

**WETTING AND SCALING RESISTANCE OF
MICROPOROUS MEMBRANES**

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Azal Alhadidi
December 2024

Copyright © 2024 by Azal Alhadidi
All rights reserved.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my thankfulness to God and acknowledge Him for all the blessings and favors that He has bestowed upon me during my time in graduate school. I am thankful for good health, strength, and His favor.

I am immensely grateful to my advisor, Assistant Professor Wei Wang, for his unwavering support during my master's research. The guidance from him was crucial for the successful completion of the study presented in this thesis. His support and passion for my area of research played a vital role in my research accomplishments.

I am also deeply thankful to the Graduate School and the Department of Mechanical, Aerospace and Biomedical Engineering of the University of Tennessee Knoxville for enabling me to pursue my study.

Finally, I want to express my sincerest thanks to my family, friends, and colleagues for their unwavering encouragement and support during my studies. Without their personal cheerleading, my life would have been far more challenging and less enjoyable. I owe a special debt of gratitude to my husband, Anees, and my sons, Ibrahim and Ali, for their extraordinary support and love. I also wish to extend my thanks to my siblings and parents, particularly, my late mother, who had hoped to witness this moment in my life.

ABSTRACT

Membrane distillation (MD) has garnered attention as a viable technology for treating hypersaline water, wastewater, and seawater by utilizing low-grade thermal energy to transport water vapor through hydrophobic microporous membranes. In the MD process, one side of hydrophobic microporous membranes directly contacts heated feed water, while the other side is in contact with the cold cleaned water. However, the application of MD desalination has significant issues, which limit its practical application. First, membrane pore wetting can lead to contamination of the treated water. Second, scaling is another challenge in MD process. Moreover, most microporous membranes used in MD have been modified with materials that are toxic, such as per- and polyfluoroalkyl substances (PFAS). Therefore, it is of great importance to understand the mechanism governing membrane pore wetting and develop novel method to fabricate microporous membranes with high wetting and scaling resistance. In this work, the influence of various surfactants with different charges and molecular structures on membrane pore wetting was studied. It is found that the properties of surfactants have significant influence on the wetting potential. Our results suggest that contact angle and surface tension are not suitable for predicting the wetting resistance of microporous membranes for MD process. Furthermore, we have developed a new method, which enables the fabrication of PFAS-free microporous membranes using polydimethylsiloxane (PDMS) brush. Our membranes display improved wetting and scaling resistance when comparing to the commercially available hydrophobic membranes.

TABLE OF CONTENTS

Chapter One Introduction	1
Chapter Two Fundamentals of Wetting.....	4
2.1 Introduction.....	4
2.2 Wetting on Smooth Surface.....	5
2.3 Wetting on Textured Surface.....	8
2.4 Role of Re-Entrant Texture	10
2.5 Role of Per- and Polyfluoroalkyl Substances (PFAS).....	10
2.6 Porous Membrane with High Wetting Resistance.....	12
Chapter Three Effects of Surfactant Properties on Membrane Wetting	15
3.1 Introduction.....	15
3.1.1 The Use of Surfactants in Tuning Wetting Behavior.....	16
3.1.2 Surfactants Induced Pore Wetting in Membrane Distillation (MD).....	19
3.2 Materials and Experimental Setup.....	20
3.2.1 Materials	20
3.2.2 Surface Tension Measurements	20
3.2.3 Contact Angle Measurements	23
3.2.4 MD Experiments.....	23
3.3 Results and Discussion	25
3.3.1 Surface Tensions of Surfactant Solutions.....	25
3.3.2 Contact Angles of Surfactant Solutions.....	30
3.3.3 Effects of Surfactants on Induction Time of Membrane Wetting.....	30
3.3.4 Relationship between Membrane Wetting and Contact Angle.....	37
3.4 Conclusion	38
Chapter Four Enhancing Wetting and Scaling Resistance of Porous Membrane.....	40
4.1 Introduction.....	40
4.1.1 Use of PFAS in Fabricating Membranes	40
4.1.2 PDMS Brushes.....	41
4.2 Materials and Experimental Setup.....	42
4.2.1 Materials	42

4.2.2 Membrane Modification	44
4.2.3 Contact Angle Measurements	44
4.2.4 Scaling Test.....	44
4.3 Results and Discussion	47
4.3.1 Contact Angle Results.....	47
4.3.2 Scaling Performance	50
4.4 Conclusion	57
Chapter Five Summary	59
List of References	61
Vita.....	74

LIST OF TABLES

Table 3.1. Surfactants with different properties.....	18
Table 4.1. The apparent advancing contact angles θ_{adv}^* and apparent receding contact angles θ_{rec}^* of various liquids on the front side of 0.22 μm pristine PVDF and PDMS-PES membranes	52
Table 4.2. The apparent advancing contact angles θ_{adv}^* and apparent receding contact angles θ_{rec}^* of various liquids on the back side of 0.22 μm pristine PVDF and PDMS-PES membranes	53
Table 4.3. The apparent advancing contact angles θ_{adv}^* and apparent receding contact angles θ_{rec}^* of various liquids on the front side of 0.45 μm pristine PVDF and PDMS-PES membranes	54
Table 4.4. The apparent advancing contact angles θ_{adv}^* and apparent receding contact angles θ_{rec}^* of various liquids on the back side of 0.45 μm pristine PVDF and PDMS-PES membranes	55

LIST OF FIGURES

Figure 2.1. Young's contact angle on smooth surface.....	6
Figure 2.2. Methods for measuring advancing and receding contact angles	7
Figure 2.3. (a) Wenzel state and (b) Cassie-Baxter state on textured surface	9
Figure 2.4. Different textures: (a) concave texture and (b) convex texture.....	11
Figure 2.5. Direct contact membrane distillation process.....	13
Figure 3.1. Different types of surfactants.	17
Figure 3.2. Molecular structures of the five surfactants.	21
Figure 3.3. Surface tension measurements using (a) pendant droplet method and (b) inverted pendant bubble method.....	22
Figure 3.4. Experimental setup for contact angle measurements at (a) room temperature and (b) 60 °C.....	24
Figure 3.5. Surface tensions of (a) SDS, (b) DTAB, and (c) Triton X-100 solutions at room temperature	26
Figure 3.6. Surface tensions as a function of time at 60 °C for 1 M NaCl solutions containing (a) SDS, (b) DTAB, (c) CTAB, (d) Triton X-100, and (e) Tween 20 at different surfactant concentrations.....	28
Figure 3.7. Equilibrium surface tensions for 1 M NaCl solutions containing surfactants of different concentrations at 60 °C.....	29
Figure 3.8. Contact angles on smooth PVDF sheet for DI water and 1 M NaCl solutions containing surfactants of different concentrations: (a) SDS. (b) DTAB, and (c) Triton X-100	31
Figure 3.9. Apparent contact angles on porous PVDF membrane for DI water and 1 M NaCl solutions containing surfactants of different concentrations: (a) SDS, (b) DTAB, and (c) Triton X-100	32
Figure 3.10. The apparent static contact angles of surfactant solutions with different surface tensions on the PVDF membranes at 60 °C	33
Figure 3.11. The induction time of membrane wetting in MD for (a) surfactants of the same carbon chain length but different charge types, (b) positively charged	

surfactants of different chain lengths, and (c) non-ionic surfactants of different molecular structures and weights.....	34
Figure 3.12. Schematic illustration of the effects of surfactant-membrane interactions on MD wetting behavior when comparing (a) anionic and cationic surfactants and (b) surfactants with different molecular weights	36
Figure 3.13. The induction time of membrane wetting as a function of apparent contact angle of the surfactant solution measured at (a) room temperature ($\sim 20\text{ }^{\circ}\text{C}$) and (b) $60\text{ }^{\circ}\text{C}$. The error bars represent the standard deviation calculated from three independent measurements	39
Figure 4.1. Molecular structure of chlorine-terminated PDMS.....	43
Figure 4.2. Schematic showing the fabrication of PDMS-PES membrane	45
Figure 4.3. Schematic showing the setup for scaling experiment.....	46
Figure 4.4. Apparent contact angle as function of surface tension for $0.22\text{ }\mu\text{m}$ (a) PDMS-PES and (b) PVDF	48
Figure 4.5. Apparent contact angle as function of surface tension for $0.45\text{ }\mu\text{m}$ (a) PDMS-PES and (b) PVDF	49
Figure 4.6. Images showing different liquids beading up on or wetting membranes	51
Figure 4.7. Scaling resistance of $0.22\text{ }\mu\text{m}$ membranes at (a) 0 rpm and (b) 100 rpm	56
Figure 4.8. Scaling resistance of $0.45\text{ }\mu\text{m}$ membranes at (a) 0 rpm and (b) 100 rpm	58

CHAPTER ONE

Introduction

A crucial factor that significantly impacts the ability of human society to maintain its well-being, health, and overall sustainability is the limited access to clean and safe drinking water. This pressing concern poses a threat to the sustainable progress of human civilization.¹ To conquer this challenge, it requires innovative solutions for conserving, protecting water sources, and limiting pollution. Recently, membrane distillation (MD) technique has shown great potential for treating wastewater, brackish water, and seawater.

MD is a thermal-driven separation process that uses a microporous, non-wettable membrane to allow the transport of water vapor through pores from heated feed water to condense on the cold side.² In other words, the key principle of the MD process is to split two aqueous liquids at different temperatures using a hydrophobic microporous membrane.² MD demonstrates an outstanding ability to withstand high salinity, provide an effective barrier against inorganic ions and non-volatile contaminants, enable the utilization of low-grade thermal energy, and offer the potential for the extraction and reclamation of valuable resources from the process.^{3,4} However, it is essential to address potential issues associated with this technology such as membrane pore wetting and scaling.^{4,5} Also, to enhance the functionality of the membranes, this technology typically utilizes harmful substances such as per- and polyfluoroalkyl substances (PFAS) to modify the microporous membranes. MD membranes require a hydrophobic property because only water vapor is allowed to pass through membrane pores. Usually, surfaces with hydrophobic property have water contact angles greater than 90°.⁶

In 1963, Bodell conducted pioneering study using such technology.⁷ In the 1980s, W. L. Gore and Associates developed porous polytetrafluoroethylene membranes, which have sufficiently high wetting resistance for membrane distillation.⁸ In recent decades, various microporous membranes have been developed, such as polyvinylidene fluoride (PVDF),^{5,9-11} polytetrafluoroethylene (PTFE),^{12,13} and polypropylene (PP) membranes.¹⁴⁻¹⁶ Recently, extensive research has focused on PVDF membranes for MD application.¹⁷

However, these membranes often experience pore wetting issue when it is in contact with liquids with low surface tensions.

In MD process, membrane pore wetting occurs when the feedwater permeates into the membrane pores, leading to contamination of the treated water.¹⁸ Among other substances in the feedwater, surfactants can have significant impacts on the process of membrane wetting. Nevertheless, the mechanisms through which different surfactants affect membrane pore wetting are still not fully understood. It is crucial to thoroughly investigate and understand the influence of surfactants on the membrane pore wetting in MD process. Study on how ionic and nonionic surfactants with varied molecular structures induce membrane pore wetting is needed. This is important for enhancing the efficiency of MD membranes and ensuring the sustainability and viability of MD technology in water treatment application.

Moreover, scaling (i.e., formation and deposition of inorganic substances on the membrane surface) poses another challenge to the effectiveness of the MD process. The precipitation and creation of mineral scales that adhere firmly to the membrane surface can significantly affect the efficiency of MD process.¹⁹ The existence of scales diminishes both the water flux and the lifespan of the membrane, thereby affecting the cost and energy efficiency of desalination systems. Effectively managing this scaling phenomenon can lead to improved performance and sustainability of MD technology.

Furthermore, PFAS are commonly used to enhance the wetting resistance of MD membranes.²⁰ PFAS have many unique properties, such as high chemical and thermal stability, hydrophobicity, and high resistance to friction.^{21, 22} The properties of PFAS have resulted in their extensive use in various industrial applications. However, the use of PFAS raises serious concerns about the potential risks that substances can cause to human health and ecological systems.^{23, 24} The potential risks presented by PFAS to human health and the environment have garnered considerable concerns.²⁵ An innovative and sustainable approach, which allows the fabrication of PFAS-free MD membranes with high wetting and scaling resistance is in dire need.

We aim to tackle the issues discussed above by 1) Investigating how ionic and nonionic surfactants with varied molecular structures affect the wetting behavior of MD

membranes; and 2) Developing a new surface modification technique using polydimethylsiloxane (PDMS) brush, which allows the fabrication of PFAS-free, microporous membranes with high wetting and scaling resistance.

CHAPTER TWO

Fundamentals of Wetting

2.1 Introduction

Wetting is an essential concept in surface science that describes the interaction between a liquid and a solid surface. Understanding how liquids form droplets on different surfaces is important for various scientific and industrial applications, such as adhesion, self-cleaning, fluid drag reduction, heterogeneous nucleation, and the formation of coffee rings.²⁶

Historical investigations on wetting behavior have been documented for hundreds of years.²⁷⁻²⁹ This reflects endless interest in this complex natural phenomenon. The extensive pursuit of knowledge has led to the formulation of significant concepts such as capillary action or capillarity.³⁰ In 1706, Hauksbee made some of the earliest detailed observations, noting that liquids rise higher in narrow tubes regardless of the presence of a vacuum.³¹ A decade later, Jurin illustrated that the maximum height of liquid ascent is inversely proportional to the diameter of the tube.³² In 1751, Segner identified surface tension as a fundamental property of liquids.³³ In 1805, Young noted the contact angle between a liquid and a solid, demonstrating that the contact angle denoted as θ_Y is formed when the liquid comes into contact with the surface. This observation helped elucidate multiple factors that affect wettability. The properties of both the liquid and the solid, including surface tension, chemical composition, and roughness, all contribute to determining the wettability of a solid surface. The surface tension is a characteristic of liquids that derives from intermolecular interactions at the air-liquid interface. On the other hand, solid surface energy is an important property of solids, and it is analogous to the surface tension of liquids. In addition to liquid surface tension and solid surface energy, surface roughness is another important factor that directly impacts the wettability of a surface. Rough surfaces can enhance wetting behavior by providing additional surface area for the liquid to interact with. This increased roughness creates micro-environments that can trap air or liquid, influencing how the liquid spreads. Moreover, the chemical composition of the surfaces such as hydrophilic or hydrophobic

characteristics further modifies the wetting behavior, often in conjunction with the effect of surface roughness. Therefore, the combined effects of surface tension, surface energy, and surface roughness all contribute to the wetting behavior of a liquid on a solid surface.

2.2 Wetting on Smooth Surface

When a liquid droplet comes into contact with a smooth solid surface, the contact angle θ_Y adopted by the droplet is determined by the Young's equation (**Figure 2.1**):³⁴

$$\cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

Where γ_{SV} , γ_{LV} , and γ_{SL} are the solid surface energy, liquid surface tension and the solid-liquid interfacial tension, respectively. Depending on the contact angle, the solid surfaces can be classified as hydrophilic surfaces ($\theta_Y < 90^\circ$) and hydrophobic surfaces ($\theta_Y \geq 90^\circ$).

In addition to the contact angle θ_Y , the wettability of a surface by a liquid is also characterized by contact angle hysteresis $\Delta\theta$, which is the difference between the advancing and receding contact angles of a liquid droplet:³⁵

$$\Delta\theta = \theta_{adv} - \theta_{rec} \quad (2.2)$$

where θ_{adv} and θ_{rec} are the advancing and receding contact angles, respectively.

There are two techniques for measuring advancing and receding contact angles. The first method involves pumping liquid into and out of a droplet, as illustrated in **Figure 2.2a**. When the liquid is pumped into the droplet, its volume increases. Subsequently, the triple-phase contact line will move with a constant contact angle. This is the advancing contact angle, which is the maximum contact angle a liquid can form on the solid surface. When the liquid volume decreases, the triple-phase contact line will recede with a constant contact angle, which is the receding contact angle (i.e., the minimum contact angle a liquid displays on the solid surface). The second technique that can be utilized to measure advancing and receding contact angles is the "tilted plate".³⁶ The solid surface on which a droplet initially rests on is gradually tilted. When the droplet initiates motion on the surface, the contact angle formed on the trailing edge of the droplet is the receding contact angle, and the contact angle on the leading edge of the droplet is the advancing contact angle, as depicted **Figure 2.2b**.

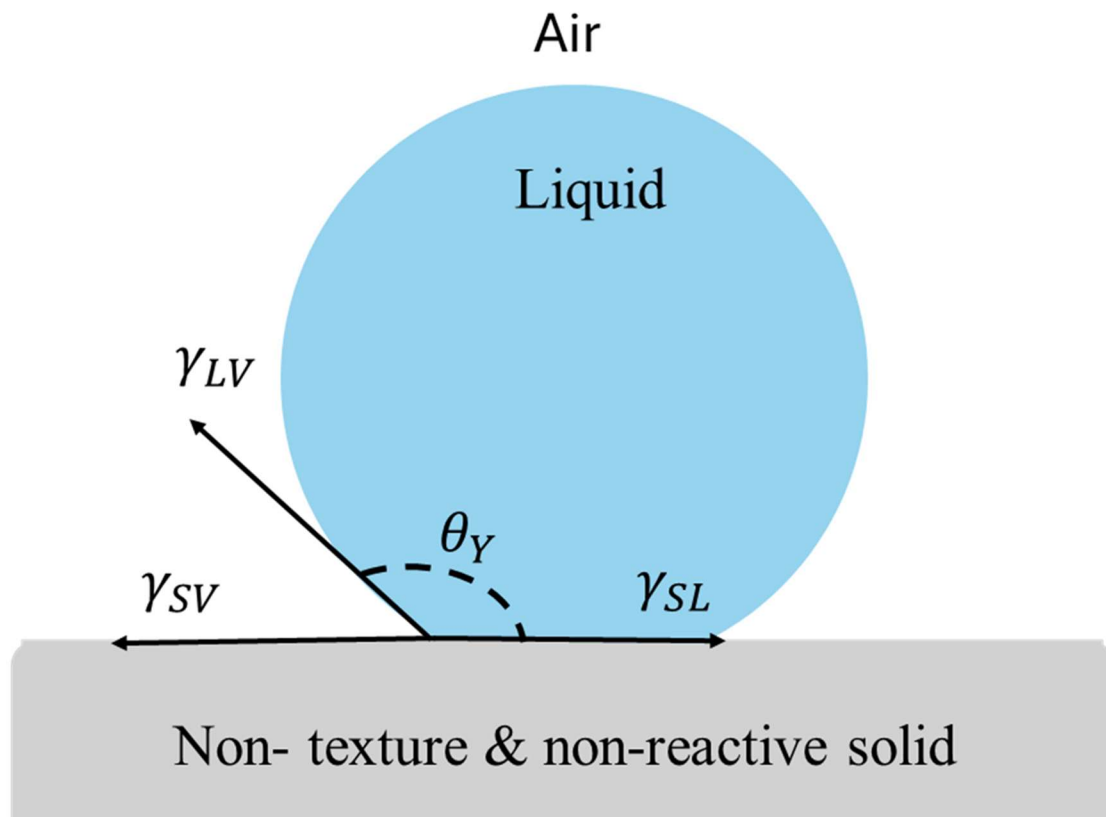


Figure 2.1. Young's contact angle on smooth surface.

