OIL DROPLET BEHAVIOR AT THE MEMBRANE SURFACE DURING FILTRATION OF OIL-WATER EMULSIONS

By

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ABSTRACT

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Oily wastewaters are produced in large volumes by petrochemical, automotive, and several other major industries. Difficult to treat, these waste streams pose significant environmental risks. Treatment required for environmental compliance may be expensive and constitutes a financial burden for companies in both public and private sectors. Membrane-based separations are often the best treatment technology capable of removing micron-sized oil droplets. Membrane fouling, however, remains a major deterrent for broader acceptance and adoption of membranes in large scale wastewater treatment. The importance of elucidating the fundamental mechanisms of membrane fouling by emulsified oil is in the value of that knowledge for decreasing the operational costs that managing membrane fouling entails. Two strategies are to modify either the membranes or the emulsions so as to limit the egregious forms of fouling that decrease water throughput. This study combined real-time direct visualization tests with microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) membranes in the presence of crossflow to observe the different patterns of membrane fouling by oil. Experimental variables included membrane pore size, surfactant concentration, concentration of divalent ions, as well as membrane charge and hydrophilicity. All experiments employed hexadecane-in-water emulsions stabilized with sodium dodecyl sulfate (SDS). Visualization tests using the Direct Observation Through the Membrane (DOTM) system with MF membranes revealed three characteristic stages of membrane

fouling: 1) droplet attachment and clustering, 2) droplet deformation, and 3) droplet coalescence. The qualitative visualization work was supplemented with quantitative modeling that described the forces acting on an oil droplet pinned at an entry to a pore on the membrane surface as a way to predict the eventual fate of that droplet. Force models predicted a critical droplet size corresponding to the droplet removable by the crossflow shear, which was validated by direct visualization observations. Permeate flux analysis indicates that membrane fouling by emulsified oil is controlled by droplet coalescence and crossflow shear: the transport of oil to the membrane surface by the permeate flow is balanced by the shear-induced removal of the droplets that coalesce to exceed a critical size. In contrast, DOTM tests with NF membranes and SDS-stabilized oil-water emulsions in the presence of divalent cations revealed the formation of oil films due to favorable droplet-droplet and droplet-membrane interactions needed for coalescence. A range of membrane and emulsion characteristics were screened, and the results indicate that droplet stability, electrical charge and a membrane's affinity for oil govern oil fouling behavior. The study also points to the possibility of managing membrane fouling by oil via the manipulation of the ionic composition of the dispersed phase. By promoting coalescence with conditions of a moderate affinity between droplets and membranes; oil droplets could reach a critical size and be removed by the crossflow shear prior to forming a contiguous film on the membrane surface.

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KEY TO SYMBOLS

α	angle of repose
γ̈́	shear rate
θ	contact angle
μ_{oil}	dynamic viscosity of the hexadecane (dispersed phase)
μ_w	dynamic viscosity of water (continuous phase)
$ ho_{oil}$	density of oil
$ ho_w$	density of water
σ	interfacial tension
ϕ	wall correction factor
Во	Bond number
Ca _{cf}	capillary number associated with crossflow
Ca _{pf}	capillary number associated with permeate flow
Ca _{crit}	critical capillary number characteristic for oil break-up condition
C_f	initial concentration of oil in the feed emulsion
C_p	concentration of oil in the permeate
d_{drop}	oil droplet diameter
d_{drop}^{crit}	critical diameter of the droplet
d_{pore}	membrane pore diameter
F _b	buoyancy force
F _D	drag force

F_{g}	gravity force
F _j	drag force due to permeate flow
F _{lift}	lift force
F_{tot}^n	sum of forces acting on an oil droplet in the direction normal to the membrane surface
F_{tot}^{τ}	sum of forces acting on an oil droplet in the direction parallel to the membrane surface
g	acceleration due to gravity
Н	height of the membrane channel
j	permeate flux
l	lever arm of the moments on an oil droplet
М	sum of moments acting on an oil droplet
ΔP	transmembrane pressure
ΔP_{crit}	critical transmembrane pressure required for an oil droplet to enter a membrane pore
R	rejection of oil by the membrane
Re	Reynolds number
R_m	hydraulic resistance of the membrane
v_{cf}	crossflow velocity
\bar{v}_{cf}	average crossflow velocity in the membrane channel
W	width of the membrane channel

CHAPTER ONE

Overview of Dissertation

Industrial wastewaters containing finely-distributed oil-water emulsions pose environmental risks if they are not treated properly. Often membrane-based separations are the best treatment technology capable of removing micron-sized oil droplets, but a major drawback to membrane separation is the issue of fouling. The motivation for this study was to solve or at least drastically limit the problem of membrane fouling caused during the separation of oil-water emulsions. However, before this problem can be solved the underlining behavior and characteristics of membrane fouling by emulsified oil must be understood. Chapters 2-4 represent different research projects that each led to a manuscript, which is either published or is in preparation for submission.

Chapter 2 is the result of a comprehensive literature review that provides a broad overview of the state of knowledge concerning pressure-driven membrane-based separations of oil-water emulsions. The results of the review revealed disagreement and major lapses in the understanding of membrane fouling by oil-water emulsions, which prompted the investigative studies outlined in Chapters 3 and 4.

Chapter 3 represents a published paper in the Journal of Membrane Science that described a study with model synthetic oil-water emulsions and microfiltration

membranes to examine the subsequent oil fouling behavior during crossflow filtration tests. The study employed a direct visualization technique that had previously only been used to study the membrane fouling behavior of suspensions of solid, nondeformable particles. This study proved that the Direct Observation Through the Membrane (DOTM) system was capable of imaging the fouling behavior of emulsified oil at the membrane surface in the presence of crossflow. Previously, the DOTM system had only been used with brittle anodized alumina (Anopore) membranes, but this study showed that polycarbonate track-etch (PCTE) membranes could also provide the necessary transparency when wet to provide guality optical resolution for imaging the membrane fouling by oil as it developed. The ability to use PCTE membranes with the DOTM system increases the value of the comparison of membrane pore size, as the pore diameter of PCTE membranes can range from 0.01 µm to 30 µm, whereas Anopore membranes are limited to pore diameters between 0.02 µm and 0.2 µm. Our study used PCTE membranes and Anopore membranes with pore diameters of 5 µm and 0.02 µm, respectively. The qualitative results of the DOTM study prompted the development of a force balance to explain quantitatively what caused the oil droplets to remain pinned at the entry to a pore on the membrane surface.

Chapter 4 builds on the results from Chapter 3, which led to subsequent DOTM studies to elucidate the effects of salinity, surfactant concentration, membrane surface characterization and permeate flux on the observed oil fouling behavior. This study was the first to produce transparent (when wet) nanofiltration (NF) membranes for the use in the DOTM setup. The transparent NF membranes were prepared using an Anopore

membrane with 0.02 µm pore diameter and a layer-by-layer deposition technique with alternating polyanionic electrolytes and polycationic electrolytes to modify the surface chemistry of the membrane and shrink the pore size. The ability to produce transparent NF membranes was an important result from this study as it opens the door for new DOTM studies including the coupling between fouling by oil and concentration polarization of rejected ions.

Chapter 5 summarizes the overarching conclusions from Chapters 2-4 focusing on the observed characteristic membrane fouling behavior by emulsified oil as a function of membrane pore size, surfactant concentration, concentration of divalent ions, membrane surface chemistry and permeate flux. The recommendations for limiting the egregious forms of membrane fouling by emulsified oil based on the results of this work are also presented.

Chapter 6 outlines possible venues for continuing this work and building upon the results described in Chapters 3-5.

CHAPTER TWO

Separation of oil-water emulsions by pressure-driven membrane processes: A review

2.1 Introduction

Oil-water emulsions are formed as end products, by-products and waste products from numerous industries (e.g., oil and gas, pharmaceutical, food and beverage, cosmetic, metal working, mining and paint). One of the largest environmental concerns related to oil-water emulsions is the industrial wastewater referred to as produced water, a by-product of oil and gas extraction processes. The United States generated ~21.2 billion barrels (bbl; 1 bbl = 42 U.S. gallons) of produced water in 2012, which is the most recent estimate [1]. The permitted oil and grease (O&G) limits for treated produced water vary depending on the location of the discharge and the country that has domain over that location. The United States Environmental Protection Agency (USEPA) has set offshore produced water discharge regulations for O&G with a daily maximum limit of 42 mg/L and a monthly average limit of 29 mg/L [2].

Produced water treatment differs between onshore and offshore facilities based partially on space and weight restrictions, but also due to different treatment concerns. Onshore facilities are more focused with reducing salt content, whereas offshore facilities are primarily concerned whether the concentration of O&G will meet discharge limits. The

first step of produced water treatment involves a free water knockout vessel or a similar oil/water separator used to separate the free oil – large droplets are easily removable by gravity separation methods. In the United States, polishing treatments are rarely used to remove the dispersed or dissolved oil from onshore produced water as only ~3% of the produced water will be discharged into the environment and < 1% is treated for beneficial reuse [1]. Instead, ~46% of onshore produced water is reused in future oil or gas extraction wells, ~47% is disposed of via deep injection wells and ~3% is lost to evaporation [1]. Conversely, more than 80% of offshore produced water in the United States is discharged into the ocean and therefore must meet the USEPA's limits for O&G [1]. The technologies commonly employed to remove dispersed and dissolved oil, grease and other organics from produced water include the following: physical separation methods (e.g., hydrocyclone, centrifuge and filtration), coalescence via added chemicals or media coalescers, flotation aided by bubbles of air or gas, combined physical and chemical processes (e.g., compact flotation unit that combines centrifugal forces, gas flotation and flocculating chemicals and a CTour system that uses gas condensate to extract hydrocarbons from water), solvent extraction (e.g., macro-porous polymer extraction), adsorption (e.g., organoclay, activated carbon, zeolite, copolymers, resins and swelling glass) and oxidation using combinations of ozonation, cavitation and electrochemical decomposition [2-5].

Physical separation includes advanced separators that rely on the difference in specific gravity between oil droplets and the continuous phase of produced water (e.g., corrugated plate separators, American Petroleum Institute (API) gravity separators,

inclined plate separators, hydrocyclones and centrifuges [3, 5]. Other physical separation treatment options include media filtration devices (e.g., sand filters, walnut shell filters and multimedia filters containing anthracite or garnet [3]) and membrane filtration (e.g. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes). A critical comparison between the technologies used for the treatment of produced water is their removal capability, and Table 1 indicates the diameter of the smallest particle or droplet that can be removed by commonly used treatment options.

Table 1:	Particle size removal capabilities of technologies used for the
	treatment of produced water [6].

Technology	Particle Size Removed (µm)
American Petroleum Institute (API) gravity separator	150
Corrugated plate separator	40
Induced gas flotation without chemical addition	25
Hydrocyclone	10-15
Mesh coalescer	5
Media filter	5
Induced gas flotation with chemical addition	3-5
Centrifuge	2
Membrane filter	0.01

A substantial fraction of oil in produced water is comprised of micron-sized oil droplets that can only be removed in a timely manner by a few technologies, and of those membrane separation is one of the most cost effective [7, 8]. Pressure-driven membrane filtration processes include the use of MF, UF, NF and RO membranes based on the nominal pore size and removal capability of the membrane, but the diversity of membranes is constantly expanding. Synthetic membrane materials include polymers, ceramics or metals, while membrane configurations and types include flatsheet, tubular, multichannel tubular, hollow fiber, track-etch, slotted pore filters and microchannel cells. Membrane filtration can be operated in either the crossflow regime where there is tangential shear at the membrane surface or in the dead-end regime. The review's analysis of pressure-driven membrane-based separations of oil-in-water emulsions includes studies with all of the membrane materials, configurations, types, pore sizes and operational regimes mentioned.

The widespread acceptance of membrane filtration for the treatment of produced water is hindered by the egregious forms of membrane fouling that occur during the separation of oil-water emulsions. After membrane fouling occurs there are different processes used to remove the oil from the membrane surface and restore the water flux such as hydraulic cleaning (e.g., water flushes and water back flushes), chemical cleaning and mechanical cleaning (e.g., air back pulses, ultrasound, vibrational cleaning and sponge cleaners sent through the interior of tubular membranes). However, membrane cleaning is costly in terms of time and money as the treatment must be temporarily stopped, the possible cost to use chemicals or sponges and their disposal, significant capital investments for equipment [9], and if cleaning doesn't remove the oil fouling layer the membrane cartridges will have to be disposed of and replaced.

Numerous studies have used experimental flux-based analyses, numerical models (e.g., film filtration model, blocking law theory, cake filtration and gel layer formation), CFD analyses and visualization techniques (e.g., membrane autopsies, optical

microscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, Direct Observation Through the Membrane (DOTM), Optical Coherence Tomography (OCT), Electrochemical Impedance Spectroscopy (EIS) and Ultrasonic Time-Domain Reflectometry (UTDR)) to elucidate the mechanisms of membrane fouling by emulsified oil so as to modify the membranes or the emulsions to limit the egregious forms of fouling. The purpose of the review is to provide a compilation of the literature concerning pressure-driven membrane-based separations of oil-in-water emulsions so as to provide a better understanding of the membrane fouling behavior exhibited by oil droplets. There are many types of emulsions including simple emulsions (e.g., oil-inwater emulsions and water-in-oil emulsions), multiple or complex emulsions (e.g., water-in-oil-in-water emulsions and oil-in-water-in-oil emulsions) and Pickering emulsions where the dispersed phase is stabilized by colloidal particles. The review will only include studies with oil-in-water emulsions, but it will incorporate work with both industrial oily wastewater (e.g., produced water, bilge water and metal rolling mill wastewater) and synthetic model emulsions with varying types of oil (e.g., kerosene, crude oil, diesel oil, cutting oil, dodecane, hexadecane, vegetable oil, soybean oil, sunflower oil and mineral oil).

2.2 Proposed mechanisms to explain oil fouling behavior

The blocking laws were derived to explain mechanisms of membrane fouling by particles. Four separate mechanisms were proposed: complete blocking, standard blocking, intermediate blocking, and cake filtration. Complete blocking describes the situation where a particle completely covers the pore entrance, thereby reducing the number of channels through which water could permeate. Standard blocking occurs when particles deposit inside the membrane pores and reduce the pore volume through which permeation could occur. Intermediate blocking is a fouling mechanism where the membrane surface is becoming more fouled via a combination of complete and early stages of cake formation on the membrane surface. Cake filtration mechanism corresponds to the situation where multiple layers of particles form a secondary membrane on the membrane surface; the secondary membrane may improve rejection as the feed must transverse both the fouling layer and the membrane, but it decreases the membrane's permeability by increasing the overall hydraulic resistance to the permeate flow. Numerous studies have attributed membrane fouling by oil-water emulsions to one or more of the blocking laws or cake filtration. However, there are a few key reasons to explain why the blocking laws and cake filtration might not apply to oil droplets. First, Hermia derived the blocking laws for solid, spherical, non-deformable particles [10] while oil droplets are generally deformable and may coalesce. Second, some of the studies were conducted in the crossflow regime, which enables several particle back-transport mechanisms in addition to diffusion due to the concentration gradient; this contradicts the assumption of no back-transport made in the derivation of

blocking laws. Even within the studies that did conduct the tests in the dead-end regime, there is disagreement between which blocking laws are applicable. Many studies report that one type of blocking law is observed during the early parts of the tests and then the type of fouling changes to a different blocking mechanism, often cake filtration.

In five separate studies membrane filtration tests were conducted in the dead-end regime, so that the blocking laws could be used to describe the fouling by emulsified oil, and yet all of the conclusions were different. The results of the studies were as follows: incomplete intermediate blocking occurred [11], complete blocking followed by cake filtration after a long transition period [12], cake filtration [13], intermediate blocking for ~18 minutes and then the fouling transitioned into cake filtration [14] and intermediate blocking for 1 to 10 minutes followed by cake filtration [15]. These five studies are only a subset of the studies that used the blocking laws to explain the fouling behavior of oil droplets on the membrane surface, and the majority did so with tests operated in the crossflow regime. The disagreement within the literature concerning oil fouling behavior is evident from just this small sample of studies.

Another mechanism that was proposed to explain oil fouling behavior is formation of a gel layer on the membrane surface. Lipp et al. used a film model to explain how the flux follows gel-polarized behavior when the oil concentration in the feed is < 10% (v/v) [16]. The oil gel layer develops and increases in depth on the membrane surface throughout the length of the filtration as more oil is rejected by the membrane. A similar study

showed that the gel layer was highly compressible as measured by the changing hydraulic resistances [17], and this fits with the understanding of the deformability and possible coalescence of oil droplets. Iritani et al. used a non-coalescing kerosene emulsion and observed the formation of a highly compressible gel layer that had a porosity much lower than that of a hexagonal close packing of non-deformed spheres [18].

2.3 Membrane fouling by emulsified oil: overview of experimental studies

There is vast literature on pressure-driven membrane separation of oil-in-water emulsions. The majority of studies were focused on the preparation or modification of membranes either to limit fouling or produce surfaces that could easily be cleaned. A sizeable, but relatively small fraction of the published work offers interpretation of fouling mechanisms. Many related questions remain unanswered. The present paper overviews literature on the mechanisms of membrane fouling by emulsified oil, identifies knowledge gaps and provides a perspective on possible future research directions. Section 2.3.1 focuses on the studies with MF and UF membranes, where the only shear produced at the membrane surface would be from the crossflow. Section 2.3.1 also presents literature review on the topic of dynamic filtration and dynamic membranes used for the separation of oil-in-water emulsions. Section 2.3.2 covers studies that used NF and RO membranes while hybrid treatment systems with membranes are discussed in section 2.3.3.

The types of membrane geometry include flat and tubular and there are a number of module designs that utilize these membrane types. Flat membranes are used in plateand-frame and spiral-wound modules, whereas tubular membrane configurations are used in tubular, capillary and hollow fiber modules, where the approximate membrane diameters are > 10 mm, 0.5 - 10 mm and < 0.5 mm, respectively. All of these membrane configurations and modules were tested in a number of studies with MF and UF membranes to gain a better understanding of the separation of oil-in-water

emulsions, while only flat-sheet and ceramic disk membranes were tested in studies with NF and RO membranes. Hollow fiber NF membranes are produced commercially, but to our knowledge there are no published reports on the use these membranes for the pressure-driven separation of oil-in-water emulsions.

2.3.1 Pressure-driven processes: microfiltration and ultrafiltration

The pressure-driven processes of microfiltration and ultrafiltration are capable of separating micron-sized oil-in-water emulsions at relatively low transmembrane pressures (0.1 - 2 bar for MF and 1 - 5 bar for UF) and high flux rates, which in 1996 were reported as > 50 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ for MF and 10 – 50 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ for UF [19]. However, membrane permeabilities have improved over the last 20 years; for example, GE reports specific permeate flux for their membranes of > 100 L·m⁻²·h⁻¹·bar⁻¹ for MF and $1 - 70 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for UF [20]. The nominal pore diameter for MF membranes is > 0.1 µm and it is between 2 nm and 100 nm for UF membranes. Studies based on pressure-driven separations of oil-in-water emulsions with MF membranes were conducted with the following membrane configuration types: polymeric flat-sheet [11, 12, 18, 21-41], polymeric tubular [42-45], ceramic tubular [17, 26, 44, 46-61], ceramic tubular with multiple channels [62-65], ceramic flat disk [12-15, 26, 66, 67], hollow fiber [68-70], microporous glass tubular [71, 72], membrane with slotted pores [73-78], metal membrane with conical pores [79, 80] and a few other specialty membranes such as silica-supported polyvinylpyrrolidone membranes [81] and flexible TiO₂/Fe₂O₃ composite membranes [82]. The configurations and modules of UF membranes used during

studies of pressure-driven separation of oil-in-water emulsions consist of the following: polymeric flat-sheet [16, 17, 30-32, 40, 41, 83-117], polymeric tubular [118-123], ceramic tubular [17, 124-128], ceramic tubular with multiple channels [65, 129-132], ceramic flat disk [133] and hollow fiber [45, 69, 70, 125, 134-138].

Despite the large number of studies with different membrane configurations and modules, there is surprisingly little agreement on the mechanisms of membrane fouling by emulsified oil and the structure of the resulting fouling layer. The variance could be attributed to the variability in operating conditions (e.g., crossflow velocity, transmembrane pressure and temperature), emulsions (e.g., type and concentration of oil and surfactant, ionic composition of the dispersion medium) and membranes (e.g., configuration, material, surface chemistry and pore size).

Approximately three quarters of published MF and UF studies used synthetic emulsions rather than real oily wastewaters. The benefit of using well characterized model emulsions is the possibility of designing experiments to identify induvial effects of various emulsion properties (interfacial tension, droplet charge, presence of colloids, salinity, type of oil and oil concentration) on membrane fouling. In contrast, the exact composition of real oily wastewaters is often not known and they may be too complex to characterize definitively. However, if the membrane filtration system is proven to produce high flux rates and limit the egregious forms of fouling with a synthetic model emulsion, then it would be advantageous to challenge the membrane with complex oily wastewaters to determine if the membrane is robust enough to be used during industrial

applications. Approximately 23% of the studies tested the membrane filtration systems with real oily wastewaters.

The types of oil used in studies with MF and UF membranes include the following: crude oil [13-15, 44, 59, 70, 74, 75, 77, 78, 84, 85, 108, 109, 117, 133, 136, 139], vegetable oil including olive oil and soybean oil [31, 32, 54, 74, 76, 82, 86, 88, 93, 95, 96, 103-107, 110, 127, 130, 132], kerosene [18, 22, 25, 27, 33, 46, 55, 79, 100, 117, 128, 140], hexadecane [28, 37, 39, 41, 70, 88, 110], dodecane [11, 12, 21, 26], isododecane [135], isooctane [88], *n*-decane [126], decane [60, 61], 1,2-dichloroethane [38], *n*-hexane [38], toluene [28, 88], mineral oil [16, 71, 72, 121], cutting oil that is mostly mineral oil [42, 43, 68, 81, 83, 90, 91, 98, 111], sunflower oil [57, 73], linseed oil [40], canola oil [129], lubricant oil [67, 82, 117, 134], hydraulic oil 32 [62, 63, 134], gasoil [24, 30, 35], condensate gas [49, 50], engine oil [114, 141], #6 fuel oil [117], diesel [28, 88, 110, 133, 134], gasoline [115], machine oil [64], petroleum ether [88, 110], Castrol oil [102], emulsify oil - Insignia oil [116], semi-synthetic oil - Mobilcut 232 [92], soluble oil - Sarelf A that is 80% mineral oil [112], vacuum pump oil – SMR-100 [94], super vacuum pump oil – GS-1 [69], synthetic bilge water [124] and 12 other types of oil that were not characterized. A number of oily wastewaters were also tested with MF and UF membranes and those include: produced water [30, 34, 45, 50, 56, 65, 78, 85, 101, 104, 113, 120, 122, 123, 125, 136], bilge water [119, 131], degreasing wastewater [137], cutting oil wastewater [137], metal-working wastewater [47] and 9 other oily wastewaters.

The majority of studies with oily wastewaters used a number of technologies and testing procedures to determine the concentrations of the constituents in both the feed and the permeate, but the results were not always clear as many of the wastewater's contaminants were unknown. The results of a total organic carbon (TOC) analysis are often used to characterize the oily wastewater, but this method can be misleading as they can include the concentration of surfactants, sugars, alcohols, natural organic matter (NOM), or a combination of these and other organic compounds. For this reason, TOC analysis cannot be relied upon as the sole characterization method. Instead, a number of complementary characterization methods should be used to describe oily wastewater composition; the methods include chemical oxygen demand (COD), gas chromatography, total suspended solids (TSS), turbidity, ultraviolet-visible spectroscopy (UV-Vis) and infrared spectroscopy (IR).

