was circulated for 24 hours to remove air bubbles in the systems at ambient pressure before exposure to high pressure. The membranes were slowly pressurized to minimize stress on the membranes.

The first sample collection (~ 0.5 ml $\gg$ ten times the downstream volume) was discarded to purge out the bore side solution, which was injected prior to the permeation experiment, and to ensure the sample collection was at a steady state. The mass of an empty vial before permeation, the mass of the vial with condensed permeate after the permeation, and the time for permeation were recorded to obtain the permeate flow rate. The effective membrane area was obtained by measuring the outer diameter of the hollow fiber membranes in SEM (SU 8010) and by measuring the effective fiber length. The feed mixture was sampled at the start and the end of the permeate collection. The compositions of the feed mixture were measured, and the average was used as the feed composition for the permeate sample. The feed and the permeate compositions were measured by high performance liquid chromatography (HPLC) (Agilent). The UV/Vis detector was set at a wavelength of 264 nm. A Poroshell 120 EC-C18 4.6×100 mm, $4 \mu\text{m}$ column was used with a mobile phase flow rate of 0.5 ml/min. The mobile carrier phase of 99.9 vol% HPLC grade acetonitrile and 0.1 vol% trifluoroacetic acid was used. Each method ran for 30 minutes under ambient conditions. A calibration curve was drawn for the p-xylene and water mixture (Eq. (3- 6)) for a p-xylene concentration range of 20-200 ppm.

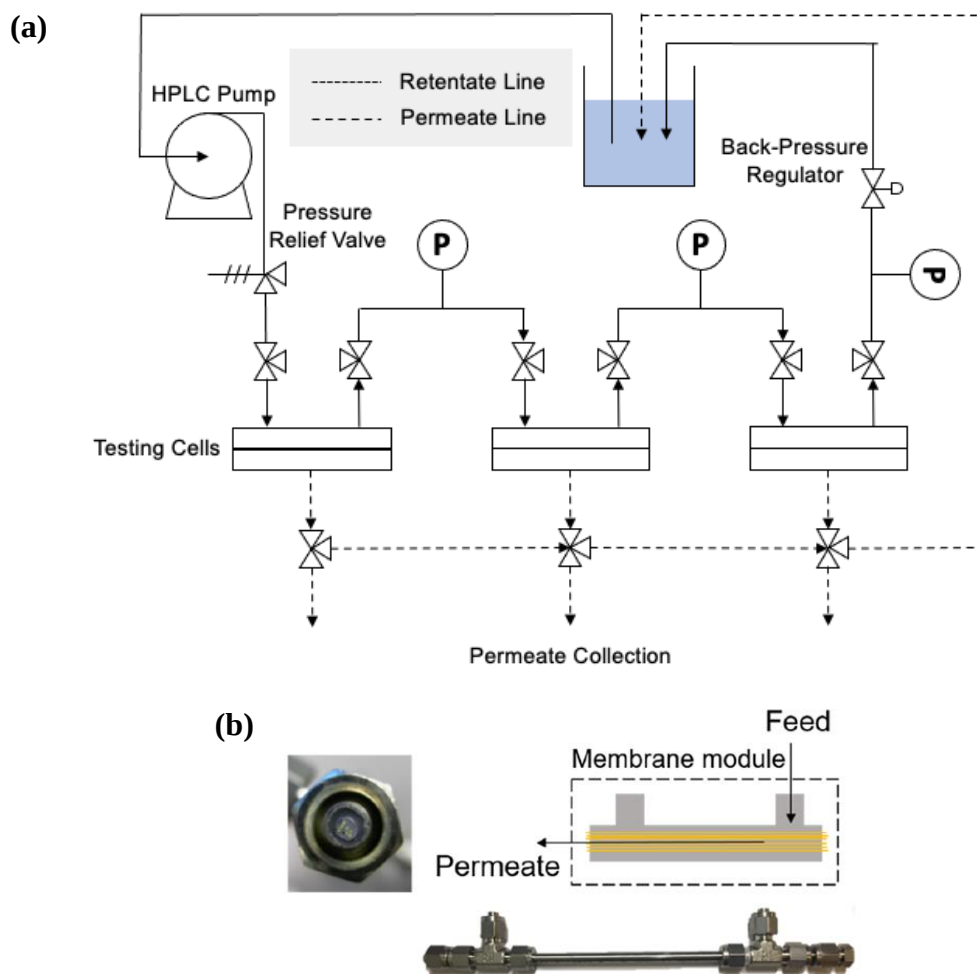


Figure 3.5. (a) Schematic of a crossflow liquid permeation systems driven by an HPLC pump and (b) Hollow fiber membrane modules used in the crossflow systems. The feed is fed to the shell-side and the permeate is collected on the bore side of the hollow fiber membranes [15].

Table 3. 3 Calibration curves for determining p-xylene concentration in water mixture using HPLC

Equations	R^2	
$y = 0.0574x^2 + 6.2645x$	0.9529	(3- 6)

3.4.9 Pervaporation Permeation

Liquid DI water transport in CMS hollow fiber membranes was conducted in a custom-built crossflow pervaporation system (Figure 3.6). Two high-pressure mechanical syringe pumps (500D, Teledyne Isco) were operated in a dual-pump mode for a continuous flow system. The hollow fiber CMS membranes were tested in the reverse osmosis modality before being tested in pervaporation. After the RO experiments, the wet fiber membranes were stored in the water to prevent damage to the fiber membranes during drying. Then, similar to the reverse osmosis setup, the DI water feed was fed to the shell side of the membrane at a flow rate of 10 ml/min. The downstream of the membrane was purged with a sweep He gas at a flow rate of 20 sccm to create a chemical potential gradient across the membrane. The pervaporation experiments were also conducted at room temperature. The initial permeate collection (~ 0.5 ml $\gg$ ten times the downstream volume) was disregarded to purge out the bore side solution, which was injected prior to the experiment, and to collect the permeate at a steady-state. The permeate was collected in a 60 ml septum vial contained in a liquid nitrogen cooling bath to condense the vapor permeates. The mass of an empty vial before permeation, the mass of the vial with condensed permeate after the permeation, and the time for permeation were recorded to obtain the permeate flow rate.

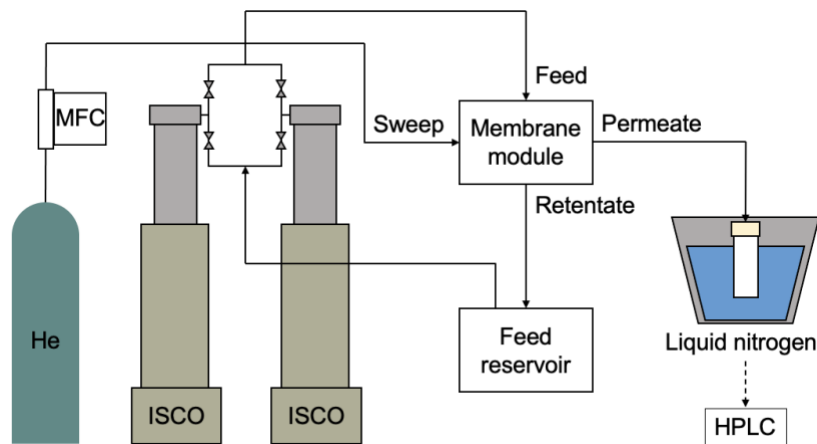


Figure 3.6 Schematic of a crossflow pervaporation system driven by a dual syringe pump crossflow system.

3.4.10 Neutron Total Scattering

Neutron time-of-flight total scattering data for lightly ground samples of carbon molecular sieves (CMS) loaded within 3 mm (OD) quartz capillaries were collected using the mail-in service at the NOMAD beamline at Oak Ridge National Laboratory [16], with a total collection time of 24 min at room temperature. Specifically, the PDF data was calculated from the total neutron scattering data first by correcting for instrumental aberrations (e.g., subtracting air and container scattering contributions). The resulting data is normalized for neutron atomic form factors to afford the reduced total structure function, $F(Q) = Q(S(Q)-1)$, where Q is the scattering vector ($4\pi\sin(\theta/\lambda)$, $\text{\AA}^{-1}$). The PDF, $G(r)$, is obtained through the Fourier transformation of the total structure function (Eq. (3- 7)) such that

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q(S(Q) - 1) \sin Qr \, dQ \quad (3- 7)$$

affording a real-space distribution of atom-atom pair distances. The data were corrected for background noise using the automated routines at the NOMAD beamline. nPDF was calculated using a scattering range $0.04 \text{ \AA}^{-1} \leq Q \leq 31.4 \text{ \AA}^{-1}$ with $Q_{\text{damp}} = 0.017 \text{ \AA}^{-1}$ and $Q_{\text{broad}} = 0.019 \text{ \AA}^{-1}$. Q_{damp} and Q_{broad} are Gaussian envelopes used to correct for limited Q resolution and increased noise at high Q , respectively. Peaks were analyzed and fitted using fityk [17].

3.4.11 Small Angle X-ray Scattering

SAXS experiments were carried out using a PANalytical Empyrean diffractometer with a Cu-LFF source ($\lambda = 1.5425 \text{ \AA}$). A continuous scan was collected within the range $0.115 < 2\theta < 5.005$ with a step size of 0.01° and collection time of 0.88s per step. Data were corrected for background noise (mylar sample holder) and fitted using SasView [18].

3.5 References

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CHAPTER 4. DIRECT EVIDENCE OF THE ULTRAMICROPOROUS STRUCTURE OF CARBON MOLECULAR SIEVES

This chapter discusses the structural studies on PIM-1 derived CMS using characterization including neutron total scattering, small angle X-ray scattering, and gas physisorption. This chapter is adapted from ‘Y.H. Yoon, D. O’Nolan, M.L. Beauvais, K.W. Chapman, R.P. Lively, Direct evidence of the ultramicroporous structure of carbon molecular sieves. *Carbon* 118002 (2023).’ The study in this chapter is performed in a highly collaborative approach. The key contributions from the coauthors are highlighted as the following: Conceptualization of the study and the analysis of neutron total scattering and small angle X-ray scattering were conducted by Daniel O’Nolan (Georgia Institute of Technology). Analysis of neutron total scattering was assisted by Michelle L. Beauvais (Stony Brook University), and Karena W. Chapman (Stony Brook University).

4.1 Introduction

The membrane separation properties of carbon molecular sieve (CMS) materials regularly exceed those of traditional polymeric materials and mixed matrix membranes (MMMs) [1–4]. The attractive separation properties of CMS materials are attributed to their bimodal pore size distributions, which are typically comprised of micropores (7-20 Å) and ultramicropores (<7 Å) (Figure 4. 1). Moreover, the solution processability of CMS polymer precursors and relative ease of fabrication via post-processing pyrolysis affords a

broad availability of membrane and adsorbent form factors (e.g., thin films and hollow fibers).

In the context of separation science, the transport of molecules through these materials is based on a combination of size, shape, and sorbate-sorbent affinity. Energy-efficient air purification [5], olefin/paraffin separations [3,6], xylene isomer purification [1,7], and natural gas separations [8,9] have been demonstrated. A 'sorption-diffusion' model can describe the membrane separation transport: molecules are adsorbed onto the membrane structure's surface and then diffuse through the structure via activated "jumps." The separation performance is the product of kinetically-driven diffusion and equilibrium-driven sorption for each component in a mixture. Diffusion through CMS materials can exhibit enthalpic and entropic selectivity, depending on the relative differences in guest size and shape, respectively.

Despite the long research history of porous carbon materials, structural insight into CMS remains elusive due to the disordered nature of these materials. Several microstructural and textural studies have given qualitative insight into the structure. A deeper insight into the structure-property relationships of CMSs can potentially enable a new generation of materials amenable to molecular design and modeling. Indeed, structural databases on amorphous materials have begun to emerge but currently lack structures for CMS materials [10]. CMS typically exhibits no long-range order (i.e., crystalline order); qualitative models hypothesize carbonaceous strands that self-assemble into plates, which imperfectly pack to create well-defined bimodal pores (Figure 4. 1) [11]. The narrow distribution of pores suggests that there must be a clear driving force that governs the material assembly and structure on this length scale.

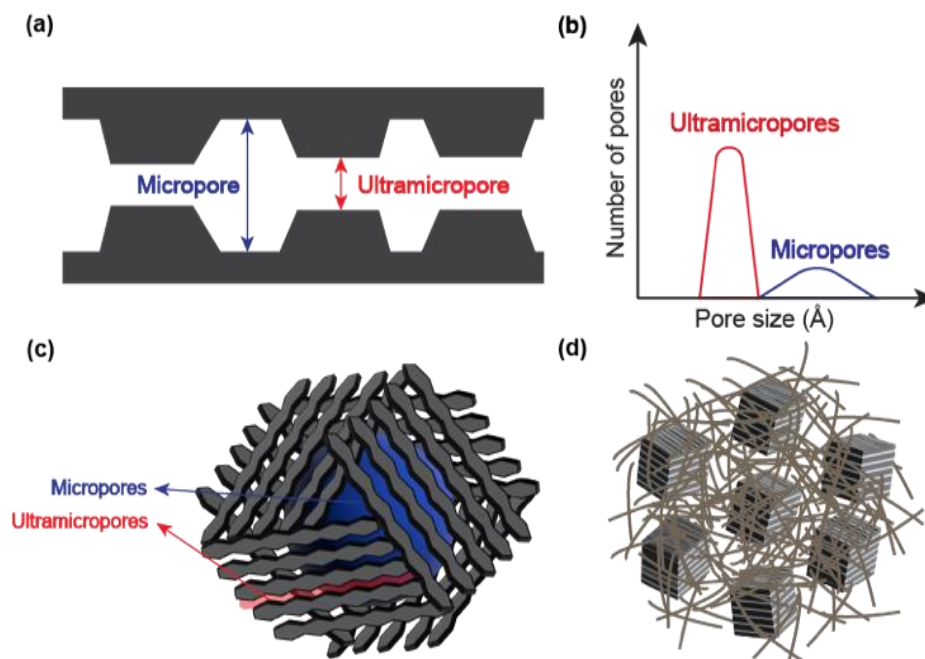


Figure 4. 1. Hypothesized microstructure of CMS. (a) Classical idealized view of slit-like bimodal distribution of micropores. (b) Generalized bimodal pore size distribution of CMS consisting of ultramicropores and micropores. (c) Updated CMS structure hypothesis from Koros et al. highlighting the arrangement of carbonaceous plates around microporous voids [11,12]. (d) These microporous cells are thought to be dispersed within a disordered array of graphenic strands that did not assemble into plate-like structures [13]. Copyrights with permission from Elsevier.

CMS membranes are derived from the controlled pyrolysis of polymer precursors, which are often linear, glassy polymers. Control over the pyrolysis reaction steps drives reproducible carbonization of the polymers and organization into the microporous turbostratic structure. Importantly, the porous microstructure of CMS materials can be precisely controlled ($\pm 0.1\text{\AA}$) by adjusting the pyrolysis temperature ramping profile, pyrolysis atmosphere, and final pyrolysis temperature [14,15]. High- T_g glassy polymers (typically polyimides) are often favorable as precursors because of their thermal stability. Pyrolysis of CMS generally follows three thermal treatment steps: 1) ramping, 2) soaking, and 3) cooling (Figure 4. 2). Koros et al. [11,12] postulated a CMS formation mechanism in which the polymer precursor forms rigid and aromatized "strands" through

fragmentation and aromatization during the ramping step. These short and imperfect strands are mobile at pyrolysis temperatures and thought to pack in parallel into imperfect "plates." These plates then form imperfect "cell" structures during the soaking and cooling steps. The neighboring cells coalesce to form a repeating matrix of micropore cells with ultramicroporous slit walls (Figure 4. 1. These repeating but non-ordered structural units are thought to give rise to the well-defined micropores in CMS materials. Recent analysis on polyimide-derived CMS materials proposed a new structural feature called "orphan strands,"[13] which form a minority continuous network of disordered ultramicropores between the microporous cells (Figure 4. 1d).

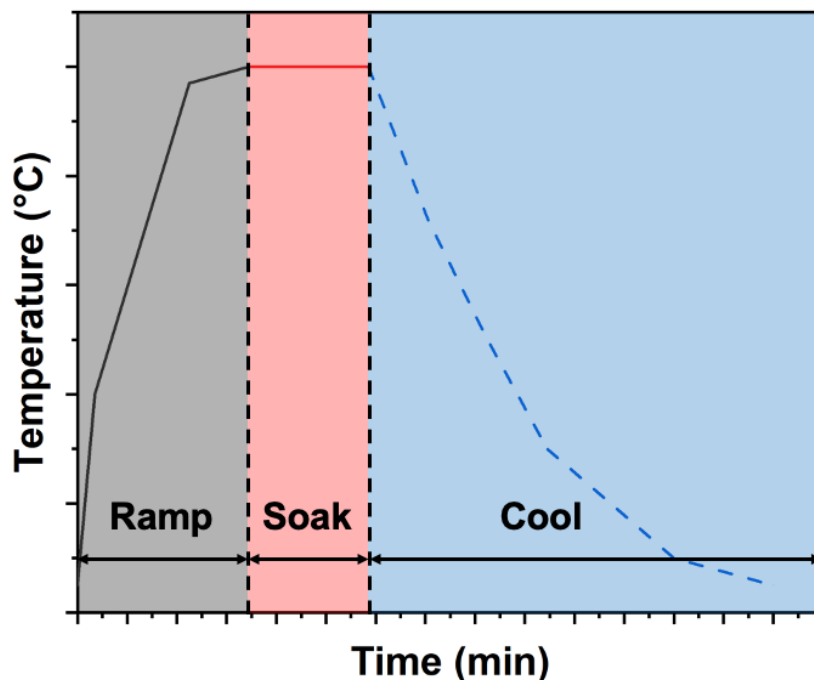


Figure 4. 2. Pyrolysis temperature ramping profile for CMS fabrication from polymer precursor. Copyrights with permission from Elsevier [11]

The amorphous nature of CMS materials (and porous carbons in general) results in a tenuous understanding of structure-property relationships, although the hypotheses noted

above are useful in guiding CMS research. Many CMS materials have very small pores that are inaccessible to traditional pore size analysis measurements, which further obfuscates linking the microstructure of these important materials to their guest transport properties. Moreover, the long-range atomic order of these structures is limited, leading to broadening of diffraction peaks. Diffraction data for CMS materials typically reveals periodic interlayer separation that is not equal to the pore size distributions but can be correlated to changes in gas transport rates, for instance [12,16].

Total scattering approaches consider diffuse scattering that includes both ordered and disordered structural features and may be a powerful technique in understanding amorphous materials such as CMS. While traditional powder diffraction may reveal the inter-planar spacing of graphitic structures, reflections cannot always be readily observed due to amorphization or highly diffuse scattering. Correcting for instrumental aberrations and normalization of scattering data using atomic form factors affords the total structure function ($S(Q)$), which better reveals these interplanar spacing, particularly in diffuse scattering data. The experimental pair distribution function (PDF, $G(r)$) captures the weighted probability of atom-atom correlations at specific radial distances (r), thus revealing the local atomic structure. More detailed descriptions of total scattering are provided elsewhere [17]. Small-angle scattering is sensitive to scattering density fluctuations on the nanoscale and can be applied to evaluate pore/particle size and shape distributions.

Ma et al. [18] reported H_2 assisted pyrolysis for PIM-1 (PIM = polymer of intrinsic microporosity) derived CMS resulted in enhanced membrane performance. PIM-1 derived CMS membranes pyrolyzed under 4% H_2 balanced with argon (**4% H_2 PIM-1-CMS**)

showed ~ 15 times increased p-xylene ideal permeability with minimal decrease in p-xylene/o-xylene selectivity (from 25.0 to 18.8) compared to CMS membrane fabricated under pure argon pyrolysis (**PIM-1-CMS**). The pore structure of **PIM-1-CMS** and **4% H₂-PIM-1-CMS** were investigated using cryogenic (77 K) N₂ physisorption, and the pore size distribution was obtained employing the 2D-NLDFT model developed by Micromeritics for a carbon material with infinite slit pores. Essentially no nitrogen uptake was obtained in **PIM-1-CMS**, while **4% H₂-PIM-1-CMS** had large N₂ uptakes (0.216 cm³/g at high activities), a result that we replicate here (Figure 4. 3a). Interestingly, the **PIM-1-CMS** and **4% H₂ PIM-1-CMS** showed similar p-xylene uptake of 1.10 mmol/g and 1.06 mmol/g, respectively, at the saturation vapor pressure at 55 °C. The similar uptake of p-xylene implies similar pore volumes that are accessible to p-xylene molecules, 0.136 cm³/g and 0.131 cm³/g, respectively. The hypothesis presented in that work was that the small ultramicropores in **PIM-1-CMS** are sufficiently small that N₂ cannot access these pores within reasonable timescales under cryogenic conditions. We explore the usage of various adsorbates (N₂, CO₂, Ne) to probe the pore size distribution of CMS samples that have been previously identified as having the ability to distinguish xylene isomers based on the difference in the shape of the isomers. We combine this textural characterization with neutron total scattering and small-angle X-ray scattering (SAXS) to gain a multiscale view of what the structure that defines the ultramicropore may look like in a series of recently reported CMSs: PIM-1 CMS derived from pyrolysis under inert conditions (**PIM-1-CMS**) and 4% H₂ gas flow (**4% H₂-PIM-1-CMS**).

4.2 Structural characterization of PIM-1 derived CMS

4.2.1 Textural analysis through gas physisorption

Carbon dioxide (0 °C or 273 K), argon (-186.15 °C or 87 K), and neon (-233 °C or 40.15 K) adsorption isotherms were measured to conduct a pore size analysis on **PIM-1-CMS** and **4% H₂-PIM-1-CMS** (Figure 4. 3 and Figure 4. 4). Ar adsorption at -186.15 °C showed similar behavior with N₂ adsorption at -196.15 °C (77 K), where the both probe molecules did not exhibit a significant uptake on **PIM-1-CMS** (Ar isotherm provided in Figure 4. 4d). It was concluded that the Ar isotherm does not provide more structural information on **PIM-1 CMS** than the N₂ isotherms, as shown in the pore size distribution plot in Figure 4. 3d. CO₂ is a reliable molecular probe molecule for carbon materials and is especially suitable for ultramicropores and micropores [19]. CO₂ adsorption can be performed at 0 °C, which enables faster approach towards equilibrium relative to cryogenic measurements of N₂ or Ar. In addition, this work explores the usage of neon as another probe molecule for accurate textural studies of ultramicroporous materials. Neon does not have a quadrupole moment like nitrogen or carbon dioxide [20], and it has a smaller molecule size (kinetic diameter: 2.75 Å) than nitrogen (kinetic diameter: 3.64 Å). The Ne physisorption isotherms were obtained at -233 °C, a temperature below its critical temperature (-228.75 °C) [21], to assist adsorbate-adsorbent interaction of neon molecules and with the pore surface. Helium, which has a smaller molecular size than neon, is a reliable probe molecule for microporous material characterization at a subcritical temperature of -269.15 °C [22,23]. Thus, it is hypothesized that the neon adsorption at -233 °C would exhibit sufficient adsorbate-adsorbent and adsorbate-adsorbate interaction to obtain reliable pore size distributions. Although the 2D-NLDFT is the state-of-the-art calculation for determining the slit-pore carbon micropore size distribution, the NLDFT model kernels for neon are yet to be established, and thus the simpler HK method was

utilized. Despite some disagreement between NLDT (a large population at 5.3 – 6.9 Å) and HK (a minor population at 4.2 – 5.3 Å and a major population at 5.3 – 6.8 Å) (Figure 4. 5) the HK calculation was found to provide a PSD with reasonable quantitative accuracy [24].

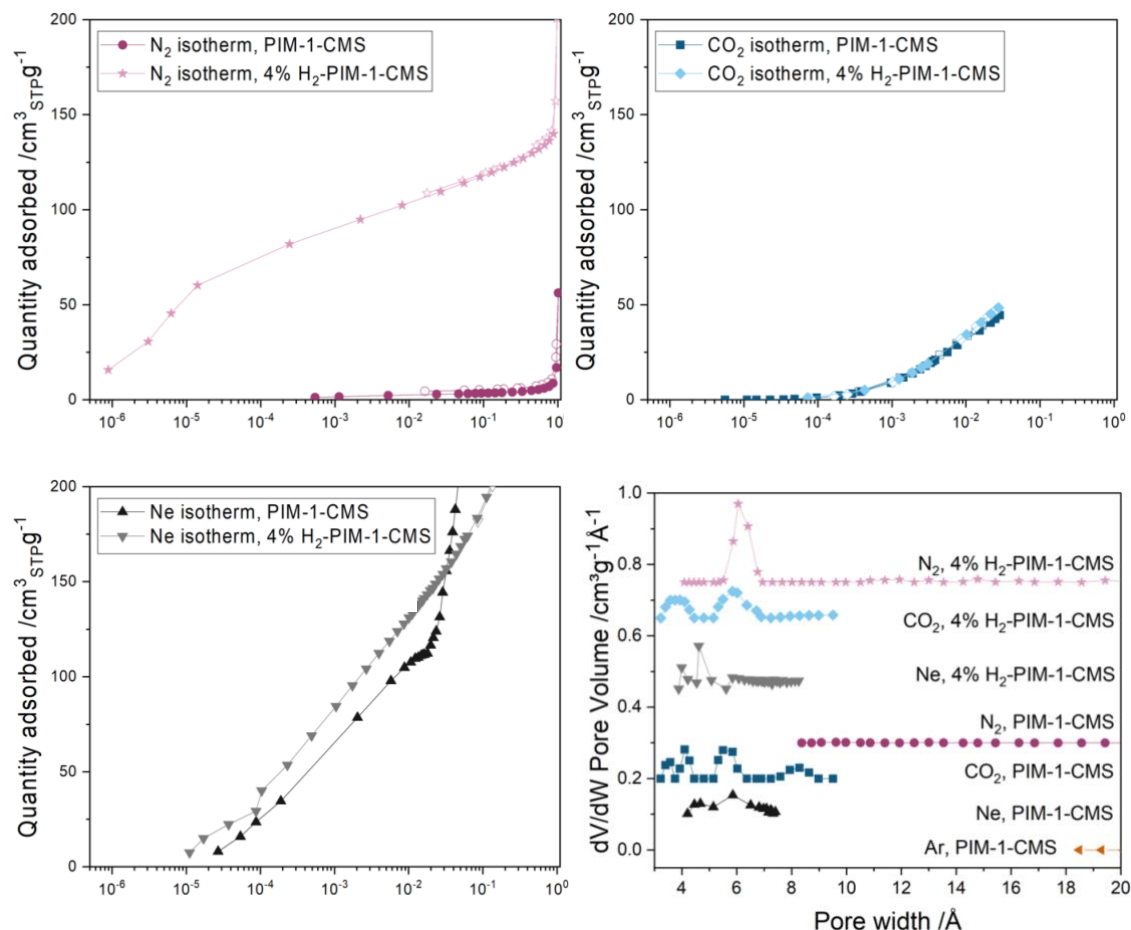


Figure 4. 3. (a-c) Gas physisorption isotherms of PIM-1-CMS and 4% H₂-PIM-1-CMS using -196.15 °C (77 K) N₂ (a), 0 °C (273 K) CO₂ (b), and -233 °C (40.15 K) Ne (c). (d) Pore size distribution (PSD) calculated from the -196.15 °C N₂, 0 °C CO₂, -233 °C Ne, and -186.15 °C Ar isotherms. The N₂ isotherms in Figure 2a are extracted from Ma et. al. [18] and the CO₂, Ne, Ar isotherms are measured in this work. The N₂, CO₂, and Ar isotherms were used in NLDT for the pore size distribution (PSD) calculation. The Ne isotherms were used in Horvath-Kawazoe (HK) PSD calculation. The PSD plots are shifted in y-axis for easier comparison of the distributions.

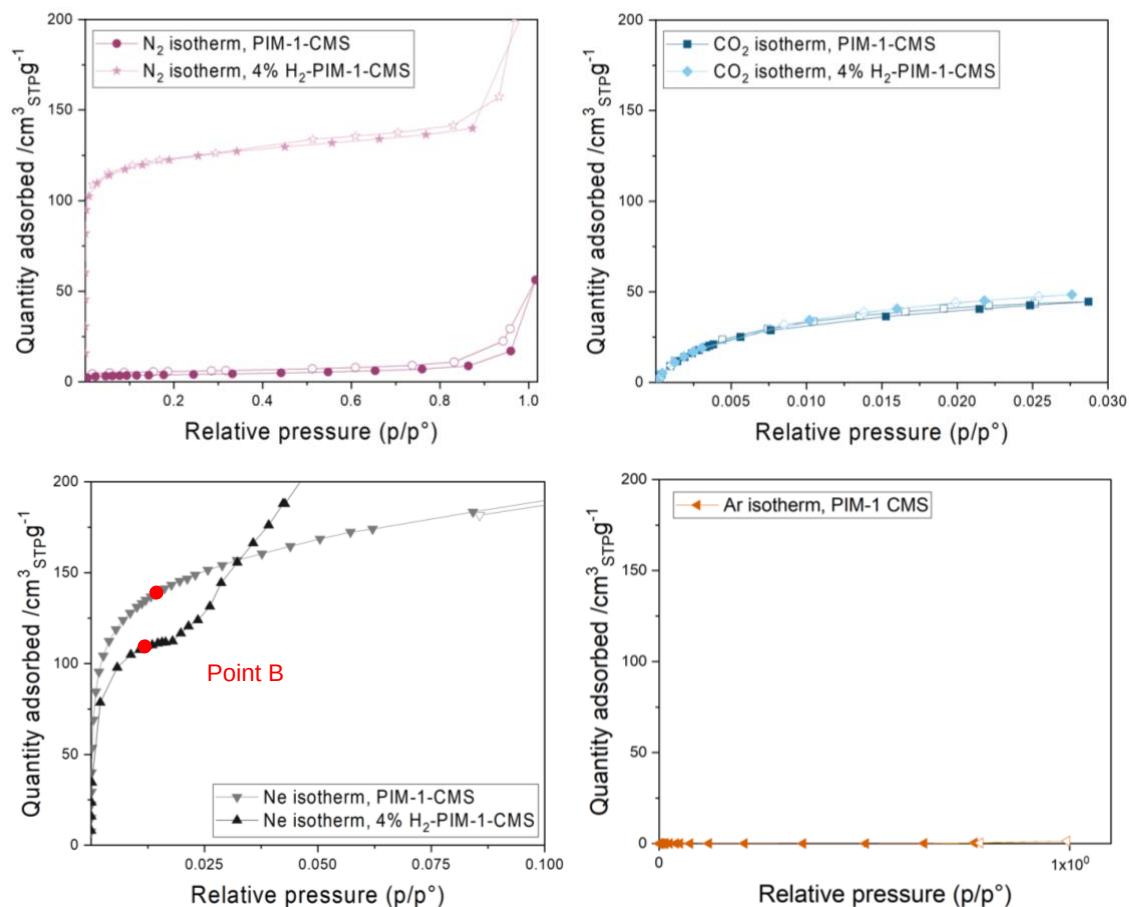


Figure 4. 4. Gas physisorption isotherms of PIM-1-CMS and 4% H₂-PIM-1-CMS using (a) -196.15 °C (77 K) N₂, (b) 0 °C (273 K) CO₂, (c) -233 °C (40.15 K) Ne, (d) -186.15 °C (87 K) Ar. Neon isotherm showed a type II isotherm exhibiting monolayer-multilayer adsorption. The Point B which indicates monolayer capacity is marked in the neon isotherms. Solid symbols are from adsorption and hollow symbols are from desorption data.

Carbon dioxide physisorption on **PIM-1-CMS** and **4% H₂-PIM-1-CMS** at 273.15 K was measured in ASAP 2020HD (Micromeritics, USA) in the 0.1-760 torr range. Analysis temperature was controlled using an ice water bath. HS-2D-NLDFT (heterogeneous surface two-dimensional non-local density functional theory) model pore-size distribution calculations were obtained from CO₂ isotherm using the MicroActive software package (Micromeritics, USA) [25].