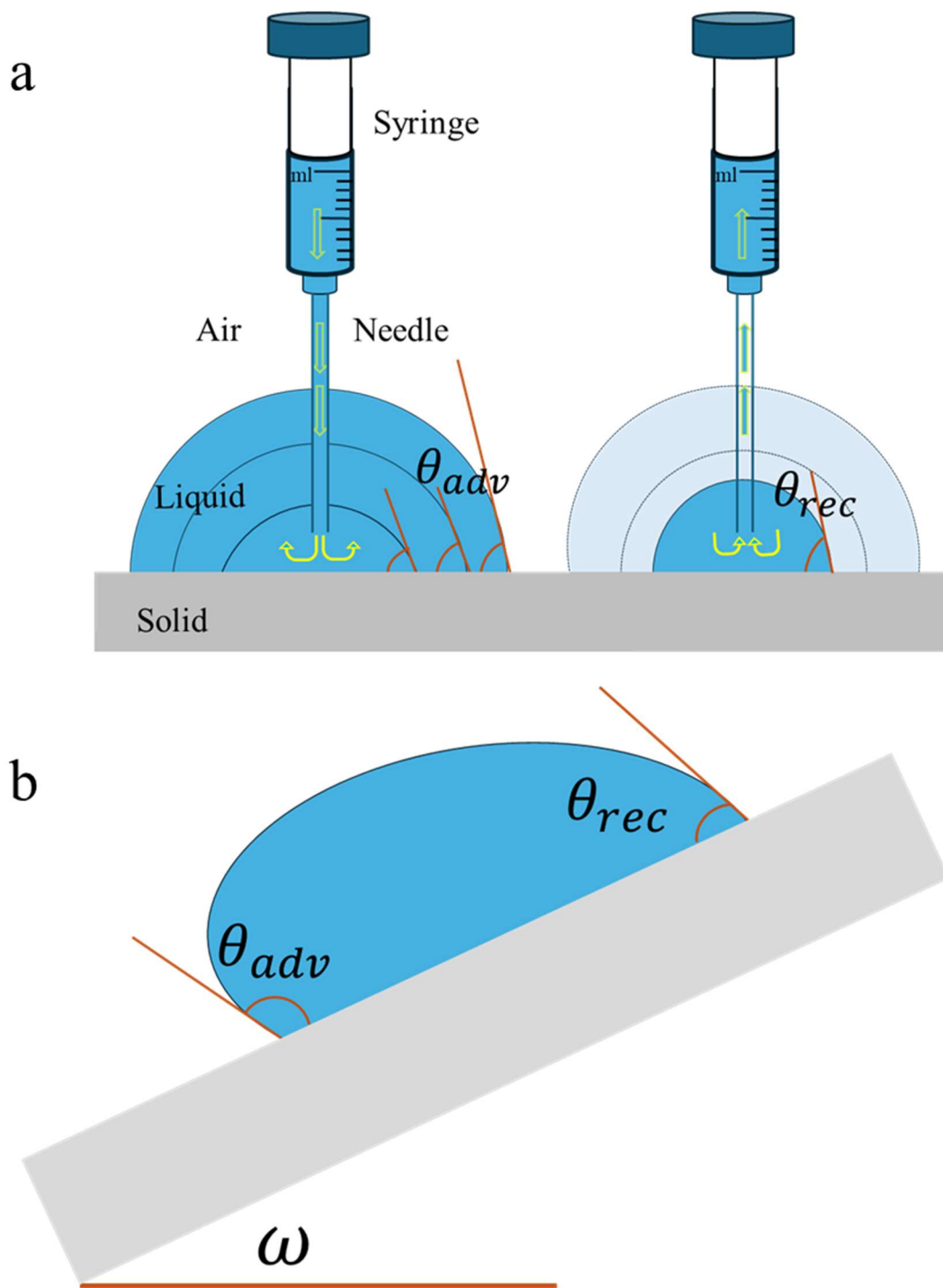


Figure 2.2. Methods for measuring advancing and receding contact angles.

In addition to the contact angles, sliding angle that is the minimum tilting angle of a solid surface, which allows the droplet to slide, is also important for characterizing the wettability. Furmidge derived a relationship that can be used to predict the sliding angle:³⁶

$$mg \sin \omega = w\gamma_{LV}(\cos \theta_{rec} - \cos \theta_{adv}) \quad (2.3)$$

where m is the mass of the drop, g is the gravitational acceleration, and w is the width of the drop. An ideally smooth, chemically uniform solid surface can show very low contact angle hysteresis.³⁷ The contact angles measured on such surfaces closely approximate Young's contact angle θ_Y .²⁶

2.3 Wetting on Textured Surface

In reality, solid surfaces are not completely smooth. The topography of solid surfaces is characterized by various micro- and nano-scale features. Thus, it becomes imperative to understand how the texture of such surfaces affect the wettability.³⁸ Theoretical models that are commonly used to describe wetting on textured surfaces are the Wenzel state (**Figure 2.3a**)³⁹ and the Cassie-Baxter state (**Figure 2.3b**).⁴⁰ In the Wenzel state, solid surfaces are completely wetted by liquid, resulting in maximum liquid-solid contact area. The apparent contact angle θ^* formed by a droplet in the Wenzel state is described by:

$$\cos \theta^* = r \cos \theta_Y \quad (2.4)$$

where r is the surface roughness.

For the Cassie-Baxter state, there are air pockets trapped between the droplet and the textured solid surface. The apparent contact angle formed by the droplet in this wetting state is described by:

$$\cos \theta^* = f_{SL} \cos \theta_Y + f_{LV} \cos \pi \quad (2.5)$$

where f_{SL} and f_{LV} are solid-liquid and liquid-air area fraction, respectively. The equation above shows that the Cassie-Baxter state can result in an apparent contact angle $\theta^* > 90^\circ$ in situations where $\theta_Y > 90^\circ$ as well as $\theta_Y < 90^\circ$. Further, low contact angle hysteresis $\Delta\theta^*$ can be achieved in the Cassie-Baxter state.^{41, 42} As a result, The Cassie-Baxter state is utilized for designing liquid-repellent surfaces with high apparent contact angles θ^* and low contact angle hysteresis $\Delta\theta^*$.

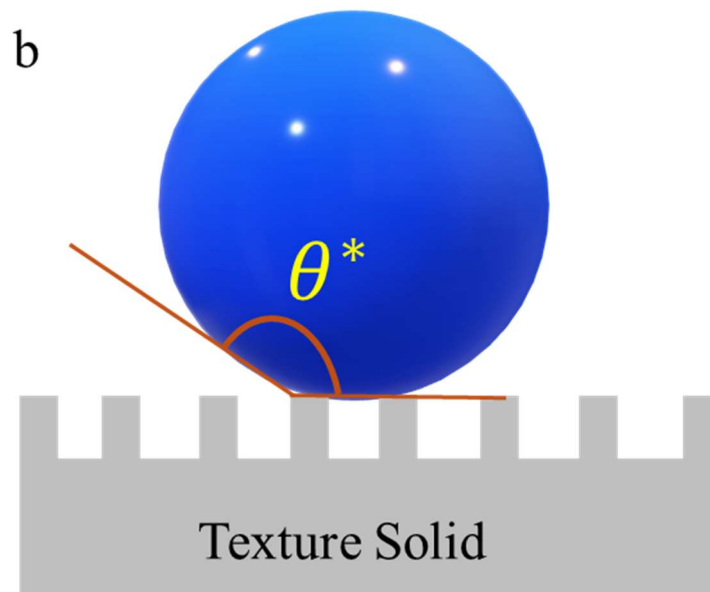
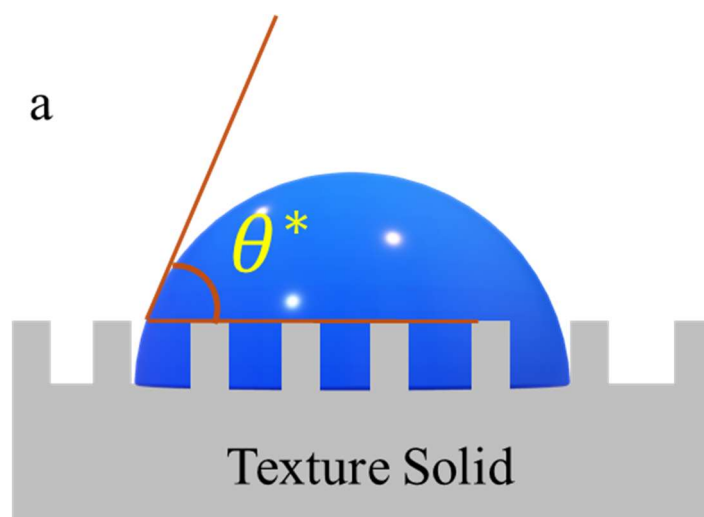


Figure 2.3. (a) Wenzel state and (b) Cassie-Baxter state on textured surface.

Based on these two configurations, it is clear that the wetting properties of a surface can be changed by altering the texture of the surface or adjusting the surface energy.⁴³ The solid surface energy can be changed through surface chemistry modification.^{44, 45}

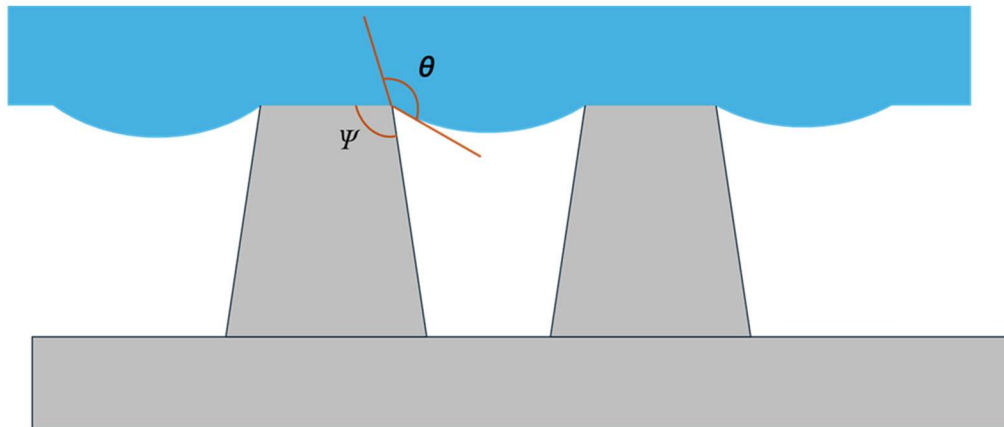
2.4 Role of Re-entrant Texture

Textured surfaces can lead to the formation of the Cassie-Baxter state for liquid droplets. However, not all textures can yield the Cassie-Baxter state for liquid droplets with low surface tensions (e.g., oils and alcohols). These liquids have Young's contact angles far below 90° on any smooth solid surface. The re-entrant texture is required for forming the Cassie-Baxter state for low surface tension liquids. **Figures 2.4a and 2.4b** illustrate two scenarios when a liquid comes into contact with two different types of textured surfaces. The symbol ψ represents the local geometric angle of the texture. If both substrates are made of the same materials and have the same surface energy, the liquid placed on these substrates will have an identical intrinsic or Young's contact angle, represented by θ_Y . A robust Cassie-Baxter state on a textured surface is possible only when $\theta_Y \geq \psi$.^{46, 47} The convex topography with ψ less than 90° are known as re-entrant textures, which is required to design textured surfaces that can resist the wetting of low surface tension liquids with $\theta_Y < 90^\circ$.

2.5 Role of Per- and Polyfluoroalkyl Substances (PFAS)

In a variety of applications, surfaces with high wetting resistance usually play a crucial role in achieving specific objectives. To this end, designing appropriate surface texture is not sufficient to meet all performance criteria.⁴⁸⁻⁵⁰ Surface chemistry modification is needed to achieve robust wetting resistance. This is because surfaces with low surface energy tend to show higher contact angles. As a result, per- and poly-fluoroalkyl substances (PFAS) with low surface energy are widely used.⁵¹ PFAS have been used to fabricate surfaces with high wetting resistance.^{52, 53} A diverse range of PFAS substances like, perfluorinated phosphates, perfluorinated silanes, fluorinated monomers, polymers, copolymers, and other fluorinated precursors, have been employed in creating superhydrophobic and superoleophobic surfaces.⁴⁸

a



b

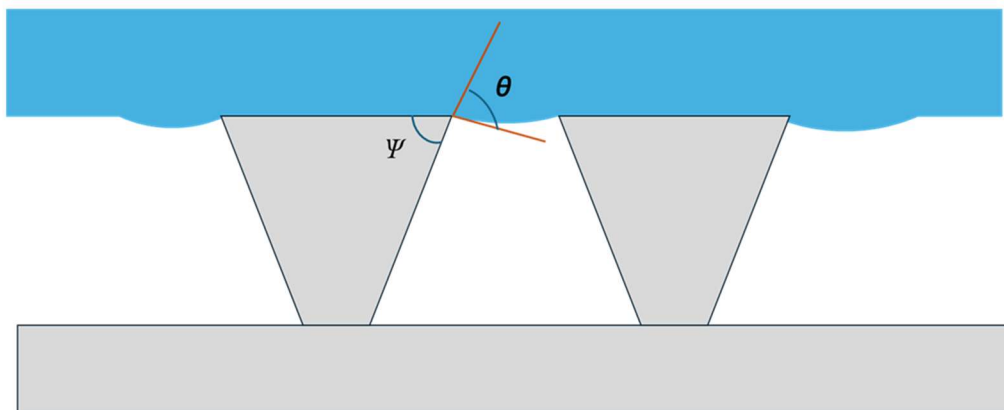


Figure 2.4. Different textures: (a) concave texture and (b) convex texture.

However, being exposed to PFAS could lead to health problems like hormonal disruptions, liver malfunction, weakened immune system, cancer, reproductive issues, and adverse impacts on cognitive abilities in children. Therefore, a pressing need is to search for alternative substances (PFAS-free) that possess the same properties like PFAS, but are more sustainable and safer for human and the environment.

2.6 Porous Membrane with High Wetting Resistance

The two primary types of membranes are inorganic membranes and organic membranes. Organic membranes are composed of various polymers such as cellulose acetate (CA), polyamide (PA), and polyethersulfone (PES), known for their cost-effectiveness, ease of production, and availability in various pore sizes.⁵⁴ Membrane-based technologies have gained significant attention in recent years due to their diverse applications including desalination, liquid separation, gas storage, and energy-related technologies.⁵⁵ In this work, we focus on two types of membranes, PVDF and PES membranes.

MD is a thermal-driven process that has applications in situations where traditional separation methods may not be feasible.⁵⁶ The efficiency of MD technology heavily depends on the properties of the membrane, particularly its wetting resistance. Highly efficient MD membranes allow only water vapor to pass through the membrane pores (**Figure 2.5**). However, they have certain limitations, prompting the need for the development of membranes with enhanced performance, including improved wetting resistance and scaling resistance.^{57, 58} These advancements are crucial for the practical deployment of MD technology.^{57, 58} These membranes with high wetting resistance are also indispensable in other applications, such as gas separation and biomedical engineering.⁵⁹ However, one of the challenges of current microporous membranes lies in striking a balance between the membrane porosity and mechanical strength while ensuring its resistance against wetting by diverse liquids. This resistance is paramount for upholding selectivity and efficiency in separation processes.⁶⁰

Membrane wetting and scaling are acknowledged as primary challenges limiting the long-term stability and salt rejection of membrane distillation technology.^{61, 62}

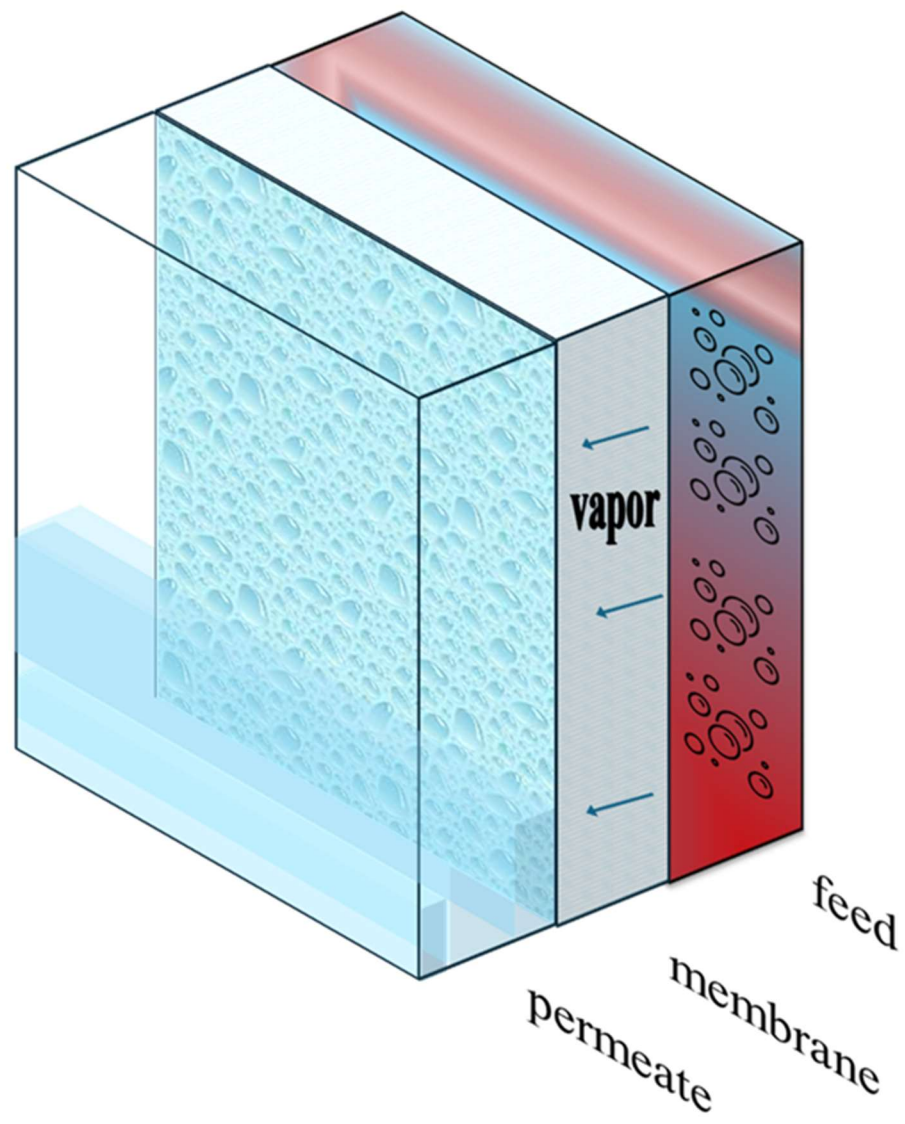


Figure 2.5. Direct contact membrane distillation process.

Pore wetting is a common occurrence in membrane processes⁶³ and is often linked with scaling on the membrane surface, as well as the presence of surfactants in the feed stream.^{8, 18} Additionally, the creation and production of these membranes require precise management of material characteristics and surface chemistry, adding complexity to the development process. Typically, membranes are chemically treated with PFAS due to their low surface energy, resulting in enhanced the wetting resistance. However, it's important to note that PFAS exposure has been linked to various health issues. Therefore, there is a need for innovative method, which enables the fabrication of wetting- and scaling-resistant membranes without using PFAS.⁵⁸

CHAPTER THREE

Effects of Surfactant Properties on Membrane Wetting*

3.1 Introduction

Exploring how the properties of surfactants affect membrane pore wetting is essential for improving membrane distillation (MD) process.⁶⁴ Pore wetting can lead to reduced salt rejection and contamination of treated water.⁴ The issue of pore wetting in microporous membranes has attracted great interest.^{3, 8, 65} MD membranes are engineered to resist the penetration of liquids into membrane pores, thereby ensuring selective permeability and operational integrity.⁶⁶ The surfactants can lower the surface tension of the feedwater and cause adsorption of surfactant molecules on the surface of membrane pores, which leads to surfactant-induced pore wetting and failed MD process.^{8, 18}

In this study, we present a comparative analysis of the wetting behaviors of various surfactants with different properties, specifically focusing on their influence on the wetting process of MD membrane.⁶⁴ We utilized multiple surfactant concentrations, allowing us to observe how the wetting potential evolves in relation to the specific type of surfactant. This investigation was conducted using the hydrophobic polyvinylidene fluoride (PVDF) membrane, which plays a critical role in the MD process. Moreover, we established a correlation between the induction time required for surfactants to initiate pore wetting and the contact angle and surface tension of the feedwater. This correlation provides valuable insights into how surfactant properties influence wetting behavior, which is essential for optimizing the membrane distillation process for more effective and efficient desalination.

* This work has been published in *Journal of Membrane Science Letters*, 2024, 4, 100077 (Ref. 64). I am one of the co-first authors. I conducted all of the measurements of surface tensions and contact angles and performed the related data analysis. The results and discussion of this published paper have been incorporated into this chapter of my thesis. This chapter also includes additional results (e.g., contact angles on smooth surfaces) of my experiments. The other co-first author is Connor Coolidge (Colorado State University). She conducted all MD experiments and performed the related analysis. The two corresponding authors of this paper are Wei Wang (University of Tennessee, Knoxville) and Tiezheng Tong (Colorado State University). Their contribution to the above published paper includes project administration, methodology, conceptualization, resources, funding acquisition, and review and editing of the paper.