Approximately 74% of the studies with MF and UF membranes measured oil rejection by the membrane. The most commonly (39% of published studies) used method to determine the concentration of oil in the feed and permeate was TOC analysis. UV-Vis analysis was used in ~31% of the studies that tested oil rejection with MF and UF membranes, while the following techniques were used in ~1 – 7% of the studies that tested rejection: COD analysis [40, 47, 99, 132, 133, 136, 137], IR spectroscopy [83, 115, 124], gas chromatography [37, 59, 125, 126, 133, 135], turbidity [16, 17, 40, 92, 98, 118], atomic absorption spectroscopy using copper as a tracer [22, 79], oil-in-water analyzer that uses solvent extraction and IR spectroscopy [39, 44, 113, 123], solvent extraction followed by gravimetrical analysis [117, 129], and fluorescence excitation

emission matrices (FEEM) [133]. The Coulter counter technique was also used to determine oil rejection, where the measured droplet sizes were converted to volumes and then to concentrations using the oil's density [33, 74, 75, 77, 80].

In most industrial applications, membranes are operated in the crossflow filtration regime, and ~71% of the studies with MF and UF membranes were tested in the crossflow filtration regime. However, dead-end filtration often allows for models to be used to characterize the fouling layer as it develops on the membrane surface (e.g. blocking mechanisms derived by Hermia [10]). This could explain why ~33% of the studies tested MF or UF membranes in the dead-end filtration regime and many of these did so to better characterize the oil fouling layer. The experiments could be conducted as constant pressure tests, constant flux tests or neither. Approximately 80% of the studies with pressure-driven MF and UF membranes conducted constant pressure experiments, and only ~8% of the studies conducted constant flux experiments.

Numerous studies compared commercial membranes with lab-prepared membranes or modified membranes to determine the superior membrane that was able to resist fouling and preserve high flux rates during the separation of oil-in-water emulsions. The filtration variables that were most often examined include the following: transmembrane pressure, crossflow velocity, temperature, type of oil or type of wastewater, oil concentration in the feed emulsion, membrane material, membrane pore size or MWCO, membrane surface chemistry usually by way of a coating, type of surfactant in

the emulsion and stability of the emulsion via different surfactant concentrations. A

number of studies have embedded carbon nanotubes or nanofibers into the membrane

matrix or used them to modify the membrane surface (Table 2).

Table 2:MF and UF membranes prepared or modified with nanofibers,
nanoparticles, or carbon nanotubes as an alternative to improve the
separation of oil-in-water emulsions.

Type of membrane	Modification	Result	Reference
Lab-prepared MF ceramic flat disk membranes	Implanted carbon nanotube grids into the porous ceramic channels via chemical vapor decomposition	The presence of carbon nanotube grids greatly improved the rejection of oil (100% rejection)	[66]
Lab-prepared UF ultrathin film of single-walled carbon nanotubes (SWCNT)	The SWCNT film was coated with TiO ₂ via the sol-gel process	Produced a flexible film capable of very high flux rates (up to 30,000 L·m ⁻² ·h ⁻¹ ¹ ·bar ⁻¹) and oil rejections of > 99%	[88]
Lab-prepared UF PVDF tubular membranes via phase inversion	Alumina nano-sized particles (Al ₂ O ₃) were added to the casting solutions	The addition of Al ₂ O ₃ particles improved membrane antifouling performance and flux recovered completely after washing	[120, 122]
Lab-prepared UF PVDF flat-sheet membranes via phase inversion	TiO ₂ /Al ₂ O ₃ nano- particles were added to some of the casting solutions	The TiO ₂ /Al ₂ O ₃ modified membranes had enhanced hydrophilicity, showed better antifouling characteristics and flux rates were easily restored with cleaning	[108, 109]
Lab-prepared UF PVDF flat-sheet mixed matrix membranes (MMMs) via phase inversion	One dimensional polyaniline (PANI)/TiO ₂ nanofibers were incorporated into the MMMs	The oil rejection was enhanced to 99% and the pure water flux was increased by 65%	[102]

Table 2 (cont'd):

Type of membrane	Modification	Result	Reference
Lab-prepared UF cross-linked electrospun PVA substrate was placed on a polyester nonwoven microfibrous substrate (PET microfilter)	Coated with: pure PVA hydrogel, PVA hydrogel incorporated with 5%, 10% and 15% surface- oxidized multiwalled carbon nanotubes (MWNTs), pure hydrophilic polyether- <i>b</i> -polyamide copolymer (Pebax), or Pebax with 6%, 8% and 12% MWNTs	High flux rates were achieved (~48 L·m ⁻² ·h ⁻ ¹ ·bar ⁻¹) and excellent oil rejection rates (99.8%) without appreciable fouling	[105]
Lab-prepared UF double-layer nanofibrous mat with an electrospun thin hydrophilic PVA nanofiber top layer and an electrospun PAN nanofibrous support layer	The PVA nanofibrous layer was remelted through water vapor exposure and then crosslinked to form a thin PVA layer	A permeate flux rate of 70 L·m ⁻ ² ·h ⁻¹ ·bar ⁻¹ and oil rejection of 99.5% were achieved	[107]
Lab-prepared UF PVDF flat-sheet membranes via phase inversion	3% of Halloysite nanotubes (HNTs) or 1%, 2% and 3% of HNTs functionalized by the grafting of 3- aminopropyltriethoxysilane (APTES) as a coupling agent were added to the casting solution	Modified membranes had improved oil rejections > 90%, and the flux recovery ratios reached ~83% after three fouling and washing cycles	[110]
Commercial multichannel (19) tubular ceramic MF membranes	The tubular membranes were modified with a nano-TiO ₂ coating	The hydrophilic nano-TiO ₂ coating prevents oil droplets from penetrating the membrane pores and helps to sustain higher fluxes than unmodified membranes	[62, 63]

Table 3 displays the results from a number of different types of membrane modifications

and coatings to improve the separation qualities of oil-in-water emulsions.

Table 3:MF and UF membranes modified with hydrogel coatings or other
surface chemistry alterations as an alternative to improve the
separation of oil-in-water emulsions.

Type of membrane	Modification	Result	Reference
Commercial polysulfone (PSF) UF flat-sheet membranes	The membranes were coated with a bifunctional hydrogel coating comprised of varying ratios of polyethylene glycol diacrylate (PEGDA) and a cationic functional monomer with an ammonium salt (RNH ₃ CI), and then cured with UV exposure	The coated membranes retained high and constant water flux during oil-water emulsion filtration, indicating outstanding anti- fouling efficiency	[95]
Lab-prepared UF membranes via an electrospun PVA nanofibrous scaffold support placed on a commercial PET non- woven substrate	A PVA hydrogel coating layer was crosslinked with the support membrane and a hydrophilic copolymer Pebax coating was applied to an electrospun PVA support	Membranes with hydrogel coatings exhibited flux rates > 19 L·m ⁻² ·h ⁻¹ ·bar ⁻¹ and oil rejections > 99.5%, which exceeded tests with uncoated membranes	[106]
Lab-prepared polyethersulfone (PES) UF flat-sheet membranes via phase inversion	Amphiphilic copolymer Pluronic F127 was added as a surface modifier to the casting solutions in different concentrations	The flux decay was minimized as the Pluronic 127 content to PES ratio was increased from 0 to 20%, and the membranes with the 20% ratio recovered up to 93% of the flux after cleaning	[86]
Type of membrane	Modification	Result	Reference
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Lab-prepared asymmetric UF membranes via phase inversion using synthesized copolymer	Polyacrylonitrile (PAN) was grafted onto cellulose acetate (CA) powder via free radical polymerization, and the synthesized CA- graft-PAN was used in the casting solution	CA-graft-PAN membranes demonstrated excellent resistance to oil fouling with good separation, and the flux was nearly completely recovered after cleaning	[87]
Lab-prepared MF ceramic flat disk membranes	A MCM-22 zeolite membrane surface modification was prepared using the secondary growth (rubbing) technique where crystals deposited on the ceramic disk membrane were rubbed manually and left to crystalize on the surface	The addition of the MCM-22 zeolite surface modification increased the oil rejection capability of the membrane throughout the length of the tests (1 hour)	[67]
Commercial MF ceramic tubular membranes	The interior of the tubular membranes were modified by in situ crystallization with the deposition of NaA zeolite	Oil rejection of > 98% was maintained throughout 80 hour tests with zeolite coated membranes but multiple membrane cleanings were needed to restore flux	[48]
Lab-prepared coal-based carbon tubular MF membranes via extrusion and carbonization	Fine coal particles were mixed with a binder to produce the extrusion paste, and the decomposition of volatile components form the pore structure	The carbon membranes were effective at separating oil emulsions as the oil rejection was > 98%	[139]

Type of	Modification	Result	Reference
membrane Commercial composite UF membranes with a thin regenerated cellulose layer on a polypropylene support	The membranes were modified by using surface-initiated atom transfer radical polymerization to graft the membrane with uniquely structured block copolymer nanolayers	The modified membranes had a lower initial flux rate during the crossflow separation of oil emulsions, but the flux remained constant and the oil rejection was higher showing that the modifications limited fouling by oil	[103, 104]
Commercial multichannel (19) tubular ceramic MF membranes	The membrane surface was modified with graphene oxide (GO) by transfer via a vacuum method and covalent bonds were formed between the GO and ceramic surface	The modified membrane displayed better oil rejection and higher permeate flux when compared to unmodified membranes	[64]
Lab-prepared UF membranes via phase inversion with CA as the main polymer in the membrane backbone	PVA was added to the casting solution in the presence and absence of polyvinyl pyrrolidone (PVP) as an additive, or PVA was cross-linked with glutaraldehyde (GA) then blended in situ with CA and PVP in the casting solution	The CA/PVA/PVP membranes had better antifouling properties than the CA/PVA membranes, but membrane with PVA cross-linked with GA had the highest flux and best antifouling ability	[114]
Lab-prepared ceramic tubular MF membranes using a slip- casting method	The tubular membranes were chemically impregnated with a zirconium citrate solution and then calcined to transform the zirconium citrate into zirconium oxide in the form of nanoparticle agglomerates	Membranes modified with zirconia showed improved separation capabilities with sunflower oil emulsions	[57]

Type of	Modification	Result	Reference
Commercial PSF UF membranes	Free-standing polymer films and the polymer coating on the PSF membranes were synthesized via free-radical photopolymerization initiated by UV-light	Coated PSF membranes had flux values 400% higher than uncoated PSF membranes, as well as higher oil rejections	[93]
Commercial PSF UF membranes	Amphiphilic organic/inorganic hybrid star-shaped polymers (SSP) were prepared by atom transfer radical polymerization and then the PSF membranes were coated with SSP using the spin-coating method	The SSP coated membranes showed better fouling resistance and higher flux recovery ability than bare PSF membranes	[94]
Commercial poly(ethylene terephalate) (PET) non-woven substrate was used as the support layer for the three-tier thin- film nanofibrous composite UF membrane	The mid-layer of electrospun nanofibrous scaffolds included PAN, cross-linked PVA and PES, and the top cellulose barrier coating layer was cast by using an ionic liquid	The three-tier membranes had permeate fluxes 2-10 times higher than commercial UF membranes as well as oil rejections > 99.5%	[31]
Commercial PSF UF membranes	A poly(ethylene glycol) diglycidyl ether–cross- linked chitosan (chi–PEG hybrid) films were produced as freestanding films or as coatings for the PSF membrane	The composite membranes demonstrated water flux values more that 5 times higher than uncoated membranes after being used for the separation of oil- water emulsions, and the oil rejection values were slightly higher	[96]

Type of membrane	Modification	Result	Reference
Commercial	Polydopamine (PD)	PD-g-PEG modified	[32]
polypropylene MF,	was deposited on	membranes showed	
poly(tetrafluoroethylene)	the membranes and	the most	
MF, PVDF MF,	then some of the	improvement of the	
poly(arylene ether	membranes were	oil fouling	
sulfone) UF, and PSF flat-	further functionalized	resistance, followed	
sheet UF membranes	with the grafting of	by the PD modified	
	PEG	membranes when	
	macromolecules to	compared with the	
	the PD layer	unmodified	
	-	membranes	
Commercial	A facile	The PDA-PEI	[38]
polypropylene MF	hydrophilization	deposition was	
membrane	method via co-	faster and the	
	deposition of	solution could be	
	polydopamine (PDA)	reused and it	
	and	created membranes	
	polyethyleneimine	with ultra-high water	
	(PEI) or just PDA	permeability,	
	was used to	allowing for the	
	decorate the	separation of oil-	
	membrane surface	water emulsions at	
		atmospheric	
Lab propored poly (condia		The febricated	[20]
acid) grafted DVDE		membranes were	[20]
aciu)-graneu F v DF		heth	
induced phase inversion		superbydrephilic and	
method		underwater	
		superoleonhohic	
		and can use gravity	
		to senarate oil-water	
		emulsions efficiently	

Type of	Modification	Result	Reference
membrane			
Lab-prepared flat- sheet MF and UF membranes via phase inversion with PVDF as the base polymer	Two complex modified PVDF copolymer additives were produced by graft-copolymerization via atom transfer radical polymerization then hydrolyzed and finally esterified before being added to the casting solution	The fabricated membranes had increased water fluxes and higher oil rejection than the PVDF control membranes	[41]
Lab-prepared hollow fiber MF and UF membranes with PVDF as the base polymer were fabricated by the common dry–wet spin phase inversion method	Two complex modified PVDF copolymer additives were produced by graft-copolymerization via atom transfer radical polymerization then hydrolyzed and finally esterified before being added to the dope solution	The modified hollow fiber membranes exhibited high water flux and low oil fouling behavior, and the fouling that did occur was easily cleaned	[70]
Commercial hydroxylated nylon flat-sheet MF membranes	The membrane surface was modified with polyelectrolyte brushes that were produced by atom transfer radical polymerization of ionic monomers	The polyelectrolyte bushes swell in water and repel oil droplets in the presence of anionic surfactants, but in the presence of cationic surfactants the brushes collapse and allow oil to pass through the membrane	[37]

One study employed a slotted pore MF membrane to reject oil-in-water emulsions composed of crude oil or vegetable oil with varying interfacial tensions under three distinct flux rates, and compared the results with a mathematical model developed to predict the 100% cut-off size for oil droplets as a function of flux rates [74]. The study produced good agreement between the model and the experimental data showing that

crude oil droplets > 4.3 µm could be completely rejected with a 4 µm by 400 µm slotted pore membrane, and it was proposed that this model could be used to predict the oil concentration in the permeate if the droplet size distribution of the feed emulsion is known [74]. A separate study with slotted pore metal MF membranes demonstrated that there was little advantage to using a slot length to slot width aspect ratio greater than 5, and when compared with cylindrical pore membranes (i.e., track-etch) the slotted pore membranes had a significantly lower pressure drop and a lower tendency to plug during the separation of deformable oil-in-water emulsions [75].

An alternative approach to membrane fouling control involves the addition of a helix inside a tubular membrane, where the pitch of the helix will adjust the rotational speed of the fluid within the tubular membrane. The use of asymmetric (conical pore) metal tubular microfilters for the separation of oil-in-water emulsions was demonstrated in two studies with and without the presence of a helical insert, where the orientation of the filter (smaller or larger side of the conical-shaped pores was facing the feed emulsion) affected the transmembrane pressure drop, but not the oil rejection [79, 80]. The use of helical inserts caused the transmembrane pressure to remain steady during the constant flux tests, but a higher transmembrane pressure was required for membranes oriented with the larger end of the conical-shaped pores facing the feed emulsion [79, 80]. Another study placed a helix inside two tubular membranes, one with 13 µm slotted pores and one with 4 µm circular pores; however, the addition of the helix introduced unnecessary resistance inside the channel that decreased the rejection of oil [73].

Dynamic filtration or shear-enhanced filtration refers to a system where the shear at the membrane surface is created by moving solid boundaries such as the membrane itself or other surfaces positioned in the membrane's proximity [142, 143]. Three studies used slotted pore tubular MF membranes operated in the dead-end regime, where the membrane module was attached to a vibrating arm to enhance the shear at the membrane surface leading to shear-induced migration and an inertial lift of droplets away from the membrane surface as a way to reduce or remove the fouling layer of crude oil or stabilized vegetable oil [76, 77]. Two of the studies proved that high oil rejection and sustainable flux were achieved with nearly constant transmembrane pressure when the membrane was oscillated at a surface shear rate of ~8100 s⁻¹, results that could not be accomplished in the absence of enhanced shear from oscillation [76, 77]. The third study showed that the oscillation of the membrane created a shear rate at the membrane's surface that was proportional to $\sqrt{v_l}$, where v_l is the lift velocity that removed droplets from the membrane surface [78]. Other studies used rotating disks adjacent to the membrane surface to enhance the shear rate as a way to increase oil rejection and decrease fouling, while sustaining high water fluxes [40, 98].

The formation of a dynamic membrane (DM) refers to a cake layer of particles that deposit on the membrane surface to create a secondary membrane to enhance the separation. The term "dynamic" recognizes that the fouling layer is formed during the separation process and can be removed with cleaning [107]. Two studies produced dynamic membranes of magnesium hydroxide on tubular ceramic MF membranes prior to separating decane oil-in-water emulsions, but the DM took 60-90 minutes to form and

it was difficult to adjust the operating conditions (crossflow velocity, transmembrane pressure) to keep the oil rejection high [60, 61]. Another study used TiO₂ particles to form a hydrophilic DM with an asymmetrical structure on the interior of a commercial tubular carbon MF membrane, but the DM took ~30 minutes to produce and the flux still decreased dramatically during the separation of an oil-in-water emulsion [144]. The use of dynamic membranes to improve the separation of oil-in-water emulsions might not be practical for industrial applications because the formation of the DM takes time that cannot be used for treatment and it involves chemical additions that increase the cost.

2.3.2 Pressure-driven processes: nanofiltration and reverse osmosis

The pressure-driven processes of nanofiltration and reverse osmosis are capable of not only separating micron-sized oil-water emulsions but also dissolved ions; the tradeoff for removing more constituents is the need for higher transmembrane pressures (5 – 20 bar for NF and 10 – 100 bar for RO) but lower flux rates that in 1996 were $1.4 - 12 \text{ L·m}^{-2}$.h⁻¹·bar⁻¹ for NF and $0.05 - 1.4 \text{ L·m}^{-2}$.h⁻¹·bar⁻¹ for RO [19], but currently GE reports flux rates of $2 - 5 \text{ L·m}^{-2}$.h⁻¹·bar⁻¹ for NF and $0.08 - 8.5 \text{ L·m}^{-2}$.h⁻¹·bar⁻¹ for RO based on their commercially available membranes [20]. There have been far fewer studies with NF and RO membranes than with MF and UF membranes. This is likely due to the fact that MF and UF are effective at removing micron-sized droplets at lower pressures and higher flux rates and thus can serve as pretreatment for NF and RO removing the need of relying on salt-rejecting membranes to remove oil. Only flat-sheet NF and RO membranes were tested in the published studies. The oils used in synthetic emulsions

included: crude oil [145], vegetable oil (e.g., olive oil and soybean oil [32, 146]), *n*decane [147], mineral oil [148], semi-synthetic oil – Mobilcut 232 [92], and gasoil [149]. Produced water emulsions were also used in separation tests with NF and RO membranes [113, 150]. Approximately ~89% of the tests with NF and RO membranes were conducted in the crossflow regime, while ~11% were conducted in the dead-end regime. None of the studies were performed as constant flux experiments, but ~78% were constant pressure tests. Oil rejection was measured in ~90% of the studies with NF and RO membranes, and ~56% of the studies used TOC to determine the separation ability of the membranes, while ~11% of the studies used each of the following methods to test oil rejection: COD [149], turbidity [92], oil-in-water analyzer that uses solvent extraction and IR spectroscopy [113], and inductively coupled plasma atomic emission spectroscopy (ICP AES) [150]. Some of the studies modified the NF and RO membranes to improve the separation of oil-in-water emulsions and those unique coatings and results are presented in Table 4. **Table 4:**NF and RO membranes modified with coatings as an alternative to
improve the separation of oil-in-water emulsions.

Type of membrane	Modification	Result	Reference
Commercial polyamide (PA) NF and PA RO flat- sheet membranes	Polydopamine (PD) was deposited on the membranes and then some of the membranes were further modified with the grafting of PEG macromolecules to the PD layer	PD-g-PEG modified membranes showed the most improvement of the oil fouling resistance, followed by the PD modified membranes when compared with the unmodified membranes	[32]
Commercial PA RO flat- sheet membranes	The membranes were coated with varying concentrations of PD in a Tris–HCI buffer	Modified membranes with PD were significantly more resistant to fouling in oil-water emulsion separation tests as judged by higher permeate flux values	[146]
Commercial thin film composite PA RO flat-sheet membranes	A series of cross-linked PEG- based hydrogels were synthesized using poly(ethylene glycol) diacrylate as the crosslinker and poly(ethylene glycol) acrylate, 2-hydroxyethyl acrylate or acrylic acid as comonomers to produce free- standing hydrogel films and coatings for the RO membranes	Hydrogel coated membranes experienced little fouling from stabilized <i>n</i> -decane emulsions as the flux value was 73% of its initial value after 24 hours of testing while the uncoated membrane's flux fell to 26% of its initial value	[147]

2.3.3 Hybrid systems with membranes

A number of studies have used hybrid systems to treat oil-in-water emulsions either by combining more than one type of membrane filtration or by using a different technology in conjunction with membrane separation. One hybrid system used to treat produced water combined UF as a pretreatment for NF to furnish a permeate that could meet discharge limits [113]. A similar study tested the treatment of metal-working fluids with a large-scale hybrid system that consisted of PVDF UF membrane units with the MWCO of either 100 kDa or 200 kDa followed by NF membrane units with good retention for organic molecules > 200 Da; the results showed that using UF membranes as pretreatment decreased the concentration polarization layer on the NF membrane, thus a permeate with lower COD and no residual turbidity was produced [92].

Intini and Liberti studied a wastewater desalination plant in the petrochemical industry that used hollow fiber ZeeWeed UF membrane modules and RO spiral wound membrane modules to produce reusable water [151]. It was determined that frequent and expensive cleaning treatments were required. Membrane autopsies of the hollow fiber UF membranes showed that irreversible fouling was occurring due to the build-up of elementary sulphur deposits on the membrane surface. The challenge was addressed by adding desulfurization upstream of the UF membrane modules [151]. The adjustment to the treatment process allowed for the 'sour' petrochemical wastewater to be treated for reuse with UF and RO membranes avoiding the irreversible fouling and the need to regularly replace membrane modules [151].

One study used four different types of MF membranes operated as membrane coalescers to enlarge the oil droplets prior to separation through three types of UF hollow fiber membranes [135]. It was shown that the hollow fiber membranes were not able to operate adequately without prior droplet enlargement from the membrane

coalescers [135]. A similar study used a hybrid system with a MF membrane operated as a coalescer that was periodically backflushed after the oil droplets partially coalesced within the pores and then the permeate was further treated with UF membranes [134].

The microfiltration of oil-in-water emulsions was assisted by gas sparging in a study by Fouladitajar et al. [24]. Higher gas flow rates were shown to lead to higher permeate fluxes due to the disruption of both the deposited cake layer and the concentration polarization at the membrane surface [24]. Similarly, Ducom et al. enhanced the separation of stabilized and non-stabilized oil-in-water emulsions with NF membranes by adding air sparging to the hybrid system; it was shown that the injection of air bubbles flowing concurrently with the feed emulsion disrupted the oil layer as it formed on the membrane surface, thus increasing the permeate flux by a factor of 2.4 for the testing conditions [148].