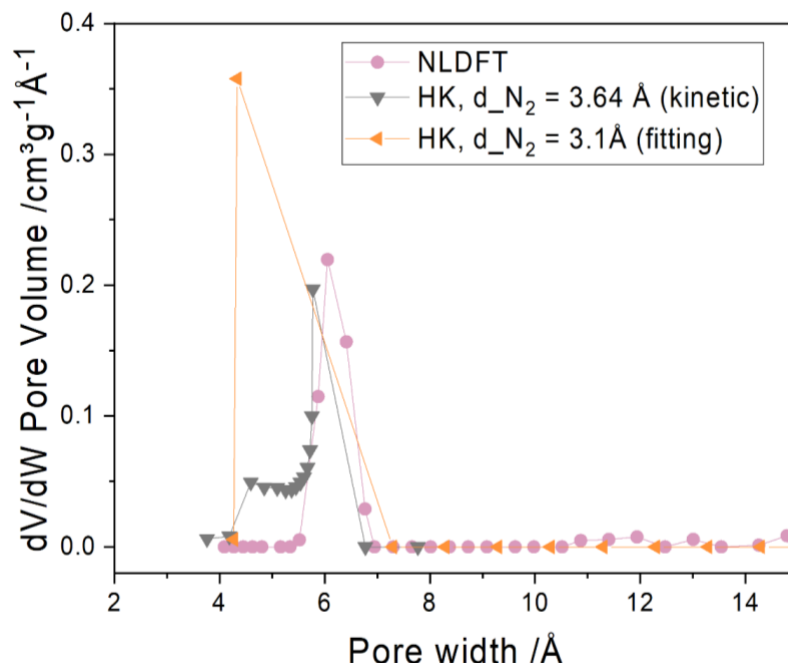


Figure 4. 5. Pore size distribution analysis on 4% H₂ PIM-1-CMS using N₂ isotherm. PSD analysis methods of 2D-NLDFT, HK using $d_{N_2,kinetic}$, and HK using $d_{N_2,fitting}$ were used. The kinetic diameter used in HK calculation exhibits better agreement with the state-of-the-art NLDFT method, compared to the fitting diameter used in HK calculation.

Argon physisorption on **PIM-1-CMS** was also measured in ASAP 2020HD, using a liquid argon bath to control the experimental temperature. NLDFT model (MicroActive, Micromeritics, USA) for carbon slit pores was used to calculate pore size distribution.

The nitrogen physisorption isotherms (Figure 4. 3a, Figure 4. 4a) were extracted from Ma et. al.[18], and HS-2D-NLDFT model (MicroActive, Micromeritics, USA) for carbon slit pores was used to determine pore size distributions (Figure 4. 3d).

Neon vapor physisorption at 40.15 K was also conducted to study the microporous structures of **PIM-1-CMS** and **4% H₂-PIM-1-CMS**. The experimental temperature at 40.15 K was maintained using a cryostat (CH-104, ColdEdge, USA) equipped with a He

compressor (CH-4A, ColdEdge, USA). The physisorption experiment was tested on a High-Pressure Volumetric Analyzer (HPVA II, Micromeritics, USA). Free space was measured using helium at both ambient and analysis temperature, followed by the neon adsorption experiment. The neon isotherms exhibiting excess surface adsorption were obtained by the quasi-Gemini free space correction calculation using MicroActive software (Micromeritics, USA). The CMS samples were degassed at 383.15 K overnight under vacuum. The equilibrium criteria of 0.03 mbar in 10 minutes or 600 min maximum was used. The temperature was controlled at 40.15 ± 0.05 K. The neon isotherm is measured in the range of 0.08 - 3000 torr. The pore size distribution from the neon isotherm was calculated using Horvath and Kawazoe (HK) method [26]. The HK method was implemented on the neon isotherms using an in-house HK Matlab code (the code is provided in Appendix A).

The in-house HK Matlab code in this work was modified from the code developed by Thompson [27] via three major changes: 1) neon molecular parameters were introduced to incorporate neon as an adsorbate, 2) the isotherm modeling of Ne and N₂ used a logarithmic isotherm instead of a Langmuir isotherm (Table 4. 1), and 3) the kinetic diameter of neon was used for the molecular diameter in HK calculation. The original HK calculation can incorporate both Henry's law and Langmuir isotherm models into the pore size calculation [26]. However, both the N₂ and Ne isotherms on PIM-1 derived CMS were better modeled using an empirical logarithmic fitting (Table 4. 1).

The molecular diameter of nitrogen for HK calculation in the past literatures has been a fitting parameter ($d_{\text{N}_2, \text{fitting}} = 3.1 \text{ \AA}$) that derived a better fit for the pore size

distribution (PSD) analyses [26]. In Figure 4. 5 the PSD of **4% H₂-PIM-1-CMS** using N₂ isotherm was obtained using 2D-NLDFT, the logarithmic-HK using $d_{N_2,fitting}$, and the logarithmic-HK using a kinetic diameter of N₂ ($d_{N_2,kinetic} = 3.64$ Å). The HK with $d_{N_2,kinetic}$ shows greater agreement with the 2D-NLDFT method compared to the HK with $d_{N_2,fitting}$. Supported by this comparison, the kinetic diameters of both Ne and N₂ molecules were used in the HK calculation. More accurate PSD analysis can be attempted via 2D-NLDFT in the future.

Table 4. 1. Langmuir and logarithmic fitting parameters of N₂ and Ne isotherms

	Langmuir				Logarithmic			
	PIM-1 CMS		4% H ₂ PIM-1 CMS		PIM-1 CMS		4% H ₂ PIM-1 CMS	
	Ne	N ₂	Ne	N ₂	Ne	N ₂	Ne	N ₂
q^{sat*} (cm ³ /g)	0.092	0.014	7.687	0.217	0.092	0.014	7.687	0.217
a	-	-	-	-	0.151	0.082	0.113	0.057
b	2430.2	5.355	34.85	54009.8	1.643	0.669	1.286	0.986
R^2	0.990	0.820	0.969	0.875	0.995	0.708	0.995	0.981

* q_{sat} for logarithmic fitting refers to the microporous capacity prior to Point B.

The CO₂ physisorption isotherms on **PIM-1-CMS** and **4% H₂-PIM-1-CMS** (Figure 4. 3b, Figure 4. 4b) display a sharp increase in the uptake in the low relative pressure region. Since the CO₂ adsorption was measured up to 1 bar, the adsorption is only measured at a low relative pressure region, which enables pore size distribution analysis up to 10 Å pores in diameter [28]. The CO₂ isotherms for both CMS samples have similar uptake capacity (with slightly higher uptake on **4% H₂ PIM-1 CMS**) at all pressures, hinting at similar pore volumes between the two samples in the micropore region below 10 Å. The pore size distribution analysis using the CO₂ isotherm and NLDFT (Figure 4. 3d) was able to reveal the ultramicropores of both **PIM-1-CMS** and **4% H₂-PIM-1-CMS**. The

CO₂ isotherm revealed ultramicropores for **PIM-1-CMS** at 3.4-3.6, 3.9-4.3, and 5.3-6.0 Å that were not accessible to cryogenic N₂ and Ar. Moreover, the CO₂ isotherm revealed ultramicropores for **4% H₂-PIM-1-CMS** at 3.4-4.2 and 5.3-6.9 Å, contrary to the cryogenic N₂ adsorption result of only 5.5-6.8 Å.

The neon isotherms on **PIM-1-CMS** and **4% H₂ PIM-1-CMS** show a reversible type II isotherm, which we interpret as being a result of monolayer-multilayer adsorption [20]. Point B (Figure 4. 4), where the linear uptake starts, implies the completion of monolayer adsorption. The uptake at Point B indicates the monolayer capacity. Therefore, the neon isotherm up to Point B was used to obtain the pore size distribution in microporous region (Figure 4. 3d) [20]. The linear uptake past Point B is interpreted as interparticle condensation between the powder samples. Ne physisorption experiments reveal a significant pore volume in **PIM-1 CMS** (137 cm³_{STP}/g at Point B) which was not detectable by N₂ physisorption (Figure 4. 3a, Figure 4. 4a). The microporous uptake of neon up to Point B of **4% H₂-PIM-1-CMS** (110 cm³_{STP}/g) exhibits similar but slightly lower uptake than that of **PIM-1 CMS**. Thus, the neon isotherms on **PIM-1 CMS** and **4% H₂ PIM-1 CMS** also show similar uptake in the microporous region consistent with the carbon dioxide isotherms. The PSD from the neon isotherm and HK analysis (Figure 4. 3d) were able to reliably reveal the ultramicropores of **4% H₂-PIM-1-CMS** (4.0-4.2, 4.6-5.1, and 5.8-6.4 Å), which yielded PSD results similar to that in the CO₂ NLDFT PSD (3.4-4.2 and 5.3-6.9 Å). Importantly, the Ne isotherm was able to reveal the small ultramicropores of **PIM-1-CMS** (4.2-5.2 and 5.2-7.3 Å) that were inaccessible to cryogenic N₂ and Ar. This technique shows potential for revealing sub-ultramicropore distributions commonly found in gas separation CMS materials. Neon physisorption may be especially useful for polar

ultramicroporous materials (e.g. oxides, zeolites, MOFs), which are more affected by the quadrupole moment of CO₂ [20]. Despite the potential of neon gas as a probe molecule for ultramicroporous PSD analysis, refinements of the experimental apparatus and PSD analysis are still required to improve the fidelity of the PSD estimates.

4.2.2 Neutron Pair Distribution Function (nPDF)

Neutron time-of-flight total scattering data for lightly ground samples of carbon molecular sieves (CMS) loaded within 3 mm (OD) quartz capillaries were collected using the mail-in service at the NOMAD beamline at Oak Ridge National Laboratory [29], with a total collection time of 24 min at room temperature. The data were corrected for background noise using the automated routines at the NOMAD beamline. nPDF was calculated using a scattering range $0.04 \text{ \AA}^{-1} \leq Q \leq 31.4 \text{ \AA}^{-1}$ with $Q_{\text{damp}} = 0.017 \text{ \AA}^{-1}$ and $Q_{\text{broad}} = 0.019 \text{ \AA}^{-1}$. Peaks were analyzed and fitted using *fityk* [30].

To further probe the structure of these CMS materials, we carried out neutron total scattering experiments to correlate to the gas sorption studies to provide qualitative structure-property relationships. The neutron PDF for both structures is similar at low *r*-region (Figure 4. 6): Both PDFs exhibit prominent peaks at ca. 1.4 Å, ca. 2.4 Å, and ca. 2.8 Å, which are characteristic of the 1,2-, 1,3- and 1,4 carbon-carbon distances for sp² hybridized carbon in an aromatic ring environment. **PIM-1-CMS** exhibited well-defined atom-atom correlations to long distances. In contrast, the intensity of peaks in the PDF for the **4% H₂-PIM-1-CMS** sample is attenuated beyond ~ 7 Å. It is important to note that the neutron PDF peaks represent the probability of finding carbon-carbon atoms in that distance and do not represent the pore sizes. However, the PDF peak attenuation beyond 7

Å indicates that the **4% H₂-PIM-1-CMS** has less longer-range ordering than the **PIM-1-CMS**, which may result in less defined micropores and loosely packed carbon structures. This correlates well with pore size distributions in this work and others [18], which shows that the use of H₂ in CMS pyrolysis gas leads to larger but less well-defined micropores.

Analysis of the 1,2-C-C and C-H peaks of neutron PDF was used to evaluate the local bonding and structure in the CMS (Figure 4. 6). Features that correspond to hydrogen-carbon distances have negative intensity owing to the negative scattering of hydrogen (¹H). Peaks of negative intensity were observed at ~1.08 Å (C-H) and 2.13-2.18 Å (H-(C)-C) in **4% H₂-PIM-1-CMS**. These distances imply H-C-C angles of 117-122°, consistent with H coordination to sp² hybridized carbon. The absence of negative peaks in the PDF for **PIM-1-CMS** indicates a low concentration of C-H bonds, below the detection limit of 10 wt% [31]. The areas of the C-C peak at 1.41 Å and C-H peak at 1.08 Å were quantified by fitting Gaussian functions to the data within fityk [30]. These were used to estimate the average C coordination within each sample after normalizing the intensities based on the neutron scattering power of the atoms. The resulting average C coordination is given below:

- **PIM-1-CMS:** C₁H_{<0.1}
- **4% H₂-PIM-1-CMS:** C₁ H_{0.132}

For **PIM-1-CMS** and **4% H₂-PIM-1-CMS**, asymmetry of the C-C peak at ~1.41 Å suggests that there may be a minor component of aliphatic C-C bonds. Fitting of a second C-C distance at a long distance (~1.55 Å) suggests that these may represent up to ~3 % of the C (**PIM-1-CMS:** 2.9 %; **4% H₂-PIM-1-CMS:** 2.5 %).

Structural models of the carbon backbone were refined against the experimental PDF data within PDFgui [32]. The PDFs for all samples could be effectively fit by a model of isolated graphitic sheets (Figure 4. 6) with nanoscale dimension (or coherence length) [33], also equivalent to graphene strands. Importantly (and consistent with CMS formation hypotheses), no discernable features can be attributed to layer-layer interactions of the type seen in graphite. **PIM-1-CMS** had larger refined nanosheet dimensions [34] of ~ 18 Å diameter ($R \sim 0.20$) while **4% H₂-PIM-1-CMS** have smaller refined nanosheet dimensions of ~ 8 Å ($R \sim 0.23 \sim 0.24$). R refers to the R -factor, which describes the discrepancy between the data and the model. Lower the R value, the fitting is better, and for amorphous carbon materials, $R \sim 0.2$ is considered a good fit [33,35].

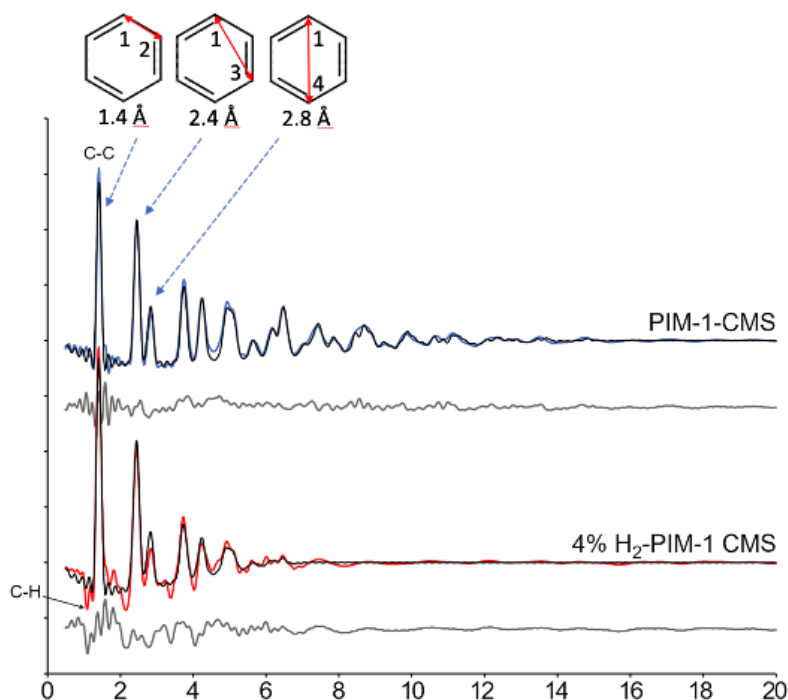


Figure 4. 6. Fits to the nPDF data for PIM-1 CMS and 4% H₂-PIM-1-CMS samples using structural models of graphene nanosheets (black) and the corresponding residuals (grey).

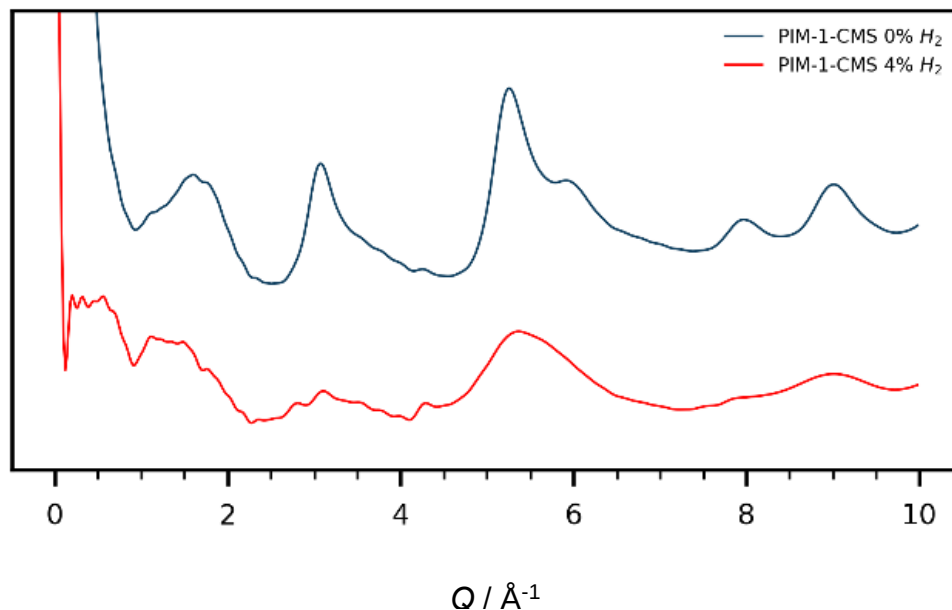


Figure 4. 7. Neutron total scattering structure function ($S(Q)$). PIM-1-CMS materials obtained under inert and reducing atmospheres. The y-axis scales linearly.

While the well-defined peaks were well fit by the models in Figure 4. 6, there are broad peaks present in the residual between the model and data. For both materials, there is a broad peak at $3.6 \text{ \AA}$ (more clearly represented in Figure 4. 7, where the PDF peak at $r = 3.6 \text{ \AA}$ is at $Q \sim 1.75 \text{ \AA}^{-1}$), which is not fit by the isolated graphene nanosheets model. We note that this distance is the same as the distance between buckminsterfullerene balls when they form a crystal lattice [36]. Inspired by this, we hypothesize that the $3.6 \text{ \AA}$ distance in the amorphous CMS materials may correspond to some non-uniform π -stacking between slightly curved, neighboring graphenic strands, resembling the surface of buckminsterfullerene balls. The graphene-like CMS strands do not exhibit a highly ordered structure of pyrolytic graphite. This lack of ordered graphitic structures is consistent with qualitative hypotheses on CMS microstructure put forth by Koros and coworkers [6,13].

4.2.3 Small Angle X-ray Scattering (SAXS)

SAXS experiments were carried out using a PANalytical Empyrean diffractometer with a Cu-LFF source ($\lambda = 1.5425 \text{ \AA}$). A continuous scan was collected within the range - $0.115 < 2\theta < 5.005$ with a step size of 0.01° and collection time of 0.88 s per step. Data were corrected for background noise (mylar sample holder) and fitted using SasView [37]. The refinement values in Table 4. 2 were used.

Table 4. 2. Refinement values SAXS fittings

	PIM-1-CMS	4%H₂-PIM-1-CMS
Wavelength (λ) / $\text{\AA}$	1.5425	
Scattering vector range (Q) / $\text{\AA}^{-1}$	0.01422 – 0.35538	
Scale	1.5785	1.136
Background	10	1
R_g / $\text{\AA}$	89.599	89.713
s	2.3983	1.6351
d	3.9997	
χ^2	1852.6	75.227

The SAXS data for both **PIM-1 CMS** and **4% H₂-PIM-1-CMS** exhibit similar monotonous trends but reveal subtle differences in their scattering inhomogeneities (Figure 4. 8). To gain a qualitative understanding of these structures, the data were fitted in the range $0.014 \text{ \AA}^{-1} \leq Q \leq 0.36 \text{ \AA}^{-1}$ with the empirically derived Guinier-Porod function [38]:

$$I(Q) = \frac{G}{Q^s} e^{\left(\frac{-Q^2 R_g^2}{3-s}\right)} \text{ for } Q \leq Q_1 \quad (4-1)$$

$$I(Q) = \frac{D}{Q^a} \text{ for } Q \geq Q_1 \quad (4-2)$$

where $Q_1 = \frac{1}{R_g} \left(\frac{3d}{2} \right)^{0.5}$, G and D are the Guinier and Porod scale factor terms, respectively, Q is the scattering vector, R_g is the radius of gyration, s is the dimension variable, and d is the Porod exponent. The Q_1 transition was refined to be *ca.* 0.1 Å⁻¹, with the large flat region affording $d = 4$. The R_g for both materials was fitted to be *ca.* 90 Å. The dimension variable component, s , can be used to describe the symmetry of non-spherical structures, with $s=0$ describing spherical, globular particles, $s=1$ describing symmetry such as rods, and $s=2$ describing symmetry such as lamellae and platelets. The dimensional variable was refined to 2.4 for **PIM-1-CMS** and 1.6 for **4% H₂-PIM-1-CMS**. These refinement results are close to 2 suggesting that both the CMS materials exhibit platelet-like structures, whereas the addition of H₂ during synthesis leads to a more rod-like structure. These findings correlate well with the PDF results that indicate smaller nanosheet dimensions for **4% H₂-PIM-1-CMS** in comparison with **PIM-1-CMS**. These SAXS refinements also correlate well with textural results, as the rod-like **4% H₂-PIM-1-CMS** would offer poorer packing than plate-like lamellae of **PIM-1-CMS**, which would lead to higher porosity.

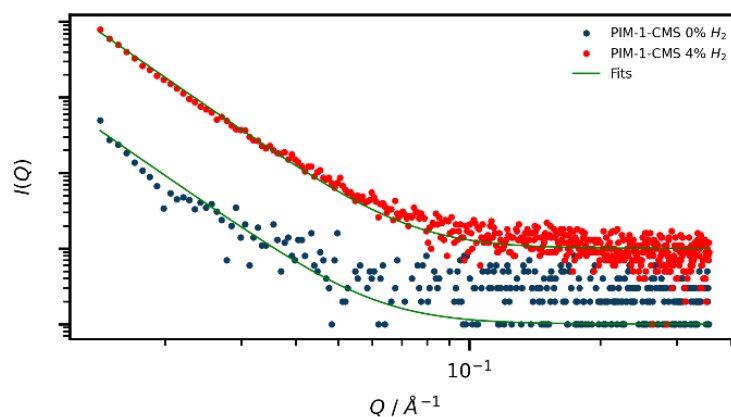


Figure 4. 8. SAXS data of PIM-1-CMS materials obtained under inert and reducing atmospheres. nPDF data are offset for clarity.

4.3 Proposed microstructure of CMS

Both materials fit reasonably well with a structural model of isolated and disordered graphitic (i.e., sp^2 hybridized C) nanosheets. Neither PDF has peaks associated with interlayer graphite distances, indicating that there is not a significant well-defined interaction between nanosheets. The refined domain size of nanosheets is smaller for the **4% H₂-PIM-1-CMS** at only 8 Å as opposed to 18 Å of **PIM-1-CMS**. While the refined domain size is typically interpreted as the overall particle size, here we interpret the finite coherence length to be the combined effect of a single graphene nanosheet of finite width in one direction and curvature in the perpendicular direction (the curvature of such a sheet leads to a reduced refined sheet dimension in the direction of the curve because the atom-atom distances would be distorted by the curvature, so atom-atom peaks in the PDF would not be present for distances beyond the flat regions). Such a combination leads to a “nanoribbon” microstructure. The 8 Å domain size for **4% H₂-PIM-1-CMS** corresponds to a 3 or more phenyl ring width across the nanoribbon, while the 18 Å domain size for **PIM-1-CMS** has >7 phenyl rings across the nanoribbon. It is also possible that the obtained domain sizes may have underestimated the full nanoribbon width due to defects in the nanoribbon structure.

The combination of gas sorption and structural analyses offers new insight into the nature of the microporous structures of **PIM-1-CMS** and **4% H₂-PIM-1-CMS**. The pore size distribution analysis from CO₂ isotherms reveals **PIM-1-CMS** to have an ultramicropore size distribution of 3.4 – 3.6 Å, 3.9 – 4.3 Å, and 5.3 – 6.0 Å. For **4% H₂-PIM-1-CMS**, pore size distribution analysis of CO₂ and N₂ sorption consistently suggest an ultramicropore size distribution of 5.3 – 6.9 Å and 5.5 – 6.8 Å, respectively. The CO₂

sorption was able to reveal smaller ultramicropore size distribution at 3.4 – 4.3 Å in **4% H₂-PIM-1-CMS**, which was not accessible to the cryogenic nitrogen.

Taking the gas sorption, neutron total scattering, and small-angle X-ray scattering studies together, the structural finding discussed here on both PIM-1-derived CMS materials corroborate previously hypothesized microstructure and transport property studies for other CMS materials. Based on the gas sorption studies, H₂ pyrolysis resulted in consistent increases in the CMS pore size, supporting the increased permeation rates of p-xylene observed in prior work [18]. The smaller PSD formation in inert atmosphere pyrolysis can be explained by the denser packing of graphenic nanoribbons, which correlates with the observation of longer-range order in the nPDF. Moreover, the SAXS results corroborate this by suggesting a more densely packed plate-like lamellae structure in the **PIM-1 CMS** sample. These findings are also in agreement with the X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) measurements on these materials [18]. In Ma et. al.'s work, XRD experiments provide information on the *d*-spacing of the **PIM-1-CMS** and **4% H₂-PIM-1-CMS** materials. The XRD *d*-spacing of the CMS is obtained from a broad reflection due to inefficient packing of the neighboring carbon planes. The *d*-spacing obtained from the center position of broad reflections represents the average inter-planar distance between the carbon layers. The XRD *d*-spacing values of **PIM-1-CMS** and **4% H₂-PIM-1-CMS** are 3.83 Å and 3.91 Å, respectively, which shows an increase in the inter-planar distance with the presence of 4% H₂ in the pyrolysis atmosphere. Such findings qualitatively suggest the increased free volume due to less dense packing, in agreement with the PSD, nPDF, and SAXS measurements conducted in this work. Prior FTIR measurements show that the **4% H₂-PIM-1-CMS** displays higher peak

intensities of the characteristic peaks of PIM-1 precursor than **PIM-1-CMS** does, which suggests the CMS pyrolyzed under H₂ exhibits a more polymer-like or random coil structure. This supports the hypothesis that the formation of a more amorphous and randomly packed structure occurs in the presence of hydrogen gas during pyrolysis. SAXS suggests that **4% H₂-PIM-1-CMS** has rod-like structural features, that is, polymeric-like structures whose paths do not overlap. Such observation supports an image of less densely packed graphenic nanoribbons, which further agree with the less defined nPDF longer-range order. Thus, **4% H₂-PIM-1-CMS** carbon structures are less dense and generally more disordered than those obtained under inert conditions.

Based on the C-H bond concentration and the refined domain size obtained from the nPDF analysis, the ultramicropore size distribution from the CO₂ physisorption studies, and the SAXS analysis, we propose a hypothetical microstructure for PIM-1-derived CMS that is consistent with qualitative structures found in the literature (Figure 4. 9). The proposed structure for **4% H₂-PIM-1-CMS** would possess 'skinny' aromatic carbon nanoribbons in agreement with the refined domain size of 8 Å. The snake strands are 3 phenyl rings across. These graphenic nanoribbons could be laid out in "snake"-like orientation, where the stacked strands from the original structure [11] (Figure 4. 1c) are connected and exist as the continuation of the graphene-like strands. The self-avoidance of the chain/ribbon, in plane, gives rise to the ultramicropores, which are found to be ~4 Å in this model, consistent with gas sorption studies. The gaps between the parallel strands of the "snake" structure act as a precisely defined ultramicropores of CMS that enhances size-selective separation performance. Based on the SAXS results where the **4% H₂-PIM-1-CMS** displays platelet-like structures (at longer length scales than those probed with nPDF)

with rod-like features, we hypothesize the "skinny" graphenic nanoribbons (a rod-like feature) to be oriented in a platelet-like structure in 2 dimension as shown in Figure 4. 9a. Moreover, based on the nPDF peak at 3.6 Å, which indicates interlayer spacing between round surfaces, the proposed structure of the platelet-like structure exhibits 3-dimensional curvature and bends (Figure 4. 9b). During pyrolysis, these nanoribbons can stack non-uniformly and could potentially inter-weave/be interleaved with other nanoribbons. The curved neighboring graphenic nanoribbons contribute to the non-uniform and turbostratic packing structure, which is detected as the nPDF peak at 3.6 Å. The gaps between these curved platelets could form the micropores detected in physisorption, which act as large sorption sites that enhances permeation in the membrane. The *d*-spacing at 3.91 Å obtained from the broad XRD peak of **4% H₂ PIM-1-CMS** would exist as a range of other interlayer spacing between graphenic nanoribbons that exist in its amorphous structure. Moreover, we hypothesize that the suggested structure of curved 'snake'-shaped graphenic nanoribbons would occupy a significant portion of the CMS structure, along with a distribution of shorter 'orphan' strands, as proposed by Sanyal et. al.[13] (Figure 4. 1d and Figure 4. 9d).

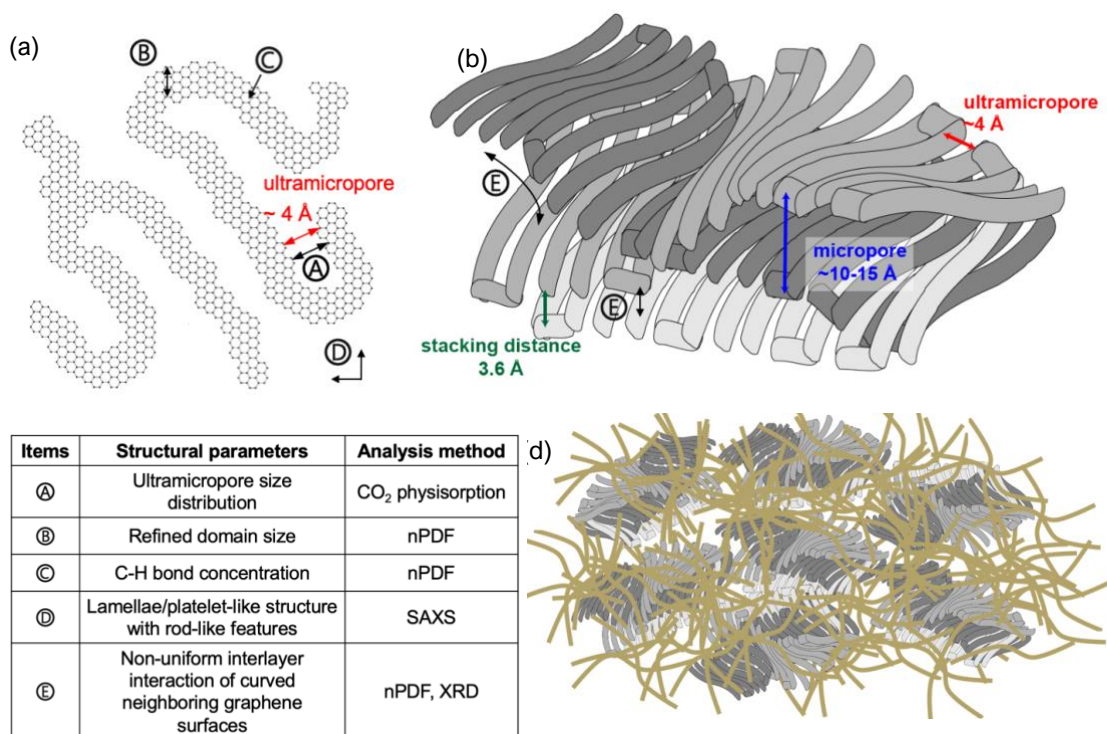


Figure 4. 9. Speculated microstructure of disrupted carbon plates that result in the creation of ultramicropores in CMS. (a) 2-dimensional schematic of the proposed carbon “snake” structure of 4% H₂-PIM-1-CMS. The slit within the “snake” forms ultramicropores. The hydrogens attached to the carbon “snake” are not indicated in the figure, but the estimated ultramicropore size of 4 Å is accounting for the hydrogens. A single chain is drawn for simplicity, but such structures could also be formed by smaller chain fragments, as hypothesized by Koros et al. (b) 3-dimensional schematic of the proposed carbon “snake” plates randomly intercalated and imperfectly packed to form micropores. The proposed figure is a simplified sketch of how the proposed “snake” plates would pack with other strands. The actual structure would consist of denser packing and the figure is not drawn to scale. (c) a table of structural source information used to propose the hypothetical structure in (a) and (b) and the corresponding analysis method used for each parameter. (d) Schematic of multiple units of packed/entangled ‘snake’-shaped graphenic nanoribbons that compose micropores and ultramicropores (drawn in grey). The graphenic nanoribbon units are enclosed by a continuous phase of randomly dispersed graphenic nanoribbon strands (drawn in gold) (FTIR [18] and SAXS).