3.1.1 The Use of Surfactants in Tuning Wetting Behavior

Surface active substances are commonly referred to as surfactants.^{67, 68} The surfactant molecule consists of a hydrophobic tail and a hydrophilic head (**Figure 3.1**). The hydrophilic head can be neutral or carry positive or negative charge.⁶⁹ The hydrophobic tail tends to be in contact with nonpolar phases.^{70, 71} Surfactants can be classified as cationic, anionic, and non-ionic surfactants based on the charge type of the head group. Surfactants have been widely used to reduce the interfacial tensions. This is because they have a distinctive capability to gather at the interface. Each type of surfactant demonstrates unique behaviors and interactions depending on its molecular characteristics. For example, a surfactant with a longer hydrocarbons chain corresponds to a greater molecular weight.^{72, 73} A larger surfactant molecule generally exhibits a lower diffusion coefficient and lower mobility within a given system.^{74, 75}

Typically, as the concentration of surfactant increases, more surfactant molecules can accumulate at the interface, causing a significant reduction in interfacial tension until an entire monolayer is established.⁷⁶ Ultimately, the interfacial tension will reach a plateau (i.e., the interfacial tension no longer decreases with increasing the surfactant concentration). Once the interface is completely covered with molecules of surfactants, a subsequent phenomenon known as micellization occurs.⁷⁶ This happens in a water-based solution when the molecules gather and arrange their hydrophobic tails facing each other and their hydrophilic groups on the outside. Essentially, a small spherical interface is formed within the solution. The surfactant concentration that allows the formation of micelles is known as the critical micelle concentration (CMC).^{76, 77}

In our study, five different surfactants with different properties are used to study the influence of surfactants on pore wetting of MD membrane (**Table 3.1**).⁶⁴ Specifically, Tween-20 and Triton X-100 are used as the representative nonionic surfactants, hexadecyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) are used as the representative cationic surfactants, and sodium dodecyl sulfate (SDS) is used as the representative anionic surfactant. These surfactants with varied molecular structures are crucial for probing the mechanism underlying the surfactant-induced pore wetting.^{64, 78, 79}

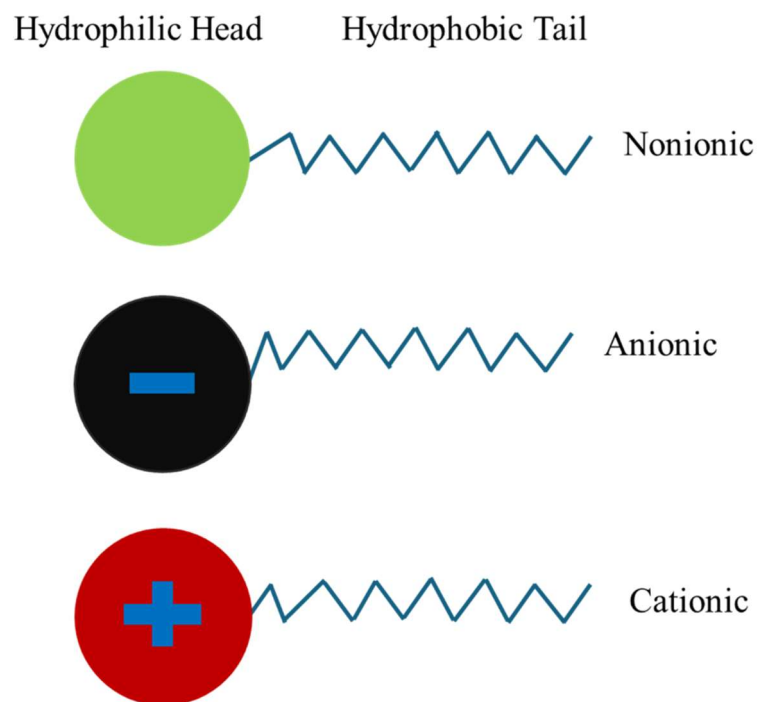


Figure 3.1. Different types of surfactants.

Table 3.1. Surfactants with different properties.

Surfactants	Abbreviation	Charge type	Molecular weight ^a (g mol⁻¹)
Sodium dodecyl sulfate	SDS	Negative	288.38
Dodecyltrimethylammonium bromide	DTAB	Positive	308.34
Hexadecyltrimethylammonium bromide	CTAB	Positive	364.45
Triton X-100	Triton X-100	Neutral	625
Tween20	Tween20	Neutral	522.68

^a Molecular weight from the manufacturers.

3.1.2 Surfactants Induced Pore Wetting in Membrane Distillation (MD)

In MD process, surfactants play a significant role in inducing the membrane pore wetting.^{8, 18, 64, 80} Pore wetting is one of the major challenges faced by MD technology and arises when the feedwater permeate through the membrane pores, leading to the contamination of the treated water product.^{5, 64} Pore wetting occurs when the transmembrane pressure exceeds the liquid entry pressure (LEP).^{8, 18} The LEP is directly related to the surface tension of the feedwater. Surfactants can reduce the surface tension of feedwater, leading to reduced liquid entry pressure and consequently pore wetting.^{8, 81} Also, the adsorption of surfactants on the membrane pores can lead to surfactant-induced wetting.^{8, 18, 80} Experiments where surfactants are gradually added to the feedwater are typically conducted to assess the wetting resistance of MD membranes.⁸¹⁻⁸³ The wetting resistance of recently developed membranes or the potential of MD for treating hypersaline wastewater has been evaluated using the critical surface tension and/or surfactant concentration at which membrane pore wetting occurs.⁸¹⁻⁸⁵ Once the surfactant concentration exceeds the critical point, MD process fails due to membrane pore wetting.⁸⁶ Moreover, assessing membrane wetting properties and determining wetting resistance typically involves measuring the contact angles of liquids with different surface tensions.^{64, 74, 75}

The potential connection between the wetting behavior of MD membranes and surfactant properties has sparked interest, yet a decisive correlation still needs to be discovered.⁶⁴ Unraveling the mechanisms of surfactant-induced wetting in MD has been the focus of multiple studies over the past few years, offering valuable insights for further exploration.^{18, 80, 87, 88} It has been demonstrated that surfactants with lower hydrophilic-lipophilic balance (HLB) possess a greater potential for adsorption onto the membrane surface, thereby boosting pore wetting.^{87, 88} Prior work has shown that electrostatic interactions play a significant role in the adsorption of surfactants onto particulate matter and minerals.⁷² Cationic surfactants exhibit the highest rate of adsorption, attributed to their electrostatic attraction to soil particles.⁸⁹ However, there is a need for further exploration to unveil the specific influence of surfactant properties such as size and charge on wetting behaviors in membrane distillation (MD).⁶⁴

3.2 Materials and Experimental Setup

3.2.1 Materials

Hydrophobic PVDF membrane and hydrophobic PVDF smooth sheet were used in this study. We used different surfactants, including sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB), hexadecyltrimethylammonium bromide (CTAB), Triton X-100, and Tween 20 (**Figure 3.2**).⁶⁴ Sodium chloride (NaCl) was dissolved in deionized water to prepare 1 M NaCl solution. Surfactants were then added to the NaCl solution at varied concentrations.

3.2.2 Surface Tension Measurements

The pendant droplet method was used to measure the surface tension of different surfactant solutions at room temperature (**Figure 3.3a**).⁶⁴ Furthermore, at the temperature of 60 °C (operating temperature of MD experiments), the dynamic surface tension measurements were also conducted for all surfactant solutions.⁶⁴ The inverted pendant bubble method was used to measure the surface tensions at 60 °C in an environmental chamber (**Figure 3.3b**). A temperature controlled was used to tune the temperature of the environmental chamber. We placed the cuvette inside the environmental chamber, and then the pre-heated surfactant solution was added to the cuvette. Subsequently, the goniometer microsyringe with the inverted stainless-steel needle was submerged in the solution. We took action to prevent evaporation, which could impact surfactant concentration and consequently the surface tension, by completely sealing the environmental chamber with aluminum foil. We generated an air bubble, which was attached to the tip of the needle, using the microsyringe. The dynamic surface tension of surfactant solution was analyzed by studying the time evolution of the bubble shape. Three measurements were performed for each surfactant solution. After performing surface tension measurement for a specific surfactant concentration, the needle and cuvette were thoroughly rinsed with deionized water, followed by ultrasonic cleaning with deionized water for three minutes. Then, the needle and cuvette were dried completely using compressed air.

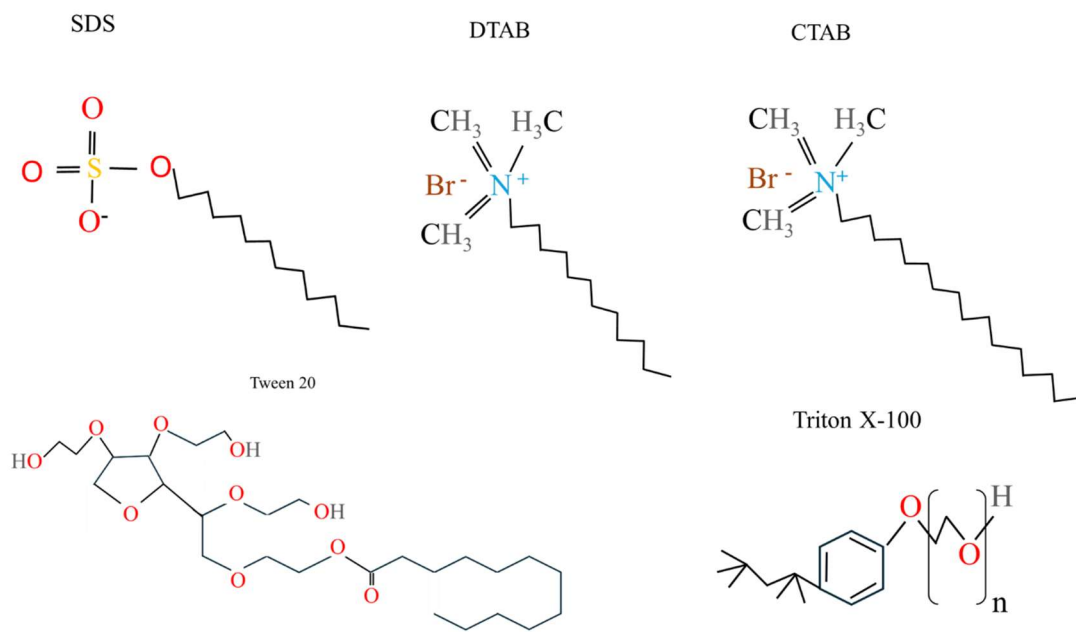


Figure 3.2. Molecular structures of the five surfactants.⁶⁴

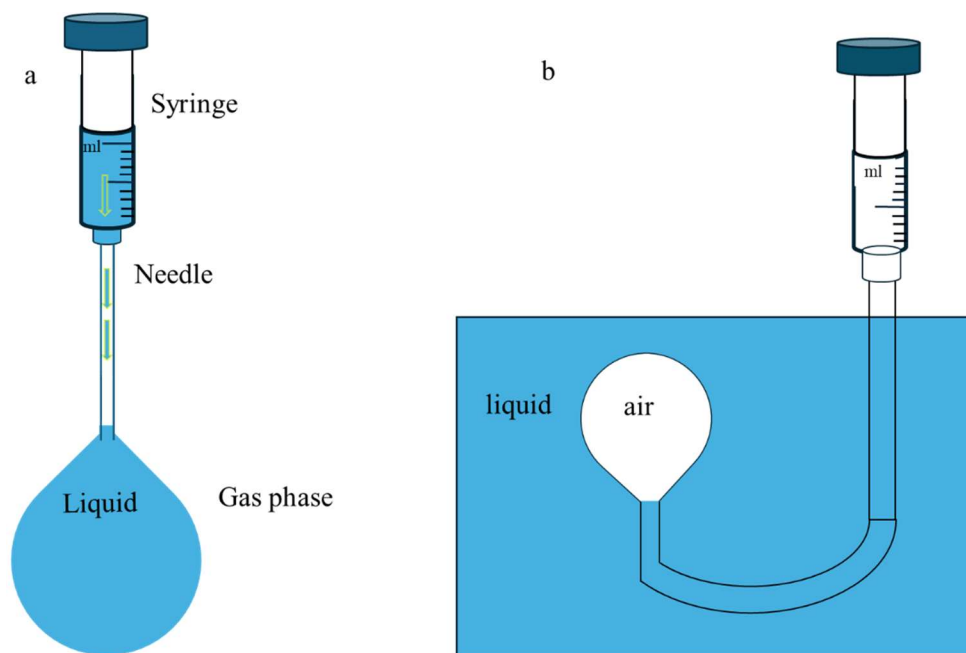


Figure 3.3. Surface tension measurements using (a) pendant droplet method and (b) inverted pendant bubble method.

3.2.3 Contact Angle Measurements

Contact angles of surfactant droplets on the PVDF sheets and porous PVDF membranes were measured using a contact angle goniometer at room temperature ($\sim 20^{\circ}\text{C}$). To guarantee reliable measurements, we discharged the surface using an anti-static gun (Milty Zerostat 3) after placing the PVDF sample on the goniometer stage. Afterward, we placed a droplet of surfactant solution with a volume of $8\ \mu\text{l}$ on the surfaces using a micropipette.⁶⁴

We measured the apparent contact angles of surfactant droplets on the PVDF membranes at 60°C degrees, which is the operating temperature in the MD process. To achieve this, we preheated the solutions in a vacuum oven at 60°C . This is followed by installing an environmental chamber on the goniometer stage. The temperature of the environmental chamber was also set to be 60°C . After the porous PVDF membrane sample inside the environment chamber reached the 60°C , we discharged the PVDF membrane surface using the anti-static gun. Subsequently, a surfactant droplet with a volume of $8\ \mu\text{l}$ was placed on the membrane surface. The apparent contact angle was measured within 10 seconds after placing the droplet on the surface. To minimize any temperature fluctuations that could affect the measurements, we preheated the pipette tips on a hot plate at 60°C before use. Three contact angle measurements were performed for each surfactant solution at both room temperature and 60°C . **Figure 3.4** shows the setup for contact angle measurements conducted at room temperature and 60°C .⁶⁴

3.2.4 MD Experiments

The MD experiments were conducted by our collaborator (Connor Coolidge and Dr. Tiezheng Tong at Colorado State University) using a custom-built system.⁶⁴ The membrane flow cell has a dimension of $77\ \text{mm} \times 26\ \text{mm} \times 3\ \text{mm}$, and the effective membrane area was $\sim 20.02\ \text{cm}^2$.⁶⁴ The feed solution with a volume of 1000 mL was processed at a temperature of 60°C , and the permeate stream was regulated at 20°C . In each experimental trial, 1 M NaCl solution was used as the feed solution. Real-time calculations of water vapor flux and salt rejection rate were carried out by monitoring the changes in weight and conductivity of

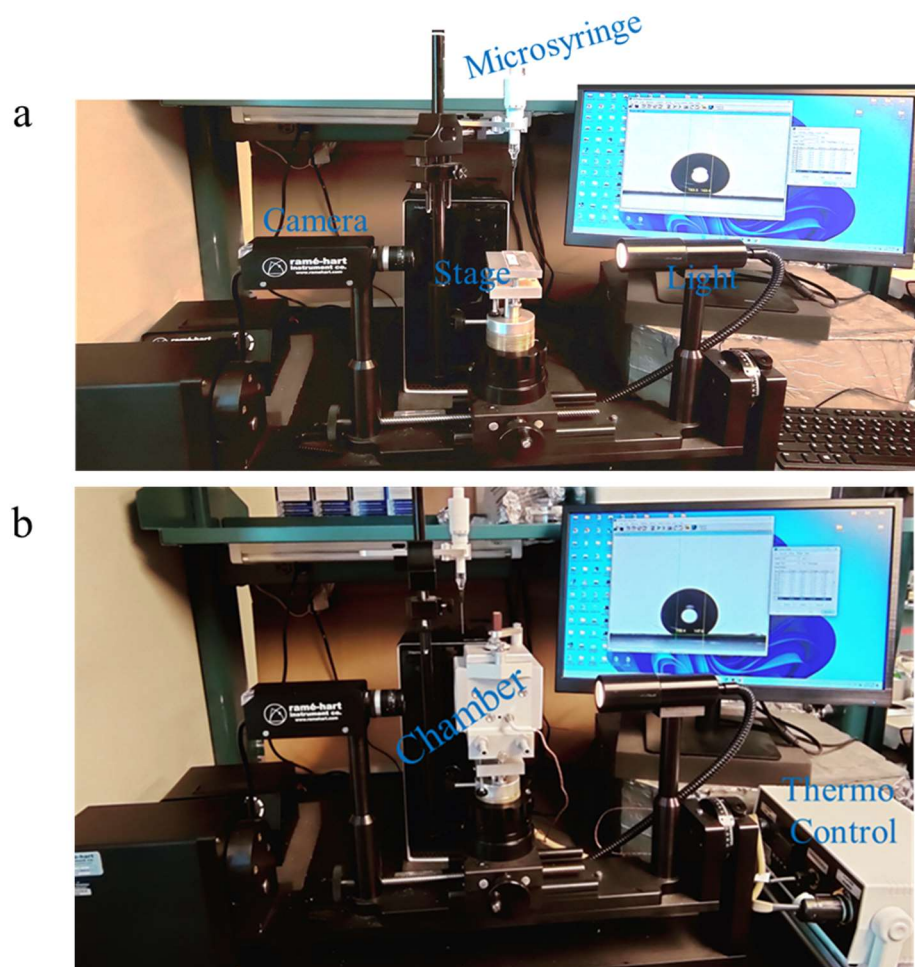


Figure 3.4. Experimental setup for contact angle measurements at (a) room temperature and (b) 60 °C.

the permeate, using precise instruments such as a top-loading digital balance from Cole-Parmer for weight and a bench-top conductivity meter from Oakton Instrument for conductivity. The MD system was allowed to run for 30 minutes to guarantee the establishment of a stable baseline flux before adding surfactant. Subsequently, the surfactant was added to the feed solution in a stepwise manner to decrease the surface tension. During this process, the mass and conductivity of the permeate were recorded at one-minute interval. The recorded data was used for computing both the water vapor flux and the salt rejection rate. The point at which the salt rejection dropped below 95% was considered as the induction time for pore wetting.⁶⁴

3.3 Results and Discussion

3.3.1 Surface Tensions of Surfactant Solutions

We measured the surface tensions of the aqueous solutions of SDS, DTAB, and Triton X-100 with different concentrations at room temperature. To study the effect of salt on the surface tension, we also conducted the surface tension measurements of these surfactant solutions in the presence of 1 M NaCl. The pendant droplet method discussed in previous section was used for the measurements at room temperature. **Figure 3.5** shows how the surface tensions of the surfactant solutions change with the surfactant concentrations. The results indicate that as the concentration of surfactant increases, there is a corresponding decrease in surface tension of surfactant solutions. As surfactant molecules accumulate at the liquid-air interface, they effectively lower the surface tension of the liquid.⁹⁰ In the presence of NaCl, same surfactant concentration leads to lower surface tension for a specific surfactant. In the case of an ionic surfactant such as SDS and DTAB, the addition of salt (e.g., NaCl) can facilitate the arrangement of the surfactants at the interface.^{91, 92} In contrast, for Triton X-100, the presence of NaCl does not result in a significant change in surface tension.⁹² Our results are in close agreement with prior studies.⁹³⁻⁹⁵

We also measured the equilibrium surface tensions of the five different surfactants in 1 M NaCl solutions at 60 °C.⁶⁴ These surfactants have either the same charge but different chain length or the same chain length but different charges. The inverted pendant bubble

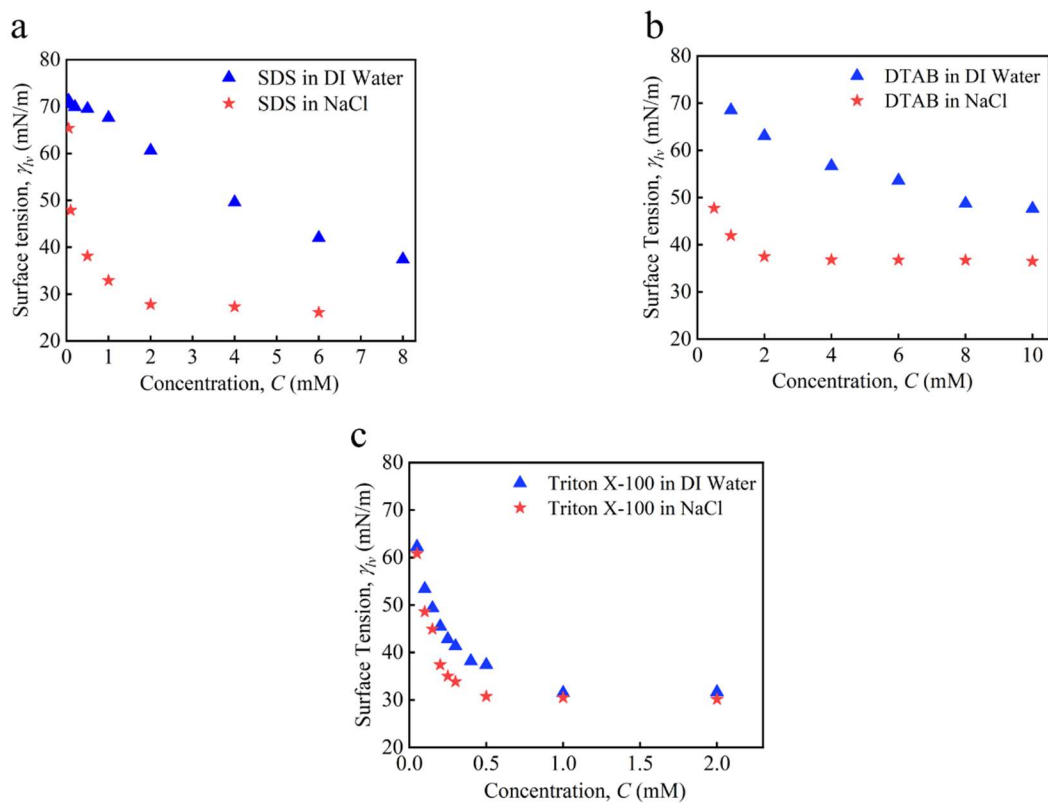


Figure 3.5. Surface tensions of (a) SDS, (b) DTAB, and (c) Triton X-100 solutions at room temperature.