Gryta et al. used a hybrid system with tubular UF PVDF membranes followed by a capillary membrane distillation (MD) system equipped with polypropylene membranes to treat bilge water [119]. The UF permeate with ~5 ppm of oil was further treated by MD to completely remove oil as well as 99.5% of the TOC [119]. Chang et al. showed that hollow fiber UF membranes were capable of producing a high quality and reusable permeate stream from degreasing wastewaters, but a hybrid UF/O₃ system was required to produce a reusable permeate from cutting oil wastewater; this was because the excess surfactants could be partially oxidized by ozone to preserve the droplets' size and limit foaming [137].

A hybrid system of coagulation–centrifugation followed by UF membrane treatment was studied for the separation of a commercial oil-in-water emulsion used in metalworking operations to determine the conditions that achieved the maximum UF permeate flux using the Taguchi methodology [152]. A destabilizing agent was used at the coagulation–centrifugation stage and then the aqueous phase was treated by a flat ceramic UF membrane operated in the crossflow regime under various flow rates, feed temperatures and transmembrane pressures [152]. The coagulation–centrifugation removed a substantial portion of the foulants allowing for a 200% increase in the UF permeate flux [152]. It was found that a cake/gel fouling layer was responsible for the flux decline; this conclusion, however, was based on the application of Hermia's blocking laws derived for dead-end filtration [152].

A separate study examined the use of electrocoagulation (EC) as a pre-treatment to MF with flat-sheet membranes for the separation of oily emulsions from the metalworking industry, and it was demonstrated that 10 minutes of EC increased the average oil droplet size to the point where the droplets were larger than the membrane pores [153]. The pretreatment reduced pore clogging and irreversible fouling of the MF membranes [153].

Mohammadi and Esmaeelifar demonstrated that wastewater from a vegetable oil factory could be treated more successfully with a hybrid system containing UF membranes when powdered activated carbon was circulated with the feed to create excess shear at the membrane surface and decrease the cake layer thickness [154].

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CHAPTER THREE

Behavior of oil droplets at the membrane surface during crossflow microfiltration of oil-water emulsions*

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Abstract

A fundamental study of microfiltration membrane fouling by emulsified oil was conducted using a combination of real-time visualization, force balance on a droplet, and permeate flux analysis. The model 0.1% v/v hexadecane-in-water emulsions contained sodium dodecyl sulfate (0.1 mM, 0.4 mM, or 0.8 mM) to regulate interfacial tension. Direct Observation Through the Membrane tests with Anopore ($d_{pore} = 0.2 \mu$ m) and track-etch ($d_{pore} = 5 \mu$ m) membranes revealed three characteristic stages of membrane fouling: 1) droplet attachment and clustering, 2) droplet deformation, and 3) droplet coalescence. In qualitative agreement with visualization results, the force balance predicted that droplets $\leq 40 \mu$ m would remain pinned at $d_{pore} = 5 \mu$ m pores while larger droplets would be swept off the surface by the crossflow drag. In a separate set of constant pressure crossflow filtration tests with track-etch membranes, the average oil rejection was $\geq 97\%$ while the permeate flux decreased to a pseudosteady-state ~10% of the initial value. The results indicate that membrane fouling by emulsified oil is controlled by droplet coalescence and crossflow shear: the transport of oil to the membrane surface by the permeate flow is balanced by the shear-induced removal of the droplets that coalesce to exceed a critical size.

3.1 Introduction

Porous membranes were first used for the treatment of oily wastewaters in the early 1970s [1-3]. Since then, research on the separation of oil-water emulsions by microfiltration (MF) and ultrafiltration (UF) membranes has been growing (Figure 1; also see Supplementary material in Appendix B of Chapter 3, Figure 13); thus enabling industrial applications [4-6]. A broad variety of MF [4, 7-12] and UF [3, 8, 13-19] membranes have been evaluated. Membrane materials ranged from polymers [7, 9, 14, 15] to ceramics [8, 13, 18, 19] to metals [10], while membrane configurations and types included flat sheet [14, 15], tubular [3, 8-10, 16, 18, 19], hollow fiber [7], track-etch [11], and slotted pore filters [12] as well as microchannel cells [20, 21]. Synthetic emulsions containing various types of oil (e. g., cutting oil [7, 9], crude oil [12, 13, 17, 19], diesel oil [19], dodecane [22], mineral oil [15], kerosene [11, 23], and edible oils [12, 16, 18]), liquid-liquid food emulsions (e. g., skimmed milk [24]) and industrial oily wastewaters (e. g., bilge water [1], metal rolling mill wastewater [25], and produced water [6, 26, 27]) were employed.



Figure 1: Number of publications with a) both "oil" and "ultrafiltration" in the title and b) both "oil" and "microfiltration" in the title. Source: Google Scholar. Retrieved: November 1, 2015.

An industrial wastewater of emerging concern is produced water, a byproduct of oil and gas extraction processes; in 2007, the global produced water output was estimated to be ~250 million barrels per day [28]. Produced water has a complex composition including suspended oil (typically, 100 to 5,000 mg/L), high salinity and various chemicals added for operational purposes. Because a substantial fraction of oil in produced water can be in the emulsified form [29], membrane separation is one of the few technologies capable of removing the small oil droplets [30, 31] to meet the discharge limit (15 to 40 mg(oil)/L depending on the country and location of the platform [32]). While membranes with sufficiently small pores can separate such emulsified oil from water the challenge of membrane fouling has prevented a broader acceptance of membranes. In the case of liquid-liquid emulsions, the issues of droplet stability, shape,

and compressibility make the already complex fouling phenomena more challenging to understand and manage.

A number of mechanistic dead-end filtration studies showed that oil droplets rejected by a membrane form a concentrated oil-water emulsion at the membrane surface [14, 15, 21, 23, 33, 34]. The deposit has been described as a gel layer but also referred to as a "cake". Lipp et al. concluded that for oil feed concentrations <10% (v/v) the permeate flux follows gel-polarized behavior that can be described by a film model [15]. Matsumoto et al. showed that the gel layer was highly compressible and had specific hydraulic resistances that were 2 to 3 orders of magnitude higher than that of yeast and polymethyl methacrylate particles [21]. Working with non-coalescing kerosene-water emulsions, Iritani et al. observed the formation of a highly compressible gel layer that may have porosity much lower (~0.02) than that of a hexagonal close packing of nondeformed spheres (0.2595) [23]. The fouling layer structure was quantified based on indirect evidence such as measured values of oil rejection and rate of permeation through fouled membranes; the specific hydraulic resistance of the fouling layer was calculated based on equations initially derived for solid-liquid separations [35, 36], which may explain the use of the term "cake" by several groups. Blocking filtration laws were also applied to analyze mechanisms of membrane fouling in several studies [19, 37-39], but with regard to the intrapore fouling this approach is questionable because the laws were derived for spherical and non-deformable particles. Direct visualization of oil droplets in a microchannel filtration cell [20, 21] confirmed that deformability has a strong impact on the separation performance: droplets larger than membrane pores

were shown to permeate the membrane at sufficiently high pressures. In the visualization work with micro channels, the size of oil droplets was either much smaller (1.5 μ m for primary droplets) or much larger than the pore size (3.8 μ m) and no buildup of a multilayer of rejected droplets was observed; thus it was neither possible to explore the effect of the variable headloss across the fouling layer nor was it possible to verify other potential permeation scenarios (e. g., percolation through a contiguous oil film).

In tangential filtration the structure of the fouling layer depends on additional transport mechanisms enabled by the crossflow. Crossflow filtration behavior of oil-water emulsions was shown to be similar to that of macromolecular solutions [16]. As demonstrated in multiple studies [13, 16, 22, 40-42] the permeate flux achieves a steady state value indicating that there is balance between convective transport of oil droplets to the membrane surface with the permeate flow and oil back-transport away from the membrane [13, 39]. NMR chemical shift selective micro-imaging was successfully applied to non-invasively visualize fouling layer in crossflow microfiltration [7, 9, 43]; it was demonstrated that a concentration polarization layer is present and slowly flows along the membrane surface [43]. The spatial resolution of the method (39 μ m [7], 94 μ m [43]), however, was not sufficient to discern droplet-scale features of the fouling layer.

Recent modeling studies explored the effect of crossflow on the behavior of an individual oil droplet pinned at a membrane micropore [44, 45]. Three main scenarios (permeation, rejection, and breakup/partial permeation) for oil droplets were identified

and shown to depend on the droplet size, shear rate, surface tension, and oil-to-water viscosity ratio. To our knowledge there have been no visualization studies that assessed such scenarios experimentally. Useful insights can be gained from the experimental and computational modeling work on membrane emulsification (e.g. [46, 47]) where a related problem is considered wherein microfilters are used to form controllable oil droplets as oil is extruded through the membrane.

The present study is motivated by the need for a better droplet-scale understanding of membrane fouling by emulsified oil. To this end, we employ a combination of real-time visualization, force balance on a droplet, and permeate flux analysis. Direct Observation Through the Membrane (DOTM) [48, 49] is used to image oil droplets at the membrane surface and visualize, in real time, the fouling layer as it forms and develops throughout the crossflow filtration process. To gain a quantitative insight into oil droplet behavior at the membrane surface, we use a simple force balance analysis and carry out a separate set of well controlled constant pressure crossflow filtration tests to understand the kinetics of permeate flux decline under the condition of membrane fouling by oil.

3.2 Materials and Methods

3.2.1 Reagents

Hexadecane (99%) and sodium dodecyl sulfate (SDS, ≥98.5%) were purchased from Sigma-Aldrich and used as received. Deionized (DI) water used in all DOTM experiments was supplied by a Milli-Q Ultrapure Water (Integral 10, Millipore) system equipped with a terminal 0.2 µm microfilter (MilliPak, Millipore); the water resistivity was approximately 18 MΩ·cm. Prior to the constant pressure crossflow tests, the DI water was filtered through a 0.2 µm microfilter (PolyCap, Whatman). Hydrochloric acid (HCI, EMD Chemicals) was diluted to 2 M before being used in the oil extraction process. Tetrachloroethylene (ultra resi-analyzed) was purchased from J.T. Baker and used as received.

3.2.2 Preparation and characterization of oil-in-water emulsions

The model emulsions were prepared by adding hexadecane to water in the presence of SDS as a stabilizing agent and stirring the resulting mixture at 1,000 rpm using a digital stand mixer (RW 20 digital dual-range mixer, IKA) for 20 minutes. Hereinafter the hexadecane-water-surfactant emulsions will be referred to as HWS-X where X is the concentration of SDS in units of mM. In all emulsions the hexadecane concentration was 0.1% v/v (773 mg/L), while the concentration of SDS was either 0.1 mM (HWS-0.1 emulsion) or 0.4 mM (HWS-0.4 emulsion) or 0.8 mM (HWS-0.8 emulsion). The

hexadecane was dyed red with Oil-Red-O dye (Sigma-Aldrich) prior to the constant pressure crossflow tests to aid in oil rejection measurements. Light scattering (Malvern Mastersizer 2000) was used to determine oil droplet size distribution in the feed emulsion using undyed hexadecane. The feed was continuously circulated through the optical cell of the Mastersizer using a Malvern sample dispersion unit mixed at 1,000 rpm. The refractive index of 1.434 for hexadecane was used as an input in the calculation of droplet size distribution. The volume-based distribution reported by the Mastersizer software was converted into a number-based distribution.

The interfacial tensions of the three emulsions were measured using a pendant drop method and a standard goniometer (model 250-F4, ramé-hart instrument co.). First, the surface tensions of the pure liquids (water and hexadecane) and the aqueous solutions of SDS were determined; as the results would later be used by the DROPimage Advanced v2.6 software during the interfacial tension measurements. A microsyringe (part no. 100-10-20) was filled with each of the liquids, which was then dispensed until a hanging pendant droplet was produced; the surface tension of the liquid was determined based on the droplet's shape as quantified by the software. The interfacial tension measurements were performed by filling the standard quartz cell (part no. 100-07-50) with each of the aqueous solutions of SDS and using a microsyringe with inverted stainless steel 22g needle (part no. 100-10-13-22) filled with hexadecane to produce a submerged pendant droplet. The interfacial tensions of the emulsions were determined by the software based on the shape of the submerged hexadecane droplets in the aqueous solutions of SDS.
3.2.3 Membranes used in DOTM and constant pressure crossflow filtration tests

Two types of hydrophilic microfilters were used: inorganic anodized alumina (Anopore) membranes with a nominal pore diameter of 0.2 µm and polycarbonate track-etch (PCTE) membranes with a nominal pore diameter of 5 µm. When wet, membranes of both types had sufficient optical transparency required in the DOTM method. The anodic alumina Anopore microfilter (Anodisc membrane filters, Whatman) has surface porosity (as reported by the manufacturer) in the 25 to 50% range and a non-deformable honeycomb pore structure with no lateral crossovers between individual straight-through pores. The other membrane chosen for the DOTM tests was the PCTE membrane (Nuclepore, Whatman) with cylindrical and narrowly distributed straight-through pores and a surface porosity of 7.9%. The PCTE membranes were treated with polyvinylpyrrolidone (PVP) by the manufacturer to create the hydrophilic surface. Table 5 summarizes manufacturer-supplied data for the membranes as well as several other characteristics that can be calculated based on simple geometrical considerations.

Table 5:Morphological characteristics of the polycarbonate track-etch (PCTE) and
Anopore membranes employed in this study
provided by the manufacturer
* provided by the manufacturer
* applies to all PCTE membranes used in this study regardless of the
supplier

Membrane characteristic	Membrane	
	ΡΟΤΕ [†]	Anopore
Pore diameter [#] , μm	5	0.2
Surface pore density [#] , pores/cm ²	4·10 ⁵	1.10 ⁹
Area of one pore, cm ²	1.96·10 ⁻⁷	3.14·10 ⁻¹⁰
Surface porosity, %	8	31
Average membrane area per one pore, cm ²	2.50·10 ⁻⁶	1.00·10 ⁻⁹
Average distance between pore centers, µm	15.8	0.32
Average distance between pore boundaries, µm	10.8	0.12

The crossflow filtration tests required a larger membrane area than the 47 mm diameter Anopore or Nuclepore membrane discs could provide, so only an alternative manufacturer's PCTE membranes (Sterlitech) with the same morphological characteristics were used in these experiments. A new membrane was used in each test.

The contact angles of hexadecane on the two membranes were measured using a standard goniometer (model 250-F4) and specialized tools provided by the ramé-hart instrument co. Each membrane was attached to the environmental fixture (part no. 100-14) with the feed side facing downward and then submerged in water (or water and SDS) when the fixture was placed in the standard quartz cell (part no. 100-07-50). The microsyringe (part no. 100-10-20) was filled with hexadecane and a single droplet was

dispensed from the inverted stainless steel 22g needle (part no. 100-10-13-22) until the droplet attached to the submerged inverted membrane. This process used the DROPimage Advanced v2.6 software to measure the contact angle between the hexadecane droplet and the membrane surface in the presence of water or water and SDS.

3.2.4 Direct Observation Through the Membrane system

Figure 2A shows the schematic of the DOTM setup. The central feature of the DOTM system is the microscope (Axio Imager.M1, Zeiss) fitted with a video camera (Digital Color video camera model TK-C921BEG, JVC) capable of capturing both still images and videos. All of the images and videos recorded during filtration tests used a 32X magnification microscope objective resulting in a total magnification of 320X. A crossflow membrane filtration cell included two acrylic windows to enable imaging of the membrane surface. The crossflow channel in the DOTM filtration cell was 109 mm long, 33.5 mm wide and 2 mm deep. Both Anopore and PCTE disk membranes with diameters of 47 mm were framed between two pieces of paper with a square cutout for the membrane in the center of the crossflow channel to facilitate the use of circular membrane disks in the rectangular crossflow channel. Araldite 2020 adhesive (Huntsman) was used to secure the membrane between the papers so that an active membrane area of 7.56 cm^2 was available for tests with Anopore, while a slightly smaller active membrane area of 2.4 cm^2 was used for tests with PCTE membranes due to the difficulty of imaging the flexible membrane. The framed membrane was held

between the two acrylic sides of the filtration cell and secured to the stage of the microscope with the permeate side of the membrane facing up towards the objective. The light emitted by the microscope's illuminator transmitted through the membrane as the images were captured by focusing through the membrane and onto its feed side. The crossflow and permeate fluxes were adjusted independently using a feed gear pump (drive model 75211-15, Cole-Parmer) and a permeate peristaltic pump (Minipuls 3, Gilson). Three pressure sensors (Cole-Parmer) were interfaced with a computer to monitor the pressure immediately upstream of the membrane in the feed line and downstream of the membrane in both the retentate and permeate lines. The permeate was collected on an electronic mass balance (PL4002, Mettler Toledo) interfaced with a computer that recorded values of permeate mass at 1 min intervals. DOTM experiments were carried out at a constant crossflow velocity of $3.6 \cdot 10^5 L/(m^2 \cdot h)$ (0.1 m/s) that translated to the Reynolds number, Re = 376. Higher crossflow velocities could not be tested because Anopore membranes were too brittle to withstand an immediate increase to high crossflow velocities; when the crossflow velocity was increased slowly the membrane became fouled before the target higher crossflow velocity (0.7 m/s) could be reached.

Throughout each DOTM experiment, the permeate rate was incrementally increased by adjusting the permeate pump setting to screen a range of fouling conditions. The continual increase in the permeate flux and the buildup of hydraulic resistance due to membrane fouling by oil led to an increase in the headloss across the membrane.

Thus, the DOTM experiments could not be classified as constant pressure or constant flux filtration tests.

3.2.5 Crossflow microfiltration system

Constant pressure crossflow microfiltration experiments were performed using a separate crossflow filtration system (Figure 2B). The filtration cell (CF042, Sterlitech) had a membrane area of 40.95 cm² and a crossflow channel that was 105 mm long, 39 mm wide and 2.3 mm deep. A gear pump (drive model 75211-10, Cole Parmer) delivered the feed emulsion to the membrane filtration cell at a constant crossflow velocity of $3.6 \cdot 10^5 \text{ L/(m^2 \cdot h)}$ (0.1 m/s) matching the crossflow velocity used in DOTM tests. The corresponding Reynolds number was higher (*Re* = 433) than in DOTM experiments (*Re* = 376) because of differences in the crossflow channel dimensions. The retentate flow was directed back into the feed tank.

Permeate samples were collected and oil contents in the samples were measured to determine oil rejection by the membrane. For each experiment, six permeate samples were taken, one every 15 minutes throughout the first 1.5 h of the 2 h test, along with one sample of the initial feed emulsion. The permeate was directed to a beaker positioned on a mass balance (Adventurer Pro AV812, OHAUS Corp. USA) and the data were automatically logged into a computer. All experiments were performed in triplicate.

3.2.6 Measurements of oil rejection by the membrane

The oil contents in both the feed emulsion and the permeate were measured for each crossflow test using a solvent extraction method. The solvent extraction procedure involved mixing the oil-in-water sample with tetrachloroethylene to extract oil into the organic phase; the method required an initial sample volume of at least 24 mL to ensure that the cuvettes could be filled properly for the measurements because only the organic solvent portion of the sample was analyzed. The initial samples could be diluted with DI water to achieve the minimum sample volume as long as the oil concentration remains above the detection limit. The feed samples (4 mL) taken before each crossflow test were diluted to one tenth of the initial concentration using DI water to achieve an excess of the necessary sample volume. In each of the crossflow tests, the six permeate samples (~4 mL) taken throughout the filtration were combined so that the oil content in the permeate could be measured without diluting the samples. The pH of each sample was adjusted to less than 2 by adding 2 M HCl dropwise, and then tetrachloroethylene was added in the 1:10 v/v proportion with respect to the sample. Next, the samples were shaken for 2 min. Once the solvent containing the dyed oil separated to the bottom of the vials it was extracted using a syringe and dispensed into a cuvette for analysis.

The oil content was determined using two separate detection methods: infrared spectroscopy (InfraCal oil in water analyzer, model CVH, Wilks) and UV-Vis spectrophotometry (MultiSpec-1501, Shimadzu). The dual detector in the InfraCal

analyzer measures hydrocarbon concentrations at 2940 cm⁻¹ with a reference at 4,000 cm⁻¹. In the UV-Vis method, oil concentration was measured based on absorption at 518 nm (maximum absorption of Oil-Red-O dye). The oil detection limits of the InfraCal and UV-Vis methods were 2 mg/L and 4.5 mg/L, respectively. The observed rejection of oil by the membrane was calculated as $R = 1 - \frac{c_p}{c_f}$ where C_p is the concentration of oil in the permeate and C_f is the initial concentration of oil in the feed emulsion.



Figure 2: Schematic illustration of the Direct Observation Through the Membrane (DOTM) apparatus (A) and the crossflow microfiltration system (B).

3.3 Results and Discussion

3.3.1 Characteristics of oil emulsions and membranes. Critical pressure for oil droplet entry into a pore

The tabulated values of the surface tensions for DI water and hexadecane are 72.8 mN/m and 27.6 mN/m [50]. The interfacial tension of hexadecane and water was measured to be 41.8 mN/m. The surface tension of the three aqueous solutions of SDS were measured to be 69.4, 66.5, and 56.9 mN/m for SDS concentrations of 0.1 mM, 0.4 mM, and 0.8 mM, respectively. These values were below the critical micelle concentration for SDS, which is in the 6 mM to 8 mM range. Based on these measurements, the interfacial tensions of the HWS-0.1, HWS-0.4 and HWS-0.8 emulsions were determined to be 39.3 mN/m, 35.0 mN/m, and 30.8 mN/m, respectively. It was assumed in this work that coalescence-induced desorption of surfactant was sufficiently fast to make the resulting transient changes in the interfacial tension relatively unimportant. The droplet size distributions (Figure 3) illustrate the effect of droplet stability on emulsion characteristics. The volume weighted mean values for the HWS-0.1, HWS-0.4 and HWS-0.8 emulsions were 109 µm, 105 µm and 93 µm. The volume-based median droplet diameter also decreased with the increase in droplet stability from 104 µm to 90 µm to 71 µm for the HWS-0.1, HWS-0.4 and HWS-0.8 emulsions, respectively. Comparison of size distribution measurements obtained in duplicate tests showed that the variation in the values of the volume-weighted mean

was 1.6%, 6.8% and 17.7% for the HWS-0.1, HWS-0.4 and HWS-0.8 emulsions, respectively.

The contact angle of hexadecane on the Anopore membrane surface was 152° and 154° in 0.1 mM SDS and 0.8 mM SDS solutions, respectively, and 151° in the absence of SDS. For the PCTE membrane, the hexadecane contact angle was measured to be 135° and 147° in 0.1 mM SDS and 0.8 mM SDS solutions, respectively, while in the absence of SDS the contact angle was 120°. Thus, both membranes were oleophobic, while the Anopore membrane could be qualified as superoleophobic [51].



Figure 3: Volume-based (A) and number-based (B) droplet size distributions for the three SDS-stabilized hexadecane-water emulsions used in the DOTM and constant pressure microfiltration tests.

The critical pressure required for an oil droplet of diameter, d_{drop} , to enter a circular pore of diameter, d_{pore} , is given by [8]

$$\Delta P_{\rm crit} = 4\sigma \frac{\cos\theta}{d_{\rm pore}} \left[1 - \left(\frac{2 + 3\cos\theta - \cos^3\theta}{4\left(\frac{d_{\rm drop}}{d_{\rm pore}}\right)^3\cos^3\theta - (2 - 3\sin\theta + \sin^3\theta)} \right)^{1/3} \right]$$
(3-1)

In eq. (3-1), σ is the interfacial tension and $\theta = 180^{\circ} - \varphi$ where φ is the contact angle between the surface of the membrane and the oil droplet at the oil/water interface. Eq. (3-1) is valid for a single non-wetting droplet pinned at an entry to a single membrane pore.