In comparison, the **PIM-1-CMS** would have wider graphenic strands with a refined domain size of 18 Å. The proposed structure also agrees with the characteristic features of **PIM-1-CMS** and **4% H₂-PIM-1-CMS**. The more curvature on the 'skinny snake' structure of **4% H₂-PIM-1-CMS** results in more imperfect stacking that is reflected in the lower density from SAXS analysis. The slightly smaller XRD *d*-spacing of 3.83 Å can also be interpreted as the most frequent interlayer spacing smaller than in **4% H₂-PIM-1-CMS** due to more closely packed nanoribbons in an inert pyrolysis atmosphere. The lower packing density explains the higher xylene isomers permeability observed in **4% H₂-PIM-1-CMS** compared to **PIM-1-CMS** [7,18].

4.4 Summary and Conclusions

A fundamental question around CMS materials is how these structures with no apparent order seemingly, paradoxically, possess well-defined and interconnected pores. Given the pyrolysis conditions and the consistency of the polymer precursor, there is a limited set of structural descriptors likely to be afforded by the product (i.e., aromatic C, H, N). Although non-crystalline, we hypothesize that structural motifs must persist throughout the entire CMS material.

Gas sorption and neutron total scattering studies were utilized to derive structural properties that were not revealed by the standard characterization techniques such as N₂ physisorption and XRD. The carbon dioxide isotherm revealed the ultramicropore size distribution of **PIM-1-CMS** (3.4-3.6, 3.9-4.3, and 5.3-6.0 Å) that was not accessible by N₂ physisorption. Despite the use of the HK method, the neon isotherm was also able to report a similar PSD of **PIM-1-CMS** and showed its potential as a probe molecule to study

ultramicroporous structures. The scattering data and SAXS data revealed that the **4% H₂-PIM-1-CMS** has a more amorphous and loosely packed structure compared to **PIM-1-CMS**, which is in agreement with the membrane performance on xylene isomer separation where the **4% H₂- PIM-1-CMS** showed higher permeability with slightly compromised selectivity [18]. The PDF and the textural analysis were combined to postulate a potential microstructure for CMS, exhibiting graphenic nanoribbons where the ribbon's self-avoidance gives rise to ultramicroporous slits. These strands pack irregularly via disordered π - π interactions and interweave to form micropores dispersed among orphan strands.

Although a clear picture on the CMS microstructure remains elusive, we have combined structural characterization and textural analysis to impart a cohesive interpretation of what ultramicropores may look like at the molecular level.

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CHAPTER 5. UNDERSTANDING THE TRANSPORT MECHANISM OF WATER AND P-XYLENE IN PVDF DERIVED CMS MEMBRANES

This chapter discusses the transport studies of water and p-xylene in PVDF-derived CMS membranes using sorption-diffusion model. This chapter is adapted from ‘Y.H. Yoon, R.P. Lively, Co-transport of water and p-xylene through carbon molecular sieve membranes. *Journal of Membrane Science* **654**, 120495 (2022).’

5.1 Introduction

The separation of miscible water and organic solvents is a common separation challenge in industrial applications. Applications include purification of produced water [1], recovery of homogeneous catalysts from water-organic reaction systems [2], and water removal from black liquor [3]. Benzene, toluene, ethyl-benzene, and xylenes (BTEX) are water-soluble aromatic hydrocarbons commonly found in contaminated or distressed water streams [4]. The BTEX compounds are volatile and toxic, making them one of the most significant contributors to hazardous pollution from produced water. In this study, p-xylene was investigated as an exemplar for a small aromatic organic solvents (e.g., BTEX) contaminant commonly found in industrial wastewater [5].

Here, we investigate membrane-based separation of miscible water-organic mixtures. The low concentration of dissolved organics in water (for instance, up to ~ 35 ppm (mol) of p-xylene dissolves in water at 298.14 K) [6] is technologically and economically challenging to separate due to the relatively low value of the purified

products. Membrane separation can operate at a steady-state, which results in easier process control and increased productivity. Moreover, the minimal usage of chemicals and negligible thermal energy requirements improve process safety, potentially enabling cost-effective separation of water and organic mixture. Moreover, there is the possibility of obtaining high purity organic products.

Carbon molecular sieves (CMS) are carbonaceous materials with a rigid and amorphous microporous structure. The CMS material is derived from a polymeric precursor -typically a linear polymer - that undergoes high-temperature pyrolysis to produce an almost-pure carbon material [7]. The proposed structure of the resulting carbon material is composed of sp^2 -hybridized carbon layers stacked in parallel, forming two-dimensional carbon sheets. The non-equilibrium packing imperfection in between the sheets form micropores (7-20 Å), and the slits in between the sp^2 -hybridized carbon layers form ultramicropores (<7 Å) (Figure 5. 1). Such a pore structure can be idealized as slit-like pores (Figure 5. 1b) with a bimodal pore size distribution. The ultramicropores provide high selectivity, while the larger micropores provide abundant sorption sites, leading to high permeability [8]. The polymer precursor of CMS is processible, enabling the creation of CMS membrane materials in commercially-relevant form factors such as hollow fiber membranes [9–12]. This study uses poly(vinylidene fluoride) (PVDF) as a polymeric precursor of the CMS. PVDF is widely used as a polymeric membrane for ultrafiltration and microfiltration due to its chemical resistance, mechanical strength, and high hydrophobicity. Compared to other common polymers for membranes such as polyimides or PIMs, PVDF is advantageous for its cost-effectiveness and commercial availability. In this work, dense film PVDF-derived CMS (PVDF-CMS) membranes were fabricated by

knife casting, crosslinking, and pyrolysis (Figure 5. 2). After film casting, the PVDF films were crosslinked by a one-pot crosslinking method as a pre-treatment to maintain their morphology during pyrolysis [9]. Upon dehydrofluorination, PVDF will form C-C double bonds via a Michael-addition reaction with the diamine crosslinker. These crosslinked PVDF films were pyrolyzed to form CMS membranes that serve as the focus of this work.

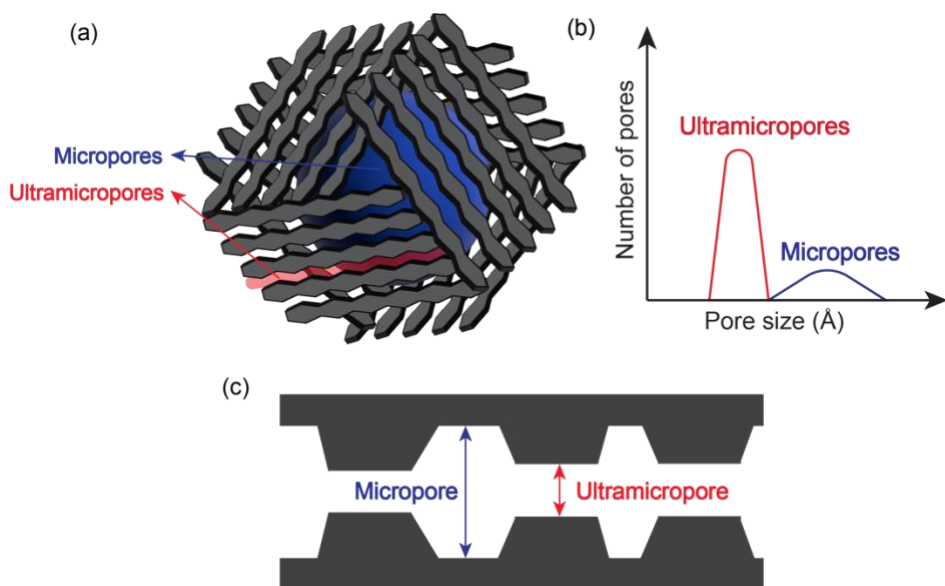


Figure 5. 1. Hypothetical structure of CMS. (a) Proposed structure of CMS membranes with a turbostratic arrangement of sp^2 -hybridized carbon sheets. (b) Bimodal distribution of CMS pores. (c) Hypothetical representation of the slit-like CMS microstructure with small ultramicropores and larger micropores. Copyrights with permission from Elsevier [13].

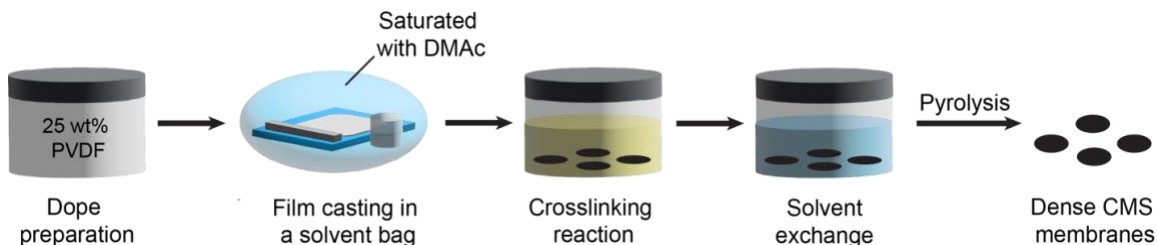


Figure 5. 2. Schematic diagram of dense PVDF-CMS membrane fabrication procedure

Here, we evaluate the transport mechanism of water and organic solvents in CMS by experimentally studying fundamental transport properties, such as sorption, diffusion, and permeation. This study aims to understand the transport mechanism of water and p-xylene molecules in microporous membranes, where the selective pore sizes (5.5-6.0 Å) approach the size of the moving molecules (kinetic diameter of water: 2.65 Å, kinetic diameter of p-xylene: 5.85 Å).

5.2 Characterization of PVDF derived CMS membranes

The PVDF-CMS membranes were characterized using N₂ physisorption (Figure 5. 3) and XRD (Figure 5. 4) to interrogate their textural and structural features. The pore size distribution was analyzed using N₂ physisorption isotherms and revealed that the PVDF-CMS exhibits a multi-modal pore size distribution. The membranes exhibit two ultramicroporous pore sizes (5.5-6.0 Å and 6.4-6.9 Å) and one larger micropore centered around 12 Å. The arrangement of these various pores is challenging to determine, but we hypothesize that the ultramicropore/micropore cellular structure discussed extensively by Koros and coworkers exists in these CMS membranes [8,14]. This cellular structure suggests that the guest species jump from microporous spaces via ultramicroporous windows. These windows provide the size and shape selectivity for many similarly-sized guest species.

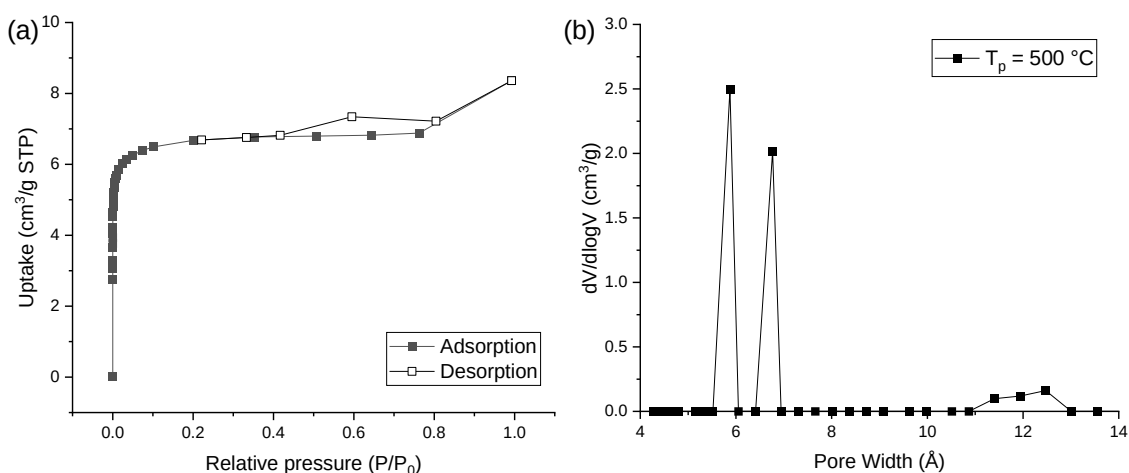


Figure 5. 3. PVDF-CMS structural studies using a cryogenic N₂ physisorption. a) N₂ isotherm in PVDF-CMS at 77 K. b) 2D-NLDFT pore size distributions calculated from cryogenic N₂ physisorption data of PVDF-CMS pyrolyzed at $T_p = 500$ °C.

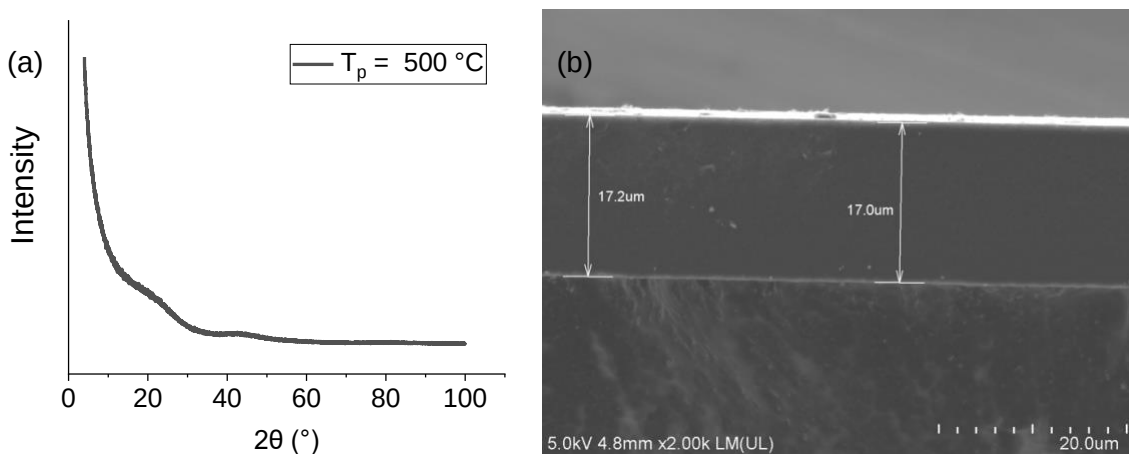


Figure 5. 4. Structural characterization on PVDF-CMS. (a) Wide-angle X-ray diffraction patterns of PVDF-CMS dense, flat membranes at $T_p = 500$ °C. (b) SEM image of a PVDF-CMS membrane cross-section.

Similar to the diffraction patterns previously reported for PVDF-CMS [9], the XRD pattern of the PVDF-CMS in Figure 5. 4 shows broad reflections around 23° and 44°, which highlights the amorphous carbon structures of CMS. The broad XRD peaks represent the center-to-center interplanar distance between carbon sheets and are not equivalent to the

pore size of CMS because the slit-like pores of CMS are formed by the random packing of the sp²-hybridized carbon sheets. Using Bragg's law, the d-spacing values of 0.380 nm and 0.210 nm are revealed, and the second d-spacing confirms the partial presence of ordered graphitic structures formed in the fabricated CMS [15].

5.3 Sorption studies on CMS membranes

The sorption behavior of water and p-xylene in PVDF-CMS membranes was investigated using experimental vapor sorption isotherms measured at various temperatures (35, 45, and 55 °C). The effective membrane area for gravimetric sorption experiments is ~ 6 cm², which is around 16 µg of CMS membrane samples for each experiment. Each experiment for isotherms and kinetic uptake curves was reproduced 2-3 times with different films produced from a different batch of polymer dopes that undergo independent crosslinking reaction and pyrolysis under the same condition.

Water sorption in PVDF-CMS was found to follow Type III isotherms according to Brunauer–Deming–Deming–Teller (BDDT) classifications (Figure 5. 5a) [16]. A type III isotherm is typically found for water sorption in non-hydrophilic carbon materials. The low water sorption in the low-activity region indicates the weak interaction between the sorbate (water) and the non-hydrophilic sorbent (CMS). As the uptake increases, sorbate-sorbate interactions begin to dominate due to the already-adsorbed water molecules and thus result in the formation of water clusters, resulting in the rapid increase in the uptake at a higher activity [17]. We find that the adsorption behavior of water in CMS is well-correlated using a Freundlich model $\left(\theta = \frac{q}{q_{\text{sat}}} = \frac{K}{q_{\text{sat}}} \cdot p^{\frac{1}{n}} \right)$ and is distinct from that of p-

xylene in CMS, which is described using a Langmuir isotherm $\left(\theta = \frac{q}{q^{\text{sat}}} = \frac{bp}{1+bp}\right)$. A Langmuir isotherm is commonly observed for organic solvents in microporous materials [9,13].

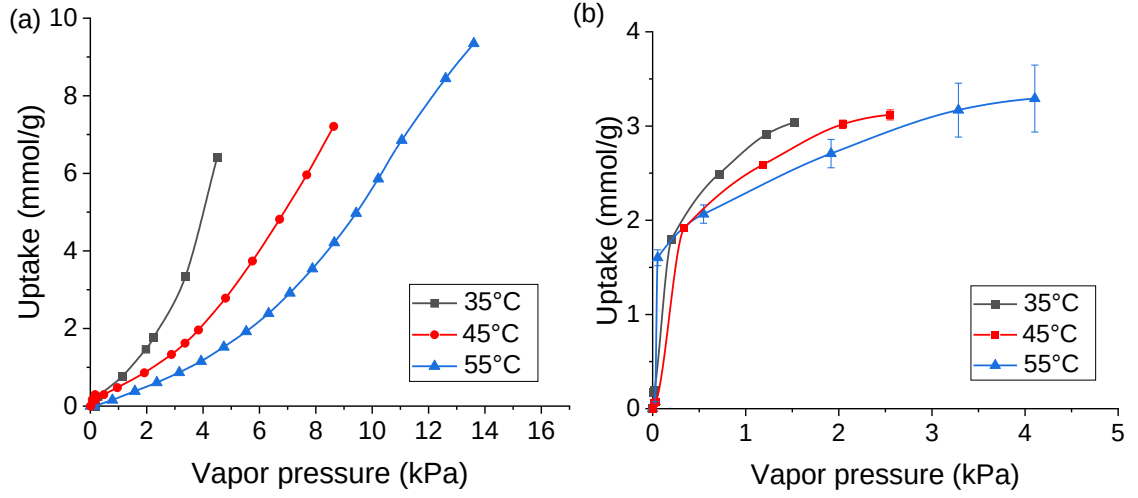


Figure 5. 5. Vapor sorption isotherms on PVDF-CMS using gravimetric vapor sorption experiment. (a) Water and (b) p-xylene sorption isotherm on PVDF-CMS at 35, 45, and 55 °C

Using the Freundlich equation to model the water isotherm, the water sorption coefficient S_w was calculated using equation (Eq. (5- 1)) [18,19]:

$$S_w = \frac{\rho_{\text{CMS}} \cdot n}{p^{\text{up}} - p^{\text{down}}} \left(K \cdot p^{\text{up}\frac{1}{n}} - K \cdot p^{\text{down}\frac{1}{n}} \right) \quad (5- 1)$$

where K and n are the empirical constants in the Freundlich equation and are dependent on adsorbates, adsorbents, and temperature; ρ_{CMS} is the density of the CMS membranes, approximated as 2.0 g/cm³ [9,13]. p^{up} and p^{down} are the vapor pressure on the membrane upstream and downstream.

The p-xylene sorption coefficient equation (Eq. (5- 2)) was also derived similarly, viz. [13]:

$$S_{pX} = \frac{\rho_{CMS} \cdot q^{sat}}{p^{upstream} - p^{downstream}} \ln \left(\frac{1 - \theta^{downstream^{sat}}}{1 - \theta^{upstream^{sat}}} \right) \quad (5- 2)$$

Assumptions of the upstream activity of 1 and the downstream activity of 0 were used to represent the experimental conditions in the Wicke-Kallenbach apparatus.

The sorption coefficients were obtained for water and p-xylene at various temperatures (35 – 55 °C) and are shown in Table 5. 1. These coefficients follow a Van't Hoff's relationship, as shown in Figure 5. 6a, such that the integral heat of sorption could be generated (Table 5. 1). p-Xylene ($-34.8 \pm 1.91 \text{ kJ/mol}$) was found to have a lower integral heat of sorption than water ($-30.0 \pm 8.17 \text{ kJ/mol}$). Moreover, the integral sorption coefficients of water are lower than that of p-xylene at all temperatures investigated, showing that water has a lower adsorption affinity to CMS. CMS is conceptually an all-carbon material and would display a non-polar environment within the micropores and thus likely have a higher affinity to non-polar p-xylene than to polar water molecules.

The integral heat of sorption of p-xylene in PVDF-CMS was compared with the integral heats of sorption of p-xylene in other microporous materials reported. The integral heat of sorption of p-xylene in PIM-1-CMS is -45 kJ/mol [13], and in MFI-type zeolite is -71 kJ/mol [20,21]. The hypothesis on why the sorption of p-xylene in PVDF-CMS has less affinity than in other microporous materials includes that the PVDF-CMS may have more non-carbon materials remaining (such as H, N, or F) on the pore surface, which does

not attract non-polar p-xylene [22]. Also, the pore size of PVDF-CMS (ultramicro pore size of 5.5 - 6.0 Å and larger micropore centered around 12 Å) [13] is larger compared to the PIM-1 CMS (pore size not accessible by N₂ physisorption) and MFI-type zeolite (5.1 - 5.6 Å) [20,21]. The larger pore size of the PVDF-CMS compared to PIM-1-CMS (not measurable by N₂ physisorption) and MFI-type zeolite can cause decreased affinity for adsorption, as the strong adsorption at micropores is induced by the overlap of force fields from opposite pore walls. McEnaney [23] has calculated the adsorption potential for slit-shaped carbon pores. This previous study showed that the maximum adsorption potential was observed from pores with a pore radius equivalent to the collision radius of the adsorbates. In those calculations, a decrease in adsorption potential was observed as the pore radius increased relative to the collision radius of the adsorbates.

Table 5. 1. Sorption properties of water and p-xylene in PVDF-CMS

	$\Delta \hat{H}_s \left(\frac{\text{kJ}}{\text{mol}} \right)$	$S \left(\frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}} \right)$			$\left(\frac{S_{\text{p-xylene}}}{S_{\text{water}}} \right)$		
		35 °C	45 °C	55 °C	35 °C	45 °C	55 °C
water	-30.0±8.17	1.94±0.12	1.09±0.05	0.92±0.04	4.20±0.28	4.63±0.20	3.76±0.19
p-xylene	-34.8±1.91	8.16±0.11	5.07±0.01	3.48±0.07			

To highlight the importance of the activity gradient in the estimation of the heat of sorption, water sorption in PVDF-CMS was further analyzed via calculation of the isosteric heat of adsorption with respect to the adsorption uptake amount (Figure 5. 6a). The lower isosteric heat of sorption at low water activities indicates the sorption is less thermodynamically spontaneous (but still spontaneous), likely as a result of weak interactions between water and non-hydrophilic CMS [24]. As the adsorption amount increases, the physisorbed water molecules facilitate clustering of water molecules using

stronger water-water interactions, which is supported by the increase in heats of adsorption at increasing uptakes. The general trend of isosteric heat of adsorption is similar to the water uptake in highly hydrophobic MFI-type zeolites [24]. PVDF-CMS shows a less steep increase of the heat of sorption, which indicates less hydrophobic characteristics potentially due to remaining -N (2.2 wt% [9], potentially left from the diamine crosslinker) and -F elements that may not have fully decomposed from the crosslinked polymeric precursor during pyrolysis. Furthermore, the enthalpy of water sorption in PVDF-CMS does not converge to the heat of condensation of water (44.0 kJ/mol at 25 °C; 42.7 kJ/mol at 55 °C). We hypothesize that water adsorption in PVDF-CMS at high activities involves both CMS-water and water-water interactions, but we cannot further support this hypothesis using the existing experimental data set.

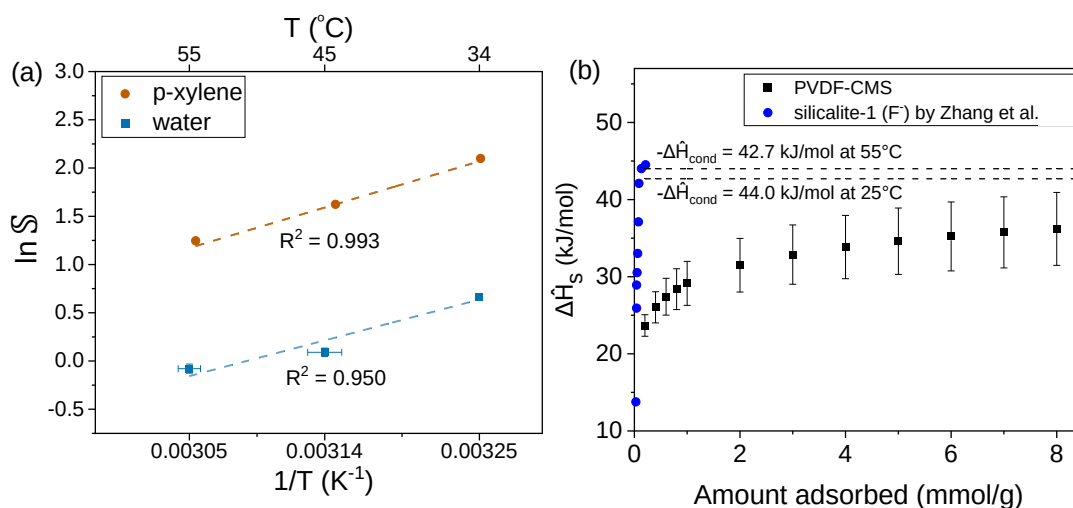


Figure 5. 6. Sorption behavior of water and p-xylene on PVDF-CMS. (a) Temperature dependence of the sorption coefficients of water and p-xylene in PVDF-CMS from 35 to 55 °C. The sorption coefficients (mol m⁻³ Pa⁻¹) were derived using an activity gradient of 1.0 on the membrane upstream and 0.0 on the downstream. (b) Isosteric enthalpy of sorption of water in PVDF-CMS and hydrophobic MFI-type zeolite silicalite-1 (F⁻) [24]. The sorption enthalpies are all negative and are plotted in absolute values.

5.4 Diffusion studies on CMS membranes

The p-xylene M-S diffusivity in PVDF-CMS was found to decrease with increasing p-xylene loading (Figure 5. 7). This is a common observation that is reminiscent of the so-called “strong confinement” diffusion case [25]. Therefore, the p-xylene M-S diffusion coefficients at zero-loading were approximated by linearly extrapolating the two lowest relative pressures measured (35 and 60 %) that passed the two criteria explained in the Experimental section. The water transport diffusion coefficients at zero-loading were approximated to be equivalent to that obtained at 20 % relative humidity. This is a reasonable assumption due to the type III water isotherm on CMS, which exhibits less than 10% loading at 20% relative humidity. The transport diffusion coefficients at zero-loading $D(0)$ is equivalent to the Maxwell-Stefan diffusion coefficients at zero loading $\bar{D}(0)$. Water M-S diffusivity was assumed to be constant at different loadings in CMS and $\bar{D}(0)$ was used as $\bar{D}$. $\bar{D}(0)$ of p-xylene was also used as $\bar{D}$ to simplify the sorption diffusion analysis. The temperature dependence of diffusion was fit using an Arrhenius activated diffusion relationship, and the activation energy for diffusion (E_D) were determined (Figure 5. 8, Table 5. 2).

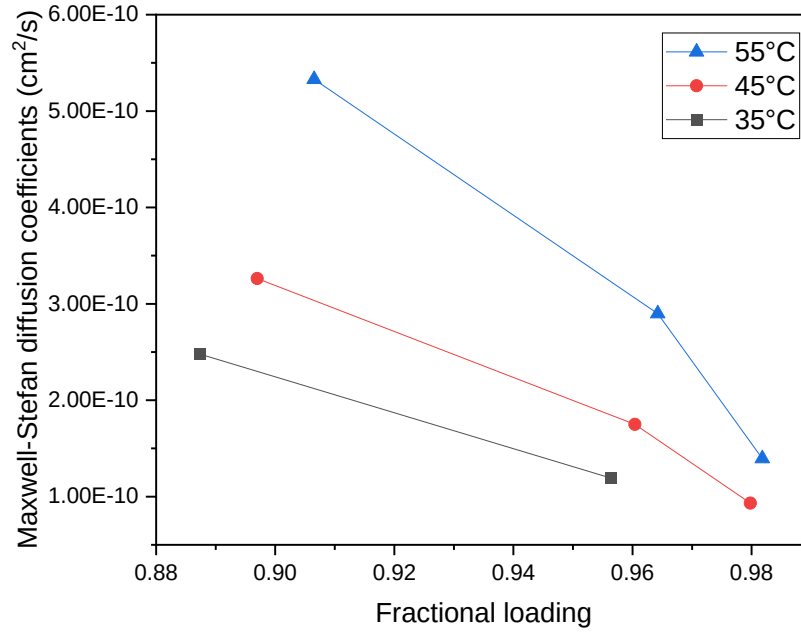


Figure 5. 7. Maxwell-Stefan diffusion coefficients of p-xylene at different fractional loadings. M-S diffusion coefficients decrease with the increase in fractional loading.