method was used to measure the surface tensions at 60 °C. In a typical measurement, a bubble was carefully generated at the tip of the inverted needle, which was submerged in the surfactant solution. The emergence of a fresh liquid-air interface triggers the surfactant molecules to be drawn to the interface, ultimately resulting in the reduction of interfacial tension due to the adsorption of surfactant molecules at the interface. The interfacial tension eventually reaches equilibrium. This process is influenced by a combination of factors, including the molecular structure and charge type of the surfactant, as well as the specific properties of the liquid environment. As a result, we thoroughly examined the change in liquid-air interfacial tension over time for each surfactant solution, as shown in **Figure 3.6**.⁶⁴ For each surfactant, the surface tension decreased as the surfactant concentration increased. The changes in surface tension over time revealed that the time required to reach equilibrium surface tension decreased with increasing surfactant concentration. This behavior can be attributed to the accelerated rate of surfactant molecule adsorption at the interface as the bulk surfactant concentration rises.⁹⁶⁻⁹⁸ For the studied surfactants, the time required to reach the equilibrium surface tension is different. This is because of the varied adsorption kinetics of different surfactants, which are affected by both the properties of the surfactant and its interaction with electrolytes (e.g., NaCl).^{91, 99} Previous research has shown that the adsorption of surfactant at the interfaces plays a crucial role in influencing the kinetics of membrane pore wetting in the MD process.⁸⁷ The different adsorption kinetics of various surfactants at the interfaces and their related transport, which have been studied in previous studies, have a substantial impact on the pore wetting process in MD.⁹⁹⁻¹⁰¹

The equilibrium surface tensions of all surfactant solutions are summarized in **Figure 3.7**.⁶⁴ This figure illustrates how the equilibrium surface tensions vary with the concentration of the surfactant. As the concentration of the surfactant increases, the surface tension consistently decreases for each surfactant. Interestingly, the surface tension of CTAB solution decreases more rapidly with increasing the surfactant concentration when comparing to DTAB solution. This result suggests that the characteristics of the surfactants (such as chain length and molecular weight) influence the surface tension.

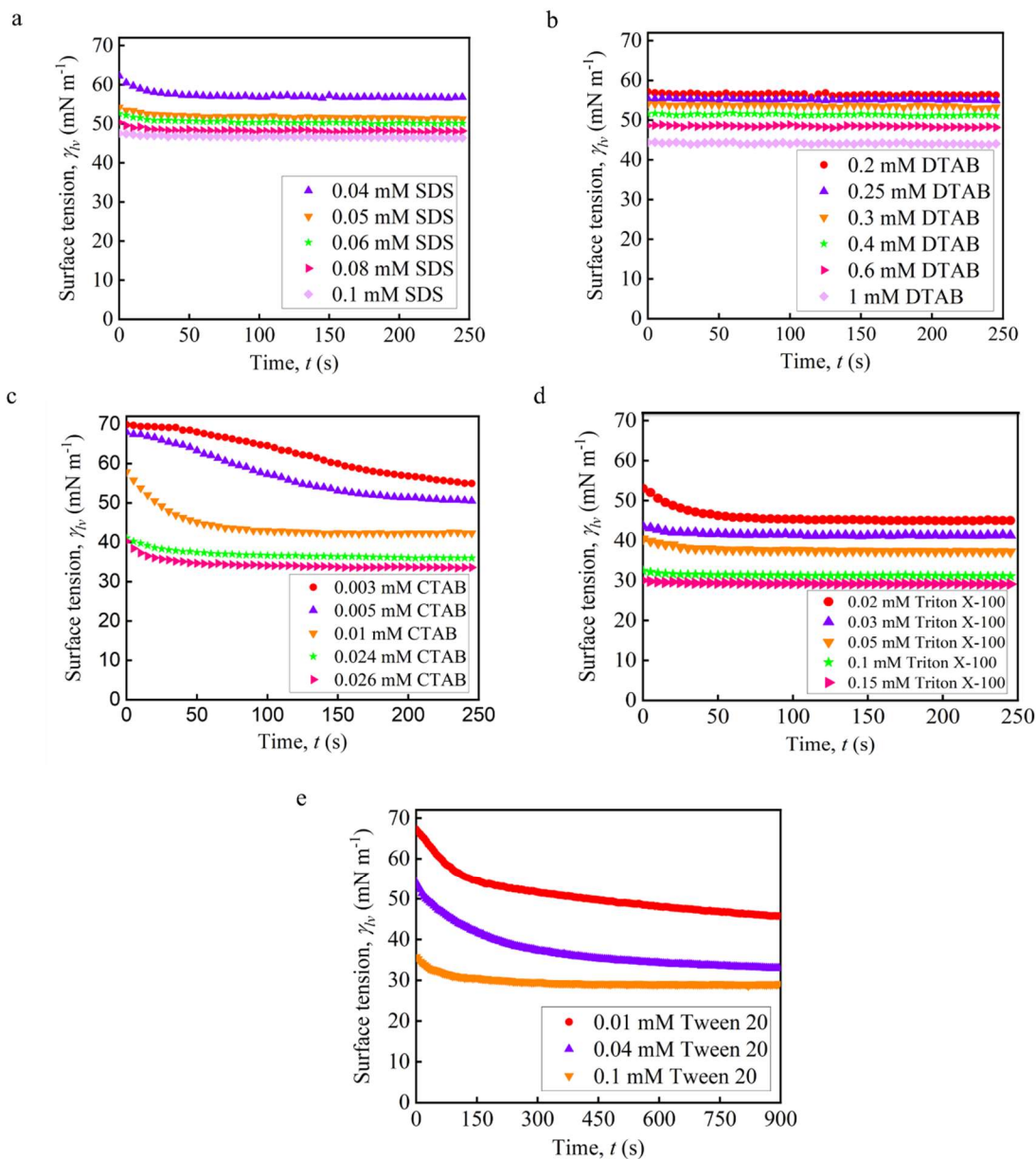


Figure 3.6. Surface tensions as a function of time at 60 °C for 1 M NaCl solutions containing (a) SDS, (b) DTAB, (c) CTAB, (d) Triton X-100, and (e) Tween 20 at different surfactant concentrations.⁶⁴

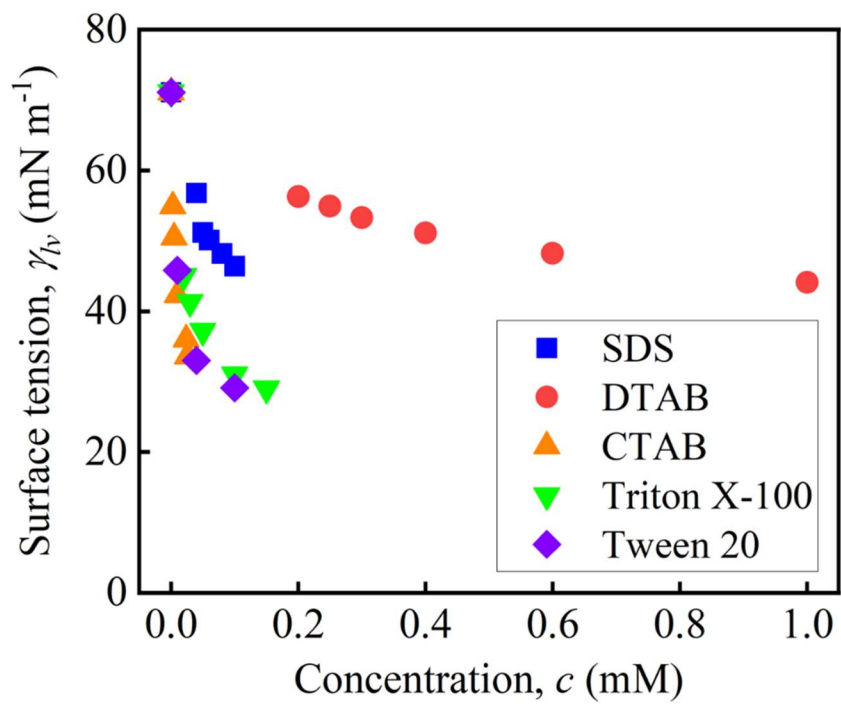


Figure 3.7. Equilibrium surface tensions for 1 M NaCl solutions containing surfactants of different concentrations at 60 °C.⁶⁴

3.3.2 Contact Angles of Surfactant Solutions

Our investigation started with the precise measurement of the contact angle formed by droplets of deionized (DI) water and sodium chloride (NaCl) solutions, which contained different surfactants with varied concentrations.⁶⁴ This experiment was conducted first at room temperature to ensure consistency and reliability in data acquisition. The initial phase of our study was carried out on a smooth sheet of polyvinylidene fluoride (PVDF), a polymer known for its hydrophobic property. **Figure 3.8** shows how the contact angle changes in response to varied concentrations of three different surfactants in both DI water and NaCl solution. As the concentration increases, the contact angle decreases for all three surfactants. This behavior can be attributed to the reduced surface tension as the surfactant concentration increases. Moreover, it is worth noting that there is a more noticeable reduction in contact angles for surfactants in the NaCl solution compared to those in DI water. Subsequently, we expanded our research to measure the apparent contact angle on microporous PVDF membrane (**Figure 3.9**).⁶⁴ The results highlight an important trend: as the surfactant concentration increases, we observe a gradual reduction in the contact angle, which is similar to the observation made on the smooth PVDF sheet.

Furthermore, at a temperature of 60 °C, a series of measurements was carried out to determine the apparent contact angles of different surfactant solutions on porous PVDF membranes. Upon analyzing the data of all surfactants, a compelling pattern emerged: apparent contact angles of the surfactant solutions decreased with increasing surfactant concentration (**Figure 3.10**).⁶⁴ However, it is worth noting that surfactant solutions with very similar surface tensions can display distinctly different contact angles on the PVDF membrane, which highlights the influence of surfactant properties on the wetting behaviors.

3.3.3 Effects of Surfactants on Induction Time of Membrane Wetting⁶⁴

To study how surfactants with different properties affect pore wetting, we measured the induction time of each surfactant at various concentrations and established a correlation with the surface tension of the feedwater (**Fig 3.11**).⁶⁴ The results in **Fig 3.11**

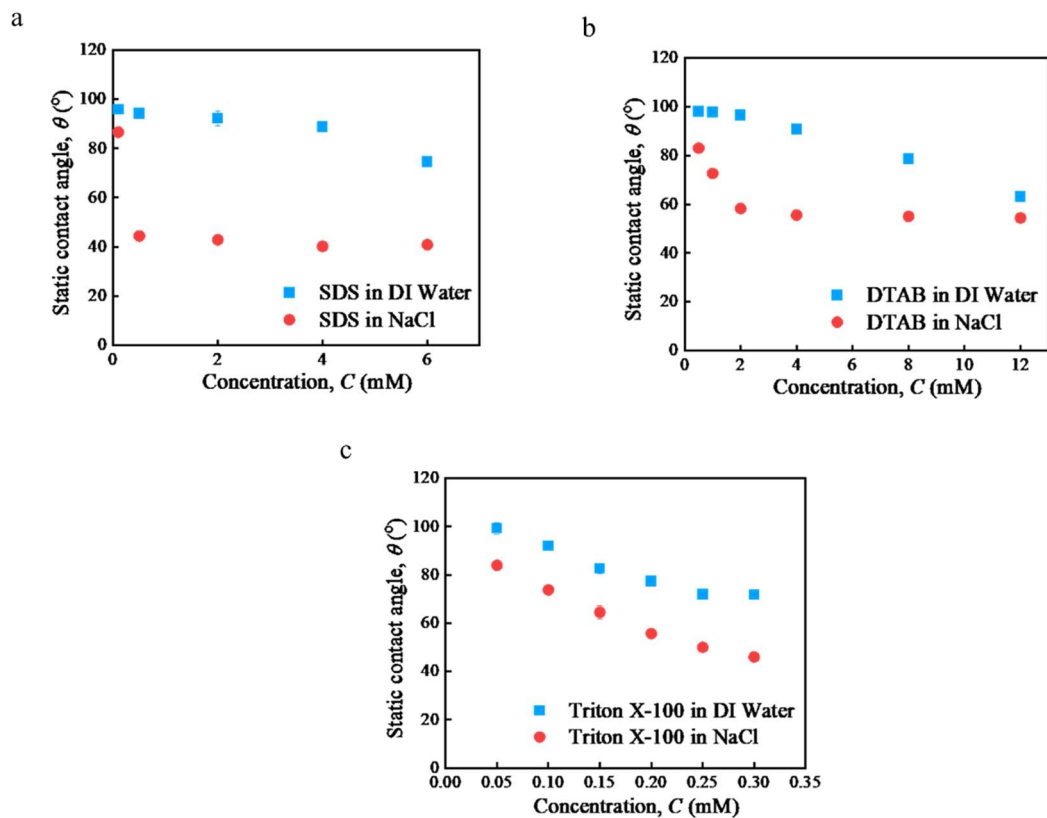


Figure 3.8. Contact angles on smooth PVDF sheet for DI water and 1 M NaCl solutions containing surfactants of different concentrations: (a) SDS. (b) DTAB, and (c) Triton X-100.

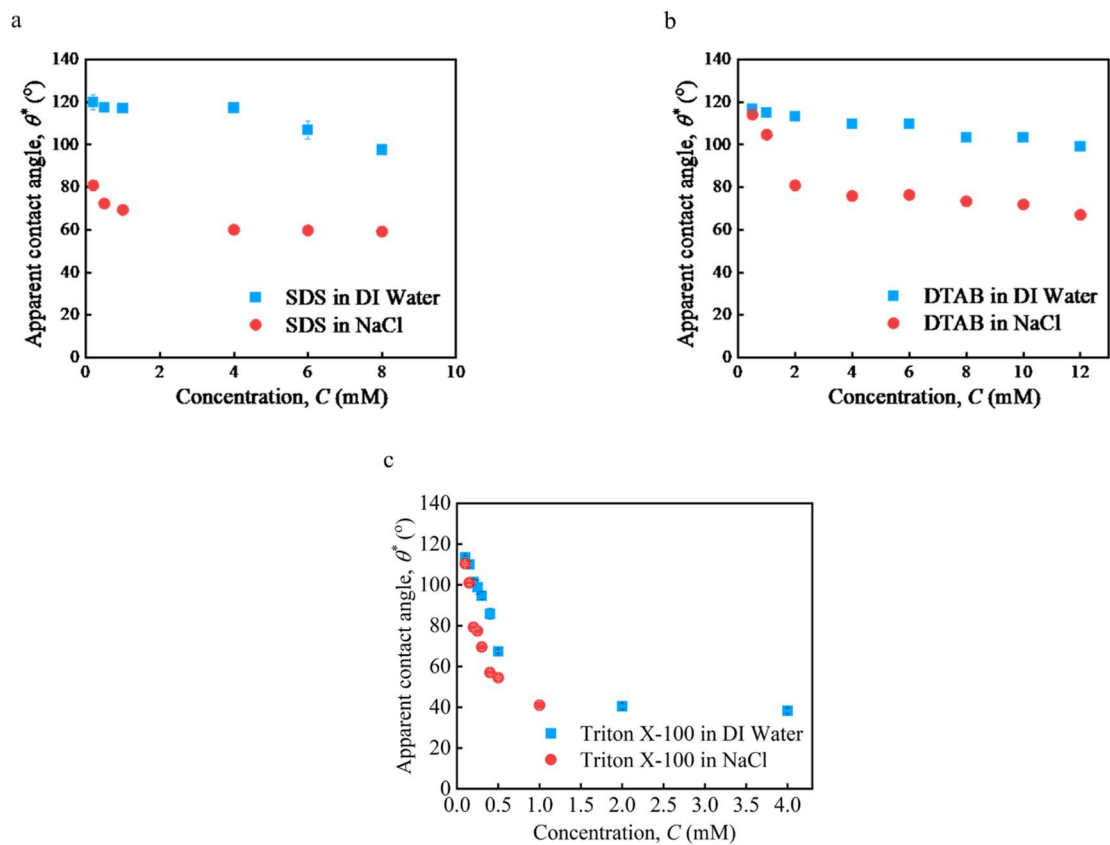


Figure 3.9. Apparent contact angles on porous PVDF membrane for DI water and 1 M NaCl solutions containing surfactants of different concentrations: (a) SDS, (b) DTAB, and (c) Triton X-100.