Figure 4: Critical pressure for an oil droplet to enter a membrane pore as a function of oil droplet size, membrane pore size, and interfacial tension of the oil-water emulsion. The calculation is based on eq. (3-1) and is for Anopore ($d_{pore} = 0.2 \mu m$) and polycarbonate PCTE ($d_{pore} = 5 \mu m$) membranes. The operational domain represents the range of oil droplet sizes in the HWS-0.1 and HWS-0.8 emulsions and the range of transmembrane pressures employed in the DOTM and constant pressure microfiltration tests.

In a computational modeling study, Darvishzadeh and Priezjev [44] have shown that numerical simulations of droplet permeation in the absence of crossflow predict ΔP_{crit} value that matches well to the value given by eq. (3-1).

Figure 4 shows how the critical pressure, ΔP_{crit} , given by eq. (3-1) depends on the droplet diameter. The grayed out area corresponds to the values of transmembrane

pressures (ΔP) and droplet sizes (d_{drop}) in the DOTM and constant pressure microfiltration tests. For the Anopore membranes ($d_{pore} = 0.2 \ \mu m$), $\Delta P / \Delta P_{crit} \sim 10^{-2}$; therefore, complete rejection of oil by these membranes could be expected and was indeed experimentally observed (see section 3.3.3.2). It is important to note, however, that eq. (3-1) was derived assuming zero crossflow on the feed side of the membrane [8, 11]. Darvishzadeh and Priezjev [44] predicted that ΔP_{crit} should increase with an increase in crossflow velocity up to a certain threshold value when the droplet breaks up. We also note that Figure 3 provides only an estimate of the actual droplet size distribution, which is dynamically changing in the membrane channel due to droplet break-up and coalescence.

In experiments with PCTE membranes ($d_{pore} = 5 \mu m$), ΔP exceeded ΔP_{crit} for smaller droplets ($d_{drop} \leq 10 \mu m$). Based on the fraction of oil mass that is in these smaller droplets (Figure 3A), the oil rejection by PCTE membranes was estimated to be ~86.3%, 92.1%, and 92.8% for HWS-0.1, HWS-0.4, and HWS-0.8 dispersions, respectively. Experimentally measured rejections were somewhat higher (see section 3.3.3.1), which can be attributed to the effects of crossflow and droplet coalescence that are not accounted for by eq. (3-1). It is also possible that the ensemble of droplets that reached the membrane was not representative of the entire droplet population as measured by light scattering or that a fraction of the entire oil mass in the feed was not transported to the membrane. The tendency for larger particles to migrate from the membrane and smaller ones to deposit was observed for latex particles via DOTM by Li et al. [48].

3.3.2 Characteristic stages of membrane fouling by emulsified oil. Capillary number

Representative DOTM images capturing the interaction of the oil droplets with the polycarbonate track-etch membrane ($d_{pore} = 5 \ \mu m$) are shown in Figure 5. Each of the three rows of images corresponds to a filtration experiment with an emulsion with a different concentration of surfactant (0.1, 0.4, or 0.8 mM) and, accordingly, different interfacial tension (39.3, 35.0, or 30.8 mN/m). The first column (Figure 5 A, E, I) shows images of clean membranes. Elongated ovals or cylinders correspond to pores that are at an angle to the membrane surface. A magnified view of the PCTE membrane pores is shown in the inset A.1 of Figure 5. The three images in the first column (Figure 5 A, E, I) correspond to t = 0. All other images (columns 2, 3 and 4) represent different fouling stages that occur at different times into an experiment depending on the concentration of the surfactant (see Figure 8 for time stamps).

DOTM experiments with hexadecane-water-SDS emulsions revealed three characteristic stages of membrane fouling: 1) droplet attachment and clustering, 2) droplet deformation, and 3) droplet coalescence:

 Droplet attachment and clustering (Figure 5 B, F, J) occurs during the early stages of membrane fouling by emulsified oil. A typical clustering scenario involves accumulation of smaller droplets around a previously attached larger droplet that is most often pinned at a pore entry.

- As a droplet cluster grows, the constituent droplets press against one another and deform, attaining increasingly angular, polyhedral shapes. These transient phenomena can be described as the *droplet deformation* stage (Figure 5 C, G, K).
- 3) Continued deformation of neighboring droplets leads to thinning of the water film in between them until the film ruptures and droplets merge [52]. This *droplet coalescence* stage (Figure 5 D, H, L) continues with larger droplets growing at the expense of smaller ones. In tests with PCTE membranes ($d_{pore} = 5 \mu m$), some of the coalesced droplets grew to be as large as ~95 μm covering multiple pores (Figure 5D).

We note that the three stages overlap in time (see section 3.3.4).

3.3.2.1 Capillary and Bond numbers. Droplet deformation and breakup

The propensity of a droplet to deform due to crossflow can be estimated using the capillary number, *Ca*, defined as a ratio of the viscous and interfacial tension forces:

$$Ca_{cf} = \frac{\mu_w d_{drop} \dot{\gamma}}{\sigma} \tag{3-2}$$

where μ_w is the viscosity of the continuous phase (water) and $\dot{\gamma}$ is the shear rate at a distance $y = \frac{1}{2}d_{drop}$ away from the membrane surface. Because the width of the membrane channel is much larger than its height ($W \gg H$) we approximate the flow field by plane Poiseuille flow between two infinite parallel stationary plates separated by distance *H*. This approximation gives the following expression for the shear rate (see Supplementary material in Appendix B of Chapter 3):

$$\dot{\gamma} = \left[\frac{d\nu_x}{dy}\right]_{y=\frac{1}{2}d_{drop}} = \frac{1}{2\mu_w}\frac{dP}{dx}\left(H - d_{drop}\right) = 6\frac{\bar{\nu}_x}{H}\left(1 - \frac{d_{drop}}{H}\right)$$
(3-3)

For the experimental conditions of DOTM tests, Ca_{cf} ranged from $4.9 \cdot 10^{-6}$ to $4.6 \cdot 10^{-4}$ for the range of droplet sizes observed on the membrane surface (1 to 95 µm). Another viscous force that acts on a droplet at a membrane surface is the drag due to the permeate flux. The importance of this effect relative to surface tension forces can be estimated using the capillary number defined as follows:

$$Ca_{pf} = \frac{\mu_w j}{\sigma} \tag{3-4}$$

where *j* is the permeate flux. For permeate fluxes employed in DOTM experiments $(1\cdot10^{-6} \text{ m/s} \le j \le 9\cdot10^{-5} \text{ m/s})$, Ca_{pf} ranged from ~3.3 $\cdot10^{-8}$ to ~2.9 $\cdot10^{-6}$. The effect of the gravitational and buoyancy forces on the droplet shape can be estimated using the Bond number, $Bo = (\rho_w - \rho_{oil})r_{drop}^2/\sigma$. For the largest droplets observed in DOTM tests $(d_{drop} = 95 \ \mu\text{m})$ and the highest concentration of surfactant (0.8 mM; $\sigma = 30.8 \ \text{mN/m})$, $Bo \cong 7 \cdot 10^{-4}$. These calculations are based on the approximation of droplets as spherical objects. The droplets are, generally, non-spherical. The contact angle of the membrane will have an effect on the droplet's shape, although both the Anopore and PCTE membranes are oleophobic causing the pinned droplets to keep a mostly spherical shape. Peng and Williams' work on membrane emulsification explains how droplets can become slightly distorted due to the presence of the pore and local hydrodynamic forces arising from the crossflow [46]; these authors also note that the buoyancy force might slightly change the shape of the droplet depending on the relative magnitude of all of the forces (see section 3.3.6).

DOTM tests offered direct experimental evidence of droplet deformation. Thus, even though viscous and body forces were relatively small (Ca_{cf} , Ca_{pf} , Bo <<1) and incapable of breaking droplets up, these forces were sufficient to change droplet shape. This effect can be partly due to the compressive forces (in the direction along the membrane surface) that are accumulative - the stress due to the drag force is transmitted through the points or areas of contact between droplets along the sequence of adjacent droplets and in the direction of the crossflow so that the highest stress is experienced by the droplet pinned at the pore entry. Such accumulating solid compressing force is a reason for compression and restructuring of membrane cakes (e. g., [53, 54]) with the difference that the drag force on particles in the membrane cake acts in the direction normal to the membrane surface. Brans et al. used CFD modeling to show that the drag force exerted by the crossflow on a particle (or, in our case, a droplet) decreases as the membrane surface coverage increases, implying that there is a shielding effect [55]. The shielding effect results in increased blockage of the pores located further downstream in the direction of the crossflow due to the decreased drag force experienced by the attaching droplets. The shielding effect might also help to explain the clustering of droplets on the membrane surface during early stages of membrane fouling.

Droplet deformation was observed for both PCTE and Anopore membranes and did not appear to depend on the membrane type despite differences in the permeate flow patterns near attached droplets. We attribute this to the fact that the permeate flux was relatively small in relation to the crossflow flux (so that $Ca_{pf} \ll Ca_{cf}$) as is typical for

most crossflow filtration systems. In dead-end filtration the membrane type may make a difference though. The average distance between pores of the PCTE membrane is ~2 orders of magnitude larger than the corresponding value for the Anopore membranes (10.8 µm versus 0.1 µm; Table 5) indicating that the stagnation point flow due to permeation enhances $\dot{\gamma}$ more in the case of PCTE membranes. This difference should be even more pronounced due to the fact that surface porosity of the Anopore membrane was 3.875 times higher than that of the PCTE membrane: the lower surface porosity of the PCTE membrane translates into higher "pore velocity" and higher local velocity close to the pore entrance.

3.3.3 Effect of interfacial tension on oil droplet behavior at the membrane surface

3.3.3.1 Microfiltration with polycarbonate track-etch membranes (d_{pore} = 5 µm)

Figure 5 demonstrates the impact that surfactant had on oil droplet coalescence and membrane fouling for a PCTE membrane. Increasing the concentration of surfactant lowers the interfacial tension causing the droplets to breakup more easily during the formation of the emulsion (see Figure 3), while at the same time limiting the coalescence of newly formed droplets. Both of these effects translate into distinctly different behaviors of the droplets at the membrane surface (Figure 5). Images in the first row (Figure 5 B, C, D) depict the membrane surface during filtration of an HWS-0.1 emulsion, composed of droplets that are on average larger than droplets in HWS-0.4 and HWS-0.8 emulsions and that tend to eventually coalesce into very large droplets

covering multiple pores. As observed in the field of view of the DOTM microscope, HWS-0.1 droplets deposited on the membrane surface ranged from 2 μ m to 20 μ m in size initially and over the ~1.5 h of filtration coalesced into droplets as large as 95 μ m. (A video of the oil droplets coalescing at the membrane surface can be found in Video 1 of the supplemental files and in Appendix B.4 of Chapter 3, Figure 16). This dynamic is quite different from the one observed with an HWS-0.8 emulsion (Figure 5 J, K, L) consisting of droplets that are initially smaller (~10 μ m) and coalesce into ~30 μ m droplets over the ~1.5 h filtration test. It should be noted that the droplets that migrate to the membrane surface and attach only represent a subpopulation of the entire emulsion.

Magnified views of the stages of *droplet clustering* and *droplet deformation* are shown in Figure 6 J.1 and Figure 6 C.1 respectively. Image J.1 shows multiple oil droplets clustering around a few membrane pores, while image C.1 illustrates oil droplets in a cluster that are deformed to adapt polyhedral shapes.

The average oil rejection by the PCTE membrane was 97.2%±0.01% and 98.5%±0.01% in filtrations of HWS-0.1 and HWS-0.8 emulsions, respectively. Some oil droplets smaller than the pore size (5 µm) permeated the membrane during the DOTM tests. Most of the smaller droplets, however, attached to the membrane surface and formed clusters; over the longer term these droplets either coalesced into droplets too large to enter membrane pores or meandered toward a pore and eventually permeated through

the membrane. Droplets larger than the pore diameter could permeate the membrane as well.



Figure 5: Transient behavior of oil droplets at the surface of polycarbonate track-etch membrane ($d_{pore} = 5 \mu m$) during crossflow microfiltration of hexadecane-water-SDS emulsions with different concentrations of surfactant: 0.1 mM (B, C, D), 0.4 mM (F, G, H) and 0.8 mM (J, K, L). Images A, E, I correspond to t = 0 when the membrane is unfouled. The direction of the crossflow ($v_{cf} = 0.1 \text{ m/s}$) was from left to right in the images. The asterisks (*) denote a specific location on the membrane to aid in the comparison of images in each row (see Figure 9 for time stamps of images shown in columns 2 - 4).



Figure 6: Magnified views of insets from Figure 5 A, J, and C: clean PCTE membrane (A.1); a PCTE membrane during *droplet attachment and clustering* stage (J.1) and a PCTE membrane during the *droplet deformation* stage (C.1).

As shown in Figure 7 a droplet ~15 µm in diameter passed through the PCTE membrane. (A video of the permeation event can be found in Video 2 of the supplemental files and in Appendix B.4 of Chapter 3, Figure 17). Notably, eq. (3-1) predicts that the pressure employed in the test (~0.01 bar) is ~8 times below ΔP_{crit} required for permeation. We attribute this discrepancy to two effects not accounted for in eq. (3-1): the presence of crossflow and the "cluster effect" when the crossflow drag on cluster-forming droplets accumulates and reaches maximum for the droplet pinned at the pore.

Another possibility for oil break-through is partial permeation resulting from a break-up of a droplet at the pore entry and permeation of only the part of the droplet that was in the pore during the "necking" process as the break-up occurred. In our earlier study [45], the break-up criterion was defined in terms of the critical capillary number, Ca_{crit} , which could be evaluated as:

$$Ca_{crit} \propto \frac{d_{pore}}{d_{drop}} \frac{1 + 1.048\lambda}{2 + 4.510\lambda}$$
(3-5)

where $\lambda = \mu_{oil}/\mu_w$. For a hexadecane-in-water emulsion, $\lambda \approx 3.44$. Even for the membrane with the smaller d_{pore} (Anopore) and the largest droplet observed in DOTM tests ($d_{drop} = 95 \ \mu m$), Ca_{cf} was still smaller than the critical value ($Ca_{cf} \approx 0.74Ca_{crit}$) indicating that partial permeation due to droplet breakup was not possible with either of the membranes.



filtration time

Figure 7: Different stages of oil droplet permeation through a 5 μ m membrane pore in the case when $d_{drop} > d_{pore}$. The top image illustrates the initial condition of a droplet pinned at an entry to the membrane pore. The sequence of images below shows the evolution of the permeating droplet; the left most image in the sequence is the same as the large image with the pore and the droplet marked. This sequence took place in less than 2 seconds.



Figure 8: Transient behavior of oil droplets at the surface of Anopore membrane ($d_{pore} = 0.2 \,\mu$ m) during crossflow microfiltration of hexadecane-water-SDS emulsions with different concentrations of surfactant: 0.1 mM (B, C, D), 0.4 mM (F, G, H) and 0.8 mM (J, K, L). Images A, E, I correspond to t = 0 when the membrane is unfouled. The direction of the crossflow ($v_{cf} = 0.1 \,\text{m/s}$) was from left to right in the images. The asterisks (*) denote a specific location on the membrane to aid in the comparison of images in the same row (see Figure 9 for time stamps of images shown in columns 2 - 4).

3.3.3.2 Microfiltration with Anopore membranes (d_{pore} = 0.2 µm)

Analogous to Figure 5, Figure 8 shows representative DOTM images from three separate filtration tests with Anopore membranes ($d_{pore} = 0.2 \ \mu m$) and different surfactant concentrations. Each of the three rows of images in Figure 8 corresponds to a filtration experiment with an emulsion with a different concentration of surfactant (0.1, 0.4, or 0.8 mM) and, accordingly, different interfacial tension (39.3, 35.0, or 30.8mN/m). As in Figure 5, the first column (Figure 8 A, E, I) shows images of clean membranes. All other images (columns 2, 3 and 4) represent different fouling stages that occur at different times into an experiment depending on the concentration of the surfactant (see Figure 9 for time stamps).

The three characteristic fouling stages are observed with the Anopore membrane as well. It is evident that the oil droplets in the emulsion decrease in size as the surfactant concentration is increased and the droplets are less likely to coalesce at the membrane surface. A comparison of images D, H and L clearly shows the impact that surfactant concentration has on the likelihood that the oil droplets will coalesce at the membrane surface. The oil droplets in image L are tightly packed together, but the lower interfacial tension provided by the 0.8 mM of SDS caused some resistance to coalescence; whereas image D shows easily coalescing deformed droplets due to the 0.1 mM of SDS and corresponding higher interfacial tension. Droplets accumulating on the surface of the Anopore membranes (Figure 8) were smaller and more narrowly distributed in size.

A comparison of the images in Figure 5 and Figure 8 demonstrate that there are two key differences in the observed droplet behavior in filtration tests with the two types of membranes. First, the droplets tended to cover the entire Anopore membrane before the clusters of droplets got compressed and possibly coalesced; whereas the oil droplets attached to the PCTE membrane tended to compress and coalesce when large portions of the membrane were still unfouled. Both Figure 5 and Figure 8 demonstrate that as surfactant concentration increases, the likelihood that the compressed droplets will coalesce decreases.

Second, DOTM filtration tests clearly showed small oil droplets passing though the 5 µm PCTE pores as well as slightly larger droplets deforming and squeezing through the pores. No evidence was captured to show that oil droplets were able to penetrate the 0.2 µm Anopore membrane pores, but the 320X magnification of the microscope used during these filtration tests was not sufficient to differentiate between the individual 0.2 µm membrane pores meaning that permeation cannot be definitively ruled out.



Figure 9: Attachment and clustering (stage 1), deformation (stage 2), and coalescence (stage 3) of hexadecane droplets on the surface of 0.2 µm pore size Anopore membrane (A, B, C) and 5 µm pore size PCTE (D, E, F) in experiments with increasing permeate-to-crossflow ratio and different surfactant concentrations: 0.1 mM SDS, σ = 39.3 mN/m (A, D); 0.4 mM SDS, σ = 35.0 mN/m (B, E); and 0.8 mM SDS, σ = 30.8 mN/m (C, F). Capital letters mark times when corresponding images shown in Figure 5 and Figure 8 were recorded. The crossflow velocity is all tests was 0.1 m/s.

3.3.4 The sequence of membrane fouling stages as a function of membrane type and emulsion stability

The DOTM tests were conducted to screen for a range of fouling conditions; the sequence and duration of the three fouling stages (see section 3.3.3) are demonstrated in Figure 9. While the three stages occur sequentially for individual oil droplets and their clusters, the stages could overlap significantly when an ensemble of droplets on the entire membrane surface is considered. With the continual step-wise increase in permeate flux in the DOTM tests, the changing behavior of oil droplets could be interpreted as either one stage or a superposition of two or three fouling stages.

The determination for the beginning of each stage was subjective and based on images and videos captured throughout each of the filtration tests. Figure 9 represents six individual experiments; three of which were conducted with PCTE membranes ($d_{pore} = 5 \mu m$) while the other three tests used Anopore membranes ($d_{pore} = 0.2 \mu m$). Both types of membranes were tested using emulsions of varying SDS concentrations (0.1 mM, 0.4 mM and 0.8 mM).

For the emulsions containing 0.1, 0.4, and 0.8 mM of SDS, PCTE filtration tests show a coalescence stage beginning at a permeate flux to crossflow flux ratio of $0.3 \cdot 10^{-3}$, $0.4 \cdot 10^{-3}$, and $0.4 \cdot 10^{-3}$, respectively. Thus, as expected, the coalescence began at a lower permeate flux to crossflow flux ratio for the least stabilized HWS-0.1 emulsion (i.e., more stable emulsions required additional drag available at higher permeate flows

to coalesce). In contrast, in the tests with the Anopore membranes, a higher permeate flux was needed to initiate the coalescence stage for the HWS-0.1 emulsion $(j/v_{cf} = 0.27 \cdot 10^{-3})$ than for more stable HWS-0.4 and HWS-0.8 emulsions $(j/v_{cf} = 0.12 \cdot 10^{-3} \text{ and } 0.15 \cdot 10^{-3}$, respectively). One possible explanation for this trend is that higher stability facilitates droplet's movement along the surface leading to larger clusters and higher likelihood of coalescence. The above interpretations are based on a small sample size and, therefore, are tentative. One consistent trend that was observed for each of the three emulsion types was that the coalescence began at higher permeate fluxes for PCTE membranes pointing to the general conclusion that pore morphology (Table 5) affects oil coalescence at the membrane surface; the reasons for this trend are not yet clear.

3.3.5 Constant pressure crossflow filtration tests

A separate set of crossflow filtration experiments (Figure 2B) with PCTE membranes $(d_{pore} = 5 \ \mu\text{m})$ only were performed in the constant transmembrane pressure regime. (This was in contrast to the flux-controlled DOTM tests (sections 3.3.2 - 3.3.4) wherein by adjusting the pumping rate, the permeate flux was incrementally increased throughout each experiment leading to corresponding increases in the transmembrane pressure.) The retentate was returned to the feed tank positioned at a height that created just enough pressure to make the initial permeate flux match the permeate flux during the coalescence stage of the DOTM tests (~4.2·10⁻⁵ m/s); these experimental conditions are represented by stars in Figure 9 D and F. The three replicate filtration

experiments with HWS-0.1 emulsions (Figure 10A) showed significantly more variability in the decline of permeate flux than what was observed in tests with the HWS-0.8 emulsions (Figure 10B). This difference is consistent with the higher stability of HWS-0.8. Momentary increases in the permeate flux during the last hour of the HWS-0.1 tests occurred when large oil droplets left the filtration cell into the retentate stream. The large oil droplets swept off the membrane opened up more membrane area for permeation and could have blocked the retentate line leading to a transient increase in the backpressure to give higher permeate flux. The flux data from the constant pressure filtration tests (Figure 10) corroborate the qualitative DOTM results (Figure 5) for the coalescence stage of fouling: as the large oil droplets formed and grew with the HWS-0.1 emulsions, after ~1 h of continual coalescence at the membrane surface the droplets were sufficiently large for the crossflow drag to remove them from the membrane (see section 3.3.6). In contrast, during tests with more stable HWS-0.8 emulsions, oil droplets did not coalesce to the point that the crossflow drag could dislodge them from the membrane surface.



Figure 10: Permeate flux behavior in crossflow microfiltration tests with HWS-0.1 emulsions (A) and HWS-0.8 emulsions (B) and PCTE membranes $(d_{drop} = 5 \ \mu\text{m})$. The experiments were performed in a constant pressure regime ($\Delta P = 0.2 \text{ bar}$) and with a constant crossflow velocity, $v_{cf} = 0.1 \text{ m/s} (3.6 \ 10^5 \text{ L/(m^2 \cdot h)})$. The hydraulic resistance of clean membranes averaged over tests 1 - 3 with HWS-0.1 and tests 1 and 3 with HWS-0.8 was $(3.37 \pm 0.11) \cdot 10^{10} \text{ m}^{-1}$; the hydraulic resistance of the clean membrane in test 2 with HWS-0.8 was $4.98 \cdot 10^{10} \text{ m}^{-1}$.