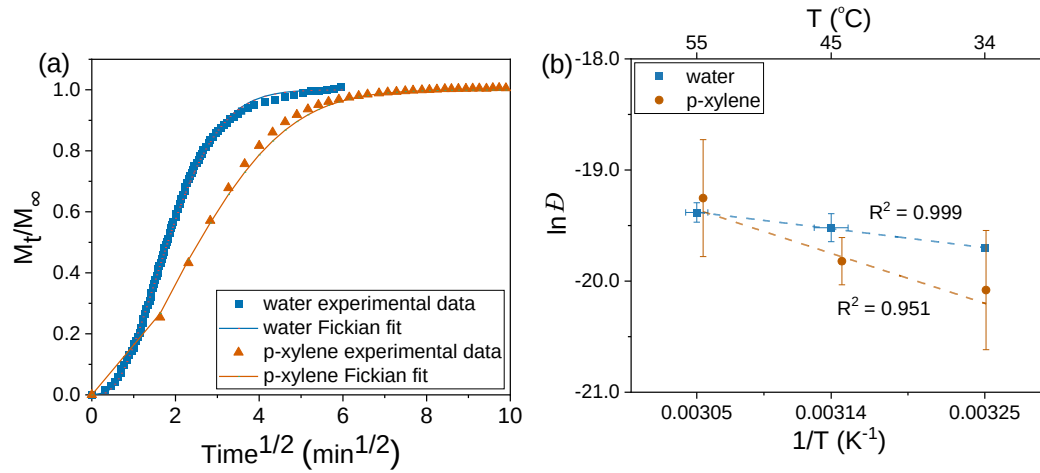


Figure 5. 8. (a) Kinetic sorption curve of water and p-xylene in PVDF-CMS at 35 °C. The solid line is the Fickian fit (Eq. (5- 3)) to the experimental data (points). (b) Temperature dependence of the Maxwell-Stefan diffusivity of water and p-xylene in PVDF-CMS from 35 to 55 °C.

$$\frac{M_t}{M_\infty} = 1 - \exp(-\beta t) \left(\frac{D}{\beta \ell^2} \right)^{\frac{1}{2}} \tan \left(\frac{\beta \ell^2}{D} \right)^{\frac{1}{2}} - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp \left(-\frac{(2n+1)^2 \pi^2 D t}{4 \ell^2} \right)}{(2n+1)^2 \left[1 - (2n+1)^2 \left\{ \frac{D \pi^2}{(4 \beta \ell^2)} \right\} \right]} \quad (5-3)$$

Table 5. 2. Diffusion properties of water and p-xylene in PVDF-CMS

	$E_D \left(\frac{\text{kJ}}{\text{mol}} \right)$	$D_o \left(\frac{\text{cm}^2}{\text{s}} \right)$	$D \left(10^{-9} \frac{\text{cm}^2}{\text{s}} \right)$			
			35 °C	45 °C	55 °C	
water	12.7±1.19	4.07×10^{-7}	2.79±0.01	3.33±0.42	3.83±0.33	
p-xylene	33.7±7.61	9.58×10^{-4}	1.90±1.02	2.47±0.52	4.35±2.29	
	$\frac{D_{o,w}}{D_{o,pX}}$	4.24×10^{-4}	$\frac{D_w}{D_{pX}}$	1.47±0.79	1.35±0.33	0.88±0.47

The activation energy of diffusion is the energy required for molecules to make diffusive jumps through the membrane, and we hypothesize that the dominant resistance to these molecular jumps is across the selective ultramicropore passages. The activation energy of p-xylene (33.7±7.61 kJ/mol) is greater than the activation energy of water (12.7±1.19 kJ/mol), indicating that the p-xylene molecules require more energy to make the activated diffusive jump across the CMS membrane, which is consistent with typical size-based diffusion separations. It is important to note that the p-xylene activation energy of diffusion is approximated as the extrapolated value at zero loading, and the water activation energy of diffusion at zero loading is approximated with the diffusion at less than 10 % loading.

We observed that the activation energy for the diffusion of water in PVDF-CMS (12.7±1.19 kJ/mol) is lower than the activation energy of diffusion in water-water systems

(18 kJ/mol) [26]. The activation energy for the diffusion of water in CMS is the energy required to make the activated jump through the ultramicropores. In contrast, the activation energy for self-diffusion in water is composed of the activation energy to form a vacancy and the activation energy to move the vacancy. We hypothesize that at the conditions used to estimate the activation energy of diffusion in CMS (very low loadings of water in the CMS membranes) the diffusing water molecule has less guest-guest interactions and thus a lower activation energy of diffusion relative to water molecules in the liquid state. However, we cannot distinguish such differences in guest molecular dynamics using our current experimental protocols. Moreover, even for self-diffusion, it is possible to have lower activation energy in a microporous solid than in a bulk liquid. The activation energy is lower when the interaction potential is very uniform along the pore walls and when the molecules mostly move along the pore walls such as water in carbon nanotubes [27,28].

Despite the significant difference in the activation energies of diffusion, water exhibits diffusion selectivity of 0.9-1.5 at a range of temperatures over p-xylene.

5.5 Permeation studies on CMS membranes

5.5.1 Prediction of pure component permeability based on sorption-diffusion model and comparison to experimental permeabilities.

Based on our hypothesis that the water transport in CMS occurs via the sorption-diffusion model, water permeability in PVDF-CMS was estimated in Table 5. 3 using the S-D model with the experimental parameters in Table 5. 1 and Table 5. 2 as inputs. We compare our S-D estimates (based on experimental parameters) with experimental permeation results, as shown in Figure 5. 9 and Table 5. 3.

The S-D modeled permselectivities possess similar values within a 2-3 fold to the experimental pure component permselectivity data, supporting our hypothesis that these molecules transport via the S-D mechanism. The ideal permselectivities of p-xylene over water are greater than 1 at all temperatures for both S-D and experiments. Our analysis suggests that the ideal permselectivity is sorption dominated, as the sorption selectivity of p-xylene over water is greater than 1, and the diffusion selectivity of p-xylene over water is close to 1.

This is further underscored by our estimates of the activation energy of permeation acquired from the S-D model (Table 5. 3), which are estimated by the addition of the sorption enthalpy and activation energies of diffusion (Eq. (5- 4)). The activation energy estimated using the S-D model for water was found to be negative (-18.0 ± 8.25 kJ/mol), which was validated from experimental measurements (-5.71 ± 1.00 kJ/mol) of the activation energy of permeation. The S-D modeled activation energy for permeation of p-xylene was found to be a small negative value (-1.12 ± 7.84 kJ/mol) near zero. The experimentally measured activation energy for permeation of p-xylene revealed a positive value (14.2 ± 2.38 kJ/mol).

The negative activation energy of water permeation indicates that sorption controls the permeation process, and the positive activation energy of p-xylene permeation indicates that diffusion controls p-xylene permeation. This is in agreement with recent publications that report kinetically-controlled transport of xylene isomers in PIM-1 derived CMS [13]. It is interesting to note the different transport behavior in organic solvents in CMS compared to the transport of organics in polymers, which generally exhibits sorption-dominated transport [29,30]. The fact that the permeation of water is controlled by sorption

is likely a result of both the low affinity of water to CMS and the minor diffusion limitation of water molecules in the ultramicropores of CMS. Meanwhile, the kinetic diameter of p-xylene is close to the limiting ultramicropore size of the CMS membranes, thus driving up the activation energy of diffusion of p-xylene relative to water to the point that p-xylene permeation is controlled by diffusion.

$$E_{\text{p}} = E_{\text{D}} + \Delta\hat{H}_{\text{S}} \quad (5-4)$$

Although the permselectivities are in good agreement between the S-D model and the experimental permeation results, we find statistically significant deviations in the permeation rates and the activation energies of permeation for both water and p-xylene. Interestingly, both p-xylene and water are observed to have ~8x higher permeation rates than those estimated via the S-D model. Also, both demonstrates more positive activation energies of permeation in experiments than the S-D estimation. There are a variety of potential reasons for this discrepancy. The S-D model calculation includes a series of measurements and calculation which imputes compounding errors in the final estimation. The M-S diffusion coefficient at zero loading was used throughout the model calculation, despite the loading gradient in membranes during permeation. Moreover, the diffusion coefficient at zero loading was estimated with the best assumptions for both p-xylene and water.

Table 5. 3.Permeability properties of water and p-xylene in PVDF-CMS of (1) pure S-D model calculated permeabilities, (2) pure WK measured permeabilities, and (3) mixture WK measured permeabilities. Unit activity feed and zero activity on the downstream.

		$E_{\mathbb{P}}$ $\left(\frac{\text{kJ}}{\text{mol}}\right)$	$\mathbb{P}\left(10^{-12}\frac{\text{mol}\cdot\text{m}}{\text{m}^2\cdot\text{s}\cdot\text{Pa}}\right)$			$\left(\alpha_{\frac{\text{p-xylene}}{\text{water}}}\right)$		
			35 °C	45 °C	55 °C	35 °C	45 °C	55 °C
(1)	water	-18.0±8.25	0.54±0.0	0.37±0.0	0.35±0.0			
Pure S-D			3	5	3	2.87±1.5	3.43±0.8	4.28±2.2
calculated	<i>p</i> -xylene	-1.12±7.84	1.55±0.8	1.25±0.2	1.51±0.8	5	6	9
			3	7	0			
			$\mathbb{P}\left(10^{-12}\frac{\text{mol}\cdot\text{m}}{\text{m}^2\cdot\text{s}\cdot\text{Pa}}\right),$ (Temperature, °C)			$\left(\alpha_{\frac{\text{p-xylene}}{\text{water}}}\right),$ (Temperature, °C)		
(2)	water	-5.71±1.00	4.47±0.2	4.25±0.4	4.05±0.2			
Pure WK			2 (40)	2 (45)	1 (54)		1.68±0.10	2.09±0.11
measured	<i>p</i> -xylene	14.2±2.38	7.01±0.0	7.13±0.0	8.47±0.0	-	(45)	(54)
			4 (42)	8 (45)	7 (54)			
(3)	water	11.6±0.70	2.19±0.1	2.30±0.0	2.58±0.3			
Mixture			0 (42)	3 (45)	7 (54)	5.67±0.40	5.37±0.23	4.65±0.80
WK	<i>p</i> -xylene	-2.53±0.43	12.4±0.6	12.4±0.5	12.0±1.1	(42)	(45)	(54)
measured			5 (42)	1 (45)	5 (54)			

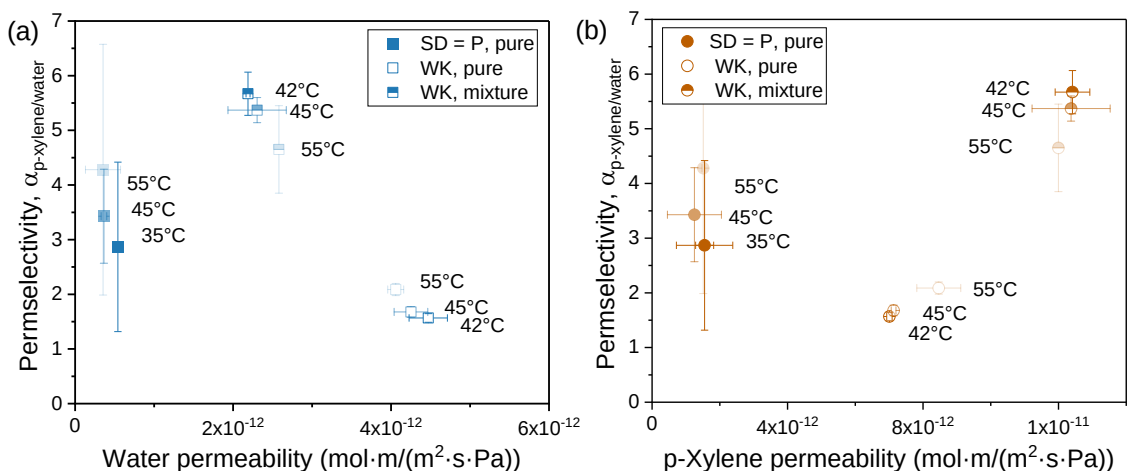


Figure 5. 9. Permeability versus permeability plots at change in temperatures. Permeability and permselectivity of water (a) and p-xylene (b) are modelled using S-D (solid symbol), and measured in pure component WK (empty symbol) and mixture component WK (half-filled symbol) experiments. The gradient in color signifies the change in temperature and it gets lighter as the temperature increases.

5.5.2 Comparison of pure component permeability with the mixture permeability

As we are ultimately interested in the transport of water and p-xylene mixtures, we explored the relative permeation rates of water and p-xylene vapors at unit activity (i.e., $p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^{\text{sat}} = 1$, $p_{\text{pX}}/p_{\text{pX}}^{\text{sat}} = 1$) through the CMS membranes. The permeation experiment result at different temperatures of (42, 45, and 55°C) are provided in Table 5. 3.

An interesting observation was made in the mixture setting: the p-xylene permeability was improved while the water permeability was hindered compared to the pure component permeation. The permselectivity of p-xylene/water was also improved relative to pure component permeation estimates and S-D model estimates. This result provides some evidence for a competitive sorption-selective separation of p-xylene over water. We hypothesize that the p-xylene competitively adsorbs to the micropores of CMS and hinders the sorption and the subsequent transport of water. It is likely that water has

difficulty accessing the microporous system to the same extent found in the pure water permeation case, as the p-xylene has a strong affinity for the CMS and forms a “liquid-like” adsorbed fluid within the micropores. As p-xylene and water liquids are immiscible outside of the dilute regimes, this liquid-like adsorbed fluid could partially exclude water from the microporous regions (Figure 5. 10).

The 1.4-1.8x increase in the permeability of p-xylene relative to the pure component case is at first an odd observation. Although the permeability of p-xylene is higher than water, the diffusion coefficient of water is still almost certainly higher than p-xylene even in the mixture case. We speculate that the p-xylene diffusion coefficient is increased in the presence of water via mutual diffusion effects. Mutual diffusion correlations such as the Vignes correlation highlight this effect, viz.,

$$D_{\text{pX-H}_2\text{O}} \cdot \mu_{\text{mix}} = (D_{\text{pX}}(0) \cdot \mu_{\text{H}_2\text{O}})^{x_{\text{H}_2\text{O}}} \cdot (D_{\text{H}_2\text{O}}(0) \cdot \mu_{\text{pX}})^{x_{\text{pX}}} \cdot \left[1 + \frac{\partial \ln \gamma_{\text{pX}}}{\partial \ln x_{\text{pX}}} \right] \quad (5-5)$$

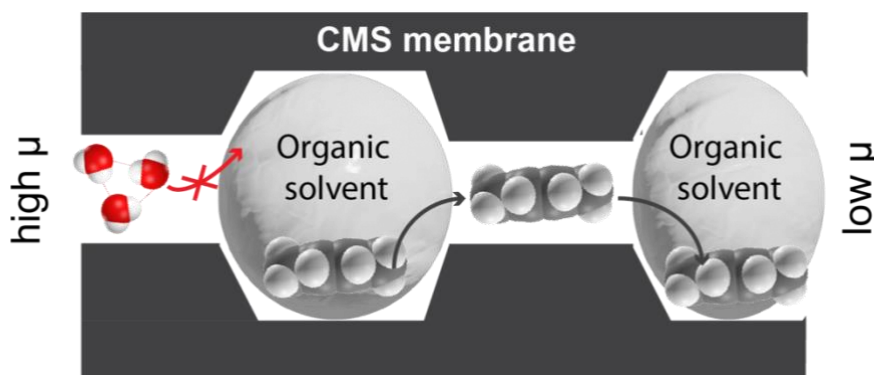


Figure 5. 10. Schematic hypothesis of water and p-xylene mixture transport in CMS. p-Xylene competitively adsorbs to CMS micropores that limits the diffusional transport of water clusters.

The sorbed-phase mole fractions of water and p-xylene as well as the sorbed phase activity coefficients are difficult to determine in these complex mixtures, but the increases in p-xylene permeabilities observed are consistent with this effect using reasonable estimates for the unknown parameters.

Moreover, an Ideal Adsorbed Solution Theory (IAST) [31] calculation was conducted as a proof-of-concept analysis for the binary mixture adsorption (Figure 5. 11). Sorption selectivities were calculated as $selectivity_{1/2} = (x_1/x_2)/(y_1/y_2)$, where x is an adsorbed phase mole fraction and y is a gas phase mole fraction. Sorption selectivities were calculated at a mole ratio of 0.01:0.99 = p-xylene:water and the selectivities of water/p-xylene and p-xylene/water is reported in Figure 5. 11a and b, respectively. Despite the probable violation of the ideal gas assumption of the IAST calculation, the competitive sorption of p-xylene over water was estimated to exhibit enhanced p-xylene sorption selectivity over water in mixture.

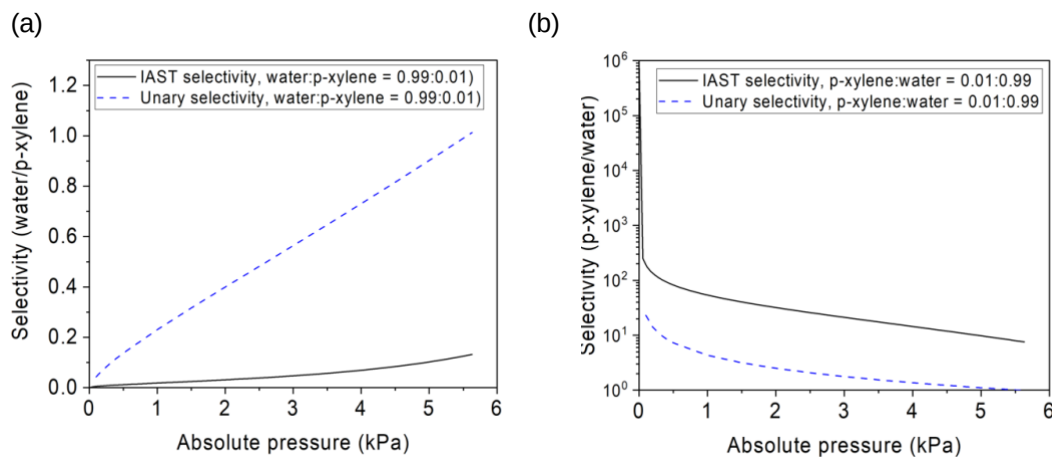


Figure 5. 11. Ideal adsorbed solution theory calculated sorption selectivity for p-xylene and water mixture at molar ratio of p-xylene:water = 0.01:0.99 at 35°C

Another interesting observation is found in the activation energy of permeation in mixture compared to that in the pure system. In the pure component permeation, the permeability of water decreases and the permeability of p-xylene increases as the temperature increases (Figure 5. 9). The trend reverses in a mixture, as the water permeability in the mixture increases and p-xylene permeability in the mixture decreases with temperature. This is also shown by the reversed sign of the activation energy of permeation of water and p-xylene in mixture (Table 5. 3). Based on the S-D model, the water transport in the mixture exhibits diffusion-controlled movement, and the p-xylene transport in the mixture is sorption-controlled. We suggest that the competitive sorption of p-xylene over water is the limiting step that the transport of p-xylene in the mixture is controlled by sorption. Also, we postulate that the competitively adsorbed p-xylene blocks the diffusion passage of water clusters such that the transport of water in the mixture is limited by diffusion (Figure 5. 10).

5.5.3 Speculation on water and p-xylene separation in CMS membranes in a pervaporation modality

Although the primary research aim of this study is to understand the transport mechanism of water and organic molecules in CMS, the separation performance of water and p-xylene mixture in our CMS was compared against a literature report by Jian et al., who used a PVDF hollow fiber (HF) membrane [32]. Jian and coworkers reported that the PVDF HF membranes operated in a pervaporation set up with a dilute 120 ppm of benzene in the aqueous feed stream resulting in a separation factor up to 1834 (Table 5. 4). The separation factor for mixture unit activity of p-xylene/water separation in PVDF-CMS in WK is only 3.1. However, in pervaporation, the separation factor is composed of a

separation factor from a thermodynamic vapor-liquid equilibrium and a separation factor from the membrane (Eq. (5- 6)) [33]. Due to the high activity coefficient of infinitely dilute benzene in water ($\gamma_{\text{benzene}}^{\infty} \sim 25000$) [34], the VLE separation factor for benzene in water is very high, thus providing a large VLE thermodynamic factor to the separation factors observed by Jian et al. We removed this thermodynamic factor to more accurately compare the contributions of the membranes. This analysis shows that the PVDF-CMS exhibits much higher permselectivity of p-xylene/water than benzene/water in polymeric PVDF HF (Table 5. 4).

Table 5. 4. Comparison of vapor permeation water-p-xylene separation in PVDF-CMS with pervaporation water-benzene separation in PVDF hollow fiber membranes

Membrane, separation system	Organic component	Feed concentration	Temperature (°C)	Separation factor, β	Permselectivity, $\alpha_{\text{organic/water}}$
PVDF-CMS, vapor permeation	p-xylene	Unit mixture activity	45	3.1	4.9
PVDF hollow fiber[32], pervaporation	benzene	120 ppm	25	1834	0.16*

*Permselectivity was calculated based on the reported results.[32]

The p-xylene activities will be very low in practical xylene-contaminated water. We expect that the p-xylene sorption amount at low p-xylene activity will be similar to that of higher activities because the p-xylene follows a relatively sharp Langmuir isotherm (Figure 5. 5b), with high uptake achieved at low fugacity. Moreover, an Ideal Adsorbed Solution Theory (IAST) [31] calculation (Figure 5. 11) for a 0.01:0.99 mole ratio of p-xylene:water mixture, predicts that the competitive sorption selectivity towards p-xylene will increase at a dilute concentration of p-xylene in water. Thus, the removal of dilute

organic solvent from aqueous solutions via a pervaporative CMS membrane would likely be an energy efficient approach, as the small amount of organic solvent would permeate out as phase-changed vapors and the large volume of purified liquid water would be collected in the retentate.

$$\beta_{\text{pervap}} = \beta_{\text{evaporation}} \times \beta_{\text{membrane}} = \frac{\text{ratio in feed vapor}}{\text{ratio in feed liquid}} \times \frac{\text{ratio in permeate vapor}}{\text{ratio in feed vapor}} \quad (5-6)$$

5.6 Summary and Conclusions

This work investigates the potential of using CMS membranes as high-performance membranes for miscible water and organic solvent separation (i.e., dilute organics in water). While CMS has been widely studied for gas and organic solvent separations, water separation in CMS membranes is rarely demonstrated. This work presents the potential of CMS membranes for water/organic separations as organic-permeable membranes. The transport fundamentals of water and p-xylene, as an example common organic solvent found in industrial wastewater, was studied in polyvinylidene fluoride (PVDF) derived CMS to understand and control the use of the CMS membrane for this complex class of separations. The transport mechanism of water and p-xylene were both explained using the sorption-diffusion (S-D) model, which matched reasonably well with experimental permeabilities. The S-D model and pure component permeation experiments reveal that p-xylene is selective over water due to the sorption selectivities. The mixture permeation

experiments demonstrated an increase in the selectivity of p-xylene over water, presenting preliminary evidence for a competitive sorption-selective separation mechanism.

It is important to identify some critical limitations to this study. The key limitations include that the water transport diffusivity at zero-loading to obtain the Maxwell-Stefan (M-S) diffusivity was measured at 20 % relative humidity. Water loading of <10% fractional occupancy was used instead of the ideal zero-loading due to experimental difficulties associated with ultra-low relative humidities. This can impart error on the permeability estimated via the S-D model. Moreover, the use of Freundlich's equation for the measured water isotherm does not follow the mathematical expression that the Fickian (transport) diffusivity at zero loading is equal to the M-S diffusivity ($D = \bar{D} \times n$). Therefore, the Fickian diffusivity at 20 % relative humidity was assumed to be closed to the diffusivity at zero loading, and was also assumed to be close to the M-S diffusivity at zero loading. Also, the permeability estimated via the S-D model is obtained from the extrapolated values at unit activity to model the experimental permeation tested in the unit activity. Furthermore, the study utilized macroscopic methods to measure diffusion. Microscopic methods are needed, especially with the existence of hyperskin [35] in CMS that controls permeation.

The mixture vapor permeation experiment revealed greater separation performance than the pure component permeation studies predicted. We hypothesized that the higher separation performance of the mixture is due to the competitive sorption-selective separation mechanism, which can be further studied in the future. Finally, the potential to use the PVDF-CMS as a hollow fiber membrane in pervaporation setup has been proposed

to effectively remove the dilute p-xylene from water to enable high recoveries of product water.

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CHAPTER 6. STRUCTURE-TRANSPORT RELATIONSHIPS OF WATER-ORGANIC SOLVENT CO-TRANSPORT IN CARBON MOLECULAR SIEVE (CMS) MEMBRANES

This chapter discusses the transport of water and p-xylene in PIM-1-derived and PVDF-derived CMS membranes that possess various pore size distributions and surface chemistry. The structure-transport relationship of water-organic solvent transport in CMS membranes will be discussed.

6.1 Introduction

CMS materials are is amorphous and carbonaceous material with a rigid microporous structure derived from a pyrolyzed polymeric precursor. A microstructural development hypothesis for CMS materials has been proposed by Koros et al. to describe the precisely controlled bimodal pore size distribution in the amorphous carbon material [1,2]. According to this hypothesis, the CMS pyrolysis typically involves three steps: 1) ramping, 2) soaking, and 3) cooling. During the first stage, the CMS structure formation mechanism proposed by Koros et al. [1,2] explains that the polymer precursor undergoes fragmentation and aromatization, thus forming rigid and aromatized “strands.” These short strands exhibit mobility at pyrolysis temperatures and imperfectly align in parallel to create imperfect “plates.” During the soaking and cooling steps, these plates further assemble into imperfect microporous “cell” structures. The neighboring cells then merge, forming a repeating pattern of micropore cells with ultramicroporous slit walls. Moreover, a recent study on CMS derived from polyimide has introduced a new structural feature called

“orphan strands,” [2] which form a minority continuous network of disordered ultramicropores located between the microporous cells. Another recent hypothesis on PIM-1 derived CMS structure [3] proposes a similar hypothetical structure that comprises sp^2 hybridized carbon nanoribbons oriented to form two-dimensional curved carbon sheet layers. The imperfect packing and weaving between these curved layers create micropores, and the slits between the nanoribbons, which compose the carbonaceous plane, become ultramicropores.

The CMS pore structures can be visualized as slit-like pores with bimodal pore size distribution. The bimodal pore structure offers a unique combination of high selectivity from the ultramicropores and high permeability from the abundant sorption sites in the larger micropores. The processibility of the polymer precursor makes it possible for the CMS membranes to be manufactured in commercially relevant forms, including hollow fiber membranes. In this study, a polymer of intrinsic microporosity-1 (PIM-1) is utilized as the polymeric precursor. PIM-1 was chosen as the polymer precursor as the PIM-1-derived CMS has been successfully fabricated into hollow fiber membranes for liquid separation [4,5] and also has shown its versatility in adjusting the microstructure by adjustments in the pyrolysis atmosphere [5].

In Chapter 5 [6], the transport of water and p-xylene in polyvinylidene fluoride (PVDF)-derived CMS was investigated using a sorption-diffusion (SD) transport model. Sorption and diffusion coefficients were experimentally measured from a gravimetric sorption experiment, and permeabilities were calculated using the SD model with appropriate driving forces. Experimental permeabilities were then measured in a Wicke Kallenbach (WK) vapor permeation system and were compared to the calculated values,

which suggested that water and p-xylene transport in PVDF-derived CMS follows the SD mechanism. Despite the molecular size difference between water (2.6 Å) and p-xylene (5.8 Å), the PVDF-CMS membranes were more selective towards p-xylene due to sorption selectivity and behaved as organic concentrating membranes in water-organic separation.

This chapter investigates the structure-transport relationship of water-p-xylene transport in CMS materials. First, we controlled the pore size distributions of PIM-1-derived CMS membranes at a molecular size level by adjusting the pyrolysis condition. Then, the transport properties were examined using the SD model. The sorption and diffusion coefficients of water in PIM-1 derived CMS are examined, and the SD-modeled permeability is tested against the experimental permeability. Furthermore, the structure-transport relationship was examined by conducting the vapor permeation experiments of water and p-xylene in various CMS membranes. The membrane performance and the activation energies for permeation are investigated to understand the structure-transport relationship of water and p-xylene co-transport in various pore size distributions of CMS.

6.2 Fabrication of CMS membranes with various pore size distribution

The CMS samples were pyrolyzed in various gas atmospheres and at different maximum pyrolysis temperatures, as reported in detail in Chapter 3, Table 3.1. The fabricated CMS samples are named in this work as **[precursor]_[pyrolysis atmosphere]_[final temperature in °C]_CMS**.

6.3 Characterization of various CMS membranes

The ultramicropores and micropores below 10 Å of various CMS samples were examined by carbon dioxide physisorption at 273 K up to 1 bar ($P/P^{\text{sat}} = 0.3$) to study the microporous structure below 10 Å. The CMS microstructure was tailored by adjusting the 1) polymer precursor, 2) pyrolysis atmosphere, 3) the final pyrolysis temperature (T_p), and 4) the pyrolysis temperature profile. First, the polymer precursor was varied between PIM-1 and PVDF. Secondly, different pyrolysis atmospheres were utilized, including Ar, 4% H₂ balanced with Ar, and CO₂. Thirdly, the final pyrolysis temperatures of 500 and 800 °C were tested. Lastly, the pyrolysis temperature profile was varied by eliminating the 2-hour hold step. These adjustments allowed for a systematic exploration of the CMS microstructure and its dependence on the parameters of interest.

Figure 6. 1a and Table 6. 1 shows the CO₂ uptake (kinetic diameter = 3.3 Å) in the microporous volumes within the CMS samples at 273 K. The **PIM-1_Ar_500_CMS** shows the lowest microporous volume, followed by **PIM-1_4% H₂_500_CMS**, **PIM-1_CO₂_500_CMS**, **PVDF_Ar_500_CMS**, **PIM-1_CO₂_800_no_hold_CMS**, **PVDF_CO₂_500_CMS**, and **PIM-1_CO₂_800_CMS**. First, the PIM-1-derived CMSs that are pyrolyzed under different conditions were compared. By introducing the 4% H₂ in the pyrolysis atmosphere, the **PIM-1_4% H₂_500_CMS** shows increased micropore volume, as observed in previous studies [3,5]. PIM-1 derived CMS pyrolyzed under CO₂ at the same pyrolysis temperature of 500 °C shows a similar micropore volume as 4% H₂ pyrolysis; both are a significant increase relative to Ar pyrolysis at the same pyrolysis temperature. The PIM-1-derived CMS pyrolysis under CO₂ was also conducted at an elevated temperature of 800 °C, which led to ~40 % increase in micropore volume at $P/P^{\text{sat}} = 0.03$ compared to CMS pyrolyzed under CO₂ at $T_p = 500$ °C. This is an interesting

observation, as the increase in pyrolysis temperature under an inert Ar environment on polyimide or PIM-1 precursors has shown more tightly packed CMS structures in both micropores and ultramicropores [5,7]. Moreover, the PIM-1-derived CMS pyrolysis under CO₂ at 800 °C was conducted with no hold (**PIM-1_CO₂_no hold_800_CMS**), to understand the effect of the hold step in pyrolysis. It showed a decreased micropore volume compared to **PIM-1_CO₂_800_CMS**.

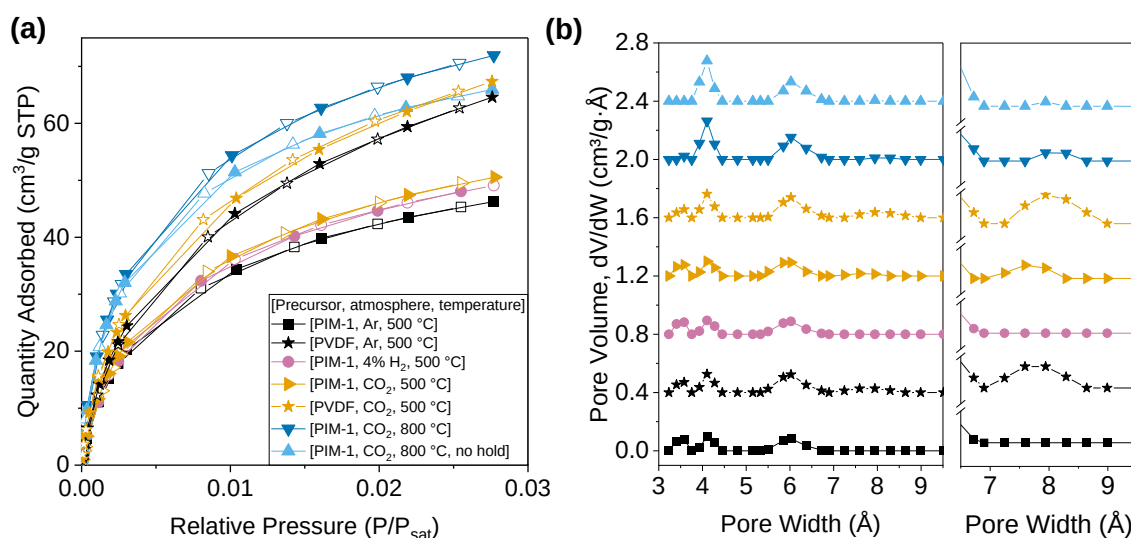


Figure 6. 1. a) Carbon dioxide isotherms on various CMS materials measured at 273 K. Solid symbols are adsorption points, and hollow symbols are desorption points. b) The pore size distribution in the microporous region using 2D-NLDFT.