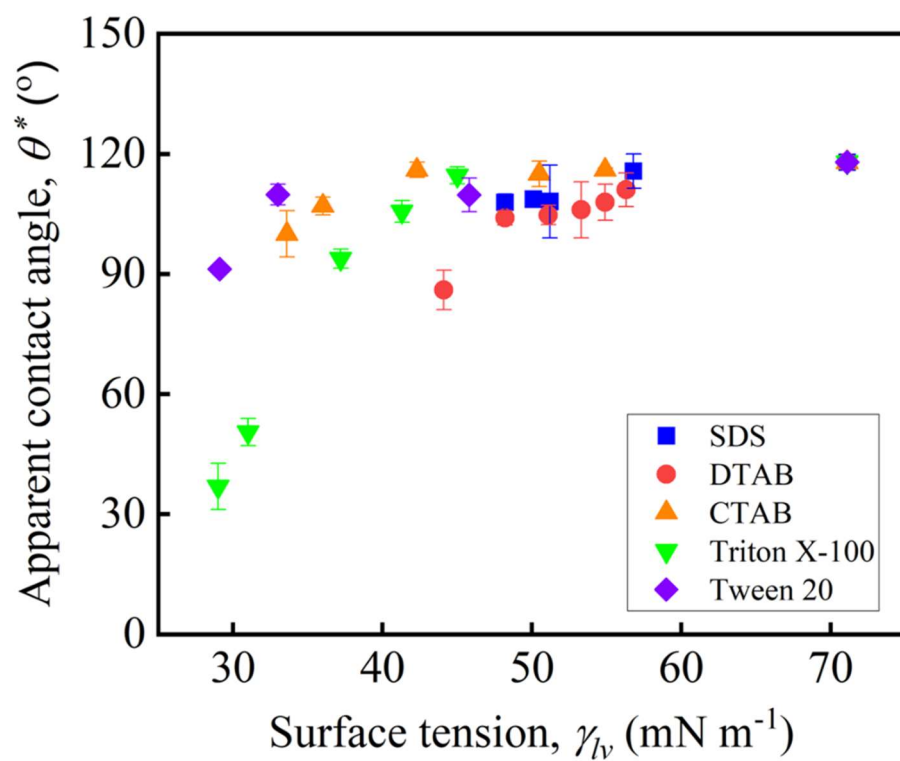


Figure 3.10. The apparent static contact angles of surfactant solutions with different surface tensions on the PVDF membranes at 60 °C.⁶⁴

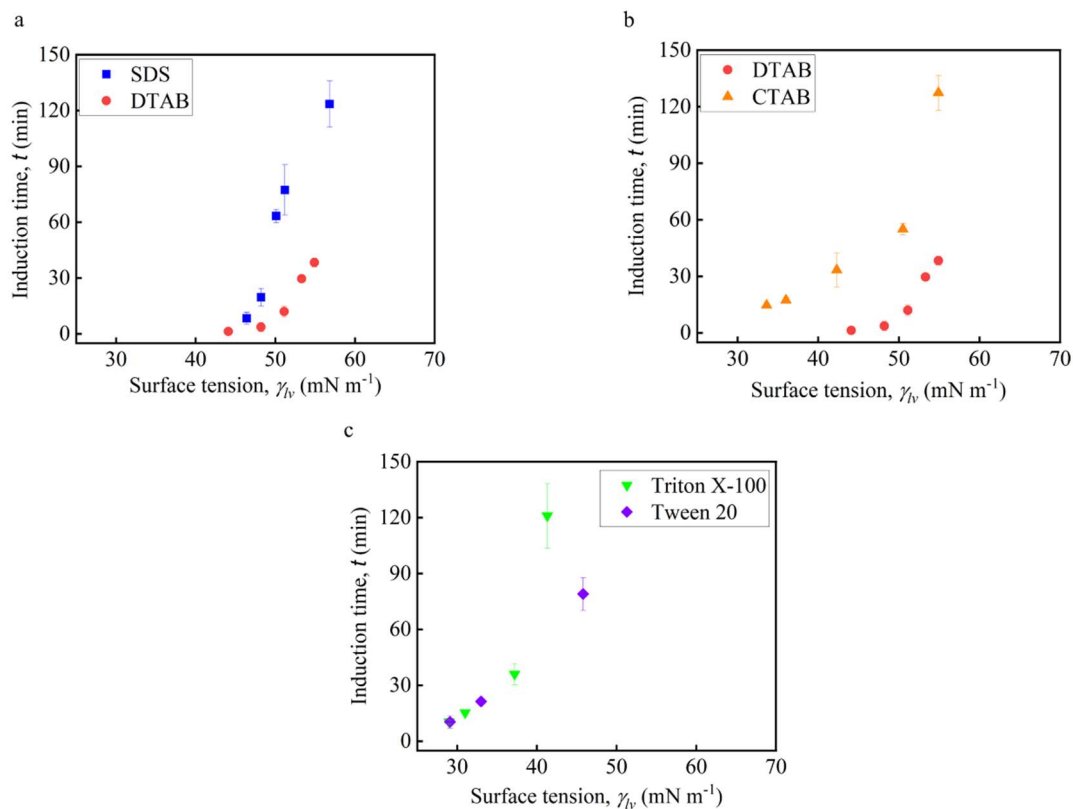


Figure 3.11. The induction time of membrane wetting in MD for (a) surfactants of the same carbon chain length but different charge types, (b) positively charged surfactants of different chain lengths, and (c) non-ionic surfactants of different molecular structures and weights.⁶⁴

revealed that SDS exhibited a longer induction time than DTAB at similar feedwater surface tensions despite their identical carbon chain lengths. For instance, SDS took approximately 77 minutes to induce wetting at a feedwater surface tension of ~ 51 mN/m, which is much longer than DTAB (~ 12 minutes) at a very similar surface tension (~ 51 mN/m).⁶⁴ This result indicates that positively charged DTAB leads to a much faster rate of pore wetting than negatively charged SDS. The distinct kinetics of pore wetting between SDS and DTAB can be attributed to their unique electrostatic interactions with the membrane surface, which has a negative charge. It is important to recognize that the electrostatic interaction is less effective under high salinity conditions. However, Li *et al.* conducted a comprehensive study that revealed an anionic polyelectrolyte's efficacy in removing cationic pollutants in various high salinity brines.¹⁰² This finding emphasizes the possibility of electrostatic interaction occurring even in environments with high salinity. Indeed, debates still exist regarding the mechanism of pore wetting induced by surfactants. The autophilic effect, which assumes that the adsorption of surfactants on the hydrophobic surface reverses surface wettability to hydrophilic, has been used to explain membrane wetting in MD.^{4, 103, 104} According to this theory, the electrostatic attraction between DTAB and the negatively charged PVDF membrane⁵ results in easier adsorption of DTAB onto the membrane surface and consequently a faster pore wetting, whereas the adsorption of SDS is retarded due to its electrostatic repulsion by the PVDF membrane surface (**Figure 3.12**).⁶⁴ Wang *et al.* suggests that the transport of surfactants to the wetting frontier by advective transport and diffusion is the key to inducing pore wetting during MD desalination.^{18, 80, 87} According to this theory, the electrostatic repulsion between the PVDF membrane and SDS hinders the transport of SDS towards and inside the membrane pores, thereby slowing the reduction of surface tension for solution near the wetting frontier and the consequent migration of the liquid-air interface towards the distillate. Compared to CTAB, DTAB has a smaller molecular weight and a shorter carbon tail, demonstrating lower induction time and higher capability of inducing pore wetting. The results for non-ionic surfactants mirrored those for cationic surfactants, where Tween 20 with a smaller molecular weight, displayed a shorter induction time to initiate membrane wetting than Triton X-100. The variations in wetting

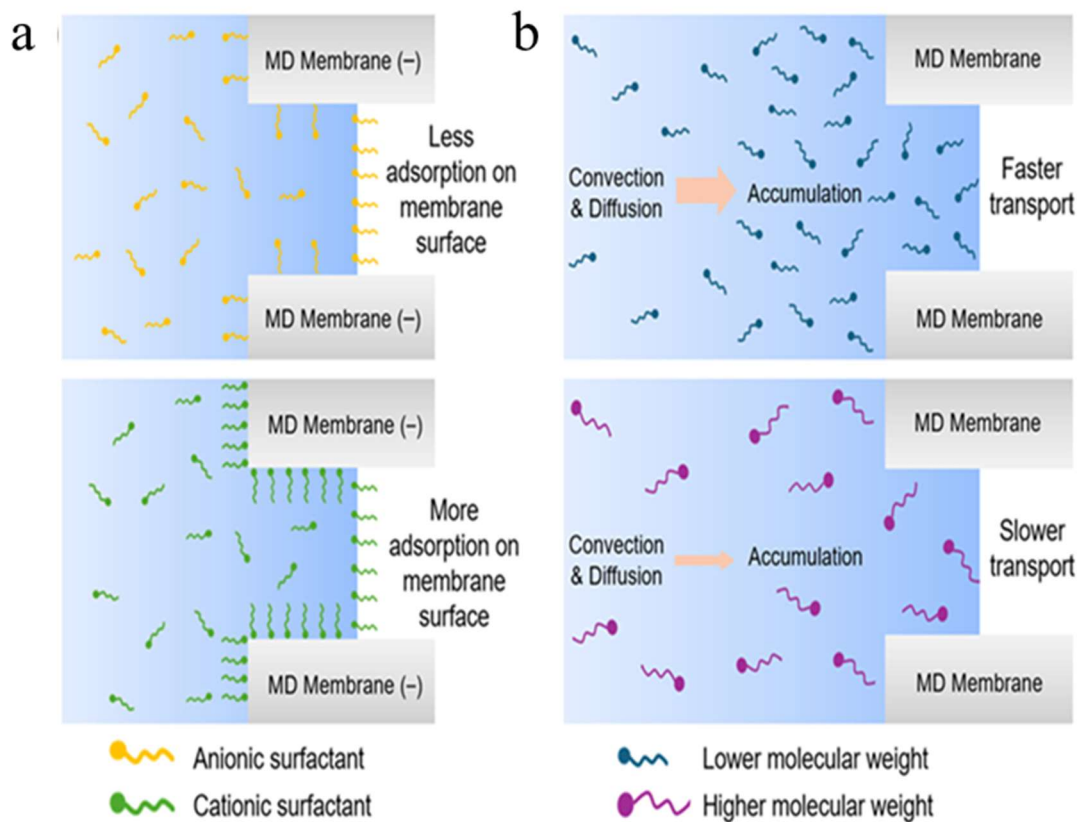


Figure 3.12. Schematic illustration of the effects of surfactant-membrane interactions on MD wetting behavior when comparing (a) anionic and cationic surfactants and (b) surfactants with different molecular weights.⁶⁴

behavior between surfactants with the same type of charge were probably driven by the difference in the rate of molecular diffusion, which determines the time required to reduce the feedwater surface tension at the wetting frontier.^{89, 105} The surfactants of higher molecular weights (e.g., CTAB and Triton X-100) possess smaller diffusion coefficients, and thus a smaller number of surfactants are able to transport to the wetting frontier within the same timeframe, leading to longer induction times.⁶⁴

Further, the results of this study contradict the belief that surfactants with a lower HLB, or greater hydrophobic characteristics, tend to be more capable of inducing wetting.^{64, 87, 88} As such a statement was obtained using a single molar concentration with highly variable surface tensions,^{87, 88} its validity needs to be revisited. In the current study, the cationic and non-ionic surfactants with higher HLB (i.e., DTAB and Tween 20) indeed exhibited higher wetting capabilities. Our results are consistent with a recent publication where surfactants with higher HLB values were more likely to induce membrane wetting.⁷⁴ The authors explain that the weaker hydrophobic-hydrophobic affinity between surfactant and membrane allows surfactants with higher HLB (and correspondingly lower hydrophobicity) to stay in the feed solution in free states, as opposed to absorbing into the membrane pore wall, thereby reducing feed solution's surface tension and membrane LEP more effectively.⁷⁴ Additionally, the membrane surfaces attached by surfactants of higher HLB are more hydrophilic, aiding in the formation of hydrophilic channels and further promoting wetting.⁷⁴ Our results demonstrate that when surfactants with varying properties are tested at comparable surface tensions, higher hydrophobicity of surfactants does not necessarily enhance the wetting potential.⁶⁴ Instead, molecular properties such as size and charge should be considered when evaluating the wetting potential of surfactant-containing solutions.

3.3.4 Relationship between Membrane Wetting and Contact Angle

We investigated the correlation between the time it takes for pores to become wetted and the apparent contact angles measured at both room temperature and 60 °C for the same surfactant solutions.⁶⁴ As shown in **Figure 3.13**, although a higher apparent contact angle generally resulted in a longer pore wetting time, the pore wetting time could

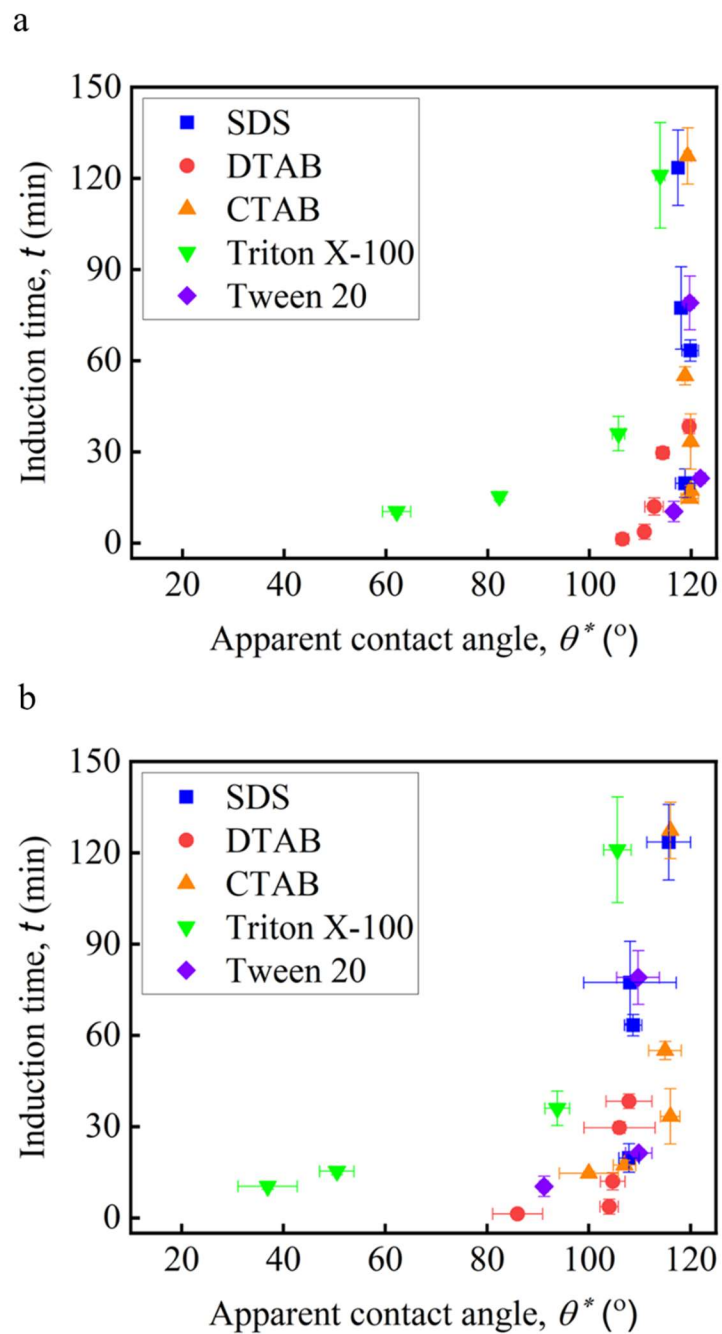


Figure 3.13. The induction time of membrane wetting as a function of apparent contact angle of the surfactant solution measured at (a) room temperature (~ 20 $^\circ\text{C}$) and (b) 60 $^\circ\text{C}$. The error bars represent the standard deviation calculated from three independent measurements.⁶⁴

significantly vary for the same (or very similar) contact angles.⁶⁴ For instance, when the apparent contact angle at room temperature was approximately 120°, the pore wetting time ranged from approximately 120 minutes to around less than 20 minutes. A similar pattern was observed when using the apparent contact angles at 60 °C (e.g., when the apparent contact angle was around 110°). These findings indicate that the apparent contact angle of aqueous solutions containing surfactants on the membrane surface (regardless of the temperature at which the contact angle is measured), which has been widely used to indicate solution wetting potential, is an unreliable indicator for evaluating the solution wetting potential in the MD process.^{82, 106-109} Indeed, based on our results, it seems unlikely that a single parameter can accurately predict membrane pore wetting caused by surfactants under MD conditions due to the complex nature of the issue. We expect that creating a predictive model for forecasting pore wetting caused by surfactants will likely involve multi-parameter modeling, which considers various surfactant and membrane properties.⁶⁴

3.4 Conclusion

We studied the influence of surfactants with different properties on the pore wetting of MD membrane. Our results showed that different types of surfactants with the same surface tension have different wetting behaviors in membrane distillation. It is crucial to recognize how factors such as charge type, chain length, and molecular weight significantly impact wetting behavior. Not only that, but we also observed that the cationic surfactants demonstrated a greater wetting capability than that of anionic surfactants of similar size. This difference is likely attributed to the electrostatic attraction between the surfactant molecules and the surface of the membrane. Moreover, the surfactants with identical charges but different molecular sizes exhibited different wetting behaviors. Specifically, surfactants with larger molecular sizes demonstrated reduced wetting potential as a result of their slower rates of transport to the membrane surface. Furthermore, our results clearly show that traditional measures of wetting potential, such as apparent contact angle and solution surface tension, cannot be relied upon to predict the wetting behavior of MD.

CHAPTER FOUR

Enhancing Wetting and Scaling Resistance of Porous Membranes

4.1 Introduction

The membrane distillation (MD) process necessitates utilizing functional microporous membranes with anti-wetting and anti-scaling properties. The MD membranes are commonly fabricated using polymer materials and modified with per- and polyfluoroalkyl substances (PFAS), which have exceptional features such as thermal stability, high wetting resistance, anti-scaling capability, and more.¹¹⁰ PFAS are human-made chemicals comprising numerous individual varieties of chemicals.^{51, 111}

Although PFAS have many unique properties, it has been reported that being exposed to PFASs could lead to health problems like hormonal disruptions, liver malfunction, weakened immune system, cancer, reproductive issues, and adverse impacts on fetal development and cognitive abilities in children.¹¹² The detrimental health effects of PFAS are not confined to humans; they equally pose a significant threat to animals and livestock.^{112, 113} It appears that the issue of PFASs contamination will persist and negatively affect living organisms and the environment. This issue should demand immediate attention and concerted efforts to mitigate its harmful effects. However, MD relies on the use of microporous hydrophobic membranes, which typically were treated by PFAS to optimize their wetting resistance, scaling resistance, and other essential characteristics.¹¹⁴

Hence, there is an urgent need for innovative method, which allows the fabrication of sustainable microporous membranes with high wetting and scaling resistance for MD process. In this study, we have developed PFAS-free membranes by applying chlorine-terminated polydimethylsiloxane onto microporous polyethersulfone (PES) membranes.

4.1.1 Use of PFAS in Fabricating Membranes

Since the 1940s, PFAS have been manufactured, which are an extensive group of chemicals containing numerous unique varieties.¹¹¹ PFASs are valued for their exceptional thermal and chemical durability, as well as their resistance to water and

oil.¹¹⁰ Their lasting characteristics and their aversion to water and oil make PFAS extremely valuable in industrial and commercial applications. For instance, they have been extensively utilized as textile protectants, anti-stain, personal care products, pesticides, fire-fighting foams, emulsifying agents, and more.¹¹⁵ Additionally, PFAS play a significant role in the fluoropolymer industry, which has had a profound influence on global development over the past 70 years.¹¹⁶ For example, PVDF is anticipated to experience significant growth because of its expanding usage in lithium-ion batteries and architectural coatings. The advances in the chemical processing, cookware, bakeware, and medical sectors are also significant factors propelling the fluoropolymer industry.¹¹⁶ There is a study which outlines various techniques used in the creation of fluoropolymer based membranes, such as phase inversion, electro-spinning, sintering, stretching, track etching, and others.¹¹⁷ Recently, the utilization of electro-spinning to produce PVDF nano-fiber membranes has made it simpler to create hydrophobic membranes for the MD process.

Furthermore, it has been suggested that for achieving specific features for fluoropolymer-based membranes, there are two effective strategies.¹¹⁸ The first approach involves innovating new materials and refining the formation conditions and parameters to create membranes with the necessary properties. The second strategy involves enhancing the existing membranes to better fit particular processes.¹¹⁸ Surface coating, surface grafting, blending, and filling are all valuable methods for modifying the properties of fluorinated polymeric membranes.

4.1.2 PDMS Brushes

PDMS is non-toxic and highly hydrophobic material.^{119, 120} Its thermal and chemical stability is attributed to the strength of the Si-O bond, which makes it crucial for various applications.^{121, 122} The use of PDMS brushes that are flexible, long-chain macromolecules for surface modification originated in 1970 when Vermeulen *et al.* deposited a PDMS brush layer on a glass surface using a vapor phase reaction for 16 hours.¹²³ This method can be used to covalently bond flexible macromolecule brushes like PDMS to a solid surface in order to repel liquids.¹¹³ The concept behind this is that the high flexibility of the macromolecules allows them to act as a lubricating layer for

liquids with a wide range of surface tensions.¹¹³ Since these molecular structures are covalently bonded to the surface, they cannot be dissolved or displaced by the contacting liquids. PDMS-coated surfaces show excellent resistance to high temperature, photodegradation, and scratching.^{113, 114} Moreover, these layers are only a few nanometers thick, making them have minimal impact on the appearance and heat conductivity of coated surfaces.^{113, 114}

PDMS brushes have been used to enhance liquid repellency,¹²⁴ create ice-phobic coatings,¹²⁵ and enable liquid transportation without loss.¹²⁶ Furthermore, they have been used to fabricate surfaces with low contact angle hysteresis.^{37, 127, 128} The low contact angle hysteresis observed on PDMS brush-modified surfaces is due to their liquid-like property.¹²⁸ This property results from the brush-like structure and its low glass transition temperature, which allows the surface to remain mobile and prevents contact line pinning.³⁷ The unique combination of properties makes PDMS brushes a particularly intriguing material for enhancing wetting resistance of solid surfaces.

The primary objective of this study is to create an innovative method that allows the fabrication of microporous membranes with high wetting and scaling resistance without using PFAS. This is achieved by grafting the PDMS brushes on the PES membrane surface through liquid phase modification. This study involved a comparative analysis that was carried out to evaluate the wetting and scaling resistance of the PDMS brush-modified membranes and the commercially available PVDF membranes.

4.2 Materials and Experimental Setup

4.2.1 Materials

Two different microporous PES membranes with pore sizes of 0.22 μm and 0.45 μm were employed. The hydrophobic PVDF membranes with pore sizes of 0.22 μm and 0.45 μm were also used for comparison. The chlorine-terminated PDMS was supplied by Gelest (**Figure 4.1**). The tetraethoxysilane (TEOS), n-hexane, ethanol, sodium dodecyl sulfate (SDS), and calcium sulfate were purchased from Fisher. All materials and chemicals were used as received.