В

In analogy with the cleaning effect of the crossflow during the separation of colloids and larger solid particles, the crossflow appears to lead to pseudo steady state permeate flux during the separation of liquid-liquid emulsions. In the former case, the membrane deposit of solid particles grows into a thick multilayer structure ("membrane cake") that constricts the membrane channel to a point where the crossflow velocity becomes sufficiently high to scour the fouling particles at a rate equal to the rate of their addition to the cake due to permeate flow. In the latter case of the separation of liquid-liquid emulsions, the deposited droplets generally do not seem to form multilayer deposits (although occasional deposition of smaller droplets on top of the larger ones was observed in DOTM tests); instead, droplets coalesce until the size of the coalesced droplet is sufficiently large for the crossflow drag force to overcome the permeation drag and sweep the droplet off the membrane surface. Because the main mechanism of flux decline appears to be pore blockage by droplets, the % decline of the flux can be interpreted as the % of blocked pores. For example, the ~95% decline in the permeate flux observed in tests with HWS-0.8 emulsions (Figure 10B) indicates that only ~5% of the surface pores remain open while the rest of the pores are plugged by droplets pinned at pore entries. In other studies [7] the low values of flux after fouling by oil were attributed to the very high hydraulic resistance of the oil layer on the membrane surface. Our results show that low flux can be achieved even at sub-monolayer coverage and is due to pore plugging by oil droplets. This should be more pronounced for Anopore and track-etch membranes that both have straight-through pores than for membranes with pore interconnectivity typical for polymeric membranes prepared by phase inversion.

3.3.6 Force balance on an oil droplet pinned at an entry to a cylindrical pore

The force balance analysis employed in this work follows the approach we applied earlier to solid particles on the membrane surface [56]. The moment of hydrodynamic forces acting on a particle about its point of contact with a surface (pivot) can be used as a criterion of whether the particle remains pinned on the surface or is swept off [57]. Herein we apply such criterion to the case of an oil droplet resting at the entry to a cylindrical pore of a membrane (Figure 11; also see Supplementary material in Appendix B of Chapter 3, Figure 15).



Figure 11: Hydrodynamic forces acting on an oil droplet positioned at the entry to a cylindrical pore of a membrane. The angles θ and α are the droplet's contact angle and angle of repose, respectively. See the text for the definitions of forces. Forces are not drawn to scale. In DOTM tests, the microscope was located above the semitransparent membrane (i.e. on the permeate side) and the focal plane of the microscope was on the feed side where oil droplets were accumulating.

The moment of the sum of forces acting tangentially to the membrane surface, F_{tot}^{τ} , around the pivot A is $F_{tot}^{\tau} \ell \cos(\alpha)$, where α is the angle of repose and ℓ is the lever arm of the moment (α and ℓ defined as shown in Figure 11; also see Supplementary material in Appendix B.2 of Chapter 3). The moment of the sum of forces acting normal to the membrane surface, F_{tot}^{n} , around the pivot A is $F_{tot}^{n} \ell \sin(\alpha)$ (presuming the net force points upward).
The sum of moments (of forces) is given by:

$$M = \ell(F_{tot}^{\tau} \cos \alpha - F_{tot}^{n} \sin \alpha)$$
(3-6)

Eq. (3-6) written for the zero value of the net moment of all forces acting on the oil droplet:

$$F_{tot}^{\tau} = F_{tot}^{n} \tan \alpha \tag{3-7}$$

can be solved to determine the diameter of the largest droplet that remains pinned at the membrane pore.

 F_{tot}^{τ} is equal to the drag force, which can be approximated using a modified Stokes equation [58]:

$$F_{tot}^{\tau} = F_D = C_1 3\pi \mu_w d_{drop} \left[v_{cf} \right]_{y=\frac{1}{2}d_{drop}}$$
(3-8)

where the crossflow velocity, v_{cf} , is evaluated as the fluid velocity at the center of the droplet (i.e. at a distance $\frac{1}{2}d_{drop}$ away from the membrane surface) and $C_1 = 1.7009$ is a coefficient that accounts for the presence of the membrane. It can be easily shown (see Supplementary material in Appendix B.1 of Chapter 3) that $[v_{cf}]_{y=\frac{1}{2}d_{drop}} = 3\bar{v}_{cf}\frac{d_{drop}}{H}$, where \bar{v}_{cf} is the average crossflow velocity in the membrane channel. In all DOTM and constant pressure crossflow filtration tests, the crossflow rate was maintained at the same value so that $\bar{v}_{cf} = 0.1$ m/s.

The force F_{tot}^n is the sum of all hydrodynamic forces that act on the droplet in the direction normal to the membrane surface:

$$F_{tot}^n = F_j - F_{lift} + F_b - F_g \tag{3-9}$$

The sum of buoyancy and gravitational forces is given by

$$F_b - F_g = (\rho_w - \rho_{oil})g \frac{\pi d_{drop}^3}{6}$$
(3-10)

The drag force exerted on the droplet in contact with the membrane surface by the flow permeating the membrane, F_i , is given by a modified version of the Stokes law:

$$F_j = \phi 3\mu_w \pi d_{drop} j \tag{3-11}$$

that includes the wall correction factor, ϕ , derived by Goren [59] for a particle in contact with a thin membrane:

$$\phi = \sqrt{\frac{R_m d_{drop}}{3} + 1.072^2} \tag{3-12}$$

where R_m is the hydraulic resistance of the membrane. The expression (3-12) is chosen because a thin membrane is a better representation of the straight-though pore membranes such as PCTE and Anopore than the boundary condition of an infinite porous half-space that Sherwood employed [60] in deriving an alternative expression for the wall correction factor.

The inertial lift force, F_{lift} , on a droplet attached to a wall is given by [61]

$$F_{lift} = 0.576 \rho_w \dot{\gamma}^2 d_{drop}^4$$
(3-13)

where $\dot{\gamma}$ is the shear rate of an unperturbed flow; we estimate $\dot{\gamma}$ by the value of the shear rate half a droplet diameter away from the membrane surface (eq. (3-3)). Note that eq. (3-12) and eq. (3-13) are for solid, non-deformable particles. Applied to oil

droplets the expressions may provide estimates but not exact answers because of the finite viscosity of the oil and a partial entry of droplets into pores.

For membranes with d_{pore} = 5 µm, the condition given by eq. (3-7) is met for droplets with $d_{drop}^{crit} \approx 40 \ \mu m$ in 0.1 mM SDS solution (Figure 12) and $d_{drop}^{crit} \approx 36 \ \mu m$ in 0.8 mM SDS solution (not shown). For droplets of this critical size, the tangential $(F_{tot}^{\tau} \ell \cos \alpha)$ and normal $(F_{tot}^n \ell \sin \alpha)$ components of the moment balance each other out because the lift force ($F_{lift} \propto d_{drop}^4$) counteracting the permeate drag grows to be sufficiently large. Thus, the force balance analysis predicts that droplets $\leq d_{drop}^{crit}$ would remain pinned while larger droplets would be swept off the surface by the crossflow drag. This prediction is in a qualitative agreement with visualization results. The deviations can be attributed to the approximate nature of the force balance calculations. Figure 10 presents an idealized scenario where a symmetric droplet interacts with an unperturbed flow. In reality, most droplets are positioned in the vicinity of other droplets, and as such the drag force exerted by the crossflow on the droplets should decrease due to the shielding effect. Further, the force balance relies on the assumption that the droplet is positioned on one pore. However, as was observed in DOTM tests (e.g., Figure 5 C, D, G, H, L) there may be multiple pores under one droplet. A calculation that is based on the PCTE membrane morphology data (Table 5) and droplet geometry shows droplets larger than 25 µm cover, on average, more than one pore. For example, the droplet of d_{drop}^{crit} = 40 µm covers, on average, between 2 and 3 pores.



Figure 12: Moment balance on an oil droplet of diameter d_{drop} positioned at a cylindrical pore ($d_{pore} = 5 \mu m$) of a PCTE membrane. Conditions: $j = 8.78 \cdot 10^{-5} m/s$; $\bar{v}_{cf} = 0.1 m/s$; $\theta = 135^{\circ}$ (0.1 mM SDS solution); $\mu_w = 1.002 \cdot 10^{-3} \text{ kg/(m·s)}$; $\rho_w = 998 \text{ kg/m}^3$; $\rho_{oil} = 770 \text{ kg/m}^3$; $R_m = 3.37 \cdot 10^{10} \text{ m}^{-1}$. The expression for the lever arm of the moments, ℓ , is provided in the Supplementary material in Appendix B of Chapter 3.

The results indicate that membrane fouling by emulsified oil is controlled by droplet coalescence and crossflow shear: the transport of oil to the membrane surface by the permeate flow is balanced by the shear-induced removal of the droplets that coalesce to exceed a critical size. Thus, membrane surfaces that promote droplet coalescence may be more resistant to membrane fouling by oil when operated in a crossflow configuration as long as intrapore fouling is avoided and droplets are removed prior to the formation of a contiguous film. The fouling dynamic may be different for more stable oil droplets where compressible multilayer gel emulsions of low hydraulic permeability are likely to form and control permeate flux.

3.4 Conclusions

The study describes the first application of a direct visualization technique to capture real-time images of a membrane surface under conditions of fouling by emulsified oil in the presence of crossflow. DOTM experiments with hexadecane-water-SDS emulsions revealed three characteristic stages of membrane fouling by oil: 1) droplet attachment and clustering, 2) droplet deformation, and 3) droplet coalescence. Increasing concentration of SDS from 0.1 mM to 0.8 mM decreased the interfacial tension of the emulsion from 39.3 mN/m to 30.8 mN/m, shifted the size distribution of suspended droplets toward smaller sizes and stabilized the emulsion as manifested by a decreased propensity of droplets to coalesce on the membrane surface. Droplet permeation was observed for droplets sized slightly above the membrane pore size and smaller. PCTE membranes (d_{pore} = 5 µm) rejected at least 97% of oil while Anopore membranes (d_{pore} = 0.2 µm) appeared to reject oil completely. The force balance on an oil droplet pinned on a single pore at the membrane surface predicted the critical size of a droplet that is not swept away by the crossflow; the predicted droplet diameter of ~40 µm was in gualitative agreement with the DOTM observations in experiments with 5 µm pore size membranes. A separate set of crossflow filtration tests in a constant pressure regime with 5 µm pore size membranes demonstrated that permeate flux reaches a steady state value. The results indicate that membrane fouling by emulsified oil (in this study's range of interfacial tensions), is controlled by droplet coalescence and crossflow shear: the transport of oil to the membrane surface by the permeate flow is balanced by the shear-induced removal of the droplets that coalesce to exceed a critical size. This is in

contrast to the scenario where viscoelastic multilayer deposit (i.e. gel emulsion) of low hydraulic permeability controls the permeate flux. Additional work with emulsions of varying degrees of stability would help elucidate the relative importance of these two fouling scenarios under different conditions. APPENDICES

APPENDIX A

Conversion of droplet size distributions from volume-based to number-based and surface area-based

The following describes the process of converting volume-based droplet (or particle) size distributions to number-based distributions and surface area-based distributions.

List of terms:

- $d_{i AVG}$ = Average droplet diameter for an incremental size range, *i*
- d_{i_lower} = Droplet diameter for the lower boundary of an incremental size range, i
- d_{i_upper} = Droplet diameter for the upper boundary of an incremental size range, i
- *i* = Specific incremental size range of droplet diameters
- j = AII of the incremental size ranges of droplet diameters
- N = Last incremental size range
- n_i = Number of droplets within an incremental size range, i
- NF_i = Number fraction for an incremental size range, *i*
- sa_i = Surface area of individual droplets in an incremental size range, *i*, based on the average droplet diameter for the size range, $d_{i AVG}$
- SA_i = Combined surface area of all droplets within an incremental size range, *i*
- v_i = Volume of individual droplets in an incremental size range, *i*, based on the average droplet diameter for the size range, $d_{i_{AVG}}$
- V_i = Combined volume of all droplets within an incremental size range, *i*

 V_{tot} = Total volume of all droplets

 VF_i = Volume fraction for an incremental size range, i

A.1 Conversion of volume-based droplet size distributions to number-based distributions

The volume-based droplet size distributions were gathered from tests conducted with a Malvern Mastersizer 2000, where the instrument provided data as a specific volume in %, VF_i , for each incremental size range of droplet diameters, *i*, in µm. The average droplet diameter, d_{i_AVG} , was calculated for each incremental size range of droplet diameters.

$$d_{i_AVG} = \frac{d_{i_upper} + d_{i_lower}}{2}$$
(A-1)

The volume of individual droplets, v_i in μ m³, within an incremental size range of droplet diameters was calculated with eq. (A-2) based on the average droplet diameter for each size range, $d_{AVG i}$, as determined by eq. (A-1).

$$v_i = \frac{4\pi}{3} \times \left(\frac{d_{i_AVG}}{2}\right)^3 \tag{A-2}$$

The combined volume of droplets within each incremental size range of droplet diameters equates to the number of droplets multiplied by the volume of those droplets as shown by eq. (A-3).

$$V_i = n_i v_i \tag{A-3}$$

The Mastersizer instrument provided volume fractions as % for each incremental size range of droplet diameters, but these values had to be deconstructed in order to

calculate the number-based size distributions. The volume fraction for the first incremental size range is shown by eq. (A-4), where N represents the last incremental size range.

$$VF_1 = \frac{n_1 v_1}{n_1 v_1 + n_2 v_2 + \dots + n_N v_N}$$
(A-4)

A simplified version of the volume fraction equation for the first incremental size range is given by eq. (A-5).

$$VF_1 = \frac{n_1 v_1}{\sum_{i=1}^N n_i v_i}$$
(A-5)

The general expression that applies to every incremental size range is shown by eq. (A-6), where i represents the specific incremental size range of concern and j represents all of the incremental size ranges.

$$VF_i = \frac{n_i v_i}{\sum_{j=1}^N n_j v_j} \tag{A-6}$$

The numerator of eq. (A-6) can be replaced with V_i from eq. (A-3) and the denominator of eq. (A-6) expresses the total volume of all droplets in the dataset; therefore eq. (A-6) can be further simplified to eq. (A-7).

$$VF_i = \frac{V_i}{V_{tot}} \tag{A-7}$$

Eq. (A-7) can be rearranged to eq. (A-8).

$$V_i = V F_i V_{tot} \tag{A-8}$$

The droplet size distribution expressed as a number fraction for an incremental size range is shown by eq. (A-9).

$$NF_{i} = \frac{n_{i}}{n_{1} + n_{2} + \dots + n_{N}}$$
(A-9)

The data concerning the number of droplets within an incremental size range, n_i , was not provided by the Mastersizer instrument; therefore in eq. (A-10) the values of n_i from eq. (A-9) were replaced with the expression $\frac{V_i}{v_i}$ from eq. (A-3).

$$NF_{i} = \frac{\frac{V_{i}}{v_{i}}}{\frac{V_{1}}{v_{1}} + \frac{V_{2}}{v_{2}} + \dots + \frac{V_{N}}{v_{N}}}$$
(A-10)

The expression for V_i from eq. (A-8) was substituted into eq. (A-10)

$$NF_{i} = \frac{\frac{VF_{i}V_{tot}}{v_{i}}}{\frac{VF_{1}V_{tot}}{v_{1}} + \frac{VF_{2}V_{tot}}{v_{2}} + \dots + \frac{VF_{N}V_{tot}}{v_{N}}}$$
(A-11)

Finally, V_{tot} cancelled out of eq. (A-11) to reveal an expression with variables that were either provided by the Mastersizer instrument or could be easily calculated using this conversion.

$$NF_{i} = \frac{\frac{VF_{i}}{v_{i}}}{\frac{VF_{1}}{v_{1}} + \frac{VF_{2}}{v_{2}} + \dots + \frac{VF_{N}}{v_{N}}}$$
(A-12)

Eq. (A-12) was further simplified

$$NF_i = \frac{\frac{VF_i}{v_i}}{\sum_{j=1}^N \frac{VF_j}{v_j}}$$
(A-13)

A.2 Conversion of volume-based droplet size distributions to surface area-based distributions

The conversion from volume-based droplet size distributions to surface area-based distributions provides numerical values for the total surface area of droplets within a specific incremental size range of droplet diameters, *i*. The surface area of individual droplets, sa_i in μ m², within an incremental size range of droplet diameters was calculated with eq. (A-14) based on the average droplet diameter for each size range, $d_{AVG i}$, as determined by eq. (A-1).

$$sa_i = 4\pi \times \left(\frac{d_{i_AVG}}{2}\right)^2 \tag{A-14}$$

The combined volume of all droplets, V_i in μ m³, within an incremental size range of droplet diameters is given by eq. (A-15)

$$V_i = \frac{VF_i}{100} V_{tot} \tag{A-15}$$

where VF_i is the volume fraction as a % for an incremental size range of droplet diameters as provided by the Mastersizer instrument, and V_{tot} is the total volume of all droplets in the dataset, which is also the concentration of oil in the emulsion expressed in μm^3 .

The number of droplets, n_i , within an incremental size range of droplet diameters is determined by eq. (A-16), where v_i , in μm^3 , represents the volume of each droplet within an incremental size range of droplet diameters.

$$n_i = \frac{V_i}{v_i} \tag{A-16}$$

Finally, the combined surface area of all droplets, SA_i in μ m², within an incremental size range of droplet diameters was calculated with eq. (A-17)

$$SA_i = n_i sa_i \tag{A-17}$$

APPENDIX B

Supplementary Material: Behavior of oil droplets at the membrane surface during crossflow microfiltration of oil-water emulsions*

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Figure 13: Number of publications with a) both "emulsion" and "ultrafiltration" in the title and b) both "emulsion" and "microfiltration" in the title. Source: Google Scholar. Retrieved: November 1, 2015.

B.1 Velocity field in the plane Couette flow

Consider unidirectional (x) flow of an incompressible fluid between two parallel stationary plates as a function of the distance, y, between the plates due to a constant pressure drop. Navier-Stokes equations are simplified to

$$\frac{d^2 v_x}{dy^2} - \frac{1}{\mu_l} \frac{dP}{dx} = 0 \tag{B-1}$$

Integrating eq. (B-1) twice with no slip boundary conditions $[v_x]_{y=0} = 0$ and $[v_x]_{y=H} = 0$ gives

$$v_x(y) = \frac{1}{2\mu_l} \frac{dP}{dx} y(H-y) \tag{B-2}$$

The maximum velocity, v_x^{max} , is achieved at the centerline of the flow (y = H/2):

$$v_x^{max} = \frac{1}{8\mu_l} \frac{dP}{dx} H^2 \tag{B-3}$$

Average velocity in the channel:

$$\bar{v}_x = \frac{1}{H} \int_0^H v_x(y) dy = \frac{1}{12\mu_l} \frac{dP}{dx} H^2 = \frac{2}{3} v_x^{max}$$
(B-4)

Shear rate is given by

$$\dot{\gamma} = \frac{dv_x}{dy} = \frac{1}{2\mu_l} \frac{dP}{dx} (H - 2y) \tag{B-5}$$

and the shear rate at the membrane wall is

$$\dot{\gamma}_w = \left[\frac{dv_x}{dy}\right]_{y=0} = \frac{1}{2\mu_l} \frac{dP}{dx} H = 6\frac{\bar{v}_x}{H}$$
(B-6)

Velocity at $y = r_{drop}$:

$$[v_x]_{y=r_{drop}} = \frac{1}{2\mu_l} \frac{dP}{dx} r_{drop} \left(H - r_{drop} \right) \cong \frac{1}{2\mu_l} \frac{dP}{dx} r_{drop} H = 6\bar{v}_x \frac{r_{drop}}{H}$$
(B-7)

and the shear rate at $y = r_{drop}$:

$$\dot{\gamma}_w = \left[\frac{dv_x}{dy}\right]_{y=r_{drop}} = \frac{1}{2\mu_l} \frac{dP}{dx} \left(H - 2r_{drop}\right) = 6\frac{\bar{v}_x}{H} \left(1 - \frac{d_{drop}}{H}\right)$$
(B-8)

The above derivation is based on the following assumptions:

- 1. The flow is unidirectional and steady
- 2. Gravity can be neglected
- 3. Fluid is Newtonian
- 4. No slip condition at the channel walls

B.2 Geometry of an oil droplet pinned at the entry to a cylindrical pore of a membrane

As can be seen by considering triangles ABC and BCD in Figure 14, the lever arm, ℓ , for drag forces on the droplet around point A and the sine of the droplet's angle of repose, α , are:

$$\ell = \sqrt{r_p^2 + [r^* \cos(\pi - \theta)]^2} = \sqrt{r_{pore}^2 + (r^* \cos \theta)^2}$$
(B-9)

$$\sin \alpha = \frac{1}{\sqrt{1 + \left(\frac{r^*}{r_{pore}}\right)^2 \cos^2 \theta}}$$
(B-10)

where the radius of curvature of the lagging part of the droplet is given by [8]

$$r^{*} = \frac{r_{pore}}{\cos\theta} \left[\frac{4 \frac{r_{drop}^{3}}{r_{pore}^{3}} \cos^{3}\theta + (2 - 3\sin\theta + \sin^{3}\theta)}{2 - 3\cos\theta + \cos^{3}\theta} \right]^{\frac{1}{3}}$$
(B-11)



Figure 14: Geometry of the oil droplet pinned at the entry to cylindrical pore of a membrane.

B.3 An oil droplet pinned at membrane pore entry: Geometrical considerations

The area covered by one droplet can be calculated based on the values of r^* (eq. (B-11); Figure 14) and θ . With this area and the cross-sectional area of one pore (Table 5) known, the average number of pores under one droplet can be calculated (Figure 15):



Figure 15: Average number of pores under one droplet.

B.4 Video evidence of oil droplet behavior at the membrane surface

The following figures represent videos that can be viewed in the supplemental files of the electronic version of this Dissertation.



Figure 16: Oil droplet coalescence at the membrane surface.

Figure 16 (Video 1) depicts multiple clusters of oil droplets pressing against one another causing the interior oil droplets to deform and become more angular in shape. As the oil droplets attempt to push closer to the pore entrances, it leads to the thinning of the water film between the droplets until the film ruptures and the droplets coalesce. The

large cluster of droplets on the top-right of the image will eventually coalesce into a \sim 95 µm droplet that covers multiple 5 µm membrane pores.





Figure 17 (Video 2) demonstrates the process through which an oil droplet of ~15 μ m in diameter can pass through a 5 μ m pore in a track-etch membrane. The oil droplet can be seen in the lower-left corner of the image as it attaches to the membrane surface and then slowly squeezes between two other droplets to force its way through the pore. As the oil droplet exits the permeate side of the membrane it can be seen floating towards the top of the image as it leaves the focal plane of the microscope. A sequence of images from this permeation event can be seen in Figure 7 of Chapter 3.

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CHAPTER FOUR

Membrane separation of saline oil-water emulsions: Effects of anion surfactants, divalent counterions and membrane surface chemistry

Abstract

The Direct Observation Through the Membrane (DOTM) method is used to explore membrane fouling by emulsified oil stabilized by an anionic surfactant (sodium dodecyl sulfate) in the presence or absence of divalent counterions (Mg²⁺). DOTM tests were performed with three optically transparent membranes - an ultrafiltration membrane (Anopore) and two nanofiltration membranes (Anopore coated with polyelectrolyte multilayer films) with oppositely charged surfaces. Observed fouling was interpreted in terms of droplet-droplet and droplet-membrane interactions. Crossflow-controlled coalescence was promoted under conditions of moderate affinity between droplets and membranes; under these conditions oil droplets could reach a critical size and be removed by the crossflow shear prior to forming a contiguous film on the membrane surface. Conversely, lower electrostatic repulsion from divalent cations facilitated droplet-droplet adhesion and led to rapid droplet coalescence resulting in membrane fouling. The low solubility of magnesium dodecyl sulfate in the thin film between droplets could be responsible for faster coalescence. Oleophobicity and surface charge of the membrane were also important factors with the most egregious fouling observed in tests with a positively charged and less oleophobic nanofiltration membrane. In

summary, droplet stability, electrical charge and a membrane's affinity for oil together govern the controllability of oil fouling behavior.