Table 6. 1. Micropore volumes of various CMS materials measured from CO₂ isotherms at 273K. The CO₂ isotherms are measured up to $P/P^{\text{sat}} < 0.03$, which has uptakes in pore sizes $< 10 \text{ \AA}$.

	Micropore volume (cm ³ /g stp) < 10 Å
PIM-1_Ar_500_CMS	46.3
PIM-1_4% H₂_500_CMS	49.1
PIM-1_CO₂_500_CMS	50.6
PIM-1_CO₂_800_CMS	71.9
PIM-1_CO₂_no hold_800_CMS	66.0
PVDF_Ar_500_CMS	64.6
PVDF_CO₂_500_CMS	67.4

A pore size distribution analysis was conducted using the CO₂ isotherms at 273 K and HS-2D-NLDFT calculation (Figure 6. 1b and Table 6. 2). The **PIM-1_Ar_500_CMS** exhibits the smallest pore volume distribution in ultramicropores in 3.4 – 4.3 Å and 5.3 – 6.7 Å. The **PIM-1_4% H₂_500_CMS** shows similar pore size distribution in 3.4 – 4.3 Å and 5.3 – 6.7 Å but with slightly increased ultramicroporous volume. **PIM-1_CO₂_500_CMS** shows similar pore size distribution in 3.4 – 4.3 Å and 5.3 – 6.4 Å but also exhibits larger micropores in the 7.2 – 7.9 Å range. The **PIM-1_CO₂_800_CMS** and **PIM-1_CO₂_no hold_800_CMS** show increased ultramicropore sizes (3.9 – 4.3 Å) and an increased pore volume in this size range, compared to **PIM-1_CO₂_500_CMS**. Their ultramicropore size distributions above 5 Å are also increased to 5.8 – 6.7 Å, as well as the increase in their total pore volume. The main difference between the CMS pyrolyzed with hold step and no hold is the existence of micropores above 7 Å. The **PIM-1_CMS_CO₂_800** showed the highest uptake in the micropore region ($> 7 \text{ \AA}$) among the PIM-1-derived CMS. On the other hand, the **PIM-1_CO₂_no hold_800** exhibited negligible

micropores in the 7-10 Å range. Such observations align with the hypothetical structural development where the graphenic carbon strands/nanoribbons align in platelet-like orientations, which imperfectly pack to form micropores. The elimination of the hold step in pyrolysis likely resulted in a less ordered arrangement that prevents the formation of micropores within the CMS.

The PIM-1-derived CMSs fabricated in this work were compared with the PVDF-derived CMS. PVDF-derived CMS was pyrolyzed under Ar at 500 °C (**PVDF_Ar_500_CMS**, which was previously studied in Chapter 5 [6]), and under CO₂ at 500 °C (**PVDF_CO₂_500_CMS**). PVDF-derived CMSs show larger micropore volume than the PIM-1-derived CMSs pyrolyzed in the same pyrolysis conditions of inert argon or carbon dioxide environment at $T_p = 500$ °C. Both PVDF-derived CMSs show the ultramicropore sizes distribution is in 3.4 – 4.3 Å and 5.5 – 6.7 Å, comparable to the PIM-1-derived CMSs. The **PVDF_Ar_500_CMS** shows micropore size in the 7.2 – 8.3 Å range, and **PVDF_CO₂_500_CMS** in 7.6 – 8.6 Å, which are in larger volumes compared to the micropores in PIM-1-derived CMS.

Table 6. 2. Pore size distribution of various CMS materials in the microporous region < 10 Å using CO₂ isotherms at 273K and 2D-NLDFT.

Pore Width (Å)	Pore Volume, dV/dW (cm ³ /g·Å)						
	PIM-1_ Ar_ 500_ CMS	PIM-1_ 4% H ₂ _ 500_ CMS	PIM-1_ CO ₂ _ 500_ CMS	PIM-1_ CO ₂ _ 800_ CMS	PIM-1_ CO ₂ _no hold_ 800_ CMS	PVDF_ Ar_ 500_ CMS	PVDF_ CO ₂ _ 500_ CM
3-4 Å	0.167	0.175	0.166	0.134	0.132	0.161	0.148
4-5 Å	0.150	0.151	0.158	0.370	0.364	0.192	0.239
5-6 Å	0.081	0.095	0.120	0.092	0.071	0.129	0.111
6-7 Å	0.122	0.129	0.124	0.244	0.215	0.188	0.215
7-8 Å	0	0	0.037	0.010	0.005	0.067	0.059
8-9 Å	0	0	0	0.010	0	0.014	0.045
9-10 Å	0	0	0	0	0	0	0

Overall, the gas physisorption experiments suggest that the ultramicropore and micropore size distributions of CMS are tailorable by varying the precursor and the pyrolysis condition. Compared to the conventional Ar pyrolysis, the pyrolysis atmosphere of 4% H₂ induces increased ultramicroporous volume, and CO₂ also causes an increase in the ultramicropore and the micropore volume. The increase in pyrolysis temperature under a CO₂ environment also results in increased ultramicropore and micropore volume. The hold step at maximum pyrolysis temperature seems to play a role in the structural arrangement of micropores. In general, the PVDF-derived CMS shows higher microporous volume compared to the PIM-1-derived CMS.

The chemical compositions of different CMS samples were examined using XPS survey scans. The XPS data (Figure 6. 2) were collected from CMS powder samples, which are ground from dense CMS films. Therefore, the collected chemical composition should represent the average composition of the membrane material. The PIM-1-derived CMS showed an increase in carbon element percentage at a higher pyrolysis temperature of 800

°C, explained by the higher degradation and carbonization at the higher temperature. Moreover, the PVDF-derived CMSs showed a distinct fluorine composition that is likely a residual from the PVDF precursor.

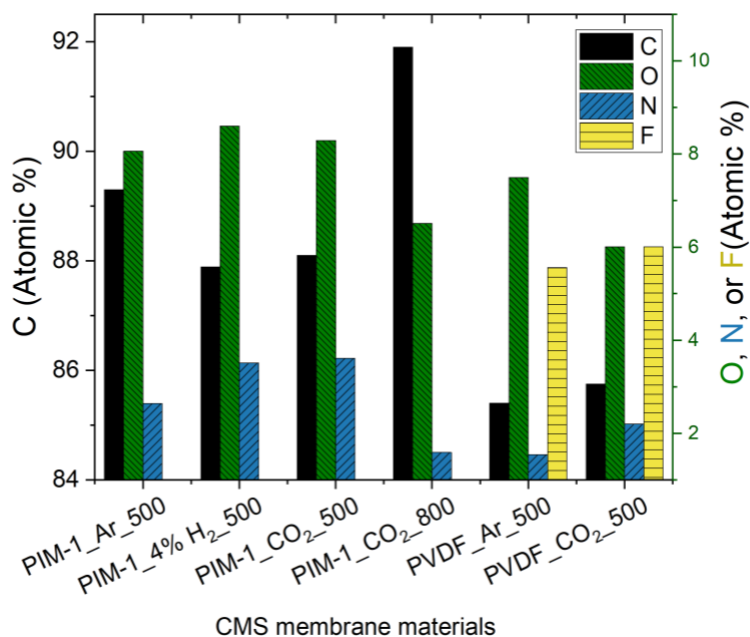


Figure 6. 2 Carbon, oxygen, nitrogen, and fluorine atomic composition in PIM-1- and PVDF-derived CMS powders obtained from XPS Survey scans.

The **PIM-1_4% H₂_500_CMS**, **PIM-1_CO₂_800_CMS**, and **PIM-1_CO₂_no hold_800_CMS** were further studied to investigate the transport behaviors of water and p-xylene in various CMS structures. Pure water and p-xylene vapor isotherms were obtained at 35 °C on various PIM-1 derived CMS dense films, including **PIM-1_4% H₂_500_CMS**, **PIM-1_CO₂_800_CMS**, and **PIM-1_CO₂_no hold_800_CMS** (Figure 6. 3). Then the isotherms were compared to the water and p-xylene isotherms for **PVDF_Ar_500_CMS** obtained from Chapter 5 [6]. The vapor uptakes from 5 to 75 % relative pressure were obtained using the automated gravimetric vapor sorption instrument (VTI SA+, TA

instrument), and the water uptakes at unit activity were obtained by soaking the dense CMS film membranes in liquid water. The unit activity water uptake was used to estimate the p-xylene uptakes at unit activity, assuming that the pores are fully occupied by the liquid adsorbates and that the adsorbates will exhibit liquid-like densities within the micropores.

A distinct difference in the water isotherms was observed between PVDF-derived CMS and PIM-1-derived CMS. **PVDF_Ar_500_CMS** exhibits a distinct Type 3 isotherm according to Brunauer–Deming–Deming–Teller (BDDT) classifications [8,9]. Type 3 isotherms are commonly observed for water adsorbing onto non-hydrophilic materials. The low uptake at low relative humidity shows the weak interaction between the water adsorbates and the non-hydrophilic sorbents. As the activity increases, the uptake of adsorbates increases due to increasing adsorbate-adsorbate interaction with the already-adsorbed water molecules and forming water clusters in the sorbent material [10]. On the other hand, the PIM-1-derived CMS materials do not exhibit such a concave-shaped isotherm, suggesting stronger interactions between the water adsorbates and the CMS materials. We speculate that the non-hydrophilic property of the PVDF-derived CMS is due to the remaining fluorine from the PVDF precursor, as observed from the XPS scans (Figure 6. 2). The p-xylene vapor isotherms on both CMS materials show similar Langmuir-type isotherms, commonly observed for organic components adsorbing to microporous material.

A distinct difference is observed where the PIM-1-derived CMS shows significantly lower p-xylene uptakes than the **PVDF_Ar_500_CMS**. Such difference can be attributed to the less pore volume available for the liquid adsorbents in the PIM-1 derived CMS.

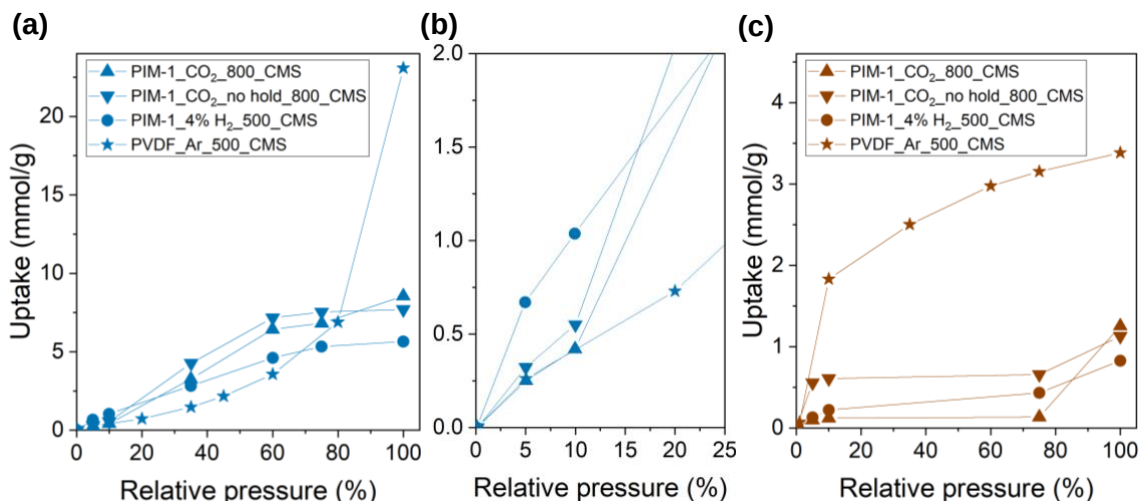


Figure 6. 3. Water (blue) and p-xylene (brown) vapor isotherms in the range of (a) 0 to 0.75 activity and (b) 0 to 0.2 activity on PIM-1 derived CMS dense films using gravimetric vapor sorption at 35 °C. The unit activity uptakes were obtained from a liquid water-soaking experiment. The isotherms for PVDF_Ar_500_CMS were adapted from [6].

6.4 Sorption-diffusion transport study of water on PIM-1 derived CMS membrane

The transport of water and p-xylene in **PVDF_Ar_500_CMS** has been investigated in previous work [6] and was shown to approximately follow the SD model. Moreover, the transport of p-xylene in PIM-1 derived CMS in **PIM-1_Ar_500_CMS** and **PIM-1_4% H₂_500_CMS** has also been shown to closely follow the SD model [5,11]. Here, to study if the transport of water follows the SD model in PIM-1-derived CMS, the sorption coefficient (S) and the Maxwell-Stefan diffusivity ($\bar{D}$) as the diffusion coefficient was derived from gravimetric vapor sorption experiments.

The transport properties of water in **PIM-1_4% H₂_500_CMS** were experimentally obtained. The gravimetric water vapor sorption experiment was conducted on a dense film **PIM-1_4% H₂_500_CMS** samples (Figure 6. 4, Table 6. 3). For simplicity, the water isotherm on **PIM-1_4% H₂_500_CMS** was modeled using a cubic

polynomial equation, $\theta = \frac{q}{q^{\text{sat}}} = a \cdot p^3 + b \cdot p^2 + c \cdot p + d$ (Figure 6. 4a). θ is a fractional uptake, q is an uptake (mmol/g), q^{sat} is a saturated uptake (mmol/g) at saturated pressure, and p is a partial pressure (kPa). An expression for the sorption coefficient was derived as (Eq. (6- 1)). The detailed derivation of the sorption coefficient expression is provided in Chapter 2.

$$\mathbb{S} = \frac{(\rho_{\text{CMS}} \Gamma q^{\text{sat}} \nabla \theta) \cdot \ell}{p^{\text{up}} - p^{\text{down}}} \quad (6- 1)$$

ρ_{CMS} is the density of the CMS membranes, approximated as 2.0 g/cm³ [11,12]. Γ is the thermodynamic correction factor, ℓ is the thickness of the membrane, p^{up} and p^{down} are the vapor pressure on the membrane upstream and downstream. The experimental upstream and downstream activities obtained from the pure component WK vapor permeation ($a_{\text{water}}^{\text{upstream}} = 0.85$ and $a_{\text{water}}^{\text{downstream}} = 0.21$) were utilized in the estimation of the sorption coefficients. The sorption coefficient of water in **PIM-1 _4% H₂_500_CMS** was calculated as $2.8 \frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}$.

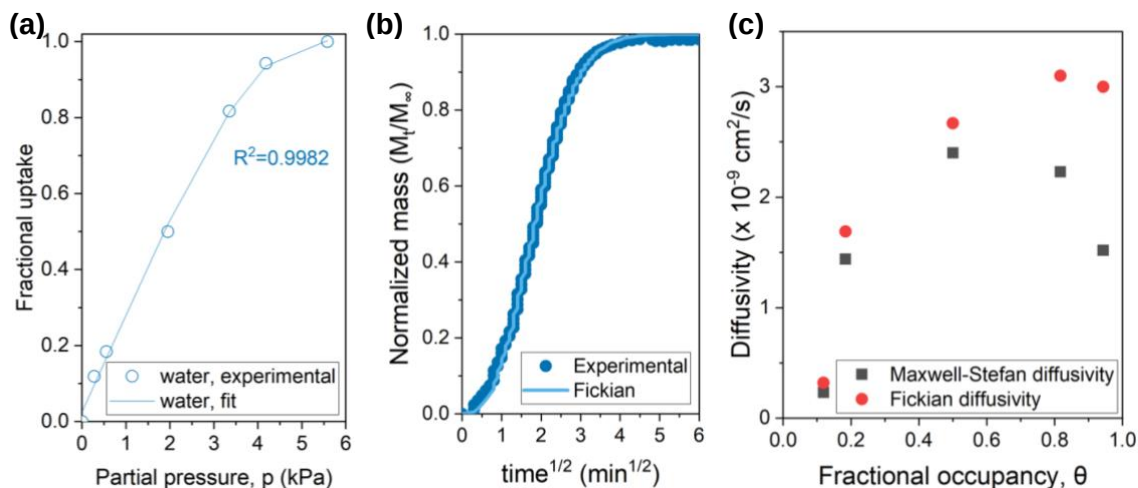


Figure 6. 4. Vapor sorption isotherms of water on PIM-1_4% H₂_500_CMS. The experimental data are represented as circle points, while the cubic polynomial modeled fit is depicted by the line plots. b) Transient uptake curve of water on PIM-1_4% H₂_500_CMS at an activity of 0.6. c) Maxwell-Stefan diffusivity and Fickian diffusivity of water on PIM-1_4% H₂_500_CMS with respect to the fractional occupancy of guest loading. All the water uptakes were measured at 35 °C.

The diffusion coefficient of water was obtained based on the kinetic sorption curve in Figure 6. 4b. The transport diffusivities were obtained by fitting the transient curves to the Fickian transport equation (Eq. (6- 2)) at different sorbate loadings. Then the Fickian diffusivities were thermodynamically corrected (Eq. (6- 3)) to obtain the MS diffusivities. The MS diffusivity at a water activity of 0.53 was used in the SD model calculation to represent the experimental conditions in the WK permeation apparatus, where the upstream and downstream of the membrane activities were averaged. The MS diffusivity at an activity of 0.53 was interpolated from the MS diffusivity at an activity of 0.35 and 0.6 (Figure 6. 4a and b). This is a current limitation of our work, as we do not have a full understanding of the guest loading gradient within the membrane. Thus we resort to using an MS diffusivity at a fractional occupancy that we feel is representative when averaged over the length of the membrane, assuming that the guest loading gradient is linear across

the membrane. The diffusion coefficients, D , of water in **PIM-1_4% H₂_500_CMS** were derived as $2.3 \times 10^{-9} \frac{\text{cm}^2}{\text{s}}$. The diffusion coefficient of water in **PIM-1_4% H₂_500_CMS** is comparable to that in **PVDF_Ar_500_CMS**, $2.8 \times 10^{-9} \frac{\text{cm}^2}{\text{s}}$. While this might be initially surprising, our PSD analysis suggests the presence of significant volumes of >3.4 Å limiting ultramicropores in both samples, and water (kinetic diameter = 2.65 Å) is sufficiently small enough that it is largely insensitive to these minor changes in the limiting ultramicropore dimensions.

$$\frac{M_t}{M_\infty} = 1 - \exp(-\beta t) \left(\frac{D}{\beta \ell^2} \right)^{\frac{1}{2}} \tan \left(\frac{\beta \ell^2}{D} \right)^{\frac{1}{2}} - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp \left(-\frac{(2n+1)^2 \pi^2 D t}{4 \ell^2} \right)}{(2n+1)^2 \left[1 - (2n+1)^2 \left\{ \frac{D \pi^2}{(4 \beta \ell^2)} \right\} \right]} \quad (6-2)$$

$$D = \frac{D}{\Gamma} = D \frac{d \ln q}{d \ln f} \quad (6-3)$$

The gravimetric vapor sorption experiment was also conducted with p-xylene on **PIM-1_4% H₂_500_CMS** (Figure 6. 3 and Figure 6. 5). In Figure 6. 5, the p-xylene isotherm on **PIM-1_4% H₂_500_CMS** is modeled with the fifth degree polynomial equation, $\theta = \frac{q}{q_{\text{sat}}} = a \cdot p^5 + b \cdot p^4 + c \cdot p^3 + d \cdot p^2 + e \cdot p + f$. The experimental upstream and downstream activities obtained from the pure component WK vapor permeation ($a_{\text{p-xylene}}^{\text{upstream}} = 0.85$ and $a_{\text{p-xylene}}^{\text{downstream}} = 0.00$) were also utilized in the estimation of the p-xylene sorption coefficients. The sorption coefficient of p-xylene is also obtained

using (Eq. (6- 1)) as $1.2 \frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}$. As the uptake of p-xylene into our CMS films was too slow to reliably measure using gravimetric vapor sorption techniques, we obtained the diffusivity of p-xylene by back-calculating from the experimental permeabilities and sorption coefficients, (i.e., $P/S=D$). The diffusion coefficient of p-xylene in **PIM-1_4% H₂_500_CMS** is obtained as $5.4 \times 10^{-11} \frac{\text{cm}^2}{\text{s}}$ using the SD model (Table 6. 3).

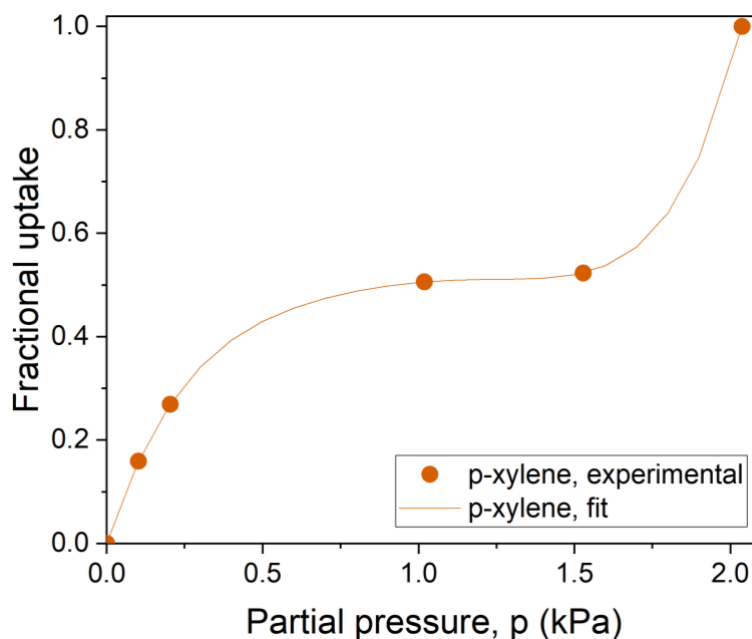


Figure 6. 5 Vapor sorption isotherms of p-xylene on PIM-1_4% H₂_500_CMS. The experimental data is represented by the circle points, while the fifth degree polynomial modeled fit is depicted by the line plots. The p-xylene uptake at unit activity was obtained from a liquid water-soaking experiment, assuming that the solvent-accessible pores are fully occupied by the liquid water adsorbents.

Table 6. 3. Sorption-diffusion model estimates of water and p-xylene vapor permeabilities in PIM-1-CMS_4% H₂_500 vapor permeation and comparison with pure component experimental permeabilities obtained via WK.

	T	S	D	$\mathbb{P}^{SD}$	$\mathbb{P}^{WK}$
	°C	$\frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}$	$10^{-11} \frac{\text{cm}^2}{\text{s}}$	$10^{-15} \frac{\text{mol} \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$	$10^{-15} \frac{\text{mol} \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$
Water	35	2.8	227.3	634.3	2779.5
p-Xylene	35	1.2	5.4*	6.5	6.5

*Obtained from $\mathbb{P} / S = D$

As shown in Table 6. 3. the Maxwell-Stefan sorption-diffusion model was able to reasonably estimate the permeability of water ($\mathbb{P}^{SD}$) within a factor of 4 of the experimental permeability ($\mathbb{P}^{WK}$). The water permeability prediction was 4 fold smaller than that of the experimental permeability, where the difference could be the result of some small defective pathways in the CMS membranes in permeation experiments; similar findings were observed in the case of the PVDF CMS.

The diffusion coefficients, D , of water and p-xylene in **PIM-1_4% H₂_500_CMS** were derived to be $2.3 \times 10^{-9} \frac{\text{cm}^2}{\text{s}}$ and $5.4 \times 10^{-11} \frac{\text{cm}^2}{\text{s}}$, respectively, resulting in the diffusion selectivity of water over p-xylene of 42. Moreover, the sorption selectivity of water over p-xylene is obtained as 2.5.

6.5 Water and p-xylene permeation in various CMS membranes

A pure component and mixture water and p-xylene vapor permeation in various CMS membranes were measured in the WK vapor permeation system. Both pure and mixture permeation experiments were conducted at three temperatures (38, 45, and 55 °C),

and the saturator temperature was controlled at 35 °C. The pure component vapor feed stream was generated from two saturators installed in series equipped with glass wool demister to ensure a saturated vapor stream. The mixture feed stream was also generated from two saturators in series containing a liquid mixture of water and p-xylene, and the vapor stream had a p-xylene partial pressure of 2.05 kPa and a water partial pressure of 4.77 kPa. This work includes permeation experiments on the PIM-1-derived CMS membranes, and the **PVDF_Ar_500_CMS** permeation data are excerpted from Chapter 5 [6].

The mixture permeation of water and p-xylene at 38 °C is provided in Figure 6. 6. Comparing **PVDF_Ar_500_CMS** to other PIM-1 derived CMS, the **PVDF_Ar_500_CMS** shows an organic-selective separation, where $\alpha_{\text{water/p-xylene}} < 1$, while the PIM-1 derived CMS shows water-selective separation ($\alpha_{\text{water/p-xylene}} > 1$). This is mainly attributed to the low water sorption affinity observed in **PVDF_Ar_500_CMS** (Figure 6. 3a). Moreover, as studied in Chapter 5, the diffusion-selective contribution to water p-xylene separation in **PVDF_Ar_500_CMS** is not sufficiently large ($D_{\text{water}}/D_{\text{p-xylene}} \sim 1.5$ at 35 °C) to overcome the strong sorption selectivity of p-xylene ($S_{\text{p-xylene}}/S_{\text{water}} \sim 4.2$ at 35 °C). On the other hand, the PIM-1-derived CMS membranes are selective towards water permeation by exhibiting mixture $\alpha_{\frac{\text{water}}{\text{p-xylene}}}$ of 1010, 72, and 54 from **PIM-1_4% H₂_500_CMS**, **PIM-1_CO₂_800_CMS**, and **PIM-1_CO₂_800_no hold_CMS**, respectively.

The high permselectivity in water selective separation can be attributed to both the sorption and diffusion selectivity in PIM-1-derived CMS. As shown in the SD transport

study in **PIM-1_4% H₂_500_CMS**, the diffusion coefficient of water in **PIM-1_4% H₂_500_CMS** is comparable to that in **PVDF_Ar_500_CMS**, which is reported to be $2.8 \times 10^{-9} \frac{\text{cm}^2}{\text{s}}$ (Chapter 5, [6]). On the other hand, the D of p-xylene in **PIM-1_4% H₂_500_CMS** is ~ 35 times slower than that in **PVDF_Ar_500_CMS**, which is reported as $1.9 \times 10^{-9} \frac{\text{cm}^2}{\text{s}}$ (Chapter 5, [6]). In addition to being slightly sorption-selective towards water over p-xylene ($S_{\text{water}}/S_{\text{p-xylene}} \sim 2.5$ at 35 °C), the **PIM-1_4% H₂_500_CMS** is significantly diffusion-selective towards water ($D_{\text{water}}/D_{\text{p-xylene}} \sim 42$ at 35 °C), resulting in a water-selective separation in water and p-xylene mixture, in contrast to **PVDF_Ar_500_CMS**, which exhibited a p-xylene-selective separation due to stronger sorption selectivity.

We also observe that the separation performance of the PIM-1-based CMS materials could be varied dramatically by varying the pyrolysis conditions. A decrease in water permeability is observed in the order of **PIM-1_4% H₂_500_CMS**, **PIM-1_CO₂_800_CMS**, and **PIM-1_CO₂_800_no hold_CMS**. High water permeability in **PIM-1_4% H₂_500_CMS** is attributed to the high sorption affinity for water, which is seen in the vapor sorption isotherm in Figure 6. 4b. Both the CO₂ pyrolyzed CMS exhibits suppressed water uptake in the low activity region, which suggests weaker interactions between water and the CMS samples. These weaker interactions ultimately result in reduced water permeability due to smaller sorption coefficients (Figure 6. 6). Moreover, the CO₂ pyrolyzed CMS with no hold exhibits slightly reduced water permeability, which we attributed to the insufficient formation of micropores.

These differences in water permeability and p-xylene permeability led to an increase in $\alpha_{\text{water/p-xylene}}$ in the order of **PIM-1_CO₂_800_no hold_CMS**, **PIM-1_CO₂_800_CMS** and **PIM-1_4% H₂_500_CMS**. The sample PIM-1 pyrolyzed in H₂ (**PIM-1_4% H₂_500_CMS**) showed the highest water permeability and the lowest p-xylene permeability, leading to the highest mixture $\alpha_{\text{water/p-xylene}}$ of 1010 at 38 °C. Such high separation performance is attributed to the narrow distribution of ultramicropores in this material. The $\alpha_{\text{water/p-xylene}}$ of the samples pyrolyzed in CO₂ (PIM-1_CO₂_800_CMS) is significantly reduced to a value of 72 primarily due to significant increases in the p-xylene permeability and decreases in water permeability, likely due to decreases in the water sorption affinity. We speculate the p-xylene permeability increases due to the broader ultramicropore and micropore distributions in this material. Removing the pyrolysis soak (PIM-1_CO₂_800_no hold_CMS) further reduces the permselectivity to 54, and this is tentatively assigned to the insufficient organization of graphenic nanoribbons. The kinetic restriction that contributes to selective transport is mainly controlled by the slit-shaped ultramicropores, not by the larger ultramicropores formed in the continuous phase by the orphan strands [2]. Therefore, it is hypothesized that the removal of the hold step caused the insufficient organization of the graphenic nanoribbons, causing CMS to be comprised of more orphan strands than the organized platelet-like structures with graphenic slits, contributing to reduced molecular sieving separation.

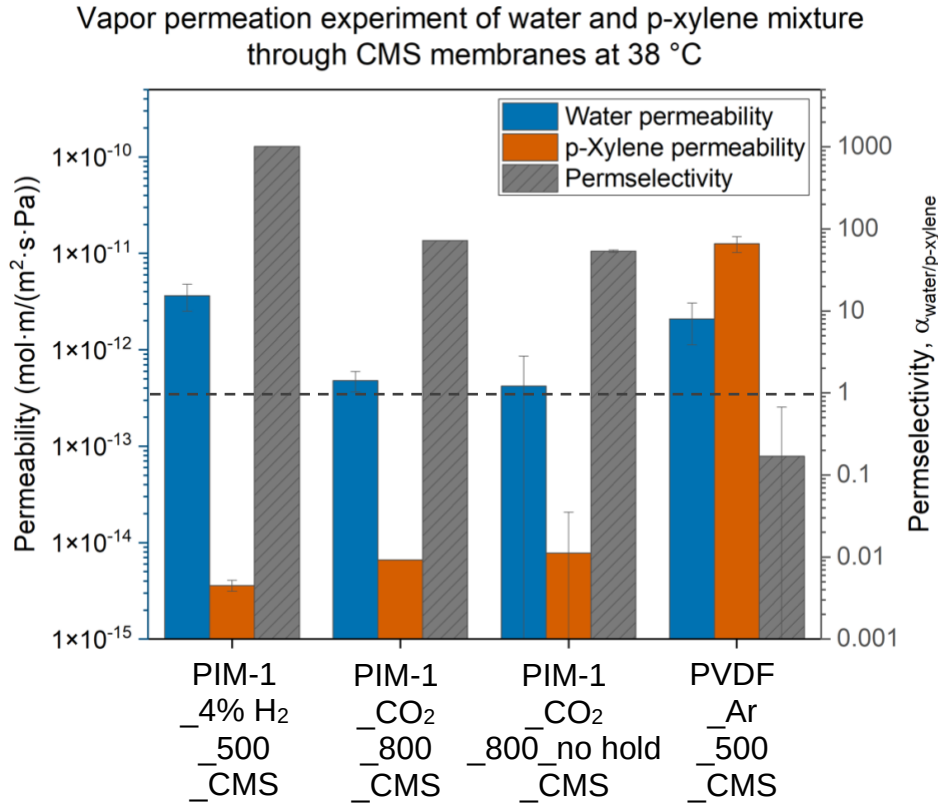


Figure 6. 6. Vapor permeation experiment of water and p-xylene mixture through various CMS membranes at 38 °C. Water activity upstream = 0.72 ± 0.01 , p-xylene activity upstream = 0.81 ± 0.09 , film thickness = $20.8 \pm 2.3 \mu\text{m}$, helium feed flow rate = 23.4 sccm, and helium sweep flow rate = 4.7 sccm for the experiments on the PIM-1 derived CMS. PVDF-derived CMS permeation measurement is excerpted from [6].