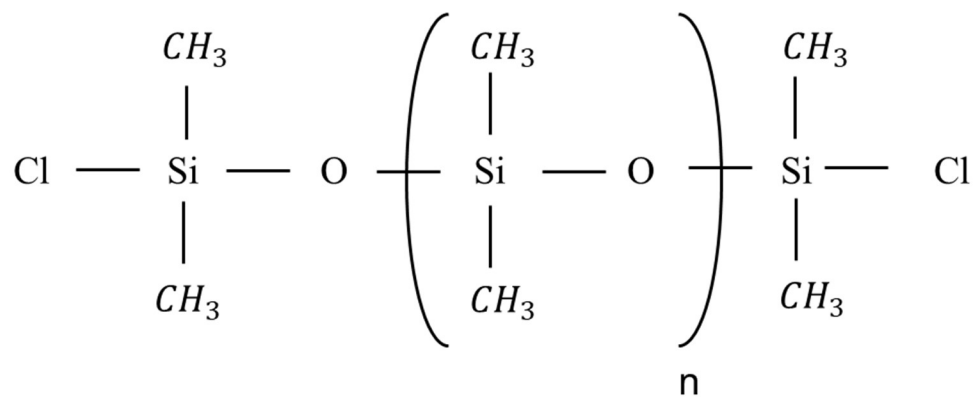


Figure 4.1. Molecular structure of chlorine-terminated PDMS.

4.2.2 Membrane Modification

The PDMS brush was grafted onto the surface of PES membranes to create microporous membranes with high wetting and scaling resistance. The procedure involved mixing 18 ml of hexane, 1 ml of chlorine-terminated PDMS, and 1 ml of TEOS. The mixture was stirred with a magnetic bar at 500 rpm for three minutes at room temperature. Meanwhile, the entire disc of the PES membrane underwent oxygen plasma treatment for 10 minutes. After that, the membrane was immersed in the prepared solution. The PES membrane was left at room temperature for 24 hours on an orbital shaker at a shaking speed of 350 rpm. After 24 hours, the membrane modified with the PDMS brush (referred to as the PDMS-PES membrane) was rinsed thoroughly with hexane and gently dried using compressed air. The modification process is shown in **Figure 4.2**.

4.2.3 Contact Angle Measurements

In this study, we examined the performance of PDMS-PES membrane and conducted a comparative analysis with the hydrophobic PVDF membranes by measuring the contact angles of liquids with a wide range of surface tensions. The contact angle measurements were performed using a contact angle goniometer (Ramé-Hart Instrument Corporation). Liquids with different surface tensions were prepared by either dissolving SDS in DI water or mixing ethanol with DI water at varied concentrations. A 10 μ L droplet of each solution was carefully placed on the surface of each sample, and the resulting images were captured and analyzed to determine the contact angle. Three independent contact angle measurements were performed on each sample.

4.2.4 Scaling Test

The scaling resistance of the membranes was evaluated using a customized setup, as illustrated in **Figure 4.3**. To create the CaSO_4 solution, we poured 1000 mL of DI water into a glass container and added 2 g of CaSO_4 . This was followed by vigorous mixing at 400 rpm using a magnetic stir bar until CaSO_4 was fully dissolved at room temperature. Subsequently, membrane attached to glass slide using double-sided tape was immersed in the CaSO_4 aqueous solution at 30° angles relative to the horizontal plane. A glass rack was utilized to support each sample. The container containing the solution and the

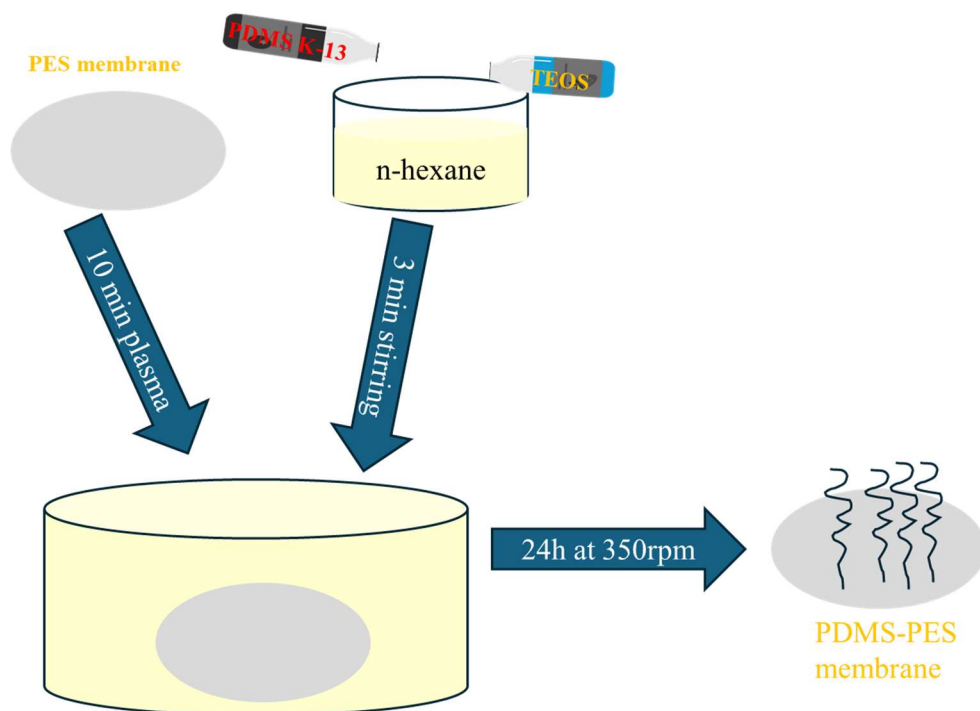


Figure 4.2. Schematic showing the fabrication of PDMS-PES membrane.



Figure 4.3. Schematic showing the setup for scaling experiment.

membrane samples were placed on a hot plate and heated to 60 °C for facilitating the evaporation. As the water gradually evaporated from the beaker, CaSO₄ precipitation occurred on the sample surfaces. To quantify the extent of scaling, we weighed the samples before and after the experiments using a microbalance. Static and dynamic scaling tests were conducted at 0 rpm and 100 rpm, respectively.

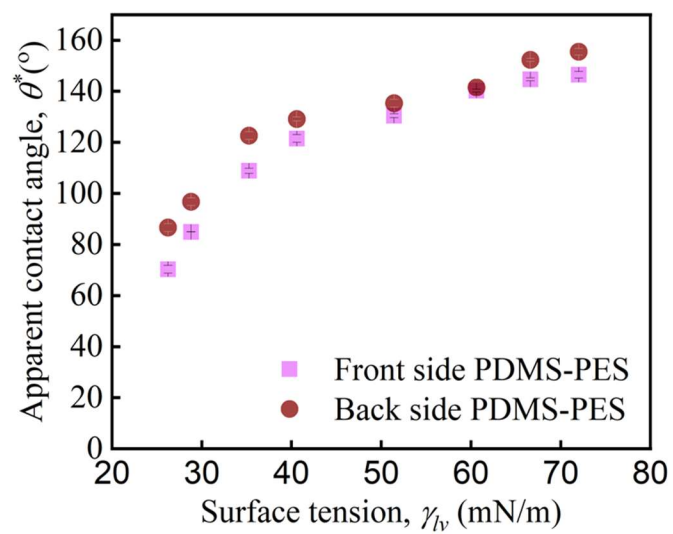
4.3 Results and Discussion

4.3.1 Contact Angle Results

The successful modification of the PES membranes with pore sizes of 0.22 μm and 0.45 μm using the PDMS brush was confirmed through contact angle measurements. Both sides of each PDMS-PES membrane were thoroughly characterized and compared to their rival, the hydrophobic pristine PVDF membrane with the same pore size. On the front side of the 0.22 μm PDMS-PES membrane, the apparent contact angles (θ^*) of liquids with different surface tensions varied from $\sim 70^\circ$ to $\sim 146^\circ$. Interestingly, when examining the back side of the same membrane, the contact angles of these liquids were notably higher, spanning from approximately $\sim 86^\circ$ to $\sim 156^\circ$ (**Figure 4.4**). Similarly, for the 0.45 μm PDMS-PES membrane, the apparent contact angles on the front side exhibited an even broader range, from $\sim 76^\circ$ to $\sim 157^\circ$ (**Figure 4.5**). The back side of this membrane displayed exceptionally high contact angles, ranging from about $\sim 93^\circ$ to $\sim 165^\circ$, revealing a marked increase in wetting resistance compared to the front side.

It is important to note that the apparent contact angles observed on PVDF membranes are considerably lower than those observed on PDMS-PES membranes with the same pore size. Furthermore, the PVDF membrane demonstrates a significant limitation, as it fails to resist the wetting of 30% ethanol. In contrast, the PDMS-PES membranes show an impressive ability to repel 60% ethanol, which has a lower surface tension compared to that of 30% ethanol. This difference underscores the superior wetting resistance of PDMS-PES when compared to the PVDF membranes. In other words, our fluorine-free microporous membranes modified using PDMS brush displayed even higher wetting resistance when comparing to the PVDF membranes, which are the fluoropolymer-based membranes. This highlights that fluorine-containing substances are not always required for creating wetting resistant surfaces for targeted applications.

a



b

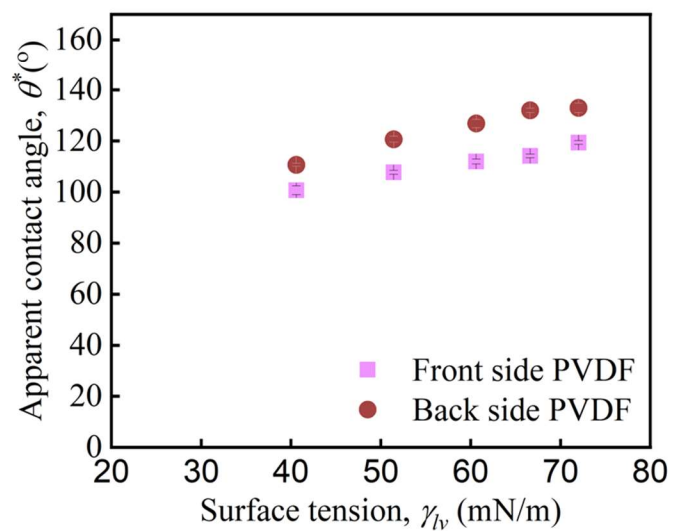
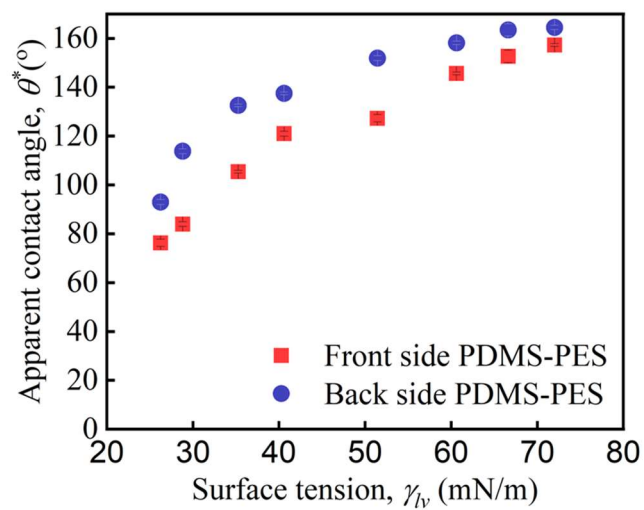


Figure 4.4. Apparent contact angle as function of surface tension for 0.22 μm (a) PDMS-PES and (b) PVDF.

a



b

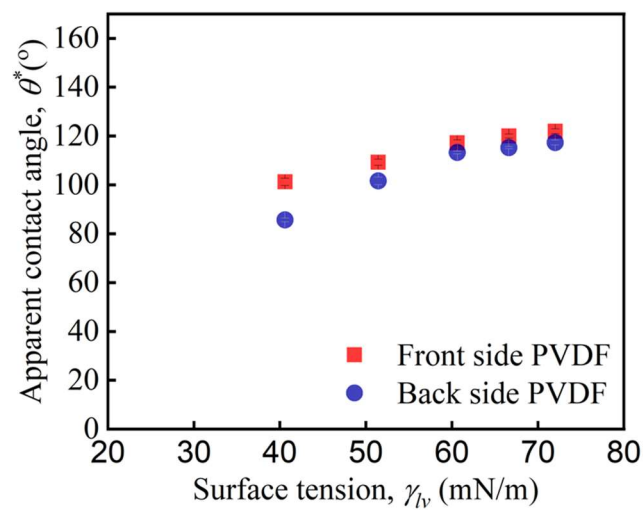


Figure 4.5. Apparent contact angle as function of surface tension for 0.45 μm (a) PDMS-PES and (b) PVDF.

The different liquid repellency of the membranes is observable in **Figure 4.6**. Additionally, the advancing contact angles θ_{adv}^* and receding contact angles θ_{rec}^* of liquids with different surface tensions on each membrane were also characterized (**Tables 4.1-4.4**). Advancing and receding contact angles were measured by continuously increasing or decreasing the volume of a droplet. The PDMS-PES membrane demonstrated higher θ_{adv}^* and θ_{rec}^* than that on the PVDF membrane.

4.3.2 Scaling Performance

The scaling tests were carried out under both static and dynamic conditions within an aqueous solution saturated with CaSO_4 . The study effectively simulates different practical scenarios that materials might encounter in real world applications. Conducting these experiments under static and dynamic conditions (i.e., 0 and 100 rpm) allows us to study the effect of fluid motion on the formation of scale on the membrane surface. The solution was heated to approximately 60 °C to expedite its evaporation, leading to the eventual precipitation of the CaSO_4 scale onto the sample surface. In assessing membranes with a pore size of 0.22 μm , a noteworthy finding emerged regarding the mass gain due to scale deposition on the back side of the PVDF membrane. This mass gain was twice as that of the PDMS-PES membrane at 0 rpm. Also, at 100 rpm, the mass gain observed on the PVDF membrane was significantly higher than that on the PDMS-PES membrane ($\sim 0.8 \text{ mg/cm}^2$ vs $\sim 0.1 \text{ mg/cm}^2$). When analyzing the anti-scaling performance of the front side of the membranes, a slight difference was observed between the front sides of the PVDF and PDMS-PES membranes for both static and dynamic conditions. In other words, the scale deposited on the PVDF membrane was slightly higher than that on the PDMS-PES membrane. These results are shown in **Figure 4.7**.

Additionally, the results demonstrate that the PDMS-PES surfaces exhibit improved anti-scaling performance compared to the PVDF surfaces for 0.45 μm pore sizes, irrespective of the testing conditions (0 or 100 rpm). Specifically, it was observed that at static conditions, the values of mass gained per unit area on the front and back sides of

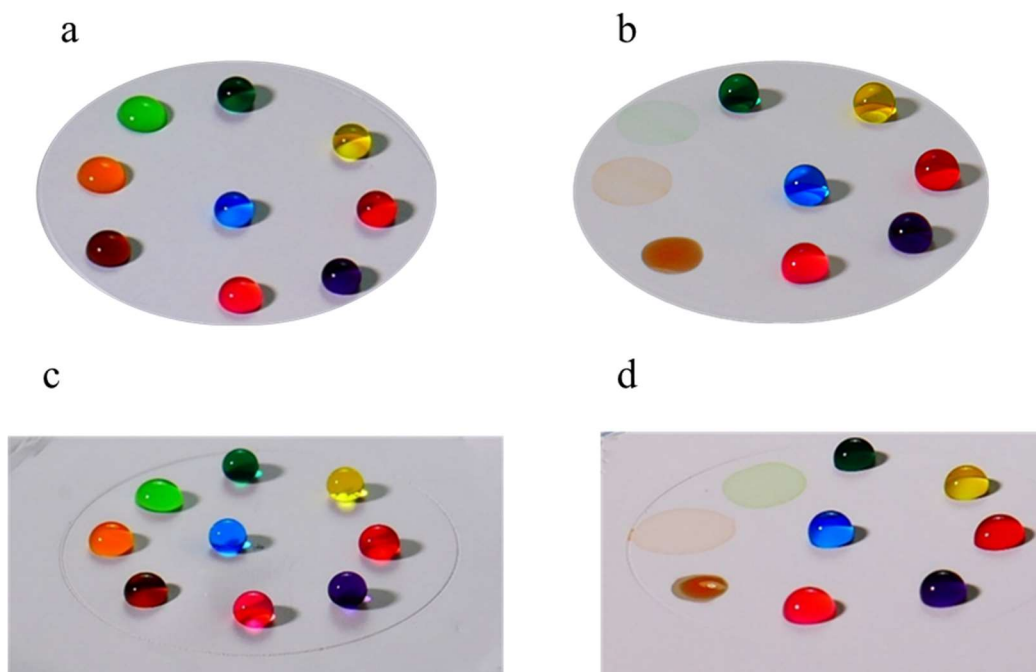


Figure 4.6. Images showing different liquids beading up on or wetting membranes. (a) 0.22 μm PDMS-PES membrane, (b) 0.22 μm PVDF membrane, (c) 0.45 μm PDMS-PES membrane, and (d) 0.45 μm PVDF. (blue) water, (dark green) 0.5 mM SDS, (yellow) 1mM SDS, (red) 1.5 mM SDS, (purple) 10% ethanol, (pink) 20% ethanol, (brown) 30% ethanol, (orange) 50% ethanol, and (light green) 60% ethanol.

Table 4.1. Apparent advancing contact angle θ_{adv}^* and apparent receding contact angle θ_{rec}^* of various liquids on the front side of 0.22 μm pristine PVDF and PDMS-PES membranes.

Liquids	Surface tension, γ (mN/m)	PDMS-PES, front θ_{adv}^*	PDMS-PES, front θ_{rec}^*	PVDF, front θ_{adv}^*	PVDF, front θ_{rec}^*
DI Water	72	153°	85°	130°	43°
0.5 mM SDS	66.61	151°	79°	126°	36°
1 mM SDS	61.4	148°	73°	125°	32°
1.5 mM SDS	60.61	144°	67°	124°	30°
10% ethanol	51.43	143°	65°	114°	29°
20% ethanol	40.59	125°	63°	101°	23°
30% ethanol	35.26	111°	47°	0°	0°
50% ethanol	28.81	91°	33°	0°	0°
60% ethanol	26.32	77°	22°	0°	0°
80% ethanol	24.7	0°	0°	0°	0°

Table 4.2. Apparent advancing contact angle θ_{adv}^* and apparent receding contact angle θ_{rec}^* of various liquids on the back side of 0.22 μm pristine PVDF and PDMS-PES membranes.

Liquids	Surface tension, γ (mN/m)	PDMS-PES, back θ_{adv}^*	PDMS-PES, back θ_{rec}^*	PVDF, back θ_{adv}^*	PVDF, back θ_{rec}^*
DI Water	72	152°	90°	152°	72°
0.5 mM SDS	66.61	151°	82°	149°	41°
1 mM SDS	61.4	139°	81°	146°	31°
1.5 mM SDS	60.61	138°	78°	142°	24°
10% ethanol	51.43	135°	74°	133°	21°
20% ethanol	40.59	127°	66°	120°	17°
30% ethanol	35.26	115°	47°	0°	0°
50% ethanol	28.81	98°	23°	0°	0°
60% ethanol	26.32	90°	16°	0°	0°
80% ethanol	24.7	0°	0°	0°	0°

Table 4.3. Apparent advancing contact angle θ_{adv}^* and apparent receding contact angle θ_{rec}^* of various liquids on the front side of 0.45 μm pristine PVDF and PDMS-PES membranes.

Liquids	Surface tension, γ (mN/m)	PDMS-PES, front θ_{adv}^*	PDMS-PES, front, θ_{rec}^*	PVDF, front, θ_{adv}^*	PVDF, front, θ_{rec}^*
DI Water	72	127°	82°	132°	35°
0.5 mM SDS	66.61	126°	72°	129°	29°
1 mM SDS	61.4	125°	67°	127°	26°
1.5 mM SDS	60.61	123°	66°	126°	24°
10% ethanol	51.43	117°	65°	122°	21°
20% ethanol	40.59	114°	62°	108°	14°
30% ethanol	35.26	100°	54°	0°	0°
50% ethanol	28.81	83°	35°	0°	0°
60% ethanol	26.32	62°	27°	0°	0°
80% ethanol	24.7	0°	0°	0°	0°

Table 4.4. Apparent advancing contact angle θ_{adv}^* and apparent receding contact angle θ_{rec}^* of various liquids on the back side of 0.45 μm pristine PVDF and PDMS-PES membranes.