4.1 Introduction

Saline oil-water emulsions represent a major waste stream of several industries such as oil and gas, mining and desalination. The efficiency of commonly used oil-water separation technologies (e.g., hydrocyclones) drops dramatically with a decrease of oil droplet size below ~10 µm [1]. Yet, the amount of oil contained in such small droplets can be sufficiently high to necessitate their removal to meet regulations on the maximum allowable concentration of oil in the discharge [2]. Membrane filters offer a viable alternative for treating such emulsions although membrane fouling remains a challenge especially for complex multicomponent feeds such as produced water. Saline emulsions present additional challenges. First, salt removal, if required, raises the cost of separation. Second, salinity alters the behavior of oil droplets during separation possibly leading to increased membrane fouling. Nanofiltration (NF) or reverse osmosis (RO) require extensive pretreatment.

The structure of the oil fouling layer as it develops on the membrane surface during the separation of an oil-water emulsion is not fully understood. Mechanistic dead-end filtration studies have described the oil deposit as a highly compressible gel layer or a "cake" based on the cake filtration blocking law derived for spherical, non-deformable particles. Our previous work [3] described the first application of a direct visualization technique - the Direct Observation Through the Membrane (DOTM) - to capture real-time images of a membrane surface under conditions of fouling by emulsified oil in the presence of crossflow. The DOTM experiments with hexadecane stabilized by sodium

dodecyl sulfate (SDS) revealed three characteristic stages of membrane fouling by oil:1) droplet attachment and clustering, 2) droplet deformation, and 3) dropletcoalescence. The study did not examine the effect that salinity has on membranefouling by oil.

The DOTM method enables direct visualization of the membrane surface and can be invaluable for understanding the behavior of micron-scale foulants in real time. A major limitation of the method, however, is the requirement that the membrane be optically transparent. Typical salt-rejecting (NF or RO) membranes prepared by phase inversion or interfacial polymerization techniques are opaque, which precludes their use in DOTM studies. To overcome this problem, we prepared NF membranes by coating an ultrafiltration (UF) support (Anopore membranes with $d_{pore} = 0.02 \ \mu m$) with polyelectrolyte multilayers. The procedure is known to render high quality salt-rejecting membranes for applications such as NF [4], forward osmosis [5], and electrodialysis [6]. Importantly, both the UF support and the PEM coatings (when wet) are optically transparent and can be used in DOTM tests.

SDS is often used to stabilize emulsions. As an anionic surfactant, it should interact strongly with divalent cations such as Ca^{2+} and Mg^{2+} that are present in natural waters in high concentrations. Typical concentrations in groundwater and surface water range from ~1 to 50 mg/L for Mg^{2+} and from ~1 to 200 mg/L for Ca^{2+} [7]. In seawater, the concentrations of Mg^{2+} and Ca^{2+} are 1,350 mg/L and 400 mg/L, respectively [8]. Nanofiltration membranes reject these cations leading to even higher concentrations in

the vicinity of the membrane surface where the ions can interact with other rejected dissolved or particulate species such as colloids and oil droplets. The resulting concentration polarization may result in precipitative fouling of the membrane by inorganic compounds with low solubility products (e.g., Mg(OH)₂, CaCO₃, CaSO₄). The extent of concentration polarization depends on permeate and crossflow fluxes but also on rejection, which in turn, is a function of relevant salt permeability constants of the membrane. We have recently measured these for MgSO₄ and a range of NF membranes including NF270 and several polyelectrolyte multilayer membranes [9]. The current study uses this information to model concentration polarization conditions that can be expected for an NF membrane operated to provide permeation at a rate typical for NF and explore how rejected salt interacts with oil droplets at the membrane surface. In addition to effects specific to divalent cations (e.g., bridging SDS molecules in the solution and on the surface of an oil droplet), dissolved ions are expected to alter the interfacial tension of the emulsion. For example, Adamczyk et al. observed a significant reduction in surface tension for an aqueous solution of cetylrimethylammonium bromide (CTAB) with an increasing electrolyte concentration of KCI [10].

We expect that there will be coupling [11] where rejected salt impacts the structure and hydraulic resistance of the fouling layer of oil while the rejected oil increases concentration polarization of rejected salts. Because the DOTM filtration cell is not designed to withstand the transmembrane pressures required for NF, DOTM tests with NF membranes were conducted in the absence of permeate flux; to understand how oil droplets behave at the membrane surface when within the mass transfer boundary layer

with high salt concentration, the concentration polarization conditions were simulated by increasing the concentration of MgSO₄ in the feed emulsion.

Minimizing droplet deposition on the membrane surface by hydrodynamic means is one strategy for decreasing membrane fouling. For droplets that do deposit on the membrane, preferred behaviors can be promoted to avoid egregious forms of membrane fouling such as complete blocking [12] of individual pores or formation of a contiguous film of oil on the membrane. For relatively unstable droplets, a preferred scenario would involve oil droplets that attach to the membrane surface in the vicinity of other oil droplets so that they could coalesce until they reach a critical size where they are swept off the membrane [3]. For more stable emulsions, a preferred scenario might be the formation of relatively thin and permeable layers of oil droplets that can be easily removed by a hydraulic flush. Sufficient stability would ensure that droplet deformation is minimal to avoid low porosity cakes. Electrostatic forces may become more important (relative to hydrodynamic interaction) for smaller droplets that can be expected in stable emulsions; under these conditions higher electrical charge on oil droplets would help minimize oil accumulation at the membrane surface and would facilitate membrane cleaning.

Whichever fouling scenario unfolds, droplet coalescence is a critical process that determines in part the rate and extent of oil layer formation on the membrane surface. Coalescence of surfactant-stabilized droplets in the bulk of the emulsion can be viewed as a last step in the sequence of several events:

- Transport of droplets in the bulk to bring them to a close separation distance near the membrane surface. This transport is governed by hydrodynamic forces and long-range (> 5 nm) droplet-droplet and droplet-membrane interactions [13]. In the classical coagulation theory, this step is described by collision efficiency.
- 2) Droplet adhesion resulting from an attractive force between droplets and a strong short-range repulsion due to surfactants. The droplets are separated by a very thin liquid film stabilized by surfactant layers. The solubility of the surfactant [14, 15] and, as a consequence, the ionic makeup of the dispersion media [16], play an important role in droplet stability. The time that the droplets reside in close proximity with respect to one another (i.e., in contact), *t_{contact}*, can be limited by droplet removal from the surface or droplet coalescence.
- 3) Drainage of the thin film of dispersion medium separating the droplets. If the film drains over a period of time, $t_{drainage} < t_{contact}$ and ruptures, coalescence occurs. There are several approaches to describing the probability of coalescence [17], with the film drainage model [18, 19] being most commonly used. The model predicts that the coalescence efficiency is given by

$$\lambda = exp\left(-\frac{t_{drainage}}{t_{contact}}\right) \tag{4-1}$$

The drainage occurs differently depending on whether the droplets are deformable and whether their interfaces are mobile [17]. In the case of deformable particles with partially mobile interfaces, drainage time is given by [20]:

$$t_{drainage} = \frac{\pi \mu_d F^{1/2}}{2(2\pi\gamma/r)^{3/2}} \left(\frac{1}{h_f} - \frac{1}{h_i}\right)$$
(4-2)
where γ (N/m) is interfacial tension, h_i and h_f are initial and critical film thickness (m), μ_d is the dynamic viscosity of oil (Pa·s), r is droplet radius (m), and F is the compressive force (N).

The same approach can be adapted to understand droplet coalescence at the membrane surface. The three membrane fouling stages identified in our previous work with oil-water emulsions can be mapped on the above stages of droplet coalescence in the straightforward manner. *Droplet attachment and clustering* corresponds to the long-range transport of droplets to the membrane surface and initial adhesion of droplets to one another. *Droplet deformation* corresponds to continual adjustment of the equilibrium shape and contact angles between droplets in response to the changing compressive (i.e., drag) force and crossflow shear. *Droplet coalescence* on the membrane surface directly corresponds to the coalescence of droplets in the bulk.

Whichever fouling scenario unfolds, droplet coalescence is a critical process that determines in part the rate and extent of oil layer formation on the membrane surface. Borrowing form the results developed for bulk emulsions, one can suppose that both $t_{drainage}$ and $t_{contact}$ are important in determining surface coalescence of droplets on the membrane surface. We hypothesize that both highly favorable and highly unfavorable droplet-membrane interactions prevent coalescence and that the intermediate affinity encourages surface coalescence most effectively. In summary, adjustments of surface chemistry of the membrane and chemical make-up of the aqueous phase appear to be practical means of regulating the fouling behavior of oil-

water emulsions. This study examined the effects of anionic surfactants and divalent counterions on membrane fouling by emulsified oil. DOTM tests were employed to visualize oil droplet behavior on surfaces of porous and nanofiltration membranes for different hydrodynamic conditions and membrane surface chemistries.

4.2 Materials and methods

4.2.1 Reagents

Hexadecane (99%), sodium dodecyl sulfate (SDS, \geq 98.5%), magnesium sulfate heptahydrate (MgSO₄(H₂0)₇ \geq 98%), poly(allylamine) hydrochloride (PAH, average Mw ~58,000), and poly(sodium 4-styrenesulfonate) (PSS, average Mw ~70,000) were purchased from Sigma-Aldrich and used as received. Potassium chloride (KCl, 99%) was purchased from J.T. Baker and used as received. DI water was supplied by a Milli-Q ultrapure water system (Integral 10, Millipore) equipped with a terminal 0.2 µm microfilter (MilliPak, Millipore); the water resistivity was ~18 MΩ·cm.

4.2.2 Preparation of oil-water emulsions. Nomenclature

The non-saline model emulsions were prepared by adding hexadecane to water in the presence of SDS as a stabilizing agent and stirring the resulting mixture at 1,000 rpm using a digital stand mixer (RW 20 digital dual-range mixer, IKA) for 20 min. Hereinafter the hexadecane-water-surfactant emulsions will be referred to as HWS-X where X is the concentration of SDS in units of mM. In all emulsions the hexadecane concentration was 0.1% v/v (773 mg/L), while the concentration of SDS was either 0.1 mM (HWS-0.1 emulsions) or 3 mM (HWS-3 emulsions). These values were below the critical micelle concentration (CMC) for SDS, which is in the 6 mM to 8 mM range [21].

The saline model emulsion was prepared the same way as non-saline emulsions, except that 804 mg/L of MgSO₄ (6.7 mM) was added to the water along with 0.1 mM of SDS prior to the addition of hexadecane. During the DOTM tests with saline model emulsions, the salinity concentration was increased by 4328 mg/L of MgSO₄ after 10 minutes to reach a total concentration of 5131 mg/L of MgSO₄ (42.6 mM). In what follows, the hexadecane-water-surfactant-salt emulsions will be referred to as HWSS-X where X is the concentration of SDS in units of mM.

4.2.3 Characterization of oil-water emulsions

Light scattering (Mastersizer 2000, Malvern Instruments) was used to determine an oil droplet size distribution in the bulk for each emulsion. During the measurement, the emulsion was continuously circulated through the optical cell of the Mastersizer using a Malvern sample dispersion unit mixed at 1,000 rpm. The refractive index of 1.434 for hexadecane was used as an input in the calculation of droplet size distribution. The volume-based distribution reported by the Mastersizer software (see Supplementary material (SM) in Appendix A of Chapter 4, Figure 28) was converted into a number-based distribution. Droplet size distributions at the membrane surface were estimated based on images captured during DOTM tests.

The interfacial tension for each emulsion was measured using the pendant drop method and a standard goniometer (model 250-F4, ramé-hart instrument co.). First, the surface tensions of the pure liquids (DI water and hexadecane) and the aqueous solutions (of

SDS only or of SDS and MgSO₄) were determined. The data would later serve as inputs to the DROPimage Advanced v2.6 software during the interfacial tension measurements. A microsyringe (part 100-10-20, ramé-hart instrument co.) was filled with each of the liquids, which was then dispensed until a pendant droplet was produced. The surface tension of the liquid was determined based on the droplet's shape as quantified by the software. The interfacial tension measurements were performed by filling the standard quartz cell (part 100-07-50, ramé-hart instrument co.) with DI water or one of the aqueous solutions (of SDS only or of SDS and MgSO₄) and using a microsyringe with inverted stainless steel 22g needle (part 100-10-13-22, ramé-hart instrument co.) filled with hexadecane to produce a submerged pendant droplet. The interfacial tension was determined by the software based on the shape of the submerged oil droplets in the different aqueous solutions.

The ζ -potential of droplets for each emulsion was measured using phase analysis light scattering (ZetaPALS, Brookhaven Instruments). The electrophoretic velocity was calculated based on the measured values of electrophoretic mobility and electric field at the particle in order to compare with estimates of the Stokes velocity for a range of droplet sizes to determine if the ζ -potential values were reliable.

4.2.4 Membranes used in DOTM tests

The DOTM method required membranes that had sufficient optical transparency when wet, and inorganic anodized alumina (Anopore) membranes met this criterion. As

reported by the manufacturer, the anodic alumina Anopore membrane (Anodisc membrane filters, Whatman) with a nominal pore diameter of 0.02 µm has surface porosity in the 30 to 35% range and a "nondeformable honeycomb pore structure with no lateral crossovers between individual pores" [22]. Some DOTM experiments were conducted with uncoated Anopore membranes as supplied by the manufacturer, but other experiments used modified Anopore membranes coated by polyelectrolyte multilayers (PEMs). The PEMs were formed using the layer-by-layer self-assembly technique [23]. The polyelectrolytes chosen for this study were poly(sodium-4-styrene sulfonate) (PSS) and poly(allylamine) hydrochloride (PAH). The preparation conditions were the same as employed by Shan et al. [9] who measured water and Mg^{2+} permeability coefficients for these membranes. The Anopore/PEM membrane where the terminal polyelectrolyte was a polyanion (PSS) was denoted by [PSS/PAH]_{4.5}, where the subscript 4.5 means that one layer of PSS was deposited on top of the four [PSS/PAH] bilayers. Similarly, the Anopore/PEM membrane where the terminal polyelectrolyte was a polycation (PAH) was denoted by [PSS/PAH]₄. A new membrane was used in each test.

4.2.5 Membrane characterization

The surface charge of each membrane was measured using an electrokinetic analyzer (EKA, Anton Paar). The ζ -potentials were determined based on a streaming potential/streaming current method with 1 mM KCI solution as the background electrolyte. All three of the Anopore membranes (uncoated and PEM-coated) were

submerged feed side down in an aqueous solution of either 0.1 mM of SDS or 3 mM of SDS. The membranes were not tested after being submerged in an aqueous solution of 0.1 mM of SDS and 6.7 mM of MgSO₄ as the salinity of the solution would interfere with the testing solution of 1 mM of KCI.

The contact angle of hexadecane on the surface of each of the three membranes (uncoated and the two PEM-coated) was measured using a goniometer (model 250-F4, ramé-hart instrument co.). The membrane was attached to the environmental fixture (part 100-14, ramé-hart instrument co.) with the feed side facing downward and then submerged in an aqueous solution of SDS or a combination of SDS and MgSO₄ when the fixture was placed in the standard quartz cell (part 100-07-50, ramé-hart instrument co.). The microsyringe (part 100-10-20, ramé-hart instrument co.) was filled with hexadecane and a single droplet was dispensed from the inverted stainless steel 22g needle (part 100-10-13-22, ramé-hart instrument co.) until the droplet attached to the feed side of the submerged membrane. DROPimage Advanced v2.6 software determined the contact angle between the oil droplet and the membrane surface in an aqueous solution.

4.2.6 Direct Observation Through the Membrane system

The DOTM setup has been described in detail previously [24]. The central feature of the DOTM system is the microscope (Axio Imager.M1, Zeiss) fitted with a video camera (Digital Color video camera model TK-C921BEG, JVC) capable of capturing both still

images and videos. All of the images and videos recorded during filtration tests used a 32X magnification microscope objective resulting in a total magnification of 320X. A crossflow membrane filtration cell fitted with two acrylic windows for visualization had a crossflow channel that was 106 mm long, 36 mm wide and 2 mm deep. The active membrane area was only 7.56 cm² and was located in the middle of the crossflow channel with the permeate side of the membrane facing up towards the objective. The light emitted by the microscope's illuminator transmitted through the membrane as the images were captured by focusing through the membrane and onto its feed side. The feed emulsion was stirred throughout each experiment by a magnetic stir plate (SP131320-33, Thermo Scientific) and stir bar, and the retentate was returned to the feed. DOTM experiments were carried out at a constant crossflow velocity of $3.6 \cdot 10^5$ L/(m²·h) (0.1 m/s) that translated to a Reynolds number, *Re*, of 377.

During experiments with HWSS-0.1 emulsions, 100 mL of the feed emulsion was extracted prior to the start of the DOTM test and was mixed with the additional 8.86 g of MgSO₄(H₂O)₇ using the stand mixer operated at 215 rpm during the first 10 min of the DOTM test. After that, the 100 mL emulsion with the added salt was slowly poured into the circulating feed emulsion so that the total concentration of MgSO₄ in the emulsion was 5131 mg/L of MgSO₄ (42.6 mM). The final concentration of MgSO₄ matched the value expected at the surface of a NF270 membrane separating MgSO₄ at the permeate flux of 95 L/(m²·h) (2.6·10⁵ m/s) [9].

Table 6 lists the DOTM tests that were conducted to explore the effect of the following variables on membrane fouling by emulsified oil: salinity, surfactant concentration, permeate flux, and membrane surface chemistry. The effect of permeate flux was only tested with uncoated Anopore membranes. Transmembrane pressures required to produce permeate flux in the NF range for the coated membranes would exceed the pressure rating of the DOTM filtration cell.

Table 6: Twelve DOTM tests carried out with three different membranes and three different emulsions. Modifier 'f' denotes that the test was conducted in the presence of permeate flux. In all cases, Anopore membranes with the pore size of 0.02 μm were employed.

Emulsion Membrane	HWS-0.1	HWS-3	HWSS-0.1
Anopore (uncoated)	Test 1	Test 2	Test 3
	lest 1f	Test 2f	Test 3f
Anopore/[PSS/PAH] ₄	Test 4	Test 5	Test 6
Anopore/[PSS/PAH] _{4.5}	Test 7	Test 8	Test 9

The DOTM experiments were performed either at zero permeate flux (for Anopore/[PSS/PAH]₄ and Anopore/[PSS/PAH]_{4.5} NF membranes) or in the constant permeate flux regime (for uncoated Anopore UF membranes). Throughout each DOTM experiment, the permeate flux was either maintained constant by the peristaltic permeate pump (Minipuls 3, Gilson) or the permeate rate was zero as the pump was turned off. The buildup of hydraulic resistance due to membrane fouling by oil led to an increase in the headloss across the membrane.

4.3 Results and discussion

4.3.1 Characteristics of oil-water emulsions

4.3.1.1 Droplet size distribution

Oil-water emulsions are dynamic: the droplet size distribution in the bulk of the feed emulsion can change with time. Hydrodynamic forces as well as droplet-droplet and droplet-membrane interactions result in selective deposition so that in general, the size distribution of droplets at the membrane surface differs from that in the feed. To elucidate this difference for the three emulsions tested, droplet size distributions were measured both in the bulk of the feed emulsions using light diffraction. The distributions on the membrane surface were estimated based on optical microscopy images obtained in DOTM experiments (Figure 18). For bulk HWS-0.1 and HWSS-0.1 emulsions, the number-based distributions showed that more 99% of droplets were smaller than 10 µm. Comparison of the size distribution data with the Kolmogorov length scale for the mixing conditions employed in this work (~25 μ m; see SM in Appendix A of Chapter 4) points to the significant role of surfactant in determining droplet sizes. The droplet size distribution for the bulk HWS-3 emulsion could not be accurately measured as the minimal required obscuration ratio could not be met due to a combination of the small droplet size and the low concentration of oil.

For each of the three emulsions, the DOTM images chosen for the characterization of droplet size distributions were taken from the tests with uncoated Anopore membranes with permeate flux of ~52 L/(m²·h) ($1.4 \cdot 10^5$ m/s) 60 s into the filtration process. The 60 s lag was sufficient for the droplets to reach the membrane surface, yet short enough to ensure that no observable droplet coalescence had occurred. The resolution of the DOTM microscope is not sufficient to discern droplets smaller than 1 µm, so the histograms do not extend beyond this limit.



Figure 18: Number-based droplet size distributions for each of the emulsions tested. The distribution in the bulk emulsion was measured by light diffraction while the sub-population of droplets that attached to the membrane surface was based on DOTM image analysis.

4.3.1.1.1 Mass transfer boundary layer for MgSO₄

The initial MgSO₄ concentration (6.7 mM) for the HWSS-0.1 emulsion was chosen based on the average Mg²⁺ concentration reported for produced waters from the Powder River Basin in Wyoming [25]. The final concentration of MgSO₄ (42.6 mM) was calculated based on the MgSO₄ concentration polarization factor for a NF270 membrane rejecting MgSO₄ at a permeate flux of 95 L/(m²·h) (2.6·10⁵ m/s) [9] assuming the diffusion coefficient for MgSO₄ (D_{MgSO_4}) of 8.5·10⁻¹⁰ m²/s [26].

4.3.1.2 Critical micelle concentration and formation of precipitates

In the presence of divalent cations, SDS may form precipitates at concentrations below its CMC (CMC_{SDS} = 8.2 mM at 25 °C [21]). For example, when CaCl₂ is added, calcium dodecyl sulfate forms, which has a CMC much smaller than that of SDS [28]. In our study, an aqueous solution of 3 mM of SDS and 6.7 mM of MgSO₄ produced a crystalline precipitate. To elucidate the 'salting out' conditions, a number of aqueous solutions were prepared with varying concentrations of SDS and as little as 0.4 mM of MgSO₄. Figure 19 summarizes these observations and approximately outlines domains with and without SDS precipitation. Pinpointing the exact boundary between the domains would require a large number of additional experiments and would still produce only an approximation as the precipitation process is kinetically limited. Avoiding precipitation is important both from the application point of view (as precipitative fouling would contribute to flux decline) and from the point of view of this study's design (as

formation of precipitates would confound the interpretation of fouling caused by oil droplets alone, which was the focus of this work). Three zones can be identified in the diagram shown in Figure 19. The dark gray zone above the filled circles in Figure 19 represents the combined concentrations of SDS and MgSO₄ where precipitation is expected. The zone below the empty circles in Figure 19 represents the region where no precipitation should occur (no observed precipitation in > 1 week) because one of the constituents was in a sufficiently low concentration. No precipitation was observed when the concentration of SDS was low (≤ 0.4 mM) even for high MgSO₄ contents. Concentrations of MgSO₄ < 0.4 mM were not tested in solutions with SDS, but no precipitation was observed when the concentration of SDS was as high as 18 mM in the absence of MgSO₄. The light gray area shown in Figure 19 represents a range for possible precipitation.



Figure 19: Solubility of SDS in the presence of MgSO₄. Light gray area represents the likely precipitation domain, the area is bounded by data points corresponding to conditions where precipitation was observed (filled circles) and where no precipitation was observed (empty circles). Due to the sparsity of the dataset, domain boundaries are approximate.