The activation energy of permeation of pure and mixed water and p-xylene in each CMS material was obtained (Figure 6. 7) by using an Arrhenius equation and by measuring the permeabilities at three different temperatures (38, 45, 55 °C). The activation energy of permeation in **PVDF_Ar_500_CMS** is also excerpted from Chapter 5 [6].

In the SD model, the activation energy for permeation can be expressed as the summation of activation energy for diffusion ($E_{D,A}$) and the integral heat of sorption ($\Delta H_{S,A}$) (Eq. (2- 10)). The activation energy for diffusion is always positive as the diffusion

increases with temperature, and the heat of sorption is always negative. Figure 6. 7 shows that the pure water permeations in all CMS membranes show negative activation energy of permeation. The negative activation energy of permeation identifies that the water transport in CMS is sorption controlled, which could be explained by either the low activation energy for the diffusion of small water molecules (kinetic diameter = 2.65 Å) or the high heat of sorption due to adsorption affinity of water to CMS. Also, pure p-xylene permeations in all CMS membranes show positive activation energy of permeation. The transport of p-xylene in CMS is diffusion-controlled, and this can be explained by the high activation energy for the diffusion of larger p-xylene molecules (kinetic diameter = 5.8 Å) or the small heat of sorption of p-xylene.

Based on what we observe from the PSD and the isotherms, the low positive activation energy of p-xylene permeation in **PVDF_Ar_500_CMS** can be attributed to both higher sorption affinity and the larger pore size distribution, compared to the PIM-1-derived CMS. All four CMS membranes show similar activation energy for water permeation, which is a result of the combination of the activation energy for diffusion and the heat of sorption.

The activation energy for permeation in pure and mixture permeation was compared. The mixture permeation in PIM-1-derived CMSs shows the same sign activation energy for water and p-xylene as the pure component permeation. In PIM-1-derived CMS, the water permeation in the mixture shows the negative activation energy of permeation, which is sorption limited as in pure component permeation. Moreover, the p-xylene permeation in the mixture shows the positive activation energy of permeation, indicating diffusion-limited transport, as in the pure component permeation. The

dominancy in sorption or diffusion in the mixture transport remains the same in PIM-1-derived CMS, which exhibits water-selective “molecular sieving”-style separation.

This is contrary to the observation in the PVDF-derived CMS, which exhibits p-xylene selectivity in mixture permeation. In this case, the water permeation in the mixture shows a positive activation energy of permeation, representing diffusion-limited transport. The diffusion-limited transport of water in the p-xylene mixture can be attributed to increased kinetic restriction by the competitively sorbed p-xylene. Moreover, the p-xylene permeation in the mixture shows a negative activation energy of permeation, indicating sorption-limited transport. Such observation corroborates the competitive sorption-driven separation of water and p-xylene, as it shows an increased contribution of p-xylene sorption to the p-xylene selective transport in the mixture separation.

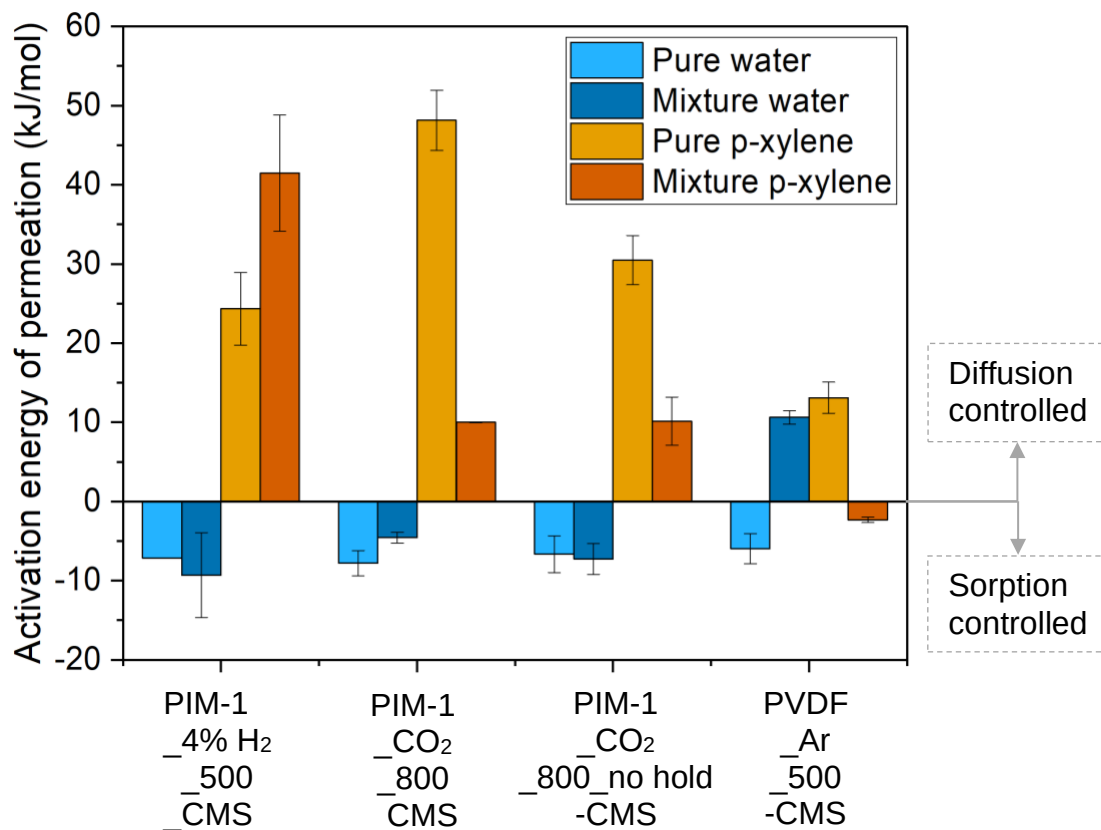


Figure 6. 7. The activation energy for permeation of water and p-xylene at pure and mixture permeation in various CMS membranes

6.6 Summary and Conclusions

The transport of water and p-xylene was studied in CMS membranes with various pore size distributions and surface chemistry. Various CMS membranes were fabricated by adjusting the 1) polymer precursor, 2) pyrolysis atmosphere, 3) the final pyrolysis temperature (T_p), and 4) the pyrolysis temperature profile. In this work, PIM-1-derived CMS membranes were investigated and compared to the PVDF-derived CMS explored in Chapter 5 [6]. The pore size distributions in CMS membranes were determined from CO₂ isotherms at 273 K and confirmed that the pore size distributions were adjusted at a

molecular scale. Furthermore, the atomic compositions of the CMS membranes were investigated via XPS, verifying that different pore surface chemistries were achieved.

The SD model study was conducted for water transport in a PIM-1-derived CMS (**PIM-1_4% H₂_500_CMS**). The sorption and diffusion coefficients were experimentally obtained using a gravimetric sorption experiment. The SD-modeled permeability and the experimental permeability were compared and validated that the water transports through the PIM-1-derived CMS in the SD model. Additionally, the sorption and diffusion selectivities of water /p-xylene were evaluated in PIM-1-derived CMS and PVDF-derived CMS. The PIM-1-derived CMS exhibited a dominating diffusion selectivity, which is in contrast to the PVDF-derived CMS, which demonstrated a sorption-selective separation [6].

The water and p-xylene permeation experiments were performed in a vapor permeation experiment using a Wicke-Kallenbach system. The water and p-xylene mixture permeation in PIM-1-derived CMS membranes showed high permselectivity of water over p-xylene, which is in agreement with the SD model transport study results. Such water-selective separation in PIM-1-derived CMS is in contrast to PVDF-derived CMS, which shows p-xylene selective separation [6]. Moreover, among the PIM-1 derived CMS, the water selective separation performance was varied by the PSD and the sorption affinity of guest molecules in CMS membranes. The **PIM-1_4% H₂_500_CMS** exhibits smaller selective pore size distribution and higher affinity to water, which resulted in the highest permselectivity of water/p-xylene. This study demonstrates the engineering of the PSD and the pore surface chemistry of CMS membranes, enabling precise control over the transport of water and p-xylene mixture.

Moreover, the activation energy for permeation of pure and mixture components was investigated to understand the structure-transport relationship of water and p-xylene co-transport in various pore size distributions of CMS. Pure water and p-xylene showed diffusion-controlled transport and sorption-controlled transport, respectively, in all CMS membranes. The water and p-xylene mixture transport in PIM-1-derived CMS shows the same diffusion-controlled and sorption-controlled transport for water and p-xylene, respectively, reflecting the molecular sieving separation. On the other hand, the mixture transport in PVDF-derived CMS shows the reverse sign in the activation energy of permeation, where the sorption-controlled transport behavior is observed from water and the diffusion-controlled transport is observed from p-xylene, which suggests the competitive sorption-selective separation.

6.7 References

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CHAPTER 7. TRANSPORT STUDIES OF WATER AND ORGANIC SOLVENT IN CMS MEMBRANES IN LIQUID-PHASE MEMBRANE PROCESSES

7.1 Overview

This chapter discusses the transport of water and p-xylene in PIM-1-derived CMS membranes in various membrane modalities using the sorption-diffusion (SD) model. The water transport in reverse osmosis (RO), pervaporation (PV), and vapor permeation (VP) was modeled by employing a simplified SD equation derived from the Maxwell-Stefan (MS) mass transfer equation. The co-transport of water and p-xylene in RO and PV was also investigated via the use of PIM-1-derived CMS hollow fiber membranes.

7.2 Introduction

Chapter 6 presented promising findings regarding the performance of PIM-1_4%_H₂_500_CMS dense film membrane for the separation of water and p-xylene. These membranes exhibited high rejection for p-xylene in VP conditions when tested with a saturated vapor feed mixture. Chapter 7 aims to extend this work to better understand the ability of these successful membranes to separate water and p-xylene in more realistic conditions. Three previous reports have discussed the use of carbon membranes derived from PIM-1 for wastewater treatment [1–3]. To the best of the author’s knowledge, no previous research has specifically investigated transport studies concerning the separation of organics from wastewater using carbon membranes in different membrane separation modalities.

Here, the aim of this study is to investigate the transport mechanism of water and p-xylene in PIM-1-derived CMS membrane in various membrane separation modalities. Specifically, the transport of water in RO, PV, and VP systems is investigated using a simplified SD equation derived from the MS mass transfer equation. The asymmetric PIM-1-derived CMS hollow fiber membranes were fabricated using dry-wet spinning [4] and applied for RO and PV membrane systems. Dense film PIM-1-derived CMS membranes were fabricated and applied in the VP system. A more accurate SD equation for VP transport has already been discussed in Chapter 6, and now the simplified equation will be employed to apply to various membrane separation modalities in which the driving forces and boundary conditions are more complicated to solve. The more robust VP predictions are used to validate the assumptions made in the simplified equation for water transport systems. Experiments on pure liquid water transport in RO and PV systems provide insights into the mechanisms governing water transport in CMS membranes. Additionally, the co-transport of water with dilute concentrations of p-xylene in RO system is explored using the SD model and compared to experimental permeation data. This analysis is further investigated to determine if sorption-vection transport plays a role in the transport of liquid water and dilute concentration of p-xylene in the CMS materials made in this work. Furthermore, the SD model is employed to predict the co-transport of water and p-xylene in CMS membranes in PV systems, and presents insights on the effect of sweep gas on the membrane downstream.

7.3 Fabrication of PIM-1 hollow fiber membrane

PIM-1 asymmetric hollow fiber membranes were fabricated and were pyrolyzed into PIM-1_4% H₂_500C_CMS asymmetric hollow fiber membranes, as shown in Figure

7. 1. These asymmetric hollow fiber CMS membranes were tested under a custom-made bench-scale crossflow permeation system for reverse osmosis separation and a custom-made bench-scale pervaporation permeation.

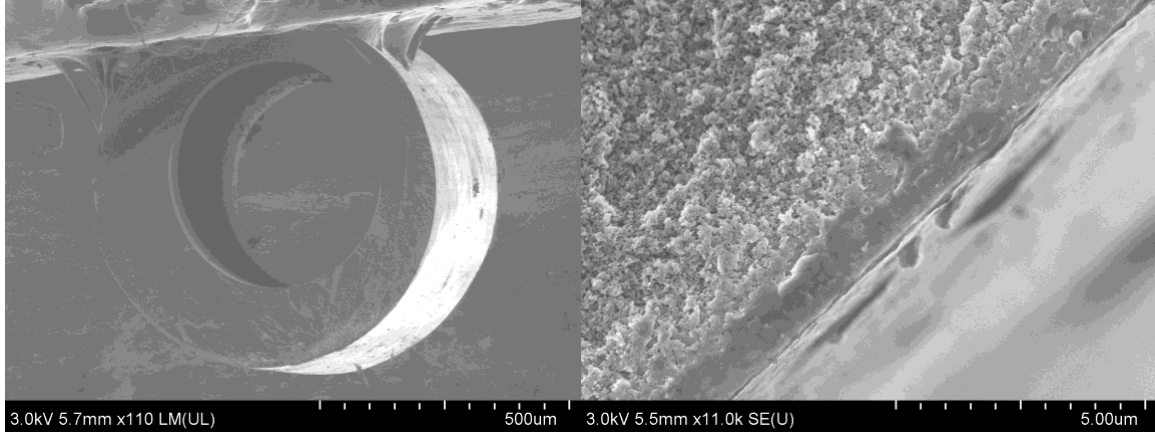


Figure 7. 1. SEM images of PIM-1_4% H₂_500C_CMS asymmetric hollow fiber membranes. The left image shows the whole cross-section of the hollow fiber membrane, and the right image shows the selective layer located on the shell side of the asymmetric membrane.

7.4 Water transport analysis in CMS membranes in RO, PV, and VP processes using the SD model

A more simplified equation was employed to estimate the fluxes of more complex membrane separation modalities such as RO and PV, in which the driving forces and boundary conditions are more complicated. The SD-modeled flux equation for a diffusive molar flux (J_i) (Eq. (7- 2)) is derived [2] from a simplified MS expression (Eq. (7- 1)).

$$\frac{x_i \nabla \mu_i}{RT} = - \sum_{\substack{j=1 \\ j \neq i}}^n x_j x_i \frac{(u_i - u_j)}{D_{ij}} \quad (7- 1)$$

$$J_i = D_i^m \rho q_i^{\text{sat}} \bar{\theta}_i^m \frac{\Delta f_i^m}{\ell \bar{f}_i^m} \quad (7- 2)$$

where x_i is the mole fraction of component i in the membrane, $\nabla\mu_i$ is the chemical potential gradient of i across the membrane. u_i is the velocity of i in the membrane, D_{ij} is the mutual MS diffusion coefficient between components i and j , where i or j could be the adsorbates or the membrane.

The simplified diffusive flux expression (Eq. (7- 2)) is derived based on two key assumptions: 1) a linear fugacity gradient, and 2) a constant average guest loading across the membrane. These assumptions enable the application of the simplified flux equation in membrane systems involving pressurized liquid stream, such as in RO. For instance, the estimation of guest molecule loading in a pressurized liquid environment (where the fugacity is $> f^{\text{sat}}$) is not feasible using vapor sorption isotherm. Hence, assuming a constant average guest loading across the membrane with a linear fugacity gradient facilitates the estimation of the guest loading even in a pressurized liquid environment. D_i^m is the MS diffusivity of i in the membrane, which is also a thermodynamically corrected diffusivity. ρ is the density of the membrane, q_i^{sat} is the saturation loading of i in the membrane, $\bar{\theta}_i^m$ is the average fractional occupancy of i in the membrane, Δf_i^m is the fugacity gradient of i in the membrane, ℓ is the thickness of the membrane selective layer, and $\bar{f}_i^m$ is the average fugacity of i in the membrane.

The estimation of pure water fluxes in PIM-1_4% H₂_500_CMS membranes in different membrane processes was conducted and compared to the experimental observations (Figure 7. 2a, Table 7. 1). The flux estimation was based on the assumption that the overall mass transfer resistance is governed by the mass transfer resistance in the selective separation layer of the asymmetric hollow fiber membranes. The parameters used

for the flux estimation were obtained from gravimetric sorption experiments as well as RO, PV, and VP pure water permeation experiments. In the RO system, a transmembrane pressure of 10 bars was applied, and the PV system employed He sweep (~18 sccm) on the downstream side of the membrane.

The MS (thermodynamically corrected) diffusivity of water, $\bar{D}_{\text{water}}^m$, was determined from a transient uptake curve using a gravimetric sorption experiment, as described in Chapter 6. The MS diffusivity of water in PIM-1_4% H₂_500_CMS shows a dependency on guest molecule loading (Figure 6. 4b). Therefore, the estimation of $\bar{D}_{\text{water}}^m$ for RO, PV, and VP involved considering each average fractional loading, $\bar{\theta}_{\text{water}}^m$, based on the experimental upstream and downstream fugacities.

The average fractional occupancy of water, $\bar{\theta}_{\text{water}}^m$, for the RO system was estimated to be 1, considering that the fractional occupancy in both the upstream and downstream would be close to 1 when exposed to a liquid phase. The $\bar{\theta}_{\text{water}}^m$ for the PV and VP systems were estimated to be 0.99 and 0.63, respectively, determined based on the experimental measurements of the upstream and downstream activities. It is worth noting that despite both PV and VP having sweep gas on the membrane downstream, the estimated $\bar{\theta}_{\text{water}}^m$ value for PV is relatively high, closer to that of RO than VP. This can be attributed to high water activity observed on the downstream of the membrane in the experiment, which is influenced by the low sweep gas flow rate employed (~18 sccm). The $\bar{\theta}_{\text{water}}^m$ estimations are based on the assumption of a linear guest loading profile in the membrane.

The MS diffusivity for the calculation of RO and PV flux, which experimentally exhibited $\bar{\theta}_{\text{water}}^m$ of 1 and 0.99, was determined at fractional occupancy $\theta = 0.94$, measured

at a relative humidity of 75 %. This value was limited by the capabilities of the gravimetric vapor sorption instrument (VTI SA+, TA instrument) used. The diffusivity for VP system was obtained by interpolation at $\theta = 0.63$. Furthermore, the sorption uptake at a unit activity, q_i^{sat} , was determined through a liquid water-soaking experiment.

It is noteworthy that the diffusivity and sorption parameters were determined at 35 °C, while the RO and PV permeation experiments were conducted at room temperature (~22 °C) as a result of current experimental capabilities (the sorption and diffusion analyzers require somewhat higher temperatures for consistent readings, and the permeation systems have not been outfitted for safe operation with heating elements). The SD-modeled fluxes were first calculated at 35 °C for RO, PV, and VP systems. Subsequently, the SD calculated fluxes of RO and PV were adjusted to the flux at 22 °C utilizing the activated energy for water permeation in PIM-1_4% H₂_500_CMS, $\Delta E_{\text{p}} = -7.2$ kJ/mol, as obtained from Chapter 6.

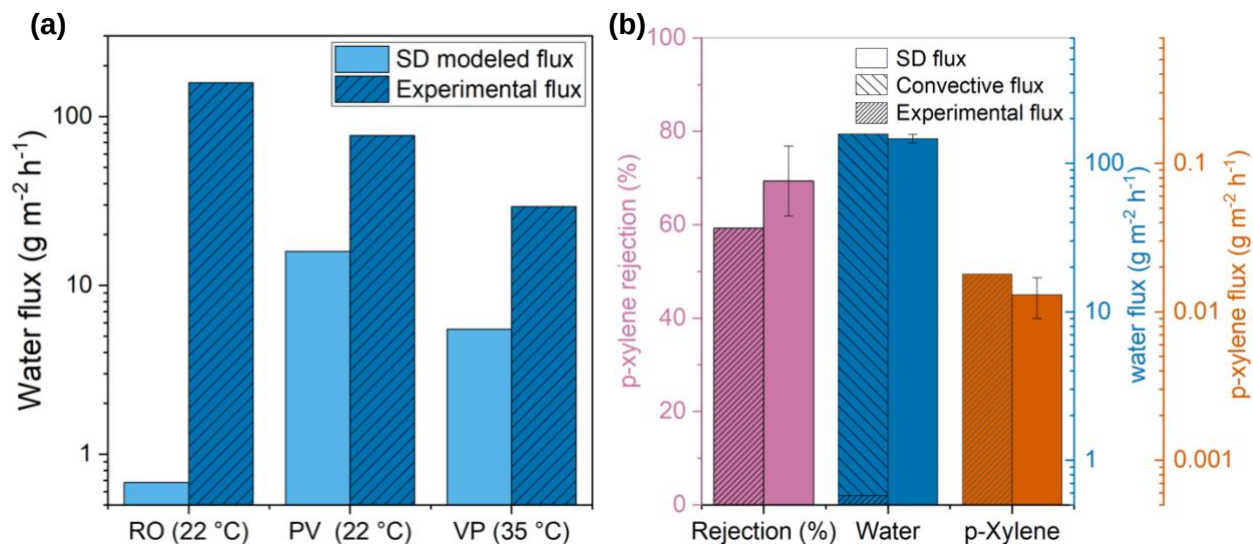


Figure 7. 2. a) Comparison of experimental water flux and the SD model calculated water flux in RO, PV, and VP modalities. b) Comparison of experimental and SD model calculated fluxes of water and dilute concentration (~290 ppm) of dissolved p-xylene. RO systems are operated at transmembrane pressure of 10 bar, and the PV system was operated at an atmospheric pressure with helium sweep on the membrane downstream at 18 sccm flow rate.

Table 7. 1. Parameters used for the calculation of the water flux in RO, PV, and VP systems using the SD model and the comparison to the experimental fluxes.

		RO	PV	VP
SD calculation	T_{SD} (°C)	35	35	35
	$\bar{D}^m$ (cm ² /s)	1.52×10^{-9}	1.52×10^{-9}	2.27×10^{-9}
	ρ (g/cm ³)	2	2	2
	q^{sat} (mmol/g)	5.65	5.65	5.65
	$\bar{\theta}^m$	1	0.99	0.63
	$p^{upstream}$ (bar)	11	1	1
	$p^{downstream}$ (bar)	1	1	1
	$f^{upstream}$ (bar)	0.0562	0.0558	0.0476
	$f^{downstream}$ (bar)	0.0558	0.0472	0.0118
	$f^{average}$ (bar)	0.0560	0.0515	0.0297
	ℓ (cm)	0.00013	0.00013	0.0023
	Flux ^{SD} (g/m ² /h) at 35 °C	0.60	14.1	5.5
	Flux ^{SD} (g/m ² /h) at 22 °C	0.68	15.9	-
Experimental data	$T^{Experimental}$ (°C)	22	22	35
	Flux ^{Experimental} (g/m ² /h)	158.5	76.9	29.3
(Flux ^{Experimental})/(Flux ^{SD})		231.8	4.8	5.3
Flux ^{Convective} (g/m ² /h) at 22 °C, $\Delta p = 10$ bar		157.9	-	-

The simplified SD expressions demonstrated reasonable predictions for the experimental fluxes in the isobaric experiments (i.e., PV and VP), with the PV and VP fluxes falling within a 5-fold difference from the experimental values. The experimental PV and VP fluxes were ~5x higher than the SD predicted fluxes, which could be a result of somewhat larger micropores or defects within the CMS hollow fiber membranes. Indeed, the SD prediction for the RO flux significantly underestimated the experimental flux by ~150x. This observation can be attributed to these defects, or larger, continuous micropores present in the CMS film membranes. These defects — if present — will play a

significant role in the flux within the pressurized RO system due to continuum-level Poiseuille flow. Such Poiseuille flow through these defects can be conservatively treated as a non-selective convective flux, which can be obtained using (Eq. (7- 3)).

$$N_{\text{total}} = J_{\text{sorption-diffusion}} + N_{\text{pore-flow}} \quad (7- 3)$$

The pore size distribution of PIM-1_4% H₂_500_CMS was investigated using cryogenic nitrogen physisorption [5] (recreated in Figure 7. 3) and has demonstrated the presence of larger micropores above 12 Å. These larger micropores and the micropores in 5 - 7 Å (Figure 6. 1) could potentially serve as defects in the membrane structure, allowing for Poiseuille flow of liquid water through these pore sizes exceeding 2-3 times the kinetic diameter of water molecules (2.65 Å). These larger micropores could have originated from either material pyrolysis process or the membrane fabrication process.

The presence of the pressure-induced pore flow through these defects raises an important consideration for the application of PIM-1_4% H₂_500_CMS in liquid separation, particularly under higher transmembrane pressures. In such cases, the flux in pore flow may become more dominant, potentially leading to reduced selectivity in the separation. The influence of these defects on the overall performance and selectivity of the membrane should be considered for the practical application of PIM-1_4% H₂_500_CMS membranes in a pressurized liquid system.

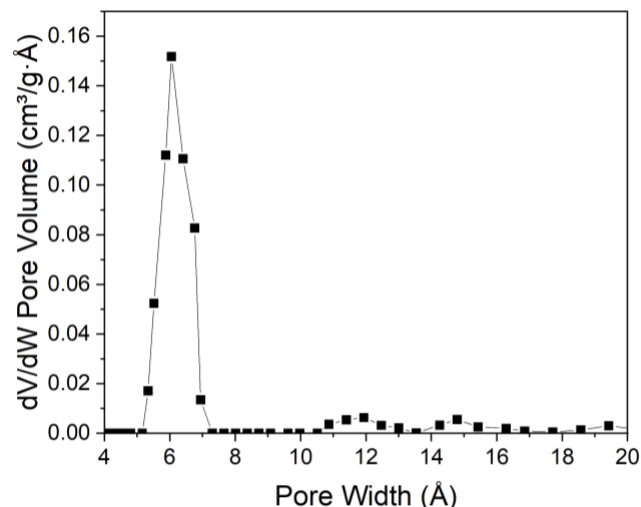


Figure 7. 3. Pore size distribution of PIM-1_4% H₂_500C_CMS obtained from cryogenic N₂ physisorption at 77K. The physisorption data are provided from Ma et al. [5], and the pore size distribution is calculated using HS-2D-NLDFT (MicroActive software, Micromeritics, USA).

The study of water transport in CMS membranes across different membrane separation modalities holds significant importance in our understanding on how liquid separation of aqueous streams can be engineered. By investigating the pure water transport in CMS membranes used in RO, PV, and VP, we can gain insights into the transport mechanisms involved, which would be useful to explore the transport of water and dilute concentrations of dissolved p-xylene in these various membrane systems.

7.5 Water-p-xylene mixture transport analysis in CMS membranes in the RO process using the SD model

The ~290 ppm concentration of p-xylene dissolved in water was separated in PIM-1_4% H₂_500_CMS membranes in the RO system. Previous studies have indicated that the liquid transport of water and dilute concentrations of organic solvent in carbon membrane follow sorp-vection mechanism, provided that the organic solvents sorb

sufficiently strongly into the membrane [2]. In the sorp-vection mechanism, the dilute concentration of organics present in the feed is competitively adsorbed onto the carbon membrane. The concentrated organic component is then carried through the membrane by the bulk flow of water. This results in the concentration of the organics on the permeate side, despite the higher chemical potential of the organics on the permeate side compared to the feed side.

Similarly, it was hypothesized that the transport of water and dilute concentration of p-xylene in PIM-1_4% H₂_500C_CMS is also composed of diffusive transport and the bulk flow effect of water. The Lightfoot equation (Eq. (7- 4)) [6] was utilized to approximate the total flux of water and p-xylene. The molar diffusive fluxes of water and p-xylene were calculated using (Eq. (7- 2)) and were converted to mass diffusive flux, j_i , to be applied in (Eq. (7- 4)).

$$n_i = j_i + \bar{w}_i(n_{\text{total}}) \quad (7- 4)$$

n_i is the total flux of i , $\bar{w}_i$ is the average mass fraction of i in the membrane, including the membrane, and n_{total} is the total flux of all the components in the system.

The isotherms of water and p-xylene in PIM-1_4% H₂_500_CMS exhibit complex non-Langmuir isotherms (Figure 7. 4), making it challenging to model the water and p-xylene mixture isotherms for application in the Maxwell-Stefan formulation [7,8]. As a result, in the calculation of diffusive flux (Eq. (7- 2)) of water and p-xylene in a mixture system, the fractional occupancy of component i in the binary mixture system, $\bar{\theta}_{i,\text{binary}}^m$, was obtained using a simplified estimation of sorption selectivity (Eq. (7- 7)) [2]. The

sorption isotherm for water was modeled using the linear model of Henry's law (Eq. (7-5)). This simplification facilitated the calculation of uptake under pressurized liquid conditions, where the fugacity exceeds the saturation fugacity, f^{sat} (which is simply the vapor pressure of the pure liquid). Henry's law assumption was justified by the nearly linear uptake curve observed in the water isotherm on PIM-1_4% H₂_500_CMS (Figure 7.4a, $R^2 = 0.978$). The p-xylene isotherm exhibited a complex isotherm model, which was modeled using a fifth-degree polynomial (Eq. (7-6)) for simplicity, as previously discussed in Chapter 6 (recreated in Figure 7.4b).

$$q_{\text{water}} = K_{\text{water}} f_{\text{water}} \quad (7-5)$$

$$q_{\text{p-xylene}} = a \cdot f_{\text{p-xylene}}^5 + b \cdot f_{\text{p-xylene}}^4 + c \cdot f_{\text{p-xylene}}^3 + d \cdot f_{\text{p-xylene}}^2 + e \cdot f_{\text{p-xylene}} + f \quad (7-6)$$

q_i (mmol/g) is the uptake of component i in the membrane, K_{water} (mmol/g/kPa) is Henry's constant for water in the membrane, and f_i is the fugacity (kPa) of i on the bulk fluid phase on the upstream or downstream of the membrane. a, b, c, d, e and f are fifth degree polynomial fitting constants for p-xylene isotherm.

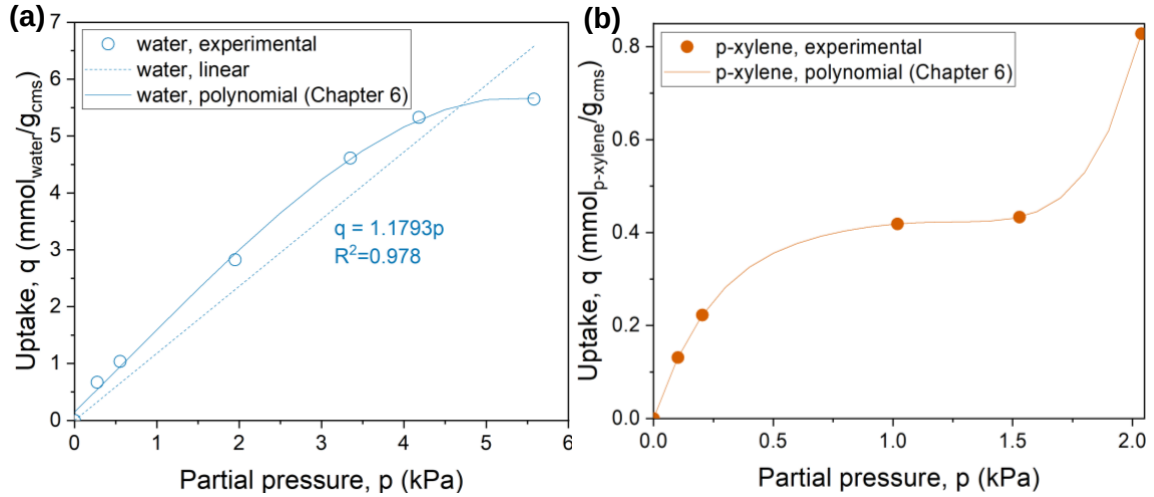


Figure 7. 4. The vapor uptake isotherms of (a) water and (b) p-xylene in PIM-1_4% H₂_500_CMS. The data points represented by circles are obtained from experimental vapor sorption isotherms discussed in Chapter 6. The dashed line represents the linear model employed in this chapter for estimating water uptake, and the R² is provided for the linear model fitting. The solid lines depict the polynomial models fitted, adapted from Chapter 6.