Liquids	Surface tension, γ (mN/m)	PDMS-PES, back θ_{adv}^*	PDMS-PES, back θ_{rec}^*	PVDF, back θ_{adv}^*	PVDF, back θ_{rec}^*
DI Water	72	149°	91°	130°	41°
0.5 mM SDS	66.61	146°	76°	125°	23°
1 mM SDS	61.4	145°	74°	123°	18°
1.5 mM SDS	60.61	142°	71°	120°	13°
10% ethanol	51.43	140°	69°	112°	9°
20% ethanol	40.59	137°	61°	96°	7°
30% ethanol	35.26	126°	54°	0°	0°
50% ethanol	28.81	115°	31°	0°	0°
60% ethanol	26.32	104°	21°	0°	0°
80% ethanol	24.7	0°	0°	0°	0°

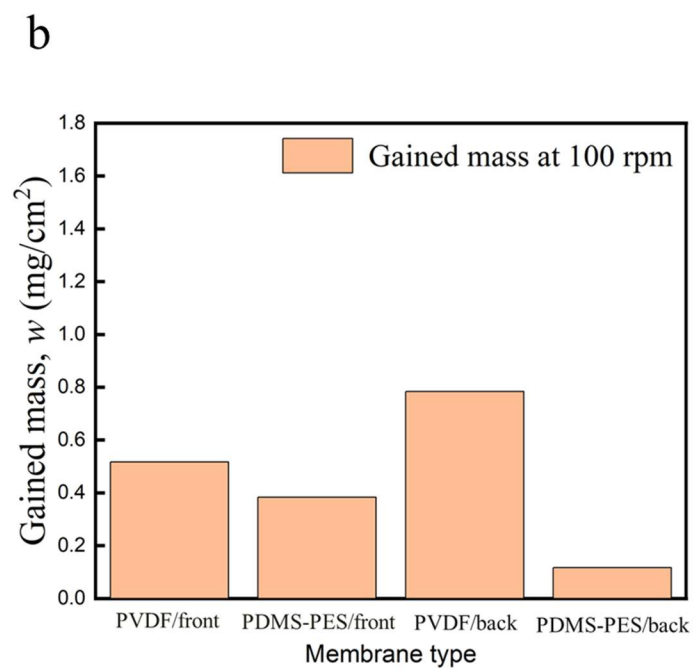
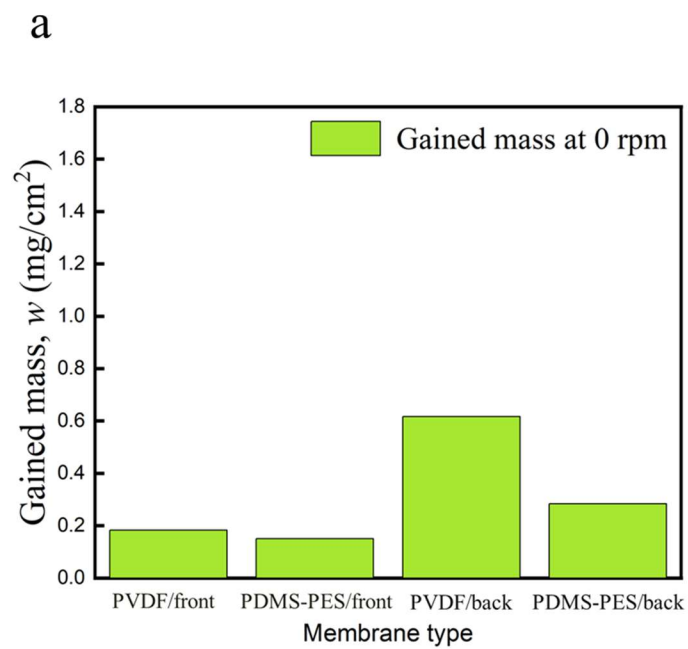


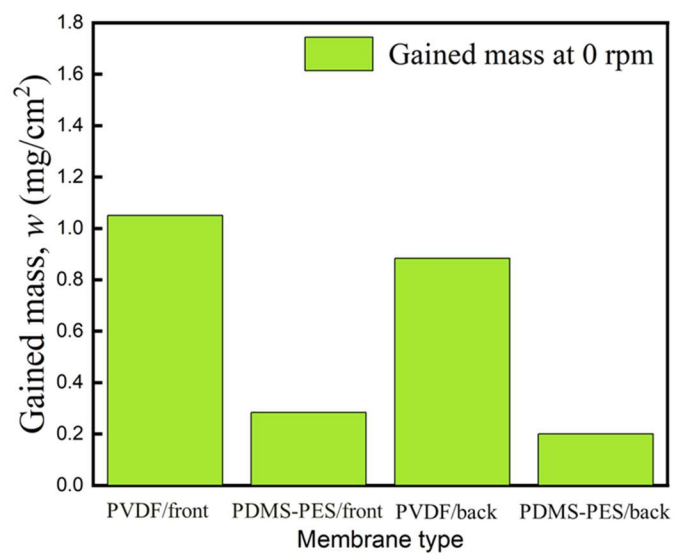
Figure 4.7. Scaling resistance of 0.22 μm membranes at (a) 0 rpm and (b) 100 rpm.

the PVDF membrane is much higher than that on the PDMS-PES membrane (**Figure 4.8**). This significant difference underscores the enhanced scaling resistance of the PDMS-PES surfaces in various operational scenarios.

4.4 Conclusion

To address the need for sustainable membranes with high wetting resistance and scaling resistance, we have developed innovative surface modification method, which allows the fabrication of such membranes using PDMS brush. This advancement was achieved through the strategic modification of microporous PES membranes with chlorine-terminated PDMS brush. Our findings can potentially lead to the creation of high-performance membrane specifically tailored for membrane distillation process. Our PDMS-PES membranes can resist not only water but also low surface tension liquids like 60% ethanol. The high apparent contact angles measured on the surfaces of the PDMS-PES membranes indicate the enhanced wetting resistance of the membranes. When compared to conventional hydrophobic fluorinated membranes such as PVDF membrane with the same pore size, the PDMS-PES membranes display better wetting resistance and scaling resistance. This finding signals a new era in membrane technology, positioning itself as a pivotal player in the pursuit of efficient and environmentally friendly membrane solutions.

a



b

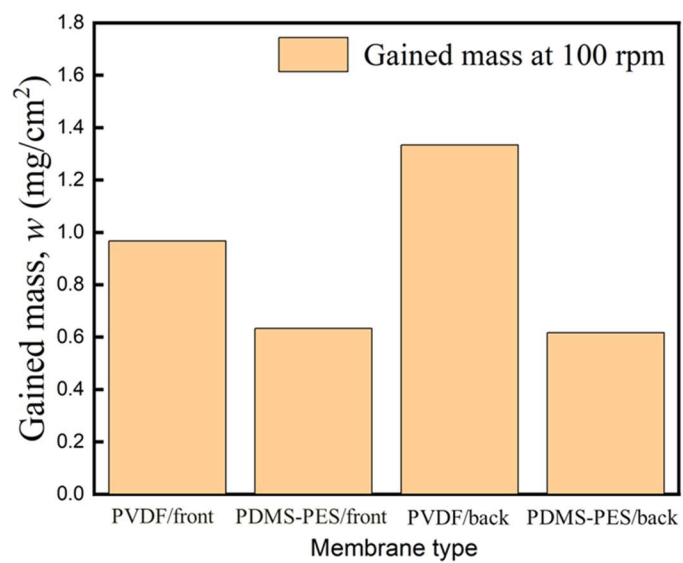


Figure 4.8. Scaling resistance of 0.45 μm membranes at (a) 0 rpm and (b) 100 rpm.

CHAPTER FIVE

Summary

After a thorough examination of the latest literature, it is apparent that there is a wealth of research dedicated to addressing the complexities associated with microporous membranes used in membrane distillation (MD). The challenges encompass various aspects such as membrane pore wetting, surface modification with per- and polyfluoroalkyl substances (PFAS), and scaling phenomenon. These issues were discussed in this thesis.

Firstly, we conducted an in-depth analysis to establish a direct correlation between the unique properties of different types of surfactants and their capability to induce pore wetting in MD desalination. By comparing the wetting behaviors of different surfactants with different charges and molecular structures, we revealed the relationship between surfactant characteristics and membrane pore wetting. Our findings unveiled that even surfactants with similar surface tensions in the feedwater can lead to different wetting potential, highlighting the profound influence of both the charge of the head group and the molecular structure of surfactants on this phenomenon. Furthermore, we demonstrated that conventional parameters, such as apparent contact angle and solution surface tension, may not serve as reliable predictors of the wetting behavior of MD membranes. This underscores the complex interplay between surfactant properties and the resulting wetting behavior.

Secondly, after comprehending the effects of surfactants in inducing pore wetting in hydrophobic microporous membranes, we proceeded to address challenges related to these membranes. These challenges entailed the development of PFAS-free microporous membranes with high wetting and scaling resistance, as PFAS have been found to be harmful to both living organisms and ecosystems due to their toxicity. The fabrication of PFAS-free microporous membranes was conducted by grafting chlorine-terminated PDMS on the surface of PES membranes to produce membranes. PES membranes with different pore sizes were used. Both sides of the resultant PDMS-PES membranes were tested, analyzed, and compared to the PVDF membranes with the same pore size. Our

PDMS-PES surface can repel liquids with very low surface tension (e.g., 60% ethanol). On the other hand, the PVDF surface was unable to withstand liquids with surface tensions lower than ~ 40 mN/m. The dynamic contact angles of different liquids on the membranes were also characterized. The results from the tests for all membranes showed that the PDMS-PES displayed higher wetting resistance than PVDF membranes. Additionally, the anti-scaling performance of the PDMS-PES and PVDF membranes was assessed. Scaling tests were carried out under both static and dynamic conditions. It was found that the PDMS-PES membranes displayed enhanced scaling resistance when comparing to the PVDF membranes with same pore size.

For future studies, more comprehensive analysis of the intricate dynamics of liquid spreading and imbibition may hold the promise of uncovering profound understandings of the critical influence of surfactants on controlling membrane pore wetting in membrane distillation. Also, factors related to membrane properties, such as the distribution of pore sizes, surface charge, and hydrophobicity, can play a significant role in influencing pore wetting. Furthermore, based on the results and findings of this thesis, there are opportunities to advance future studies in the development of PFAS-free microporous membranes with superior wetting and scaling resistance. To enhance the current PDMS-PES membrane, efforts should focus on reducing contact angle hysteresis and improving its wetting resistance to withstand liquids with lower surface tension than those examined in this thesis. Additionally, there is potential to augment scaling resistance and broaden the fouling experiments to evaluate its effectiveness in resisting organic fouling.

List of References

1. Mekonnen, M. M.; Hoekstra, A. Y., Four billion people facing severe water scarcity. *Science Advances* **2016**, 2 (2), e1500323.
2. Franken, A. C. M.; Nolten, J. A. M.; Mulder, M. H. V.; Bargeman, D.; Smolders, C. A., Wetting criteria for the applicability of membrane distillation. *Journal of Membrane Science* **1987**, 33 (3), 315-328.
3. Deshmukh, A.; Boo, C.; Karanikola, V.; Lin, S.; Straub, A. P.; Tong, T.; Warsinger, D. M.; Elimelech, M., Membrane distillation at the water-energy nexus: limits, opportunities, and challenges. *Energy & Environmental Science* **2018**, 11 (5), 1177-1196.
4. Horseman, T.; Yin, Y.; Christie, K. S.; Wang, Z.; Tong, T.; Lin, S., Wetting, scaling, and fouling in membrane distillation: state-of-the-art insights on fundamental mechanisms and mitigation strategies. *ACS ES&T Engineering* **2020**, 1 (1), 117-140.
5. Boo, C.; Lee, J.; Elimelech, M., Omniphobic polyvinylidene fluoride (PVDF) membrane for desalination of shale gas produced water by membrane distillation. *Environmental Science & Technology* **2016**, 50 (22), 12275-12282.
6. Lee, H. K.; Kim, W.; Kim, Y. M.; Kwon, Y.-N., Surface modification of polyvinylidene fluoride membrane for enhanced wetting resistance. *Applied Surface Science* **2019**, 491, 32-42.
7. Bodell, B., Silicone Rubber Vapor Diffusion in Saline Water Distillation (United States Pat. Ser). **1963**.
8. Rezaei, M.; Warsinger, D. M.; Duke, M. C.; Matsuura, T.; Samhaber, W. M., Wetting phenomena in membrane distillation: Mechanisms, reversal, and prevention. *Water Research* **2018**, 139, 329-352.
9. Zhao, F.; Ma, Z.; Xiao, K.; Xiang, C.; Wang, H.; Huang, X.; Liang, S., Hierarchically textured superhydrophobic polyvinylidene fluoride membrane fabricated via nanocasting for enhanced membrane distillation performance. *Desalination* **2018**, 443, 228-236.

10. Khayet, M.; Matsuura, T., Preparation and characterization of polyvinylidene fluoride membranes for membrane distillation. *Industrial & Engineering Chemistry Research* **2001**, *40* (24), 5710-5718.
11. Yang, X.; Wang, R.; Shi, L.; Fane, A. G.; Debowski, M., Performance improvement of PVDF hollow fiber-based membrane distillation process. *Journal of Membrane Science* **2011**, *369* (1-2), 437-447.
12. Villalobos García, J.; Dow, N.; Milne, N.; Zhang, J.; Naidoo, L.; Gray, S.; Duke, M., Membrane distillation trial on textile wastewater containing surfactants using hydrophobic and hydrophilic-coated polytetrafluoroethylene (PTFE) membranes. *Membranes* **2018**, *8* (2), 31.
13. El-Abbassi, A.; Kiai, H.; Hafidi, A.; García-Payo, M. d. C.; Khayet, M., Treatment of olive mill wastewater by membrane distillation using polytetrafluoroethylene membranes. *Separation and Purification Technology* **2012**, *98*, 55-61.
14. Xu, Z.; Liu, Z.; Song, P.; Xiao, C., Fabrication of super-hydrophobic polypropylene hollow fiber membrane and its application in membrane distillation. *Desalination* **2017**, *414*, 10-17.
15. Gryta, M., Influence of polypropylene membrane surface porosity on the performance of membrane distillation process. *Journal of Membrane Science* **2007**, *287* (1), 67-78.
16. Li, J.-M.; Xu, Z.-K.; Liu, Z.-M.; Yuan, W.-F.; Xiang, H.; Wang, S.-Y.; Xu, Y.-Y., Microporous polypropylene and polyethylene hollow fiber membranes. Part 3. Experimental studies on membrane distillation for desalination. *Desalination* **2003**, *155* (2), 153-156.
17. Khayet, M.; Feng, C.; Khulbe, K.; Matsuura, T., Preparation and characterization of polyvinylidene fluoride hollow fiber membranes for ultrafiltration. *Polymer* **2002**, *43* (14), 3879-3890.
18. Wang, Z.; Chen, Y.; Sun, X.; Duddu, R.; Lin, S., Mechanism of pore wetting in membrane distillation with alcohol vs. surfactant. *Journal of Membrane Science* **2018**, *559*, 183-195.

19. Antony, A.; Low, J. H.; Gray, S.; Childress, A. E.; Le-Clech, P.; Leslie, G., Scale formation and control in high pressure membrane water treatment systems: A review. *Journal of Membrane Science* **2011**, 383 (1-2), 1-16.
20. Du, X.; Alipanahrostami, M.; Wang, W.; Tong, T., Long-chain PFASs-free omniphobic membranes for sustained membrane distillation. *ACS Applied Materials & Interfaces* **2022**, 14 (20), 23808-23816.
21. Leung, S. C. E.; Shukla, P.; Chen, D.; Eftekhari, E.; An, H.; Zare, F.; Ghasemi, N.; Zhang, D.; Nguyen, N.-T.; Li, Q., Emerging technologies for PFOS/PFOA degradation and removal: A review. *Science of The Total Environment* **2022**, 827, 153669.
22. Gagliano, E.; Sgroi, M.; Falciglia, P. P.; Vagliasindi, F. G.; Roccaro, P., Removal of poly-and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. *Water Research* **2020**, 171, 115381.
23. Dhore, R.; Murthy, G. S., Per/polyfluoroalkyl substances production, applications and environmental impacts. *Bioresource Technology* **2021**, 341, 125808.
24. Zhi, Y.; Lu, H.; Grieger, K. D.; Munoz, G.; Li, W.; Wang, X.; He, Q.; Qian, S., Bioaccumulation and translocation of 6: 2 fluorotelomer sulfonate, GenX, and perfluoroalkyl acids by urban spontaneous plants. *ACS ES&T Engineering* **2022**, 2 (7), 1169-1178.
25. Ehsan, M. N.; Riza, M.; Pervez, M. N.; Khyum, M. M. O.; Liang, Y.; Naddeo, V., Environmental and health impacts of PFAS: sources, distribution and sustainable management in North Carolina (USA). *Science of The Total Environment* **2023**, 878, 163123.
26. Liu, Y.-M.; Wu, Z.-Q.; Bao, S.; Guo, W.-H.; Li, D.-W.; He, J.; Zeng, X.-B.; Huang, L.-J.; Lu, Q.-Q.; Guo, Y.-Z., The possibility of changing the wettability of material surface by adjusting gravity. *Research* **2020**.
27. Boyle, R., New experiments made and communicated by the Honourable Robert Boyie Esquire, about the superficial figures of fluids, especially of liquors contiguous to other liquors: likely to conduce much to the physical theory of the grand system of the

world. *Philosophical Transactions of the Royal Society of London* **1677**, 11 (131), 775-787.

28. Boyle, R., New experiments physico-mechanicall, touching the spring of the air, and its effect. **1667**. Oxford, UK: Printer to the Univ., for T Robinson.

29. Hooke, R., An attempt fo the explication of the phaenomena, observable in an experiment. Published by the honourable Robert Boyle. Printed by J. H. for Sam Thomson: London, 1661

30. Maxwell, J. C., Capillary action. *Encyclopaedia Britannica* **1876**, 5, 256-275.

31. Hauksbee, F., VIII. An experiment made at Gresham-College, shewing that the seemingly spontaneous ascention of water in small tubes open at both ends is the same in vacuo as in the open air. *Philosophical Transactions of the Royal Society of London* **1706**, 25 (305), 2223-2224.

32. Jurin, J., II. An account of some experiments shown before the Royal Society; with an enquiry into the cause of the ascent and suspension of water in capillary tubes. *Philosophical Transactions of the Royal Society of London* **1718**, 30 (355), 739-747.

33. Pomeau, Y. Surface tension: from fundamental principles to applications in liquids and in solids. Warsaw School of Statistical Physics, 2013.

34. Young, T., III. An essay on the cohesion of fluids. *Philosophical Transactions of the Royal Society of London* **1805**, (95), 65-87.

35. Sun, T.; Feng, L.; Gao, X.; Jiang, L., Bioinspired Surfaces with Special Wettability. *Accounts of Chemical Research* **2005**, 38 (8), 644-652.

36. Furmidge, C. G. L., Studies at phase interfaces. I. The sliding of liquid drops on solid surfaces and a theory for spray retention. *Journal of Colloid Science* **1962**, 17 (4), 309-324.

37. Wang, L.; McCarthy, T. J., Covalently attached liquids: instant omniphobic surfaces with unprecedented repellency. *Angewandte Chemie International Edition* **2016**, 55 (1), 244-248.

38. Erbil, H. Y., The debate on the dependence of apparent contact angles on drop contact area or three-phase contact line: A review. *Surface Science Reports* **2014**, 69 (4), 325-365.