Studies concerning the miscibility of aqueous solutions with surfactants and either monovalent or divalent salts have reported similar figures that indicate the salt's ability to decrease the critical micelle concentration (CMC) or induce a critical concentration for particle formation [28, 29]. Corrin and Harkins found that the addition of salts to aqueous solutions of detergents lowers the CMC, and this can lead to the precipitation of the surfactant in the form of crystals; data for SDS showed a seven-fold decrease in CMC with the addition of 0.354 M NaCI [29]. To our knowledge, results with MgSO₄–SDS solutions have not been published, but similar tests by lyota et al. [28] showed that the critical mole fraction of SDS to precipitate out of a solution is much larger for a CaCl₂–SDS mixture than for a NaCl–SDS mixture due to the larger

electrostatic attraction in the aggregates between Ca²⁺ and DS⁻ ions than between Na⁺ and DS⁻ ions. DS⁻ ions should be strongly attracted to the Mg²⁺ ions as well. This might explain why the HWSS-0.1 emulsion remains precipitate free, while the HWSS-3 emulsion forms crystalline precipitates. To avoid the problem of precipitation when divalent ions are present the use of non-ionic surfactants is recommended.

4.3.1.3 Interfacial tension as a function of surfactant and MgSO₄ concentrations

The interfacial tensions between hexadecane and an array of aqueous solutions containing varying concentrations of either SDS or the combination of SDS and MgSO₄ were measured to quantify the impact that SDS and MgSO₄ have on droplet stability and the 'salting out point'. Measurements could only be performed with the precipitate free aqueous solutions of SDS and MgSO₄ and were carried out using the pendant drop method. The accepted values of surface tension for DI water and hexadecane are 72.8 mN/m and 27.6 mN/m, respectively [30], and these were confirmed in our tests. The interfacial tension of hexadecane and DI water was measured to be 41.8 mN/m. The surface tensions for all of the aqueous solutions were measured first, as the results were used as inputs for the DROPimage Advanced v2.6 software during the interfacial tension measurements with hexadecane. During the filtration tests, it was assumed that coalescence-induced desorption of surfactant was sufficiently fast to make the resulting transient changes in the interfacial tension relatively unimportant.



Figure 20: Effect of surfactant (SDS) and 2-2 salt (MgSO₄) on the interfacial tension of hexadecane-in-water emulsion. Red arrows point to three emulsion types used in DOTM experiments.

Figure 20 demonstrates the impact that surfactant concentration has on the stability of an emulsion: the interfacial tension between hexadecane and an aqueous solution of SDS decreases with the addition of SDS until the CMC is reached and then the interfacial tension remains constant. The trend in the interfacial tension with an increase in the concentration of SDS is consistent with the droplet size distributions shown in Figure 18; wherein lower interfacial tensions resulted in smaller oil droplets. Figure 20 also provides quantitative results that depict the dramatic effect that MgSO₄ concentration has on interfacial tension, but these results are not consistent with the droplet size distributions. The values of interfacial tension, σ , measured for HWS-0.1 and HWS-3 emulsions were 32.7 mN/m and 18.4 mN/m, correspondingly. For HWSS-0.1 emulsion (0.1 mM SDS and 6.7 mM MgSO₄), $\sigma = 21.7$ mN/m, which is closer to the corresponding value for HWS-3; yet the droplet size distribution of HWSS-0.1 was very similar to that of HWS-0.1, and not HWS-3. This discrepancy in correlations between the interfacial tension values and the droplet size distributions for emulsions containing MgSO₄ may be due to the difference in ζ -potentials.

4.3.1.4 Droplet charge

The only difference between HWS-0.1 and HWSS-0.1 emulsions is the addition of MgSO₄. Yet, the presence of Mg²⁺ dramatically decreased the ζ -potential of oil droplets from -101 ± 22 mV for the HWS-0.1 emulsion to -58 ± 4 for the HWSS-0.1 emulsion. There was no statistical difference between the ζ -potential of oil droplets for the HWS-0.1 emulsion and the HWS-3 emulsion (ζ -potential = -112 ± 17). The large standard deviations for both the HWS-0.1 emulsion and the HWS-3 emulsion can be attributed to the absence of a background electrolyte during the measurement. Electrophoretic velocities were calculated based on the ζ -potential results in order to compare them with Stokes velocities determined for a range of droplet sizes to evaluate if the buoyancy of the droplets was significant to interfere with the ζ -potential measurement. It was determined that the electrophoretic velocity was of the same magnitude as the

Stokes velocity for droplets of ~17 µm in diameter for the HWSS-0.1 emulsion, while the HWS-0.1 and HWS-3 emulsions showed velocities of the same magnitude for droplet diameters of \geq 25 µm. Based on the measured droplet size distributions (Figure 18), HWS-0.1 emulsion contained at least 92.7% of the oil surface area in droplets \leq 25 µm in diameter. For HWSS-0.1 emulsions, droplets smaller than \leq 17 µm corresponded to 74.8% of the total droplet surface area. Thus, the ζ -potential values for these emulsions were reliable.

The effect of droplet charge is critical for droplet coalescence and it can further be explained by the relationship between frequency of encounters and high affinity. If the droplet-droplet contact time is sufficiently long, the droplet might be able to coalesce. High affinity is observed when ζ -potentials are low and droplets can approach one another due to the lack of repulsive forces. Coalescence is a two-step process highly affected by droplet charge because the droplets first must approach another droplet, and this interaction is governed by the charge of the droplets. Once two droplets are in contact with each other the second-step is coalescence, and this process is controlled by the interfacial tension of the emulsion and the size of the droplets in contact. The HWSS-0.1 emulsion containing MgSO₄ has a lower ζ -potential meaning that the droplets are more likely to get close to one another thereby increasing the frequency of encounters, and as such they have a higher propensity to coalesce. In comparison, the HWS-3 emulsion had a high ζ -potential, which lowered the affinity between droplets meaning that the droplets would repel one another and thus decreases the frequency of encounters and the possibilities for coalescence. The charge density is higher on

smaller droplets, which also explains the higher ζ -potential for the HWS-3 emulsions as its droplet size distribution was the smallest. These scenarios for droplet charge affecting coalescence were verified by DOTM imaging.

4.3.2 Characteristics of membranes

Figure 21 summarizes contact angle and ζ -potential data for the three membrane types evaluated in this work. The contact angle results indicate that both the membrane surface and the solution chemistry may be relevant for the oil fouling behavior during filtration. All of the Anopore membranes (including the two PEM-coated membranes) were oleophobic, while the uncoated Anopore 0.02 µm membrane and the Anopore/[PSS/PAH]_{4.5} membrane could be classified as superoleophobic [31].



Figure 21: Hexadecane contact angle and ζ -potential values measured for uncoated and PEM-coated Anopore membranes ($d_{pore} = 0.02 \,\mu$ m) as a function of SDS and MgSO₄ concentrations. The coatings tested include one polycation-terminated ([PSS/PAH]₄) and one polyanion-terminated ([PSS/PAH]_{4.5}) polyelectrolyte multilayers. The errors correspond to standard deviations.

В



The contact angles of hexadecane on all three types of membranes decreased with the increase of SDS concentration in the solution. The addition of MgSO₄ to the 0.1 mM SDS solution did not lead to statistically significant changes in the contact angle of hexadecane on the uncoated Anopore membrane. However, MgSO₄ did induce a decrease in the contact angle of hexadecane on both of the PEM-coated membranes. It was extremely difficult to measure the contact angle of hexadecane on the polyanion-terminated membrane (Anopore/[PSS/PAH]_{4.5}) as the oil droplets freely rolled off the submerged membrane surface. This result was dramatically different from what was observed with the polycation-terminated membrane (Anopore/[PSS/PAH]₄), where droplets attached to the submerged membrane surface and continued to wet the membrane surface. A sequence of images (see SM in Appendix A of Chapter 4, Figure 29) depicts the slow decrease in the droplet's contact angle on Anopore/[PSS/PAH]₄ from 136° to 116° as the droplet spreads on the membrane surface, but the contact angle stabilized after ~10 minutes.

The measured ζ -potentials of the three membranes show the impact that PEM coatings have on the surface charge of the membrane (Figure 21). Each membrane was soaked in a solution of either 0.1 mM SDS or 3 mM SDS for 30 min prior to the ζ -potential measurements, but the different SDS concentrations only had a statistically significant effect on the polycation-terminated membrane (Anopore/[PSS/PAH]₄). After soaking in an aqueous solution of 0.1 mM of SDS, the uncoated Anopore membrane had a ζ -potential of -5.3 ± 0.8 mV; the polyanion-terminated membrane (Anopore/[PSS/PAH]₄.5) had a ζ -potential of -28.1 ± 5.8 mV, while the polycation-terminated membrane

(Anopore/[PSS/PAH]₄) had a ζ -potential of 38.0 ± 2.3 mV. The effect of MgSO₄ on each membrane's ζ -potential was not determined as the ionic strength of the background solution (0.1 mM of SDS and 6.7 mM of MgSO₄) was much higher than that of the background electrolyte (1 mM KCI) used in EKA tests.

4.3.3 DOTM tests with oil-water emulsions

Earlier DOTM work [3] with hexadecane-water-SDS emulsions revealed three characteristic stages of membrane fouling: 1) droplet attachment and clustering, 2) droplet deformation, and 3) droplet coalescence. These experiments were carried out in a solution of SDS (0.1 mM, 0.4 mM, or 0.8 mM) and did not explore the effects that background electrolyte and membrane surface charge have on the way in which oil fouls the membrane.

The process of droplet coalescence is controlled in part by droplet-droplet and dropletmembrane interactions. Longer interactions translate into higher likelihood of coalescence. Variations in the distributions of droplet sizes recorded by light scattering (Figures 18.A, 18.B and 18.C) indicate that droplets interact in the bulk. At the same time DOTM tests provided direct evidence of droplet-droplet interactions at the membrane surface and of the importance of membrane surface chemistry (see sections 3.3.1 through 3.3.4). The time scale of droplet-droplet interactions, $t_{contact}$, is $\sim d_{drop} (\bar{G} d_{drop})^{-1} = \bar{G}^{-1}$, where \bar{G} is the mean velocity gradient. For bulk emulsions, \bar{G} can be calculated based on the emulsion volume and viscosity, impeller diameter and

mixing speed [32] (see SM in Appendix A of Chapter 4). For all emulsions used in this work, $\bar{G} \cong 1426 \text{ s}^{-1}$. In the membrane channel with a no slip boundary condition, \bar{G} is highest at the membrane surface. Approximating flow in the membrane channel using the Hagen–Poiseuille equation gives the following expression for \bar{G} (i.e., shear rate) at a distance d_n from the wall:

$$\bar{G} = \left[\frac{dv}{dz}\right]_{z=\frac{d_p}{2}} = 6\frac{v}{H}\left(1 - \frac{d_{drop}}{H}\right)$$
(4-3)

where *v* is the average crossflow velocity in the membrane channel and *H* is the height of the membrane channel (in our experiments v = 0.1 m/s and H = 2 mm). Near the membrane surface, \bar{G} is ~300 s⁻¹. Thus droplet-droplet interactions are longer in the membrane channel (~3 ms) than in the bulk (~0.7 ms) outside of membrane channel indicating that coalescence is more likely at the membrane surface. This calculation does not include the added impact of the membrane to hold droplets together for longer contact times.

Once deposited on the membrane surface, droplets may remain there for much longer and interact with other attached droplets. Droplet residence time observed in DOTM tests ranged from close to zero (corresponding to a transient contact of a droplet with the membrane surface) to many minutes (corresponding to droplets that deposited onto the membrane and remained there for the entire duration of the DOTM test).

The droplet-membrane interactions determine the affinity between the membrane and the droplets. If the droplets and the membrane have a very high affinity for one another the droplets will spread across the membrane surface leading to extensive membrane fouling. If the droplets and the membrane have a moderate affinity for one another the droplets will attach to the membrane surface and remain pinned without wetting the membrane surface. Finally, if the droplets and the membrane have a weak affinity for one another the droplets will avoid attaching to the membrane or if they do attach the connection will be weak meaning that the droplets could easily become dislodged from the membrane if droplets from the crossflow sweep past or collide with the weakly attached droplets.

The optimal droplet-membrane interaction that can separate oil droplets without major fouling is the interaction described by the moderate affinity, but this interaction needs to be accompanied by favorable droplet-droplet interactions for coalescence to occur. When favorable droplet-droplet interactions are present and the droplet-membrane affinity can be classified as moderate, the scenario allows for prolonged contact between droplets allowing them to coalesce on the membrane surface until the droplets reach a critical size causing them to be swept off the membrane surface. These droplet-droplet and droplet-membrane interactions will be explained in more detail with accompanying images and videos in the following sections based on observations from the monitored membrane area throughout different tests.

4.3.3.1 Effect of SDS and MgSO₄ on oil droplet fouling behavior on uncoated Anopore membranes

Different oil droplet fouling behaviors were observed on uncoated Anopore membranes in the presence of two varying concentrations of SDS (0.1 mM in HWS-0.1 emulsion and 3 mM in HWS-3 emulsion) as well as the combination of both SDS (0.1 mM) and MgSO₄ (6.7 mM initially) in HWSS-0.1 emulsion, as shown in Figure 22.





t = 9 min

Uncoated Anopore

HWS-3



No permeation

t = 9 min



Uncoated Anopore HWS-3

Permeation

t = 9 min





t = 9 min



Permeation

t = 9 min

Figure 22: DOTM images of the membrane surface in Tests 1, 2, 3, 1f, 2f and 3f with uncoated Anopore membranes.

4.3.3.1.1 Effect of SDS

The most dramatic difference between the emulsions containing 0.1 mM SDS and those containing 3 mM SDS was the much smaller size of droplets in HWS-3 emulsions (Figure 18) caused by the lower interfacial tension in HWS-3 (18.4 mN/m versus 32.7 mN/m for HWS-0.1). There was no statistical difference between the ζ -potentials of the HWS-0.1 emulsion (-101 ± 22 mV) and the HWS-3 emulsion (-112 ± 17 mV). These results provide an explanation for the different oil droplet fouling behavior observed in the DOTM tests. Because the ζ -potential is high, the droplet-droplet interaction in both emulsions is not favorable and the frequency of droplet-droplet encounters is relatively low. If droplets in the HWS-3 emulsion do come in contact with one another, the low interfacial tension decreases the likelihood of coalescence. The droplet-droplet interaction for the HWS-3 emulsion is slightly more favorable than the HWS-3 emulsion due to a higher interfacial tension so that the energy barrier for coalescence is smaller.

Video 3 (see supplemental files and Appendix A.6 of Chapter 4, Figure 31) from 2 minutes into DOTM Test 2f shows the small droplets of the HWS-3 emulsion attaching to the uncoated Anopore membrane surface in clusters; often the oil droplets move or adjust their position on the membrane surface as new oil droplets attach. Video 3 also shows that the interior surface of the oil droplets in the clusters becomes deformed, as discussed in our previous work [3]. No coalescence on the membrane surface was observed in DOTM Test 2 (Figure 22.C) or Test 2f (Figure 22.D, Video 3 of

supplemental files and Appendix A.6 of Chapter 4, Figure 31) with HWS-3 emulsions and uncoated Anopore membranes. This can be attributed to the unfavorable dropletdroplet interactions and the moderate affinity between the droplets and the membrane surface. Whereas, coalescence was observed on the membrane surface in all DOTM tests with HWS-0.1 emulsions. The slightly more favorable droplet-droplet interactions in HWS-0.1 emulsions coupled with the moderate affinity between the uncoated Anopore membrane and the droplets in DOTM Test 1 (Figure 22.A) and Test 1f (Figure 22.B) led to the attachment of numerous droplets eventually creating more than one layer of droplets on the membrane surface wherein surrounding droplets coalesced.

The high concentrations of surfactant in HWS-3 emulsions not only prohibits surface coalescence, but also creates a high potential for precipitative fouling when divalent cations are present.

4.3.3.1.2 Effect of MgSO₄

Most produced waters are saline or brackish [33], which is why elucidating the effect of salinity on membrane fouling by emulsified oil is critical for optimizing membrane filtration of such waters. DOTM tests allowed for the visual comparison of membrane fouling by oil in the presence and in the absence of MgSO₄. The MgSO₄ concentration was increased from 6.7 mM to 42.6 mM after 10 min into the DOTM tests with HWSS-0.1 emulsions to simulate the calculated concentration polarization values.

In the presence of MgSO₄, the electrostatic charge on droplets is lower because the Debye layer is compressed at a higher ionic strength and because of the possible bridging of dodecyl sulfate ions at the oil droplet surface by Mg²⁺ cations. As a result, droplet-droplet repulsion is weaker, the equilibrium distance between two droplets becomes smaller, and droplet-droplet encounters are more likely. At the same time, MgSO₄ also decreases the interfacial tension of the emulsion (Figure 20). The lower interfacial tension should decrease the likelihood of oil droplet coalescence, but the DOTM tests with HWSS-0.1 emulsions demonstrate that the effect of lower droplet charge outweighs the impact of the lower interfacial tension. This is evidenced by the rapid coalescence between droplets that come in contact with one another in Video 4 (see supplemental files and Appendix A.6 of Chapter 4, Figure 32) and the massive oil film formation shown in Video 6 (see supplemental files and Appendix A.6 of Chapter 4, Figure 34).

DOTM tests illustrate that the membrane can ensure prolonged contact between attached droplets, and in the case of filtration tests with HWSS-0.1 emulsions the extended contact promotes droplet coalescence due to the high droplet-droplet affinity. With electrostatic repulsion suppressed, the lower droplet stability (~0.1 mM SDS) and longer contact time lead to rapid coalescence and the possible formation of an oil film.

HWSS-0.1 oil droplets and the uncoated Anopore membrane used in DOTM Test 3 (Figure 22.E) had a moderate affinity that allowed the droplets to attach to the membrane thus promoting the frequency of encounters with other droplets, and this,

coupled with the favorable droplet-droplet interactions in the HWSS-0.1 emulsion, allowed for coalescence on the membrane surface. The additional MgSO₄ added to the emulsion after 10 min promoted more coalescence on the membrane surface as seen in Video 4 (see supplemental files and Appendix A.6 of Chapter 4, Figure 32). Due to the moderate affinity between the droplets and the uncoated Anopore membrane, droplets stayed sufficiently long at the membrane surface to coalesce until reaching a critical size when a droplet is typically removed by the crossflow shear [3]. Oil films were not formed in DOTM Test 3 (Figure 22.E) or Test 3f (Figure 22.F) with uncoated Anopore membranes and HWSS-0.1 emulsions.

4.3.3.1.3 Relative importance of the effects of salinity and surfactant concentration

The relative importance of salinity and surfactant concentration on the fouling behavior of oil droplets can be rationalized in terms of the droplet-droplet and droplet-membrane interactions. Droplet-droplet interactions affect the likelihood of droplet-droplet encounters, both in the emulsion and on a surface. For micron-size and larger droplets, these interactions are governed by hydrodynamics of the flow and electrostatic forces. The latter depend on the droplet charge and the salinity of the emulsion. Higher ionic strength leads to lower ζ -potential increasing the frequency of droplet-droplet encounters. Once droplets are in contact, the coalescence likelihood and dynamics are governed by the interfacial tension between the droplets and the surrounding liquid, which is largely a function of surfactant concentration.

DOTM tests showed that salinity had a larger impact on the oil droplet fouling behavior than the surfactant concentration. DOTM tests with saline emulsions produced the most egregious forms of membrane fouling by creating massive oil films. DOTM tests with divalent saline emulsions containing high concentrations of SDS were not possible due to the precipitation caused by this ionic surfactant. Figure 23 illustrates the four domains in the salt-surfactant space that correspond to different patterns of membrane fouling by surfactant-stabilized oil droplets in the presence of ionic surfactant.



MgSO₄ concentration, mM

Figure 23: Schematic diagram illustrating the state of emulsion as a function of SDS and MgSO₄ concentrations.

4.3.3.2 Effect of permeate flux on oil droplet fouling behavior on uncoated Anopore membranes

The main effect of permeate flux on membrane fouling by oil droplets is the added drag force that draws the oil droplets to the membrane and, for sufficiently large ratios of droplet size to pore size, increases droplet's residence time at the membrane surface. Figure 22 shows that in the three DOTM tests with permeate flux (Tests 1f, 2f, and 3f, Table 6) more droplets attached to the membrane in the first minutes of filtration than in counterpart tests with the same emulsions but in the absence of permeation (Tests 1, 2, 3, Table 6). Moreover, in Tests 1f (with HWS-0.1) and 3f (with HWSS-0.1) coalescence occurred much sooner than in the control tests without permeate flux.

In the absence of permeate flux, droplets often attached to the membrane and shortly thereafter detached or migrated along the membrane surface in the direction of the crossflow shear that was not compensated by the force of the permeate flux. Another recurring behavior pattern in the absence of permeate flux was droplet removal by crossflow shear immediately upon coalescence when the newly formed larger droplet was adjusting its point of contact with the membrane.

The three characteristic stages of membrane fouling (droplet attachment and clustering, droplet deformation, and droplet coalescence [3]) were more clearly defined in the presence of permeate flux. As the membrane surface becomes covered with oil droplets the locations through which water can permeate the membrane decrease, but

in the DOTM system the permeate flux is held constant by a peristaltic pump meaning that the water passing through the limited pores of the membrane must be flowing at a higher velocity to sustain the constant flux. The increased velocity of water passing though the membrane in turn increases the force on the droplets pinned at the membrane surface, which explains why the deformation stage is observed much more extensively in tests with permeate flux.

Droplet coalescence is a function of drainage time and residence time, where drainage time represents the time needed for the thin film of liquid between two droplets to be removed prior to coalescence, and residence time represents the contact time between droplets. The increased local velocity of water permeating through the membrane creates highly deformed droplets; thus decreasing the drainage time for droplet coalescence. At the same time, residence time is increased due to the permeate drag. The aggregate effect should be an earlier onset of coalescence as was indeed observed in DOTM tests with permeate flux.

In DOTM Test 2f (Figure 22.D), droplets of the HWS-3 emulsion were seen rapidly attaching to the uncoated Anopore membrane at the beginning of the filtration experiment, and within 7 minutes into the test the membrane was completely covered by small droplets. A large droplet that formed a second layer on top of micron-sized droplets pinned at the membrane surface was also observed (Figure 24.A). Some small droplets were seen under the edge of the large droplet; this positioning allowed the small droplets to avoid the shear force created by the crossflow drag. In a few areas

the large droplet was attached directly to the membrane surface either because it pushed the micron-sized droplets out of the way or because it coalesced with the droplets. However, these scenarios are speculative as the large droplet attached outside of the original monitored membrane area. Another instance of small droplets pinned between a large coalesced droplet and the membrane surface due to permeation was observed in Test 3f (Figure 24.B).



Figure 24: DOTM images showing a number of smaller droplets pinned between the membrane surface and an overhanging large oil droplet.

4.3.3.3 Effect of SDS and MgSO₄ on oil droplet fouling behavior on negatively charged nanofiltration membranes

Membrane characteristics - contact angle and ζ -potential - have a considerable effect on the surface coalescence of droplets. The polyanion-terminated membrane (Anopore/[PSS/PAH]_{4.5}) can be classified as a superoleophobic membrane based on hexadecane contact angles (\geq 160°) in all three of the aqueous solutions (Figure 21.A). The ζ -potential of the Anopore/[PSS/PAH]_{4.5} membrane did not show a statistically significant dependence on SDS concentration: $\zeta = -28.1 \pm 5.8$ mV in 0.1 mM SDS and ζ = -27.7 ± 3.7 mV in 3 mM SDS. DOTM tests with Anopore/[PSS/PAH]_{4.5} membranes revealed droplet coalescence on the membrane surface. However, most droplet-membrane collisions did not lead to attachment events consistent with results of contact angle measurements.