The calculation of fractional uptake in a binary adsorbent system is simplified and expressed in (Eq. (7- 7)), utilizing the single-component isotherms. It was assumed that the fractional occupancy on membrane pores is 1 (i.e., $\theta_i^m + \theta_j^m \sim 1$) where in contact with a liquid phase.

$$\theta_{i,\text{binary}}^m = \frac{q_i}{q_i + q_j} \quad (7- 7)$$

Detailed parameters for the mixture modeling can be found in Table 7. 2. The permeate mole fraction is calculated using permeate molar fluxes (Eq. (7- 8)). The separation performance in the RO system was expressed in terms of separation factor ($\beta_{i/j}$) (Eq. (7- 9)).

$$x_{i,\text{permeate}} = \frac{N_{i,\text{total}}}{N_{i,\text{total}} + N_{j,\text{total}}} \quad (7-8)$$

$$\beta_{i/j} = \frac{x_i^{\text{permeate}} / x_j^{\text{permeate}}}{x_i^{\text{feed}} / x_j^{\text{feed}}} \quad (7-9)$$

where x_i^{permeate} and x_i^{feed} are mole fraction of i in permeate and feed, respectively.

Table 7. 2 Detailed parameters used in SD model estimation of water-p-xylene mixture transport in PIM-1_4% H₂_500C_CMS RO system.

RO		p-Xylene	Water
Parameters	D^m (cm ² /s)	5.42×10^{-11}	1.52×10^{-9}
	ρ_{CMS} (g/cm ³)	2	2
	q^{sat} (mmol/g)	0.828	5.649
	x^{feed} (mole fraction)	4.73×10^{-5}	0.99995
	γ^{feed} (UNIQUAC) at 11 bar	5686	1
	$\gamma^{permeate}$ (UNIQUAC) at 1 bar	11848	1
	Δp (bar)	10	10
	f^{feed} (kPa)	0.52	5.61
	$f^{permeate}$ (kPa)	0.42	5.58
	Δf (kPa)	0.10	0.04
	Liquid mass fraction in liquid saturated membrane	0.115	
	Henry's constant, K (mmol/g/kPa)	-	1.18
	Polynomial model parameter, a	0.28	-
	Polynomial model parameter, b	-1.34	-
	Polynomial model parameter, c	2.57	-
	Polynomial model parameter, d	-2.63	-
	Polynomial model parameter, e	1.53	-
	Polynomial model parameter, f	3×10^{-10}	-
	$\theta_{m,upstream}$	0.052	0.948
	$\theta_{m,downstream}$	0.048	0.952
	$\bar{\theta}^m$ (average)	0.050	0.950
	ℓ (cm)	0.00013	0.00013
Calculation Results	Diffusive flux (g/m ² /h) at 35 °C	0.03	0.51
	Diffusive flux (g/m ² /h) at 22 °C	0.02	0.58
	Convective flux (g/m ² /h) at 22 °C	-	157.9
	Total flux (g/m²/h) at 22 °C	0.018	158.4
	$x^{permeate}$ (mole fraction)	1.93×10^{-5}	0.99998
	separation factor water/p-xylene	2.5	

The reverse osmosis water and p-xylene separation in PIM-1_4% H₂_500_CMS was experimentally performed, showing a ~69.4 % rejection of p-xylene (Figure 7. 2b, Table 7. 3) and a water flux of 147.0 L m⁻² h⁻¹. This experimental flux for water and p-xylene was then compared with the estimates from the sorption-diffusion model. As shown in the pure water permeation experiments, the SD model was unable to replicate the experimental water fluxes in the hydraulic permeation case. We assign the difference between the experimental fluxes and the SD fluxes as the “convective flux”. This convective flux was then used to estimate the water flux in the mixture permeation experiments along with the SD model flux (i.e., $N_{H_2O} = J_{H_2O} + N_{H_2O}^{PF}$, where $N_{H_2O}^{PF}$ is the convective flux from the single component permeation experiment) The flux estimates for both p-xylene and water closely aligned with the experimental fluxes (when the “convective flux” of water through the defects is considered by using the pure water fluxes under hydraulic permeation conditions, Table 7. 2), with an error of within 5% when accounting for the experimental error. The convective flux of water is assumed to be the same in the pure water and water-p-xylene mixture experiments, as the water mole fraction in the feed is near 1 in the dilute concentration of p-xylene dissolved in aqueous solution, and both pure and mixture systems are applied with the same 10 bar pressure gradient. Additionally, the separation factor of water/p-xylene was accurately estimated with an error of 25 %, also accounting for the experimental error. This sorption-diffusion calculation based on vapor phase isotherm and diffusion data successfully captured the p-xylene rejection separation in the liquid phase RO system.

The p-xylene and water permeation sorption-diffusion calculations were updated by taking into account the sorp-vection effect. It is postulated that the selective uptake of

p-xylene would be different in the defect-free micropores and the microporous defects. Accounting for the relatively large volume of water convective flux through microporous defects ($\sim 157.9 \text{ g/m}^2/\text{h}$) with respect to the diffusive fluxes of water and p-xylene (0.02 and $0.58 \text{ g/m}^2/\text{h}$, respectively), the p-xylene mass fraction in the defect-free micropores were considered negligible. Assuming that the p-xylene mass fraction in the defects approximates the feed mass fraction, the average mass fraction in membrane, $\bar{w}_i$, was approximated using the feed mass fraction. As a result, a slight increase in the p-xylene flux from 0.018 to $0.021 \text{ g/m}^2/\text{h}$ was observed, resulting in a marginal decrease in the separation factor of water/p-xylene of 2.1 , which deviates further from the experimental flux and separation factors. It is possible that water can convectively transport through the defective regions whereas p-xylene cannot, thus leading to the high separation factors that were observed in the experiment.

Table 7. 3. Comparison of calculated p-xylene and water fluxes and the separation factor with the experimental permeation results in PIM-1_4% H₂_500_CMS.

	Calculation		Experimental
	Without sorp-vection effect	With sorp-vection effect	
p-Xylene flux ($\text{g/m}^2/\text{h}$)	0.018	0.023	0.013 ± 0.004
Water flux ($\text{g/m}^2/\text{h}$)	158.4	176.7	147.0 ± 10.0
Separation factor (water/p-xylene)	2.5	2.1	3.1 ± 0.1
p-xylene rejection (%)	59.3	53.2	69.4 ± 7.5

This observation hints that the sorp-vection transport does not play a significant role in the transport of water and p-xylene in PIM-1_4% H₂_500_CMS, which differs from the findings observed in the case of DMF and water transport in PIM-1 derived carbon membrane materials [2]. White et al. [2] reported various PIM-1-derived carbon

membranes pyrolyzed above 900 °C under 4% H₂ with different ramping profiles, demonstrating sorp-vection transport for water and dissolved dimethylformamide (DMF) solution. The main factors contributing to the different transport mechanisms between these two systems are 1) pore size distribution, 2) the adsorbent affinity to the membrane material (Figure 7. 5). As an example, PIM-1 dCMS 900 °C and PIM-1 AmC, 1000 °C which exhibit good separation factors in sorp-vection transport, were discussed here for comparison purposes.

Upon comparing the pore size distribution plots derived from CO₂ isotherms at 273K, it is evident that the PIM-1 dCMS 900°C exhibits a larger pore volume in all micropore size distributions above 3.9 Å, as well as larger pore sizes above 7.2 Å, which are not present in PIM-1_4% H₂_500_CMS. The presence of sufficiently large distributions of selective pore sizes above 3 Å in both PIM-1_4% H₂_500_CMS and PIM-1 dCMS 900°C, can facilitate the diffusive and convective flux pathways for water molecules (kinetic diameter = 2.65 Å). Moreover, the presence of sufficient pore volumes in the ranges of 5.8 – 6.4 Å and 7.2 – 8.3 Å in PIM-1 dCMS 900°C may contribute to unrestricted passageways for p-xylene molecules (kinetic diameter = 5.8 Å) to be swept through with the convective water flux. On the other hand, the PIM-1_4% H₂_500_CMS, which exhibits a smaller volume of pores in the range of 5.5 – 6.4 Å and lacks pores above 7 Å, may restrict the movement of p-xylene along with the convective water flux, thereby limiting the sorp-vection transport of p-xylene via water.

Moreover, the affinities of water and the organic solvent to the PIM-1-derived carbon membrane materials are compared in Figure 7. 5b. The organic solvent uptake isotherms in both PIM-1 derived carbon membranes (p-xylene uptake in PIM-1_4%

H₂_500_CMS and DMF uptake in PIM-1 AmC, 1000 °C [2]) show similar Langmuir type sorption isotherms. On the other hand, the water isotherms in both PIM-1 derived carbon membranes (PIM-1_4% H₂_500_CMS and PIM-1 dCMS 900°C) display distinct adsorption behavior. The water isotherm on PIM-1_4% H₂_500_CMS shows high uptake at low relative pressure, whereas the water isotherm on PIM-1, dCMS 900°C shows a low uptake in the relative pressure range $< 0.1 p/p^{\text{sat}}$. Such low uptake at low relative pressure is commonly observed when water interacts with non-hydrophilic materials, indicating weak interactions between water and non-hydrophilic adsorbents. This weak sorption affinity of water and high sorption affinity of DMF results in the competitive sorption of DMF, which is then swept through the membrane by the bulk flow of water. On the other hand, water exhibits a high affinity for PIM-1_4% H₂_500_CMS, inhibiting the competitive sorption of p-xylene over water. It is also worth noting that not only the affinities but also the mass fractions of the organic solvents in aqueous solution may play a role in the fractional uptake difference between the two systems. p-Xylene in the system is only in ppm level where the DMF transporting in sorp-vection was at ~ 10 wt% range. Although it is difficult to jump to a conclusion as the activity coefficient of infinitely dilute p-xylene ($\gamma_{\text{p-xylene}}^{\infty, \text{feed}} \sim 5686$ at 11 bar) is significantly higher than the DMF in feed mixture ($\gamma_{\text{DMF}}^{\text{feed}} = 1.021$ at 2.5 wt% [2]), the selective uptake difference will play a significant role, thus a further competitive sorption study on complex water and organic solvent system would be a useful future research question.

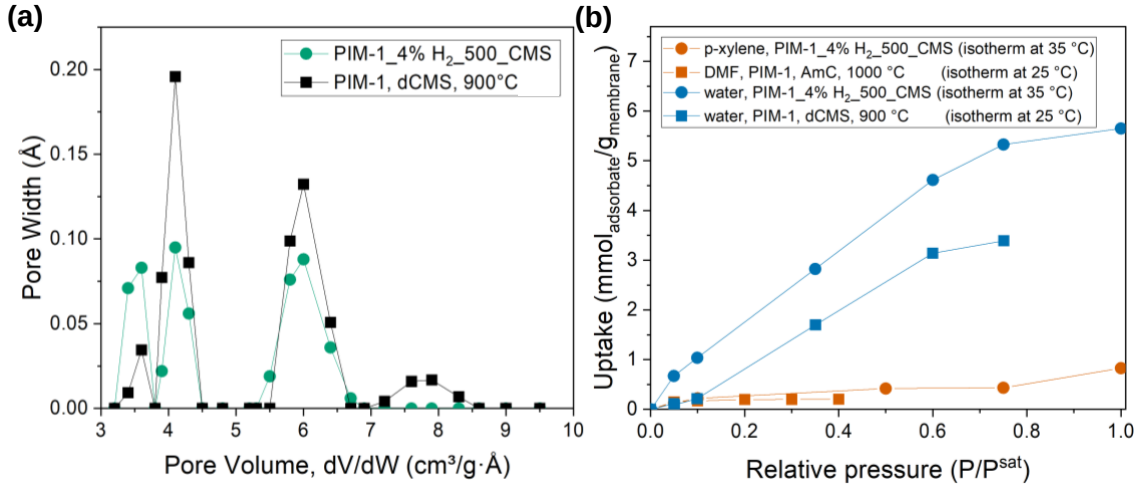


Figure 7. 5. Comparison of different PIM-1 derived carbon materials exhibiting different transport behavior for water and dissolved organic solvent membrane separation. PIM-1_4% H₂_500_CMS, studied in this chapter, is represented by circle points. The PIM-1 derived carbon material, reported to exhibit sorp-vection transport of water and DMF, is represented by square points [2] a) Micropore size distribution derived from carbon dioxide physisorption at 273K below 10 Å. b) Water and organic solvent vapor uptake isotherms. Isotherm on PIM-1_4% H₂_500_CMS is obtained at 35 °C. Isotherms on PIM-1, dCMS, 900 °C and PIM-1, AmC, 1000 °C, which exhibited sorp-vection transport, are obtained at 25 °C.

7.6 Water and p-xylene separation prediction in pervaporation system

The separation of dilute concentration of p-xylene in an aqueous solution in CMS hollow fiber membranes is predicted using the simplified SD equations. The diffusive fluxes of water and p-xylene were also calculated using (Eq. (7- 2)) and the fractional occupancy in the binary mixture system, $\theta_{i,binary}^m$, was obtained using (Eq. (7- 7)). Polynomial fittings are employed to model the water and p-xylene isotherms (Eq. (7- 6) and Eq. (7- 10), respectively), and the isotherm fittings are presented in Figure 7. 4. The details of the model fittings are provided in Chapter 6, and these models were utilized to estimate water and p-xylene uptakes with respect to the bulk phase fugacities in the upstream and downstream.

$$q_{\text{water}} = a \cdot f_{\text{water}}^3 + b \cdot f_{\text{water}}^2 + c \cdot f_{\text{water}} + d \quad (7-10)$$

a, b, c , and d are cubic polynomial fitting constants for the water isotherm. Detailed parameters for the mixture permeation modeling in pervaporation can be found in Table 7.

4. The fractional occupancies in the downstream membrane pores are assumed to be 0 (i.e., $\theta_i^m + \theta_j^m \sim 0$), assuming the downstream permeate fugacities in PV system are near zero.

In the pervaporation experiment with pure water, the fractional occupancy in the downstream was nearly 1, as indicated in Table 7. 1 with an average value of $\bar{\theta}^m = 0.99$.

This high fractional occupancy was due to the low sweep gas slow rate. However, when dealing with mixture systems in pervaporation, we estimate the downstream fractional occupancy by assuming it to be 0, as our understanding of mixture fractional occupancy is limited when it is not equal to 1.

Table 7. 4. Detailed parameters used in SD model estimation for water-p-xylene mixture transport in pervaporation PIM-1_4% H₂_500C_CMS

RO		p-Xylene	Water
Parameters	D^m (cm ² /s)	5.42×10^{-11}	1.52×10^{-9}
	ρ_{CMS} (g/cm ³)	2	2
	q_{sat} (mmol/g)	0.828	5.649
	x^{feed} (mole fraction)	4.73×10^{-5}	0.99995
	γ^{feed} (UNIQUAC) at 1 bar	11848	1
	$\gamma^{permeate}$ (UNIQUAC) at 1 bar	11848	1
	p^{feed} (bar)	1	1
	f^{feed} (kPa)	0.52	5.61
	Liquid mass fraction in liquid saturated membrane	0.115	
	Polynomial model parameter, a	0.28	-0.02
	Polynomial model parameter, b	-1.34	0.05
	Polynomial model parameter, c	2.57	1.42
	Polynomial model parameter, d	-2.63	0.15
	Polynomial model parameter, e	1.53	-
	Polynomial model parameter, f	3×10^{-10}	-
	$\theta^{m,upstream}$	0.052	0.948
	ℓ (cm)	0.00013	0.00013

The predictions of water and p-xylene separation in pervaporation using PIM-1_4% H₂_500_CMS are presented in Table 7. 5. Initially, arbitrary values were assigned to the permeate mole fraction, which were used to calculate the downstream fugacities. The upstream and downstream fugacities were then used to calculate the Δf_i^m and $\bar{f}_i^m$, allowing the calculation of the diffusive fluxes (Eq. (7- 2)). Then the calculated diffusive fluxes were used to determine the permeate mole fractions, $x_{i,permeate}$ (Eq. (7- 8)). The calculated permeate mole fraction was subsequently used to calculate the downstream fugacities, and through iterations, the final concentrations for the permeate mole fraction were obtained where the input and output permeate mole fractions converged.

In pervaporation systems where a downstream sweep gas is used, the permeate mole fraction can be diluted by the sweep gas depending on the flow rate of the sweep gas flow rate (Figure 7. 6). Therefore, the dilution factors, k_{dilution} , as defined in (Eq. (7- 11)), were varied to investigate the effect of permeate dilution on the water-dissolved organic solvent separation. The diluted permeate mole fraction, $x_{i,\text{diluted permeate}}$, was used to calculate the downstream fugacity. k_{dilution} was varied in 0.01, 0.1, to 1 to represent conditions of high dilution to minimal dilution, respectively. The effect of the dilution factor on the separation parameters (flux, transmembrane fugacity, and separation factor) are presented in Figure 7. 7 and Table 7. 5. The pervaporation system employing PIM-1_4% H₂_500_CMS for the separation of dissolved organics in aqueous solutions predicts the concentration of p-xylene in the permeate across various levels of permeate dilution.

$$x_{i,\text{diluted permeate}} = k_{\text{dilution}} x_{i,\text{permeate}} \quad (7- 11)$$

Under conditions of no dilution ($k_{\text{dilution}}=1$), where the sweep gas is used to carry the permeates to the condenser without diluting the permeate fugacities, the minimum fugacity gradients across the membrane are observed. As a result, both p-xylene and water exhibit the lowest fluxes. The separation factor of p-xylene/water was estimated to be ~559.

In contrast, under conditions of low downstream permeate activities, where the permeates are significantly diluted ($k_{\text{dilution}}=0.01$), both the p-xylene and water experience the maximum fugacity gradients across the membrane. This leads to an increase in both p-xylene and water fluxes. However, mainly due to the higher molar fraction of water in the feed stream, the feed water fugacity is higher than the feed p-xylene fugacity. Although both fugacity gradients reach their maximum values as the downstream fugacity

approaches zero, the maximum fugacity gradient value is higher for water. Consequently, the increase in water fluxes is more pronounced, resulting in a lower separation factor of p-xylene over water. This relationship between flux and separation factor with respect to the dilution of permeate via sweep flow can be utilized, depending on the desired separation performance.

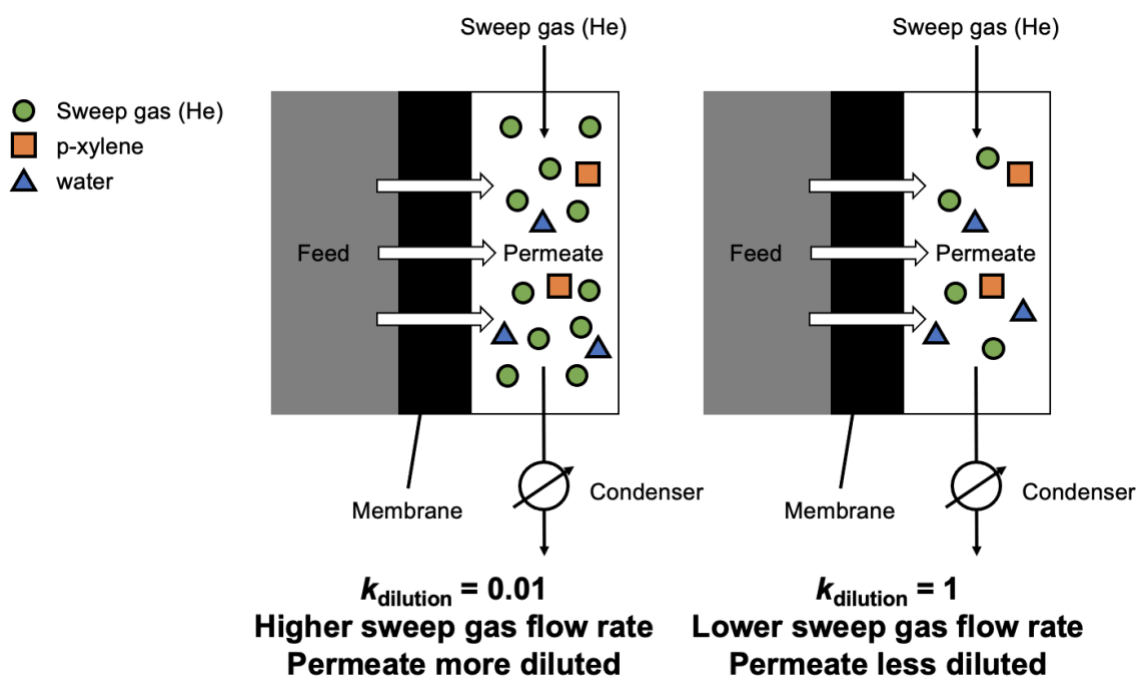


Figure 7. 6. A cartoon illustrating a pervaporation system, highlighting the varying levels of permeate dilution achieved through different sweep gas flow rates on the downstream side of the membrane. The numbers of sweep gas helium molecules, p-xylene molecules, and water molecules depicted in the diagram do not reflect the quantitative ratio between the molecules but serve as qualitative representations to demonstrate the differences between high dilution (e.g. $k_{\text{dilution}} = 0.01$) and low dilution ($k_{\text{dilution}} = 1$) conditions.

Table 7. 5. Calculation prediction of p-xylene and water separation in pervaporation using PIM-1_4% H₂_500_CMS.

Dilution factor for permeates	$x_{\text{permeate, pX}}$	$x_{\text{permeate, w}}$	Δf_{pX}	Δf_{w}	Flux _{pX}	Flux _w	SF _{pX/w}
-	Mole fraction	Mole fraction	kPa	kPa	g/m ² /h	g/m ² /h	-
0.01	4.0×10^{-4}	0.9996	1.0457	5.52	0.18184	78.2	8.3
0.1	4.7×10^{-4}	0.9995	1.0456	5.02	0.18181	65.3	10.0
1	2.6×10^{-2}	0.97	0.9979	0.15	0.16594	1.1	558.6

pX = p-xylene, w = water, SF = separation factor, α = permselectivity.

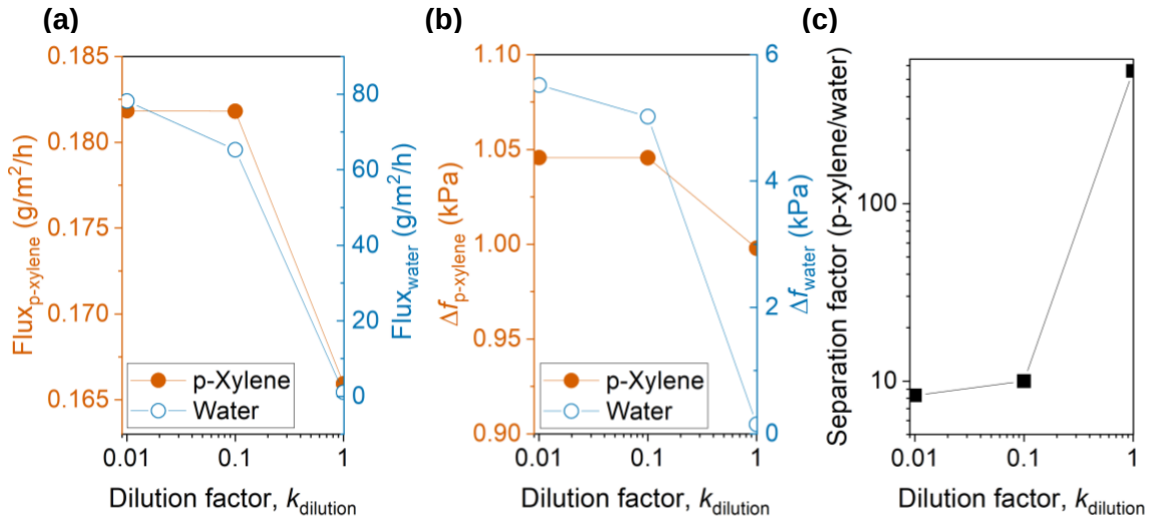


Figure 7. 7. a) Flux, b) transmembrane fugacity of p-xylene and water, and c) separation factor of p-xylene over water with respect to the dilation factor, k_{dilution} , for permeates in pervaporation separation of dilute p-xylene in aqueous mixture.

7.7 Discussion

The permeation of water-organic mixtures such as water/p-xylene through amorphous, permanently microporous structures such as carbon molecular sieves is clearly a complex process. Taken holistically, our combined data sets focusing on surface and textural analysis, diffusion and sorption coefficient measurements, and permeation measurements under different sets of driving forces suggest that there is fertile ground for

engineering CMS materials to enable different types of transport mechanisms. A common observation in VP, PV, and RO was that the predicted diffusive flux of water underestimated the experimental fluxes. This discrepancy was more evident in the pressurized RO system ($\sim 150\times$ for RO as compared to $\sim 4\times$ for VP and PV). Such a difference in fluxes for the RO case (compared with the relatively good agreement in the VP and PV cases) suggests to us that water is permeating through the H₂-pyrolyzed PIM-1 membranes via a Poiseuille-style mechanism. A potential impact of this observation is that it is likely possible to intentionally design CMS membranes such that the solvent molecule (water, in our case) permeates following a Poiseuille-flow style mechanism, which is important from a practical perspective as this transport mechanism can conceptually lead to high water fluxes. However, Poiseuille transport is often undesirable in practice as the solute molecules are often nonselectively convected through the membrane. We show here that p-xylene in the **PIM-1_4% H₂_500_CMS** sample transports only via a sorption-diffusion mechanism (i.e., via activated diffusive “hops” through the membrane ultramicropores), whereas water can transport through the same micropores – or perhaps through separate micropores not accessible to p-xylene – via a Poiseuille-style mechanism (Figure 7. 8). CMS membranes ideally consist of microporous cell structures composed of carbon plates with ultramicroporous slits, which result in interconnected ultramicropores and micropores that exhibit a narrow distribution of pore sizes. Within this distribution, there are interconnected pores that are continuous through the membrane that facilitate both diffusive fluxes of water and p-xylene (with an ultramicropore size of 3 – 4 Å). Additionally, we speculate that there exists a population of continuous pores in the 5 – 7 Å range, which are potentially created in the continuous

phase of orphan strands. These larger and less selective ultramicropores may serve as a convective pathway for water while still acting as a diffusive pathway for p-xylene (Figure 7. 8). In these slit-shaped pores, the convective transport of water may occur around the p-xylene molecules transporting via activated diffusion. Although this is a speculative interpretation, the resulting differences in the SD transport rate of p-xylene and the pore flow transport rate of water in such a situation provide interesting possible combinations of solute rejection and water flux.

Importantly, these same membranes can also be used in pervaporation applications in which the transmembrane pressure is minimized relative to RO, thus allowing the membranes to operate predominantly in a SD mode for all penetrants (i.e., water and p-xylene). From the vapor permeation experiments, we find that the PIM-1 CMS membranes are permselective for water, while the PVDF CMS membranes are permselective for p-xylene, likely due to differences in the water sorption isotherm in the two carbon membranes. Nevertheless, the high activity coefficient of p-xylene in the feed mixture allows for significant enrichment of p-xylene in the membrane permeate for both classes of membranes, suggesting an interesting path forward for both water purification and solute recovery applications via the combination of RO and PV in a membrane cascade.

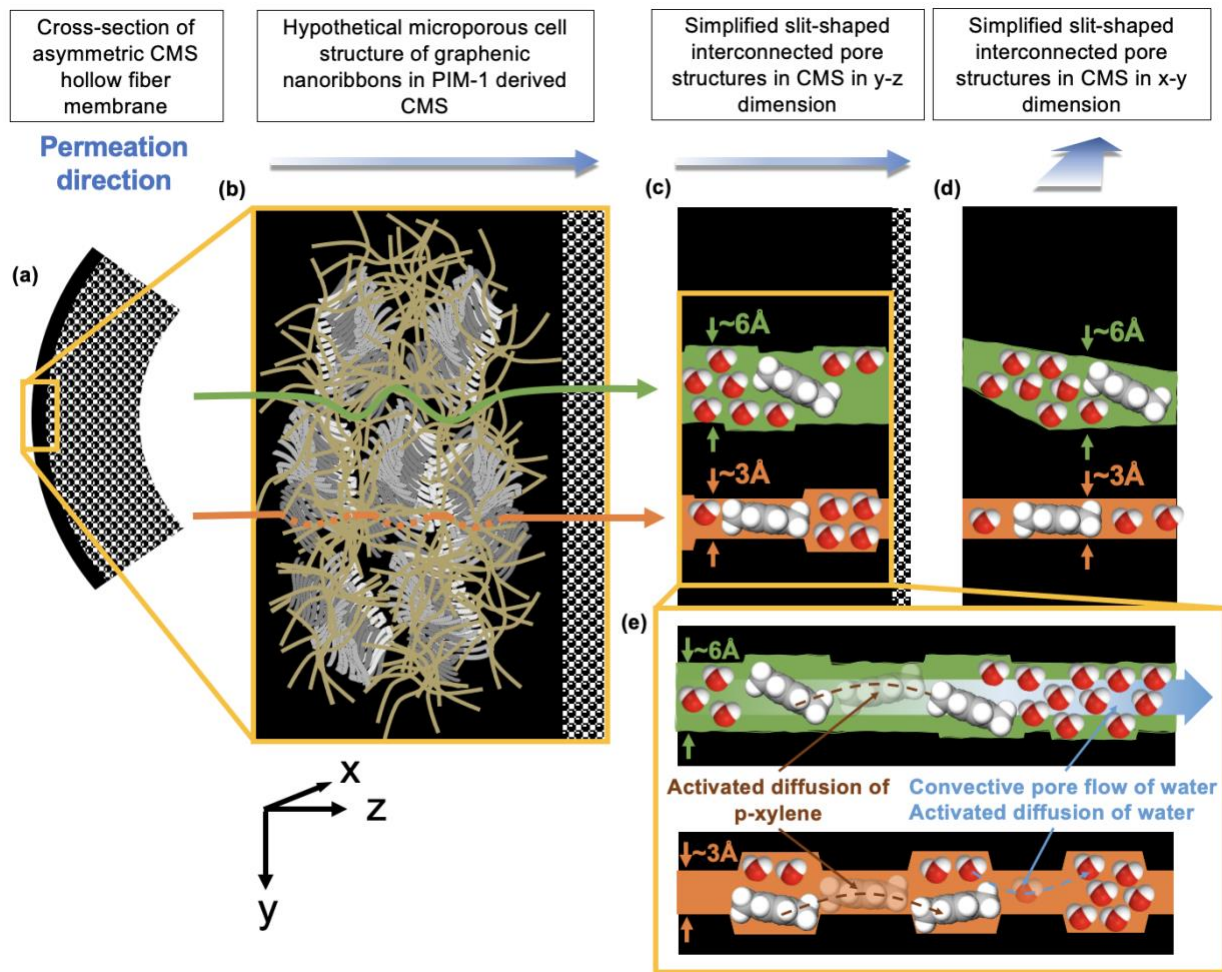


Figure 7. 8. Hypothetical schematic of water and p-xylene co-transport in PIM-1_4% H₂_500_CMS in a hydraulic permeation experiment. a) A cross-section of asymmetric hollow fiber CMS membrane. The transport of water and p-xylene occurs from the shell side to the bore side. b) A magnified schematic of the selective layer of the asymmetric hollow fiber CMS membrane. The hypothetical structure of PIM-1_4% H₂_500_CMS [9] is shown, which consists of a microporous cell matrix composed of graphenic plates with ultramicroporous gaps. The microporous cell matrix is surrounded by a network of orphan strands. c) A simplified schematic of the slit-shaped microporous structure of PIM-1_4% H₂_500_CMS. The transport pathways exist in parallel through less-selective ultramicropores (5 – 7 Å) and more selective ultramicropores (3 – 4 Å). d) A simplified schematic of the slit-shaped microporous structure of PIM-1_4% H₂_500_CMS, showing the dimension where permeate is transporting into the plane of the page. The convective transport of water in 5 – 7 Å pores may occur around the p-xylene molecules in this direction, which are transporting only via activated diffusion in the slit-shaped pores without blocking the pathway for water transport.