39. Wenzel, R. N., Resistance of solid surfaces to wetting by water. *Industrial & Engineering Chemistry* **1936**, 28 (8), 988-994.
40. Cassie, A.; Baxter, S., Wettability of porous surfaces. *Transactions of the Faraday Society* **1944**, 40, 546-551.
41. Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Öner, D.; Youngblood, J.; McCarthy, T. J., Ultrahydrophobic and ultralyophobic surfaces: some comments and examples. *Langmuir* **1999**, 15 (10), 3395-3399.
42. Callies, M.; Quéré, D., On water repellency. *Soft Matter* **2005**, 1 (1), 55-61.
43. Di, J.; Li, L.; Wang, Q.; Yu, J., Porous membranes with special wettabilities: designed fabrication and emerging application. *CCS Chemistry* **2021**, 3 (3), 2280-2297.
44. Borrás, A.; Gonzalez-Elipé, A. R., Wetting properties of polycrystalline TiO₂ surfaces: a scaling approach to the roughness factors. *Langmuir* **2010**, 26 (20), 15875-15882.
45. Prakash Chakrapani Gunarasan, J.; Ravindran, P., Significance of chemical engineering in surface wettability tuning and its boiling hydrodynamics: a boiling heat transfer study. *Industrial & Engineering Chemistry Research* **2020**, 59 (10), 4210-4218.
46. Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Robust omniphobic surfaces. *Proceedings of the National Academy of Sciences* **2008**, 105 (47), 18200-18205.
47. Marmur, A., From hydrophilic to superhydrophobic: theoretical conditions for making high-contact-angle surfaces from low-contact-angle materials. *Langmuir* **2008**, 24 (14), 7573-7579.
48. Martines, E.; Seunarine, K.; Morgan, H.; Gadegaard, N.; Wilkinson, C. D.; Riehle, M. O., Superhydrophobicity and superhydrophilicity of regular nanopatterns. *Nano letters* **2005**, 5 (10), 2097-2103.
49. Jothi Prakash, C.; Prasanth, R., Approaches to design a surface with tunable wettability: a review on surface properties. *Journal of Materials Science* **2021**, 56, 108-135.
50. Antony, R. P.; Mathews, T.; Dash, S.; Tyagi, A., Kinetics and physicochemical process of photoinduced hydrophobic↔ superhydrophilic switching of pristine and N-

doped TiO₂ nanotube arrays. *The Journal of Physical Chemistry C* **2013**, 117 (13), 6851-6860.

51. Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; De Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P., Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. *Integrated Environmental Assessment and Management* **2011**, 7 (4), 513-541.
52. Knepper, T. P.; Lange, F. T., *Polyfluorinated chemicals and transformation products*. Springer Science & Business Media: 2011; Vol. 17.
53. Gould, R. F., Contact angle, wettability, and adhesion, copyright, advances in chemistry series. ACS Publications: 1964.
54. Cui, Z.; Jiang, Y.; Field, R., Fundamentals of pressure-driven membrane separation processes. In *Membrane Technology*, Elsevier: 2010; pp 1-18.
55. Anari, Z.; Sengupta, A.; Sardari, K.; Wickramasinghe, S. R., Surface modification of PVDF membranes for treating produced waters by direct contact membrane distillation. *Separation and Purification Technology* **2019**, 224, 388-396.
56. Yao, M.; Tijing, L. D.; Naidu, G.; Kim, S.-H.; Matsuyama, H.; Fane, A. G.; Shon, H. K., A review of membrane wettability for the treatment of saline water deploying membrane distillation. *Desalination* **2020**, 479, 114312.
57. Du, X.; Zhang, Z.; Carlson, K. H.; Lee, J.; Tong, T., Membrane fouling and reusability in membrane distillation of shale oil and gas produced water: Effects of membrane surface wettability. *Journal of Membrane Science* **2018**, 567, 199-208.
58. Kamaz, M.; Sengupta, A.; Gutierrez, A.; Chiao, Y.-H.; Wickramasinghe, R., Surface modification of PVDF membranes for treating produced waters by direct contact membrane distillation. *International Journal of Environmental Research and Public Health* **2019**, 16 (5), 685.
59. Baker, R. W., *Membrane technology and applications*. John Wiley & Sons: 2023.
60. Tai, Z. S.; Othman, M. H. D.; Koo, K. N.; Mustapa, W. N. F. W.; Kadirkhan, F., Membrane innovations to tackle challenges related to flux, energy efficiency and wetting in membrane distillation: A state-of-the-art review. *Sustainable Materials and Technologies* **2023**, e00780.

61. Xiao, Z.; Guo, H.; He, H.; Liu, Y.; Li, X.; Zhang, Y.; Yin, H.; Volkov, A. V.; He, T., Unprecedented scaling/fouling resistance of omniphobic polyvinylidene fluoride membrane with silica nanoparticle coated micropillars in direct contact membrane distillation. *Journal of Membrane Science* **2020**, *599*, 117819.
62. Xiao, Z.; Li, Z.; Guo, H.; Liu, Y.; Wang, Y.; Yin, H.; Li, X.; Song, J.; Nghiem, L. D.; He, T., Scaling mitigation in membrane distillation: From superhydrophobic to slippery. *Desalination* **2019**, *466*, 36-43.
63. Warsinger, D. M.; Swaminathan, J.; Guillen-Burrieza, E.; Arafat, H. A., Scaling and fouling in membrane distillation for desalination applications: a review. *Desalination* **2015**, *356*, 294-313.
64. Coolidge, C.; Alhadidi, A. M. H.; Wang, W.; Tong, T., Effects of Surfactant Properties on Pore Wetting of Membrane Distillation. *Journal of Membrane Science Letters* **2024**, *4*, 100077.
65. Chen, Y.; Lu, K.-J.; Gai, W.; Chung, T.-S., Nanofiltration-inspired Janus membranes with simultaneous wetting and fouling resistance for membrane distillation. *Environmental Science & Technology* **2021**, *55* (11), 7654-7664.
66. Parani, S.; Oluwafemi, O. S., Membrane distillation: recent configurations, membrane surface engineering, and applications. *Membranes* **2021**, *11* (12), 934.
67. Stortini, A. M.; Cincinelli, A.; Degli Innocenti, N.; Tovar-Sánchez, A.; Knulst, J., 1.12 - Surface Microlayer. In *Comprehensive Sampling and Sample Preparation*, Pawliszyn, J., Ed. Academic Press: Oxford, 2012; pp 223-246.
68. Belhaj, A. F.; Elraies, K. A.; Mahmood, S. M.; Zulkifli, N. N.; Akbari, S.; Hussien, O. S., The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: a review. *Journal of Petroleum Exploration and Production Technology* **2020**, *10* (1), 125-137.
69. Moo-Young, M., *Comprehensive Biotechnology*. Elsevier: 2019.
70. Alam, M. S.; Siddiq, A. M.; Natarajan, D.; Kiran, M. S.; Baskar, G., Physicochemical properties and bioactivity studies of synthesized counterion coupled (COCO) gemini surfactant, 1, 6-bis (N, N-hexadecyldimethylammonium) adipate. *Journal of Molecular Liquids* **2019**, *273*, 16-26.

71. Zhu, Y.; Free, M. L.; Woollam, R.; Durnie, W., A review of surfactants as corrosion inhibitors and associated modeling. *Progress in Materials Science* **2017**, *90*, 159-223.
72. Farn, R. J. *Chemistry and technology of surfactants*; Wiley Online Library: 2006.
73. Miller, C. C., The Stokes-Einstein law for diffusion in solution. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1924**, *106* (740), 724-749.
74. Liao, X.; Wang, Y.; Liao, Y.; You, X.; Yao, L.; Razaqpur, A. G., Effects of different surfactant properties on anti-wetting behaviours of an omniphobic membrane in membrane distillation. *Journal of Membrane Science* **2021**, *634*, 119433.
75. Chen, Y.; Tian, M.; Li, X.; Wang, Y.; An, A. K.; Fang, J.; He, T., Anti-wetting behavior of negatively charged superhydrophobic PVDF membranes in direct contact membrane distillation of emulsified wastewaters. *Journal of Membrane Science* **2017**, *535*, 230-238.
76. Lewis, J., An introduction to surfactants. *Preservation of Surfactant Formulations* **1995**, 53-82.
77. Zhu, Y.; Free, M. L., Chapter 1 - Introduction to Surfactants. In *Surfactants in Precision Cleaning*, Kohli, R.; Mittal, K. L., Eds. Elsevier: 2022; pp 1-53.
78. Chang, C.-H.; Franses, E. I., Adsorption dynamics of surfactants at the air/water interface: a critical review of mathematical models, data, and mechanisms. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1995**, *100*, 1-45.
79. Starov, V. M.; Kosvintsev, S. R.; Velarde, M. G., Spreading of Surfactant Solutions over Hydrophobic Substrates. *Journal of Colloid and Interface Science* **2000**, *227* (1), 185-190.
80. Wang, Z.; Chen, Y.; Zhang, F.; Lin, S., Significance of surface excess concentration in the kinetics of surfactant-induced pore wetting in membrane distillation. *Desalination* **2019**, *450*, 46-53.
81. Rezaei, M.; Warsinger, D. M.; Samhaber, W. M., Wetting prevention in membrane distillation through superhydrophobicity and recharging an air layer on the membrane surface. *Journal of Membrane Science* **2017**, *530*, 42-52.

82. Wang, Z.; Lin, S., Membrane fouling and wetting in membrane distillation and their mitigation by novel membranes with special wettability. *Water Research* **2017**, *112*, 38-47.
83. Huang, Y.-X.; Wang, Z.; Jin, J.; Lin, S., Novel Janus membrane for membrane distillation with simultaneous fouling and wetting resistance. *Environmental Science & Technology* **2017**, *51* (22), 13304-13310.
84. Eykens, L.; De Sitter, K.; Dotremont, C.; De Schepper, W.; Pinoy, L.; Van Der Bruggen, B., Wetting resistance of commercial membrane distillation membranes in waste streams containing surfactants and oil. *Applied Sciences* **2017**, *7* (2), 118.
85. Rezaei, M.; Samhaber, W., Wetting behaviour of superhydrophobic membranes coated with nanoparticles in membrane distillation. *Chemical Engineering Transactions* **2016**, *47*, 373-378.
86. Franken, A.; Nolten, J.; Mulder, M.; Bargeman, D.; Smolders, C., Wetting criteria for the applicability of membrane distillation. *Journal of Membrane Science* **1987**, *33* (3), 315-328.
87. Wang, Z.; Chen, Y.; Lin, S., Kinetic model for surfactant-induced pore wetting in membrane distillation. *Journal of Membrane Science* **2018**, *564*, 275-288.
88. Hou, D.; Yuan, Z.; Tang, M.; Wang, K.; Wang, J., Effect and mechanism of an anionic surfactant on membrane performance during direct contact membrane distillation. *Journal of Membrane Science* **2020**, *595*, 117495.
89. Ying, G.-G., Fate, behavior and effects of surfactants and their degradation products in the environment. *Environment International* **2006**, *32* (3), 417-431.
90. Qazi, M. J.; Schlegel, S. J.; Backus, E. H. G.; Bonn, M.; Bonn, D.; Shahidzadeh, N., Dynamic Surface Tension of Surfactants in the Presence of High Salt Concentrations. *Langmuir* **2020**, *36* (27), 7956-7964.
91. Qazi, M. J.; Schlegel, S. J.; Backus, E. H.; Bonn, M.; Bonn, D.; Shahidzadeh, N., Dynamic surface tension of surfactants in the presence of high salt concentrations. *Langmuir* **2020**, *36* (27), 7956-7964.

92. Qazi, M. J.; Liefferink, R. W.; Schlegel, S. J.; Backus, E. H.; Bonn, D.; Shahidzadeh, N., Influence of surfactants on sodium chloride crystallization in confinement. *Langmuir* **2017**, *33* (17), 4260-4268.
93. Kinoshita, K.; Parra, E.; Needham, D., Adsorption of ionic surfactants at microscopic air-water interfaces using the micropipette interfacial area-expansion method: Measurement of the diffusion coefficient and renormalization of the mean ionic activity for SDS. *Journal of Colloid and Interface Science* **2017**, *504*, 765-779.
94. Das, J.; Ismail, K., Aggregation, adsorption, and clouding behaviors of Triton X-100 in formamide. *Journal of Colloid and Interface Science* **2009**, *337* (1), 227-233.
95. Ullah, I.; Baloch, M. K.; Niaz, S.; Sultan, A.; Ullah, I., Solubilizing potential of ionic, zwitterionic and nonionic surfactants towards water insoluble drug flurbiprofen. *Journal of Solution Chemistry* **2019**, *48* (11), 1603-1616.
96. Atkin, R.; Craig, V. S.; Biggs, S., Adsorption kinetics and structural arrangements of cationic surfactants on silica surfaces. *Langmuir* **2000**, *16* (24), 9374-9380.
97. Atkin, R.; Craig, V. S.; Wanless, E. J.; Biggs, S., Mechanism of cationic surfactant adsorption at the solid–aqueous interface. *Advances in Colloid and Interface Science* **2003**, *103* (3), 219-304.
98. Daniel, R. C.; Berg, J. C., A simplified method for predicting the dynamic surface tension of concentrated surfactant solutions. *Journal of Colloid and Interface Science* **2003**, *260* (1), 244-249.
99. Diamant, H.; Ariel, G.; Andelman, D., Kinetics of surfactant adsorption: the free energy approach. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2001**, *183*, 259-276.
100. Zhang, X.; Chen, B.; Wang, Z., Computer simulation of adsorption kinetics of surfactants on solid surfaces. *Journal of Colloid and Interface Science* **2007**, *313* (2), 414-422.
101. Diamant, H.; Andelman, D., Kinetics of surfactant adsorption at fluid– fluid interfaces. *The Journal of Physical Chemistry* **1996**, *100* (32), 13732-13742.

102. Li, C.; Wang, H.; Xu, X.; Liu, M.; Liu, Y.; He, S.; Qian, Y.; Li, Z., Anionic polyelectrolyte modified perovskite composite activated hydrogen peroxide to treat high-salinity organic wastewater: Dual effects of electrostatic interaction. *Chemical Engineering Journal* **2024**, *488*, 151033.
103. Chang, H.; Zhu, Y.; Huang, L.; Yan, Z.; Qu, F.; Liang, H., Mineral scaling induced membrane wetting in membrane distillation for water treatment: Fundamental mechanism and mitigation strategies. *Water Research* **2023**, 120807.
104. Nthunya, L. N.; Pinier, J.; Ali, A.; Quist-Jensen, C.; Richards, H., Valorization of acid mine drainage into potable water and valuable minerals through membrane distillation crystallization. *Separation and Purification Technology* **2024**, *334*, 126084.
105. Alves, A. V.; Tsianou, M.; Alexandridis, P., Fluorinated surfactant adsorption on mineral surfaces: implications for PFAS fate and transport in the environment. *Surfaces* **2020**, *3* (4), 516-566.
106. Ismail, M. F.; Islam, M. A.; Khorshidi, B.; Tehrani-Bagha, A.; Sadrzadeh, M., Surface characterization of thin-film composite membranes using contact angle technique: Review of quantification strategies and applications. *Advances in Colloid and Interface Science* **2022**, *299*, 102524.
107. Gekas, V.; Persson, K. M.; Wahlgren, M.; Sivik, B., Contact angles of ultrafiltration membranes and their possible correlation to membrane performance. *Journal of Membrane Science* **1992**, *72* (3), 293-302.
108. Kung, C. H.; Sow, P. K.; Zahiri, B.; Mérida, W., Assessment and interpretation of surface wettability based on sessile droplet contact angle measurement: challenges and opportunities. *Advanced Materials Interfaces* **2019**, *6* (18), 1900839.
109. Huhtamäki, T.; Tian, X.; Korhonen, J. T.; Ras, R. H., Surface-wetting characterization using contact-angle measurements. *Nature Protocols* **2018**, *13* (7), 1521-1538.
110. Usuda, H.; Mishima, Y.; Noda, K.; Toyoshima, T.; Sakurai, K.; Takamura, C.; Takahashi, A.; Minami, K.; Kawamoto, T., Vesicles exhibit high-performance removal of per-and polyfluoroalkyl substances (PFAS) depending on their hydrophobic groups. *Chemosphere* **2024**, *363*, 142818.

111. Kissa, E., Fluorinated Surfactants and Repellents. *Surfactant Science Series* **2001**, 97.
112. Death, C.; Bell, C.; Champness, D.; Milne, C.; Reichman, S.; Hagen, T., Per- and polyfluoroalkyl substances (PFAS) in livestock and game species: A review. *Science of The Total Environment* **2021**, 774, 144795.
113. Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z., An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science: Processes & Impacts* **2020**, 22 (12), 2345-2373.
114. Kujawska, A.; Kujawski, J.; Bryjak, M.; Kujawski, W., ABE fermentation products recovery methods—a review. *Renewable and Sustainable Energy Reviews* **2015**, 48, 648-661.
115. Zushi, Y.; Hogarth, J. N.; Masunaga, S., Progress and perspective of perfluorinated compound risk assessment and management in various countries and institutes. *Clean Technologies and Environmental Policy* **2012**, 14, 9-20.
116. Teng, H., Overview of the development of the fluoropolymer industry. *Applied Sciences* **2012**, 2 (2), 496-512.
117. Cui, Z.; Drioli, E.; Lee, Y. M., Recent progress in fluoropolymers for membranes. *Progress in Polymer Science* **2014**, 39 (1), 164-198.
118. Du, J. R.; Peldszus, S.; Huck, P. M.; Feng, X., Modification of poly (vinylidene fluoride) ultrafiltration membranes with poly (vinyl alcohol) for fouling control in drinking water treatment. *Water Research* **2009**, 43 (18), 4559-4568.
119. Merkel, T.; Bondar, V.; Nagai, K.; Freeman, B.; Pinnau, I., Gas sorption, diffusion, and permeation in poly (dimethylsiloxane). *Journal of Polymer Science Part B: Polymer Physics* **2000**, 38 (3), 415-434.
120. Hong, T.; Niu, Z.; Hu, X.; Gmernicki, K.; Cheng, S.; Fan, F.; Johnson, J. C.; Hong, E.; Mahurin, S.; Jiang, D. e., Effect of Cross-Link Density on Carbon Dioxide Separation in Polydimethylsiloxane-Norbornene Membranes. *ChemSusChem* **2015**, 8 (21), 3595-3604.
121. Noll, W., *Chemistry and technology of silicones*. Elsevier: 2012.

122. Yilgör, E.; Yilgör, I., Silicone containing copolymers: Synthesis, properties and applications. *Progress in Polymer Science* **2014**, *39* (6), 1165-1195.
123. Han, J. T.; Lee, D. H.; Ryu, C. Y.; Cho, K., Fabrication of superhydrophobic surface from a supramolecular organosilane with quadruple hydrogen bonding. *Journal of the American Chemical Society* **2004**, *126* (15), 4796-4797.
124. Shabanian, S.; Khatir, B.; Nisar, A.; Golovin, K., Rational design of perfluorocarbon-free oleophobic textiles. *Nature Sustainability* **2020**, *3* (12), 1059-1066.
125. Zhang, L.; Guo, Z.; Sarma, J.; Dai, X., Passive removal of highly wetting liquids and ice on quasi-liquid surfaces. *ACS Applied Materials & Interfaces* **2020**, *12* (17), 20084-20095.
126. Zhang, L.; Guo, Z.; Sarma, J.; Zhao, W.; Dai, X., Gradient quasi-liquid surface enabled self-propulsion of highly wetting liquids. *Advanced Functional Materials* **2021**, *31* (13), 2008614.
127. Khatir, B.; Shabanian, S.; Golovin, K., Design and high-resolution characterization of silicon wafer-like omniphobic liquid layers applicable to any substrate. *ACS Applied Materials & Interfaces* **2020**, *12* (28), 31933-31939.
128. Zhao, X.; Khatir, B.; Mirshahidi, K.; Yu, K.; Kizhakkedathu, J. N.; Golovin, K., Macroscopic evidence of the liquidlike nature of nanoscale polydimethylsiloxane brushes. *ACS Nano* **2021**, *15* (8), 13559-13567.

Vita

Azal Alhadidi, hailing from Babylon City, Iraq, holds the distinction of being the eldest among her siblings. She pursued her undergraduate studies at the University of Babylon, where she earned a Bachelor of Science in Mechanical Engineering in June 2006. Following her graduation, she delved into the industrial realm, initially working as a project supervisor engineer. Subsequently, she progressed to the esteemed position of group leader engineer at Babylon Provincial Council Bebel in Iraq, where she dedicated approximately five years to her professional endeavors.

In 2014, she made a momentous relocation to Australia with her two sons to support her husband, who was pursuing a PH.D. program. During this period, she selflessly volunteered as an English LOTE (Languages Other Than English) Teacher at Al-Seraj Arabic School while awaiting her husband's completion of his studies before embarking on her own academic pursuits.

In 2020, Azal made her way to Tennessee – Knoxville to commence her graduate studies, which officially began in 2021. During her academic journey, she seized an opportunity to gain practical experience as a Process Engineer/Intern at Sonoco Metal Packaging, Tennessee, for an entire semester, an experience that significantly influenced her decision to extend her master's studies.

Motivated by her fervent interest in the subject, Azal displayed an unwavering passion for the Inspired Nature class during her coursework and aspired to deepen her comprehension of this intriguing scientific realm. Consequently, upon returning to school, she was privileged to be admitted as a member of Dr. Wang's team, where she is fervently pursuing her master's degree in bio-inspired materials.

Azal is anticipated to culminate her academic journey with the attainment of a Master of Science degree in Mechanical Engineering in December 2024, marking the fruition of her educational odyssey in this field.