7.8 Conclusions

This study aims to investigate the transport mechanism of water and dissolved p-xylene in PIM-1_4% H₂_500_CMS. PIM-1_4% H₂_500_CMS has previously demonstrated high separation performance for water and p-xylene in vapor permeation from near-saturated mixture compositions in Chapter 6. Building upon these findings, the present work focuses on the liquid separation of water and a dilute concentration of dissolved p-xylene using an asymmetric hollow fiber CMS membrane.

To start with, the pure water transport in PIM-1_4% H₂_500_CMS membranes across RO, PV, and VP systems was examined using a simplified SD flux equation. The application of the simplified flux equation to the water transport in the VP system yielded accurate predictions, demonstrating similar performance to a more precise SD flux prediction presented in Chapter 6. Moreover, the diffusive water transport prediction in the PV system showed good agreement with the experimental flux. However, a notable deviation between the diffusive SD water flux estimation and the experimental flux was observed in the case of RO. This deviation can be attributed to the presence of small defects that are more significantly influenced in the pressurized RO system. The flux through defects is interpreted as convective flux.

Subsequently, the transport of a mixture of water and a dilute concentration of dissolved p-xylene in the RO system was predicted and compared with the experimental data. The RO separation experiments exhibited p-xylene rejection of ~69.4 % under 10 bar transmembrane pressure gradient. In contrast to the significant convective flux observed in water transport, the flux of the dilute concentration of p-xylene did not exhibit a convective component, as its flux was well-predicted by the SD calculations. When the convective flux of water was accounted for, the mixture flux was reasonably well estimated, as was

the p-xylene rejection ~ 59.3 %. Furthermore, despite the large convective flux of water, the PIM-1_4% H₂_500_CMS membrane did not demonstrate sorp-vection transport. This can be attributed to the membrane's high affinity for water and its small pore size distribution, which restricts the transport of p-xylene by the bulk flow of water.

The mixture transport prediction of water and a dilute concentration of dissolved p-xylene was also investigated in the PV system and exhibited an effective concentration of p-xylene on the permeate. The degree of dilution of the permeates was found to have a significant impact on the separation performance. When the permeates were minimally diluted by the sweep gas, the fluxes of water and p-xylene were low due to small fugacity gradient driving force, while exhibiting an effective concentration of p-xylene on the permeate. On the other hand, when the permeates were significantly diluted, both water and p-xylene fluxes were maximized. However, the separation factor of p-xylene/water decreases due to the higher maximum fugacity gradient of water in the presence of a dilute concentration of organic solvents in the aqueous feed. When the RO and PV data are inspected in the context of our single component sorption, diffusion, and permeation data, we hypothesize the presence of larger, interconnected micropores that enable Poiseuille-style transport of water while inhibiting such transport for p-xylene. Such a combination of pore flow and sorption-diffusion fluxes for the solvent and solute, respectively, is a potential path forward for engineering high-performance membranes with high water permeance and solute rejections.

It is important to acknowledge the limitations of this study. Assumptions were made in the SD model to simplify the flux calculations, including the utilization of a linear uptake model in the pressurized liquid system, a simplified mixture uptake approach, and the

assumption of zero total uptake at the downstream in pervaporation. Consequently, while the findings provide valuable insights into transport under different scenarios, they may not encompass the entirety of the phenomenon. Indeed, key questions exist regarding the nature of the water transport mechanism in these permanently microporous materials. Nevertheless, we believe these findings offer valuable insights into the engineering conditions necessary to achieve the desired separation performance of a membrane in a given separation modality, whether it involves the rejection or the concentration of p-xylene in the permeate stream

7.9 References

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CHAPTER 8. CONCLUSIONS AND FUTURE WORK

8.1 Dissertation Review

This dissertation sought to investigate the transport of water and organic solvents in amorphous CMS membranes. The separation of dissolved organic solvents from wastewater is a topic of interest in industries and academia. As an exemplar of a dissolved organic solvent, p-xylene was selected for investigation in this study. Here, we suggested high-performance CMS membranes as promising materials for the efficient separation of water and organic solvents. The adjustable micropores in CMS materials offered a significant advantage, allowing us to explore how different CMS structures and surface chemistries impact the transport of water and organic solvents. Gaining a comprehensive understanding of water and organic solvent transport in amorphous microporous CMS membranes with varying structures and surface chemistries is crucial for guiding material engineering and design to achieve desired separation. Given the challenges associated with computationally modeling the transport behavior in amorphous materials, our approach in this study is to experimentally investigate the transport mechanism of water and p-xylene in various CMS membrane materials.

In this work, the structure of CMS membranes was extensively investigated through gas physisorption and unconventional characterization techniques, such as neutron total scattering and small-angle X-ray scattering (SAXS). These methods provided valuable insights into the microporous structures of CMS membranes derived from PIM-1 polymer precursor. Then, the transport of water and p-xylene in CMS membranes was examined by experimentally investigating the transport mechanism in PVDF-derived CMS using a SD

transport model. As an initial approach, vapor transport was examined by experimentally determining the vapor sorption and diffusion coefficients, and the SD-modeled permeabilities were validated through vapor permeation experiments. Subsequently, the co-transport of water and p-xylene vapor mixtures was investigated in various PIM-1-derived CMS membranes, aiming to understand the relationship between CMS structure and the transport of water and p-xylene. Lastly, a PIM-1 derived CMS hollow fiber membrane was utilized to separate a liquid dilute solution of dissolved p-xylene in water, emulating a more realistic scenario of wastewater separation. The choice of a PIM-1-derived CMS in the liquid separation was informed by the impressive separation performance observed in prior vapor separation studies. The transport mechanism of water and the dilute concentration of p-xylene in liquid separation processes, such as RO and PV, was examined using a SD model. We observed that p-xylene likely follows a SD-style transport mechanism, whereas water may experience Poiseuille-style transport in the somewhat larger defects or ultramicropores within the CMS membranes studied here. The findings provided valuable insights into the engineering conditions necessary to achieve the desired separation performance, whether it involves the rejection or the concentration of p-xylene in the permeate stream.

8.2 Summary and Conclusions

8.2.1 Chapter Summaries

Water scarcity and pollution are critical global challenges that require effective wastewater management for water sustainability and environmental conservation. In the context of industrial wastewater management, the separation of water and dissolved

organic solvents plays a crucial role in mitigating water pollution risks and ensuring the availability of safe water supplies. Membrane separation offers cost-efficient and highly effective separation performances. This dissertation focuses on exploring the potential of a rigid microporous material as a membrane material that achieves the desired separation performance for water and organic solvent separation. This study investigated p-xylene as a representative aromatic organic solvent commonly encountered in industrial water.

Chapter 1 of this dissertation includes an overview of research on water-p-xylene separation, offering a broader context and highlighting the current state of the art technology in this field. Chapter 2 includes background and theory for understanding the key concepts explored in this dissertation. Chapter 3 provides detailed list of materials used and experiments conducted, offering descriptions of the experimental procedures.

Chapter 4 addresses the first objective of the dissertation, which is *to enhance our understanding of ultramicropore formation in CMS*. The unique structure of CMS materials has intrigued researchers with its paradoxical combination of seemingly disordered features and well-defined pore structures. Previous work by Ma et al. [1] demonstrated that PIM-1 derived CMS membrane pyrolyzed under 4% H₂ balanced with argon has shown improved permeability while maintaining separation efficiency, compared to the CMS from argon pyrolysis. This work aimed to explore deeper into the structure of PIM-1-derived CMS that resulted in the engineering of membrane separation. We employed CO₂ and Ne physisorption, which revealed ultramicropore size distribution not accessible through standard methods like N₂ physisorption and XRD. The comprehensive analysis of gas physisorption, neutron total scattering, and SAXS revealed that PIM-1-derived CMS pyrolyzed under 4% H₂ exhibited a more amorphous and loosely

packed structure compared to PIM-1 derived CMS pyrolyzed under Ar, which correlates with its separation performance with xylene isomers [1]. Furthermore, based on these structural characterization results, we proposed a potential microstructure for PIM-1-derived CMS, featuring graphenic nanoribbons that form ultramicroporous slits by avoiding one another in the packing process. These graphenic nanoribbon strands pack irregularly through disordered π - π interactions, forming micropores dispersed among orphan strands [2]. Although a complete understanding of the CMS microstructure remains elusive, our combined approach provided valuable insights into the molecular-level structure of ultramicropores.

Chapter 5 explores objective 2, *investigating the transport mechanism of water and p-xylene in PVDF-derived CMS membrane using a sorption-diffusion (SD) model*. The chapter investigated the potential of CMS membranes for high-performance separation of water and p-xylene. The transport mechanism of water and p-xylene vapors in PVDF-derived CMS membranes was studied using the SD model. The sorption and diffusion coefficients were experimentally determined, and the SD modeled permeability was validated by showing good agreement with experimental permeabilities. The results indicated that p-xylene exhibits selectivity over water due to sorption selectivity, and mixture permeation experiments suggest the presence of a competitive sorption-selective separation mechanism. These findings demonstrated the potential of CMS membranes for effective water/organic solvent separations as organic-selective membranes.

Chapter 6 focuses on the third objective, which is to *understand the relationship between membrane structure and transport characteristics of water and p-xylene separation in CMS membranes*. The investigation involved studying the transport of water

and p-xylene in CMS membranes with varied pore size distributions and surface chemistries. Four variables were considered in the fabrication of CMS membranes to achieve diverse pore structures and surface chemistries. CO₂ isotherms and XPS analysis confirmed the adjustment of pore size distributions at a molecular level and surface chemistries, respectively. The SD model was used to analyze the water transport in PIM-1-derived CMS, and the experimental results validated the modeled permeability. The SD transport study of water and p-xylene revealed that the diffusion selectivity is dominating in PIM-1-derived CMS, whereas the sorption selectivity is dominating in PVDF-derived CMS. Vapor permeation experiments demonstrated high permselectivity of water over p-xylene in PIM-1-derived CMS and showed that the separation performance of water and p-xylene vapors in PIM-1-derived CMS varies with different pore size distributions. Activation energy analysis revealed diffusion-controlled transport of water and sorption-controlled transport of p-xylene in mixture transport, confirming molecular sieving separation in PIM-1-derived CMS, in contrast with PVDF-derived CMS that exhibits competitive sorption-selective separation. This work showed that CMS membranes can achieve either water-selective or p-xylene-selective separation depending on the choice of polymer precursors, and the separation performance can also be engineered by adjusting the pyrolysis atmosphere, final pyrolysis temperature, and temperature profile.

Chapter 7 discusses the fourth objective, *modeling the liquid separation of water and p-xylene in PIM-1 derived CMS membrane*. The transport mechanism of water and dissolved p-xylene in PIM-1-derived CMS was investigated, focusing on the liquid separation in an asymmetric hollow fiber CMS membrane. The transport of pure water in different membrane systems (RO, PV, and VP) was analyzed using a simplified SD flux

equation. The pure water transport study showed good agreement between predicted and experimental fluxes, except for RO, which exhibits the convective flow through small defects under pressurized conditions. Furthermore, the liquid separation of a dilute concentration of p-xylene in an aqueous solution in the RO system was investigated. The SD transport was accurately predicted where the water flux comprises both diffusive and convective components, while the p-xylene flux is solely diffusive. Experimental results validated our predictions, with the system exhibiting a p-xylene rejection of ~69.4 % under a 10 bar transmembrane pressure gradient. Moreover, the liquid separation in the PV system was modeled, which demonstrates an effective concentration of p-xylene on the permeate. The findings provided valuable insights into the engineering conditions required to achieve the desired separation performance in liquid separation, whether it pertains to the effective rejection or concentration of p-xylene in the permeate stream.

8.3 Future Directions

8.3.1 Optimization of CMS hollow fiber membranes for organic selective separation in pervaporation

Chapter 6 demonstrated the remarkable water-selective separation performance of PIM-1-derived CMS membranes in vapor permeation of near-saturated mixture feed, showcasing their potential for molecular sieving separation and high rejection of organic solvents. However, Chapter 7 revealed the limited p-xylene rejection (~70%) performance of these membranes in liquid separation of dilute p-xylene in an aqueous feed using RO. The high activity coefficient of p-xylene in water resulted in high flux and low rejection of p-xylene, hindering the efficiency of the separation process. An alternative approach

focusing on concentrating the dilute organic solvents in the permeate rather than collecting purified water may be more effective, especially considering the relatively low flux achieved by CMS membranes in liquid separation.

On the other hand, PVDF-derived CMS membranes demonstrated selective separation of p-xylene in the vapor permeation, highlighting their potential for organic selective separation in a liquid environment. The PIM-1-derived carbon membranes that have shown an effective sorption-vection transport [3] have reported pore volumes ranging from 0.015 to 0.8 cm³/g (obtained from N₂ physisorption at 77K at P/P₀ ~ 0.99). On the other hand, the PVDF-derived CMS hollow fiber membranes have reported a pore volume of 0.35 cm³/g (measured by the N₂ physisorption at 77K at P/P₀ ~ 0.99) [4]. As discussed in Chapter 6, the larger microporous volume and the presence of larger micropores in the PVDF-derived CMS, coupled with its low water sorption affinity, suggest the possibility of sorption-vection transport in PVDF-derived CMS, where competitively sorbed p-xylene transport can be effectively assisted by the convective water flux. Furthermore, the utilization of the PVDF as a polymer precursor offers cost advantages and enhanced accessibility compared to PIM-1-derived CMS, making it a viable and economically attractive option for efficient liquid separation processes. The successful fabrication of PVDF-derived CMS hollow fiber membranes and their application in reverse osmosis separation of xylene isomers [4] provides a practical methodology for implementing these membranes for liquid separation applications.

8.3.2 Influence of polymer precursor's molecular weight and polydispersity index (PDI) on the structure and transport properties of CMS.

Chapter 6 investigated the transport behavior of water and p-xylene in PIM-1-derived CMS membranes that were pyrolyzed under 4% H₂ at a maximum pyrolysis temperature of 500 °C. Interestingly, discrepancies in the transport properties were observed between the same CMS membranes in this study and those previously introduced by Ma et al. [1]. The CMS membranes in this study exhibited lower sorption uptakes and permeabilities, as shown in Figure 8. 1.

We propose that these differences may arise from the varying properties in the PIM-1 precursor polymers employed, which were synthesized in the laboratory. Specifically, the molecular weight and PDI of the PIM-1 polymers differed (Table 8. 1), potentially leading to different CMS structures. Hypotheses are formulated to study the influence of these polymer properties on the CMS transport properties, based on speculated CMS structure formation mechanism. It is conjectured that higher average weight molecular mass (M_w) and lower PDI could facilitate the formation of denser structures during pyrolysis. Expanding on this idea, the large M_w could induce more entanglements, resulting in more interchain bond stresses and chain fractures that yield shorter strands. These strands, coupled with the presence of shorter polymer chains in PIM-1 with higher PDI, would reorganize during pyrolysis to form tighter carbon structures. Additionally, investigating the effects of the H₂ pyrolysis environment, which promotes sp³ bond formation over the sp² carbon backbone aromatization, on polymers with varying properties presents an intriguing avenue for future research.

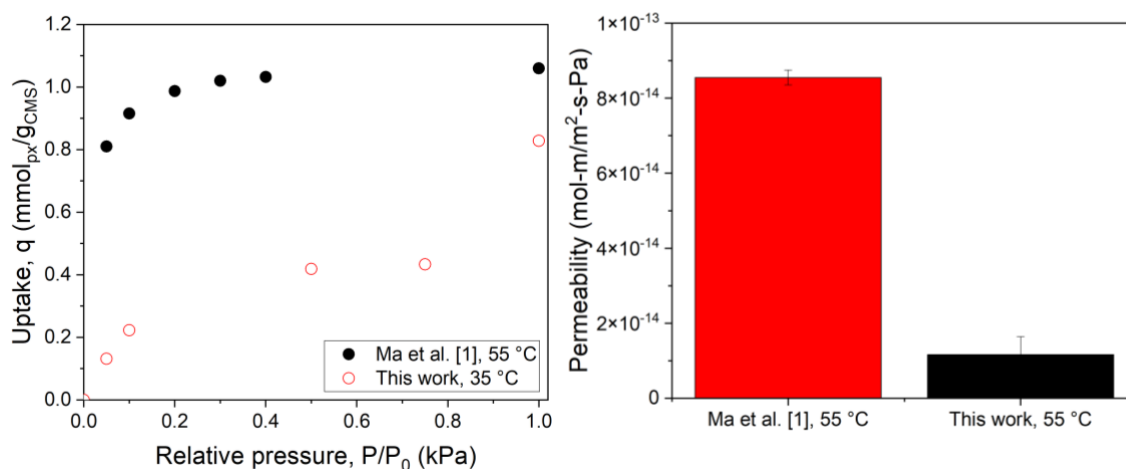


Figure 8. 1. Different transport behaviors observed from PIM-1 derived CMS pyrolyzed under 4% H₂ at a maximum temperature of 500 °C. a) p-xylene uptake isotherms. b) permeabilities of p-xylene vapors in a Wicke Kallenbach system.

Table 8. 1. Properties of synthesized PIM-1 utilized as polymer precursor for CMS membrane fabrication

	M_w	M_n	PDI
PIM-1 in Ma et al.[1]	68,000	46,500	1.5
PIM-1 in this work	157,000	27,300	5.8

8.3.3 Mutual transport studies of p-xylene and water in CMS membranes

Throughout the dissertation, the mixture transport studies on water and p-xylene in CMS membranes were performed under assumptions such as neglected mutual diffusion effects and simplified mixture sorption models. As observed from Chapters 5 and 6, the mixture separation shows distinct separation performance from the pure component permeabilities in water and p-xylene. For instance, PVDF-CMS exhibited an enhanced concentration of p-xylene in the permeate during mixture separation, suggesting a sorption-selective separation mechanism. In PIM-1 derived CMS membranes, we observed increased permselectivity of water/p-xylene in 4% H₂ pyrolyzed CMS and decreased

permselectivity in CO₂ pyrolyzed CMS. Based on the current observations, it is possible to hypothesize that the increased water selectivity in 4% H₂ pyrolyzed CMS during mixture transport can be attributed to its sorption-selective properties as evidenced by the water isotherm shape in this particular CMS. Conversely, in CO₂ pyrolyzed CMS, the transport of water and p-xylene may involve frictional coupling effects, where the faster-moving species (water) experiences delay due to interaction with the slower-moving species (p-xylene), while the slower species is accelerated by the presence of the faster species. Alternatively, the reduced water selectivity on CO₂ pyrolyzed CMS could be a result of competitive sorption, with p-xylene exhibiting a greater affinity for adsorption compared to water in the mixture system.

Therefore, mutual transport studies in diffusion and sorption would be beneficial to investigate. A pulsed-field gradient NMR (PFG-NMR) experiment can be a useful tool to measure the mutual diffusion [5] of water and organic solvent in CMS. Moreover, conducting competitive sorption measurement would be advantageous to achieve a more accurate understanding of how the adsorbates with such different sorption properties interact within CMS materials. Such insights would not only provide direct evidence of sorption selective separation in PVDF-derived CMS, but also offer valuable knowledge regarding the underlying factors influencing the enhanced or hindered permselectivity performances observed in PIM-1 CMS.

8.3.4 *Hyperskin*

A hypothesis has been made that a densely packed carbon layer called hyperskin is formed during pyrolysis on the outer surface of CMS materials [6]. This hyperskin layer

could serve as an additional barrier for diffusion through the CMS surface. The presence of hyperskin in CMS membranes can be experimentally investigated using PFG-NMR as well. The diffusivity measurement in PFG-NMR enables capturing microscopic diffusion in the absence of a macroscopic loading gradient across the film [5]. When the guest molecule is in near-infinite dilution, the self-diffusivity measured by PFG-NMR (D^*_s) and the macroscopic M-S diffusivity ($\bar{D}$) should converge. If the microscopic self-diffusivity is significantly larger than the macroscopic M-S diffusivity, it would become an experimental evidence that the hyperskin exists.

Moreover, more insights into the structural properties of the hyperskin can be deduced by comparing the activation energies derived from both microscopic and macroscopic diffusion measurements. The activation energies of diffusion would be the same if the hyperskin is composed of an increased distribution of pore blockage. On the other hand, if the hyperskin consists of smaller pores, the activation energy of diffusion would be higher in the macroscopic studies compared to that in PFG-NMR. Therefore, these comparative studies provide a means to understand the nature and properties of the hyperskin layer in CMS membranes.

*8.3.5 Investigation of the speculative convective water transport in **PIM-1_4%** **H₂500_CMS***

The speculative convective water transport through larger and less selective ultramicropores in **PIM-1_4% H₂500_CMS** (Figure 7. 8) could be further investigated as future work. Carbon dioxide (kinetic diameter = 3.3 Å) and isopentane (kinetic diameter = 5.9 Å) may be used as a probe pair that provides useful insights. This probe pair exhibits

similar kinetic diameters and polar/nonpolar properties with the water (kinetic diameter = 2.7 Å) and p-xylene (kinetic diameter = 5.8 Å) pair, potentially yielding similar transport behavior in the **PIM-1_4% H₂_500_CMS** and indicate the transport of these molecules in the suggested parallel pathways.

Moreover, the investigation of the convective water transport pathway focusing on the engineering of the CMS microstructure (Figure 7. 8) would be an interesting approach. The hypothesis posits that the manipulation of thermal soak (hold) duration in pyrolysis controls the packing of the orphan strands into the microporous structures that features selective slit pores. If we can observe the reduction of the convective water transport by increasing the CMS pyrolysis thermal soak time, it would become another experimental evidence that describes the formation of CMS microstructure and the existence of parallel pathways for water in **PIM-1_4% H₂_500_CMS**. This finding may also present another method to control the pathway for convective water transport and the water-organic solvent separation.

8.4 References

- [1] Y. Ma, M.L. Jue, F. Zhang, R. Mathias, H.Y. Jang, R.P. Lively, Creation of Well-Defined “Mid-Sized” Micropores in Carbon Molecular Sieve Membranes, *Angewandte Chemie International Edition*. **2019**, 131, 13393–13399. DOI: 10.1002/ange.201903105.
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APPENDIX A. HORVATH AND KAWAZOE (HK) PORE SIZE DISTRIBUTION MATLAB CODE FOR NEON PHYSISORPTION

The following code was modified from Joshua Thompson's dissertation [1].

```
clear all;
```

```
%parameter bank
```

```
d_C = 3.4; %Å - Carbon kinetic diameter
```

```
d_Ne = 2.75; %Å - Neon kinetic diameter
```

```
d_N2 = 3.1; %Å - Nitrogen kinetic diameter
```

```
a_C = 1.02*10^-24; %cm^3 ----- polarizability, Sams Jr., G. Constabaris, G.D. Halsey  
Jr. J. Phys. Chem., 64 (1960), p. 1689.
```

```
a_Ne = 0.39*10^-24; %cm^3
```

```
a_N2 = 1.46*10^-24; %cm^3
```

```
x_C = 13.5*10^-29; %cm^3 ----- magnetic susceptibility
```

```
x_Ne = 1.17*10^-29; %cm^3
```

$x_{N_2} = 2.0 \times 10^{-29}$; %cm³

$N_C = 3.85 \times 10^{15}$; %surface density of carbon (molecules/cm²)

$N_{Ne} = 2.3498 \times 10^{14}$; %surface density of Ne (Adsorbate)(atom/cm²)

$N_{N_2} = 6.7 \times 10^{14}$; %surface density of N₂ (Adsorbate)

$MW_{Ne} = 20.1797$; %g/mol - molecular weight of Neon

$m = 9.10938356 \times 10^{-31}$; %kg - mass of electron

$c = 3.00e8$; %speed of light; units [=] m/s

$R = 1.986$; %Ideal Gas constant; units [=] cal/mol/K

$T = 40.15$; %K - experimental temperature

$N_{av} = 6.0221409 \times 10^{23}$; %Avogadro's number

%Define Parameters

%Adsorbate Neon

$d_a = d_{Ne}$; %Å - adsorbate kinetic diameter

$a_a = a_{Ne}$; %cm³ - adsorbate polarizability

$x_a = x_{Ne}$; %cm³ -adsorbate magnetic susceptibility

$N_a = N_{Ne}$; %surface density of adsorbate, number of adsorbate (Neon) atoms per unit area (atom/cm²)

%Adsorbent Carbon

$d_s = d_C$; %Å - adsorbent kinetic diameter

$a_s = a_C$; %cm³ - adsorbent polarizability

$x_s = x_C$; %cm³ - adsorbent magnetic susceptibility

$N_s = N_C$; %surface density of adsorbent, number of adsorbent (carbon) molecules per unit area (molecules/cm²)

$d_o = (d_a + d_s)/2$; %Å

$\sigma_a = (2/5)^{1/6} * d_a$; %Å - minimum distance at zero energy between adsorbate and adsorbate

$\sigma_s = (2/5)^{1/6} * d_o$; %Å - minimum distance at zero energy between adsorbate and adsorbent

```
raw_data=xlsread('post-micromeretics 061021 PIM-1 4% H2 CMS  
40K.xlsx','Logarithmic','A30:M56'); %Copy your data file to the MATLAB folder on  
your computer
```

```
P = raw_data(:,1); %bar
```

```
P_0 =14.85; %bar - saturated pressure of adsorbate at T
```

```
n = raw_data(:,11); %mmol/g - adsorbed amount of adsorbate
```

```
n_inf = 6.57811632; %mmol/g - in logarithmic region
```

```
V = raw_data(:,13); %cm3/g - measured adsorbed amount of adsorbate in volume (not  
STP)
```

```
%Cheng-Yang Correction -- HK Model assumes Henry's law for adsorption.
```

```
%CY-correction will account for LANGMUIR behavior. 0 = no; 1 = yes.
```

```
YYcorr = 1;
```

```
%Modified HK Equations -- There are some inconsistencies in the original assumptions  
for the derivation of the HK equations. 0 = no; %1 = yes.
```

```
MHK = 0;
```

```
a = 0.1273115; %from logarithmic fit  $\theta = a \cdot \ln x + b$ 
```



```
b = 1.458618984;
```

```
%1. Guess L
```

```
guessL = linspace(1, 25,10000); %A - slit width range from 3Å to 15Å, 10000 steps
```

```
%2. Experimental e_free - free energy change during adsorption
```

```
pressuredata = length(P); %length of experimental pressure data
```

```
e_free = zeros(pressuredata,1); %generating experimental energy term
```

```
theta = zeros(pressuredata,1);
```

```
for i = 1:pressuredata
```

```
    if YYcorr ==0
```

```
        e_free(i) = R*T*log(P(i)/P_0); % cal/mol
```

```
    else
```

```
        theta(i) = a*(P(i)/P_0)+b; %logarithmic isotherm prediction
```

```
        %theta(i) = n(i)/n_inf; %experimental uptake
```

```
        e_free(i) = R*T*log(P(i)/P_0) + R*T*(1-1/(2*a))*(theta(i))); %cal/mol - logarithmic
```

```
isotherm prediction
```

end

end

%3. calculate modeled molar average interaction energy

$A_s = 6 * m * c^2 * a_s * a_a / (a_s/x_s + a_a/x_a)$; %Kirkwood-Mullar formula -
dispersion constants ($J \cdot \text{cm}^6$) - constant in Lennard-Jones potential

$A_a = 3/2 * m * c^2 * a_a * x_a$; %Kirkwood-Mullar formula - dispersion constants
($J \cdot \text{cm}^6$) - constant in Lennard-Jones potential

%4. calculate e_{avg}

RMSE = 10000*ones(pressuredata,1);

sqrt = zeros(pressuredata,1);

L_final = zeros(pressuredata,1);

e_final = zeros(pressuredata, 1);

for i = 1:pressuredata %loop for determining L for each P

```

for j = 1:length(guessL) %loop for determining e_avg for L

    sqrt(i) = 0;

    if MHK == 0

        e_model(i) = N_av * (10^10 / 100)^4 * 0.239 *
(N_s*A_s+N_a*A_a)/(sigma_s^4*(guessL(j)-2*d_o))*(sigma_s^4/(3*(guessL(j)-
d_o)^3)-sigma_s^10/(9*(guessL(j)-d_o)^9)-
sigma_s^4/(3*d_o^3)+sigma_s^10/(9*d_o^9)); %cal

    else

        M = (guessL(j)-d_s)/d_a;

        e_1 = N_s*A_s/(2*sigma_s^4)*(-(sigma_s/d_o)^4+(sigma_s/d_o)^10-
(sigma_s/(guessL(j)-d_o))^4+(sigma_s/(guessL(j)-d_o))^10)*(10^10 / 100)^4;
        %J*molecule

        e_2= N_s*A_s/(2*sigma_s^4)*(-(sigma_s/d_o)^4+(sigma_s/d_o)^10)*(10^10 /
100)^4 + N_a*A_a/(2*sigma_a^4)*(-(sigma_a/(d_a))^4+(sigma_a/(d_a))^10)*(10^10 /
100)^4; %J/molecule

        e_3 = 2*N_a*A_a/(2*sigma_a^4)*(-
(sigma_a/(d_a))^4+(sigma_a/(d_a))^10)*(10^10 / 100)^4; %J*molecule

    if M<2

        e_model(i) = e_1*N_av * 0.239; %cal

```

```

else

    e_model(i) = (2*e_2 + (M-2)*e_3)/M *N_av * 0.239; %cal

end

end

e_modelavg(i) = e_model(i);

sqrt(i) = sqrt(i) + (e_modelavg(i) - e_free(i))^2;

if e_modelavg(i) < e_free(i)

    if sqrt(i) < RMSE(i) %if sqrt(i for this j) is smaller than previous sqrt(i for j-1),

        RMSE(i) = sqrt(i); %sqrt(i) is replaced with the current value

        e_final(i) = e_modelavg(i); %code still runs if this line is deleted

        L_final(i) = guessL(j); %optimal L for each P

    end

end

end

end

d = L_final - d_s; %Å

```

```

dVdL = zeros(pressuredata,1);

for m = 1:pressuredata

    if d(m) < d_a %if the slit width is less than the adsorbate size

        d(m) = 0; %Let's say the slit width is 0

        dVdL(m) = 0; %cm3(STP)/g/A - and the differential volume is 0

    elseif m - 1 == 0 %if the initial point is some actual value

        dVdL(m) = V(m)/d(m); %cm3(STP)/g/A - extrapolates to 0

    elseif d(m) < d(m-1) %when using CY correction, there is sometimes decreasing L as
RP increases due to coverage approaching 1

        d(m) = max(d) + 1;

        dVdL(m) = 0

    else

        dVdL(m) = (V(m)-V(m-1))/(d(m)-d(m-1));

    end

end
end

```

```
%differential volume plot
```

```
figure;
```

```
plot(d,dVdL,'b');
```

```
xlabel({'Slit Width (Angstroms)'}, 'FontSize', 14);
```

```
ylabel({'dV/dL (cm3(STP)/g/Angstrom)'}, 'FontSize', 14);
```

```
%Write data to Excel (or ASC) file
```

```
user_entry = input('Enter 1 to write data to an Excel file. Enter 0 to cancel. ');
```

```
if user_entry ==1
```

```
    user_entry = input('Specify desired file name: ', 's');
```

```
    filename = user_entry;
```

```
    xlswrite(filename,[d, dVdL]);
```

```
end
```

```
clc;
```

```
d
```

```
dVdL
```

References

- [1] J.A. Thompson, Evaluation and Application of New Nanoporous Materials for Acid Gas Separations, *Georgia Institute of Technology*, **2013**.