4.3.3.3.1 Effect of SDS

Immediate attachment (within seconds) of droplets was observed in DOTM Test 7 (Figure 25.A), where the negatively charged Anopore/[PSS/PAH]_{4.5} membrane allowed negatively charged droplets to foul the membrane surface. Despite electrostatic repulsion between droplets and the membrane, the relatively low contact angle of oil on the surface of Anopore/[PSS/PAH]_{4.5} ensures prolonged contact time between droplets at the membrane surface allowing for eventual, but not immediate coalescence. Droplets of the HWS-0.1 emulsion formed more than one layer on the membrane surface even when some areas of the membrane were free of oil. This possibly illustrates that the droplet-droplet interaction was more favorable than the dropletmembrane interaction. Ten minutes into the test, droplets in the secondary layers of fouling coalesced. After 18 min, droplets from the first layer coalesced directly on the membrane surface and then continued to coalesce into an oil film.

The weak affinity between HWS-3 droplets and the negatively charged and superoleophobic Anopore/[PSS/PAH]_{4.5} membrane in DOTM Test 8 coupled with the unfavorable droplet-droplet interactions needed for coalescence led to large portions of the membrane remaining oil-free, although a few instances of droplet coalescence on the membrane surface were observed (Figure 25.B). The higher stability of HWS-3 emulsion with respect to HWS-0.1 emulsion (σ = 18.4 mN/m versus 32.7 mN/m) could explain the difference between fouling behaviors observed in DOTM Tests 7 and 8.

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4.3.3.3.2 Effect of MgSO₄

DOTM Test 9 employed the negatively charged, superoleophobic

Anopore/[PSS/PAH]_{4.5} membrane and the HWSS-0.1 emulsion with its relatively weekly charged droplets. Both the membrane and the droplets were negatively charged. Fewer droplets attached to the Anopore/[PSS/PAH]_{4.5} membrane in DOTM Test 9 (Figure 25.C) and the coalescence that took place occurred between a droplet pinned to the membrane surface and another droplet passing by in the crossflow. The coalescence occurred almost instantaneously between the two droplets that came in contact, and even though the membrane helped to facilitate the coalescence by keeping one of the droplets stationary it did not support droplet-droplet interactions where both droplets are attached to the membrane surface. Once the additional MgSO₄ was added to the HWSS-0.1 emulsion, it caused some of the droplets attached to the membrane surface to coalesce (Figure 27.B). As the test continued more coalescence was observed, and after 53 minutes a survey of the membrane showed that the majority of the surface was covered by large surface area oil films. It took 48 minutes longer for the Anopore/[PSS/PAH]_{4.5} membrane to become predominately covered with oil films by the HWSS-0.1 emulsion than it did for the Anopore/[PSS/PAH]₄ membrane in Test 6 (see section 3.3.4.2).

4.3.3.4 Effect of SDS and MgSO₄ on oil droplet fouling behavior on positively charged nanofiltration membranes

The polycation-terminated membrane (Anopore/[PSS/PAH]₄) can be classified as moderately oleophobic based on its contact angles ($106^{\circ} \le \theta \le 127^{\circ}$) with hexadecane in all three of the aqueous solutions. The ζ -potential of the Anopore/[PSS/PAH]₄ membrane decreased from 38.0 ± 2.3 mV to 27.8 ± 0.8 mV as the concentration of SDS increased from 0.1 mM to 3 mM in the aqueous solution that the membrane was soaked in prior to the measurements. With its positive charge, the Anopore/[PSS/PAH]₄ membrane had high affinity for the negatively charged droplets. DOTM tests with Anopore/[PSS/PAH]₄ membranes showed faster fouling including an earlier onset for coalescence as well as the formation of oil films in Test 5 (see section 3.3.4.1) and Test 6 (see section 3.3.4.2) (Figure 26).



Figure 26: DOTM images of the membrane surface in Tests 4, 5 and 6 with Anopore/[PSS/PAH]₄ membranes.

4.3.3.4.1 Effect of SDS

DOTM Test 5 with a positively charged Anopore/[PSS/PAH]₄ membrane and a negatively charged HWS-3 emulsion revealed egregious fouling of the membrane (Figure 26.B) despite the relatively high stability of the emulsion (σ = 18.4 mN/m ; ζ_{drop} = -112 ± 17 mV). Video 5 (see supplemental files and Appendix A.6 of Chapter 4, Figure 33), taken 11 minutes into DOTM Test 5, shows that the oil film grew at a much slower rate than in DOTM Test 6 (see section 3.3.4.2, Video 6 in the supplemental files and Appendix A.6 of Chapter 4, Figure 34), which could be attributed to the difference in droplet-droplet interactions in these emulsions. In DOTM Test 5, the membrane became completely covered with an oil film after 72 min; whereas the membrane in DOTM Test 6 (see section 3.3.4.2) was completely covered with an oil film after only 3 min. Often crevasses were observed between neighboring oil films on the membrane surface through which water could still permeate the membrane (Figure 27).

In DOTM Test 4, attachment of the negatively charged droplets to the positively charged Anopore/[PSS/PAH]₄ membrane was expected, but this test seemed to be an outlier as very little attachment was observed (Figure 26.A). The high ζ -potential of the HWS-0.1 emulsion, which limits the frequency of encounters and the contact time between droplets must have lowered the droplets' propensity to coalesce. The hexadecane contact angle was 127° for an Anopore/[PSS/PAH]₄ membrane submerged in an aqueous solution of 0.1 mM of SDS, pointing to a more oleophobic surface than that of the same membrane in aqueous solutions of either 3 mM SDS (106°) or 0.1 mM SDS

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with 6.7 mM MgSO₄ (119°). The increased oleophobicity of the membrane in the HWS-0.1 emulsion could also explain the lack of droplet attachment observed in Test 4. Another possible explanation of the lack of droplet attachment to the membrane in the observed area could be a higher local charge of the PEM coating.

4.3.3.4.2 Effect of MgSO₄

In DOTM Test 6, the negatively charged droplets attached to the positively charged Anopore/[PSS/PAH]₄ membrane (Figure 26.C). The low ζ-potential of the HWSS-0.1 emulsion and longer contact time overshadowed the impact of the low interfacial tension of the HWSS-0.1 emulsion and led to droplet coalescence within the first minute of the DOTM test. Video 6 (see supplemental files and Appendix A.6 of Chapter 4, Figure 34) illustrates the sequence of events where initially the oil droplets attach to the membrane surface and some droplets swirl in the flow field perturbed by the presence of larger attached droplets before attaching and coalescing across the entire monitored membrane area. At ~3 minutes into DOTM Test 6, a survey of the membrane surface showed that the majority of the membrane was covered by contiguous large surface area oil films. Figure 27.C and D depict the oil film growth that occurred in a different location on the membrane surface at five and six minutes into Test 6. The DOTM test that revealed the most egregious form of fouling from extensive oil films was Test 6 with the Anopore/[PSS/PAH]₄ membrane and HWSS-0.1 emulsion due to both the very high affinity between the droplets and the membrane as well as favorable droplet-droplet interactions.



Figure 27: A, B and C depict oil films separated by crevasses through which water could permeate the membrane (if permeation was allowed). D captures the moment 1 min after C where the oil film grew to cover the entire monitored membrane area trapping some water around two small droplets pinned between the membrane surface and the oil film.

4.4 Conclusions

The study presents results of direct visualization study of UF and NF membrane fouling by emulsified oil stabilized by an anionic surfactant (SDS) in the presence of divalent counterions (Mg²⁺). Three emulsions of different stabilities were characterized in terms of droplet size distribution, interfacial tension and ζ -potential. Optically transparent NF membranes were prepared by coating a UF support (Anopore membranes with d_{pore} = 0.02 µm) with polyelectrolyte multilayers. Hexadecane contact angles and surface charge were determined for each membrane type. Distinct fouling behaviors were observed and interpreted in terms of droplet-droplet and droplet-membrane interactions. Divalent cations have a dramatic effect on droplet coalescence and, by extension, on membrane fouling by emulsified oil. While MgSO₄ decreased the interfacial tension of the HWSS-0.1 emulsion; the concomitant decrease in the ζ -potential appeared to be a more dominant effect, leading to the overall increase in the droplet-droplet affinity and more facile droplet coalescence at the membrane surface. Fouling was found to be a strong function of the membrane type. The most egregious fouling was observed in tests with the positively charged and less oleophobic Anopore/[PSS/PAH]₄ membrane challenged by a HWSS-0.1 emulsion: in this system, the formation of extended oil films could be attributed to both the favorable droplet-droplet interactions and a high affinity between the droplets and the membrane. Tests with the negatively charged and superoleophobic Anopore/[PSS/PAH]_{4.5} membrane challenged by a HWS-3 emulsion showed minimal membrane fouling due to the repulsive force between the droplets and the membrane coupled with unfavorable droplet-droplet interactions. Permeate flux

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increased the attachment of droplets to the membrane surface often leading to more than one layer of oil droplets. Coalescence was promoted under conditions of moderate affinity between droplets and membranes; under these conditions oil droplets could reach a critical size and be removed by the crossflow shear prior to forming a contiguous film on the membrane surface. In summary, droplet stability, electrical charge and a membrane's affinity for oil together governed oil fouling behavior. Manipulation of the ionic composition of the dispersed phase is suggested as a means of controlling membrane fouling by emulsified oil. APPENDIX

APPENDIX A

Supplementary Material: Membrane separation of saline oil-water emulsions:

Effects of anionic surfactants, divalent counterions and membrane surface

chemistry





Figure 28: Volume-based droplet size distributions for HWS-0.1 and HWSS-0.1 emulsions. The HWS-3 emulsion's size distribution could not be determined as the obscuration ratio was not met during the Mastersizer testing.

A.2 Thin film model of concentration polarization

The thin film model was used to estimate the concentration of MgSO₄ at the membrane surface, C_m [34]:

$$\frac{C_m - C_p}{C_f - C_p} = \exp\left(\frac{J}{k}\right) \tag{A-1}$$

where C_p , C_f and C_m are the concentrations of MgSO₄ in the permeate, in the bulk feed, and in the portion of the feed directly adjacent to the membrane, respectively. The mass transfer coefficient, k, was estimated using the Sherwood correlation for MgSO₄ in the membrane cell channel [9]. *J* represents the permeate flux.

$$\frac{C_m}{C_f} = \exp\left(\frac{J}{k}\right) \tag{A-2}$$

$$k = \frac{D}{\delta}$$
(A-3)

where δ represents the boundary layer thickness, and *D* is the diffusion coefficient (*D* is 8.5·10⁻¹⁰ m²/s for MgSO₄ in water) [26].

The concentration polarization factor, PF, was calculated in eq. (A-4) for MgSO₄

$$PF_{MgSO_4} = \left(\frac{C_m}{C_f}\right)_{MgSO_4} = \exp\left(\frac{J\delta}{D_{MgSO_4}}\right)$$
(A-4)

The natural log of eq. (A-4) resulted in eq. (A-5)

$$\ln PF_{MgSO_4} = \frac{J\delta}{D_{MgSO_4}} \tag{A-5}$$

The concentration polarization factor was also determined for SDS in eq. (A-6)

$$PF_{SDS} = \left(\frac{C_m}{C_f}\right)_{SDS} = \exp\left(\frac{J\delta}{D_{SDS}}\right)$$
(A-6)

The natural log of eq. (A-6) resulted in eq. (A-7)

$$\ln PF_{SDS} = \frac{J\delta}{D_{SDS}}$$
(A-7)

Eq. (A-8) is the result of dividing eq. (A-5) by eq. (A-7)

$$\frac{\ln PF_{MgSO_4}}{\ln PF_{SDS}} = \frac{\frac{J\delta}{D_{MgSO_4}}}{\frac{J\delta}{D_{SDS}}}$$
(A-8)

A simplified version of eq. (A-8) is eq. (A-9)

$$\frac{\ln PF_{MgSO_4}}{\ln PF_{SDS}} = \frac{D_{SDS}}{D_{MgSO_4}}$$
(A-9)

Solving for the concentration polarization factor of SDS resulted in eq. (A-10)

$$PF_{SDS} = \exp\left(\frac{D_{MgSO_4}}{D_{SDS}}\right) PF_{MgSO_4}$$
(A-10)

t = 0 t = 1 min t = 10 min $\theta = 136^{\circ}$ $\theta = 122^{\circ}$ $\theta = 116^{\circ}$

A.3 Contact angle measured for hexadecane droplet on membrane surfaces

Figure 29:Evolution of a hexadecane droplet on the surface of an Anopore
membrane ($d_{pore} = 0.02 \ \mu m$) coated by a [PSS/PAH]₄ polyelectrolyte
multilayer and submerged in an aqueous solution of 3 mM of SDS.
The contact angle reached a steady-state value of 116° after 10 min.

A.4 Calculation of the Kolmogorov length scale

The following values were used as inputs:

- Impeller diameter, D = 0.05 m
- Density of the emulsion, $\rho = 997 \text{ kg/m}^3$ (approximated by that of water)
- Viscosity of the emulsion, $\mu = 8.94 \cdot 10^{-4}$ kg/m/s (approximated by that of water)
- Emulsion volume, V = 1 L
- Impeller constant, K_T = 1.26 (value for a pitched-blade turbine (45°) with 4 blades)
- Rotational speed, n = 1000 rpm
- Mixing time, *t* = 1200 s

The calculated values are:

- Reynolds number for the impeller: $N_{Re} = D^2 n \rho / \mu = 46467$
- Mixing power: $P = K_T n^3 D^5 \rho = 1.82 \text{ W}$
- Mean velocity gradient: $\bar{G} = \sqrt{P/(\mu \cdot V)} = 1425.8 \text{ s}^{-1}$
- Energy dissipation rate: $\varepsilon = P/(\rho \cdot V) = 1.82$ W/kg
- Kolmogorov length scale: $\eta = (\mu^3/(\rho^3 \cdot \varepsilon))^{1/4} = 25078$ nm

A.5 Calculation of the concentration of SDS in the bulk and on the oil-water interface

The amount of surfactant adsorbed Γ (moles per unit area), is given by the Gibbs adsorption isotherm:

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{dlogC}$$

where γ is the interfacial tension (N/m) and *C* is the concentration of the surfactant in the dissolved phase.



Figure 30: Interfacial tension vs log C dependence of SDS.

Γ can be calculated from the linear portion of the Γ versus *logC* dependence for concentrations approaching the critical micelle concentration. The experimental data and the fit are shown in Figure 30.

The calculation gives $\Gamma = 5.27 \cdot 10^{-6}$ (mole/m²), which translates into ~0.32 nm² of droplet surface area per one adsorbed SDS molecule. This is close to the cross-sectional area of the sulfate group, which is ~0.4nm² (e.g., [35]). Thus one can assume that in our system, SDS molecules at the hexadecane droplet surface are oriented in the direction normal to the droplet surface.

With the droplet-size distribution available (and after converting it from number-based to surface are based), one can use the area-per-molecule value to calculate the relative abundance of SDS molecules in the adsorbed state. For the HWS-0.1 emulsions (i.e., with SDS contents of 0.1 mM and hexadecane contents of 1mL/L), the concentration of SDS in the adsorbed state is $4.5 \cdot 10^{-4}$ mM. Thus, only 0.45% of SDS molecules are on the hexadecane surface. In other words, for every SDS molecule on the droplet surface, there are ~223 SDS molecules in the aqueous phase.

A.6 Video evidence of oil droplet behavior at the membrane surface

The following figures represent videos that can be viewed in the supplemental files of the electronic version of this Dissertation.



Figure 31: DOTM Test 2f with an uncoated Anopore membrane and HWS-3 emulsion.

Figure 31 (Video 3) from 2 minutes into DOTM Test 2f shows the small droplets of the HWS-3 emulsion attaching to the uncoated Anopore membrane surface in clusters; often the oil droplets move or adjust their position on the membrane surface as new oil

droplets attach. Video 3 also shows that the interior surface of the oil droplets in the clusters become deformed.



Figure 32: DOTM Test 3 with an uncoated Anopore membrane and HWSS-0.1 emulsion.

Figure 32 (Video 4) depicts DOTM Test 3 with an HWSS-0.1 emulsion and uncoated Anopore membrane to demonstrate that the effect of lower droplet charge outweighs the impact of the lower interfacial tension, which is evidenced by the rapid coalescence between droplets that come in contact with one another.



Figure 33: DOTM Test 5 with a positively charged Anopore/[PSS/PAH]₄ membrane and HWSS-0.1 emulsion.

Figure 33 (Video 5), taken 11 minutes into DOTM Test 5 with a positively charged Anopore/[PSS/PAH]₄ membrane and a negatively charged HWS-3 emulsion shows that

the oil film grew at a much slower rate than in DOTM Test 6 (see Video 6).



Figure 34: DOTM Test 6 with a negatively charged Anopore/[PSS/PAH]_{4.5} membrane and HWSS-0.1 emulsion.

Figure 34 (Video 6) illustrates the sequence of events from DOTM Test 6 with an HWSS-0.1 emulsion and a negatively charged Anopore/[PSS/PAH]_{4.5} membrane where initially the oil droplets attach to the membrane surface and some droplets swirl in the flow field perturbed by the presence of larger attached droplets before attaching and coalescing across the entire monitored membrane area.

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CHAPTER FIVE

Overarching conclusions

The comprehensive literature review provided a broad overview of the state of knowledge concerning membrane-based separations of oil-water emulsions, and revealed some disagreement and gaps in the current understanding of membrane fouling by emulsified oil. The need for more information and a detailed framework for describing oil droplet behavior at the membrane surface motivated the present work. The project explored membrane fouling by model oil-water emulsions with hexadecane stabilized by an anionic surfactant (SDS) in the presence or absence of divalent counterions (Mg²⁺). Two microfiltration (MF), one ultrafiltration (UF) and two nanofiltration (NF) membranes with different surface chemistries and pore sizes were employed. All membranes were optically transparent in the presence of aqueous solutions making them suitable for the Direct Observation Through the Membrane (DOTM) method. The two MF membranes were Anopore (d_{pore} = 0.2 µm) and PCTE $(d_{pore} = 5 \ \mu m)$, and the one UF membrane was Anopore $(d_{pore} = 0.02 \ \mu m)$. Transparent NF membranes were prepared by coating a UF support (Anopore membranes with $d_{pore} = 0.02 \ \mu m$) with polyelectrolyte multilayers.

The study described in Chapter 3 is the first application of a direct visualization technique to capture real-time images of a membrane surface under conditions of fouling by emulsified oil in the presence of crossflow. DOTM experiments with

hexadecane-water-SDS emulsions revealed three characteristic stages of membrane fouling by oil: 1) droplet attachment and clustering, 2) droplet deformation, and 3) droplet coalescence. The combination of qualitative DOTM results and quantitative force balance analysis for an oil droplet pinned at the entry to a pore on the membrane surface indicated that membrane fouling by emulsified oil is controlled by droplet coalescence and crossflow shear: the transport of oil to the membrane surface by the permeate flow is balanced by the shear-induced removal of the droplets that coalesce to exceed a critical size.

The study presented in Chapter 4 interpreted the distinct fouling behaviors observed during DOTM tests in terms of droplet-droplet and droplet-membrane interactions. Divalent cations were shown to have a dramatic effect on droplet coalescence and membrane fouling by emulsified oil. While MgSO₄ decreased the interfacial tension of the HWSS-0.1 emulsion; the concomitant decrease in the ζ -potential appeared to be a dominant effect, leading to the overall increase in the droplet-droplet affinity and more facile droplet coalescence at the membrane surface. Fouling was also found to be a strong function of the membrane type. The most egregious fouling was observed in tests with the positively charged and less oleophobic Anopore/[PSS/PAH]₄ membrane challenged by a HWSS-0.1 emulsion due to both the favorable droplet-droplet interactions and a high affinity between the droplets and the membrane. Tests with the negatively charged and superoleophobic Anopore/[PSS/PAH]_{4.5} membrane challenged by a HWS-3 emulsion showed minimal membrane fouling due to the repulsive force

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between the droplets and the membrane coupled with unfavorable droplet-droplet interactions.

The results presented in Chapters 3 and 4 show that droplet stability, electrical charge and a membrane's affinity for oil together govern oil fouling behavior. The study also points to the possibility of managing membrane fouling by oil via the manipulation of the ionic composition of the dispersed phase. By promoting droplet-droplet coalescence on the membrane surface under appropriate hydrodynamic conditions, one can enable the removal of oil droplets by the crossflow shear prior to the undesirable formation of a contiguous film on the membrane surface.

CHAPTER SIX

Future work: Expounding upon the understanding of oil fouling behavior

There are many opportunities to continue this research and build upon the important results presented in this study. Some of the proposed opportunities for future work adjust characteristic parameters of either the emulsion or the membrane used in the filtration tests; while other options for future work involve the design and construction of new DOTM systems capable of different types of analysis.

6.1 Proposed experiments with the current DOTM system

Table 7 summarizes proposed experiments that use the current DOTM system to gain further insights into the oil fouling behavior during crossflow filtration tests with either simple model oil-water emulsions or complex industrial oily wastewater. **Table 7:**Proposed experiments with the current DOTM system, and questions that
the experiments aim to answer.

Feed emulsion or membrane to	Questions the experiments
Model oil water emulsion with	Con the oil fouling behavior of these
monovalont salts (o.g. NaCl)	omulsions ho tostod in the absence of
	provinitative fouling?
	Doos the addition of monovalent salts
	decrease the interfacial tension of emulsions
	in a similar way to divalent salts, and if so is
	coalescence still determined by the Z_{-}
	potential of the droplets?
Model all water emulsion with model	What is the impact of the much higher salinity
sogwater (o.g. Instant Ocean sog salt	of societation on droplet stability and
mix)	coalescence near membrane surfaces?
Model ail water amulsion with non	Are emulsions stabilized by pen ionic
ionio surfactante	Are emulsions stabilized by non-ionic
	Surfactants more likely to coalesce due to the
	charged oil droplets?
Model all water emulsion with alls of	For all with lower viscosition introdroplet flow
varving viscosities (e.g. light crude oil	becomes important leading to a slip and lower
and boow crude oil)	drag force on the droplet. What is the impact
	of oil's viscosity on the droplet coalescence at
	the membrane surface?
Model oil-water emulsion in the	How do Pickering emulsions foul
presence of suspended colloids	membranes?
Produced water	Are the results from the simple model oil-
	water emulsions canable of representing the
	observed oil fouling behavior of produced
	water?
Phase inversion membranes with	Is the observed oil fouling behavior altered
complex pore space (if they can be	when the membrane porosity is dramatically
purchased or produced to be	increased and the pores are not cylindrical,
transparent when wet)	thus limiting the ability for oil droplets to
	completely plug the entrance to pores?
Membranes with slit pores	Is the observed oil fouling behavior altered
	when the slit membrane pores are oriented in
	the parallel direction vs the perpendicular
	direction with respect to the crossflow? Does
	one orientation (parallel or perpendicular) limit
	the ability for oil droplets to completely plug
	the entrance to the slit pores allowing for
	higher sustained water fluxes?

6.2 Proposed experiments with a new DOTM system capable of higher pressures

Table 8 lists a set of proposed experiments that would only be possible if a new DOTM setup could be built to withstand the transmembrane pressures needed for nanofiltration (NF) tests with PEM-coated Anopore membranes.

Table 8:Proposed experiments with a new DOTM system capable of high
pressures needed for NF and questions that the experiments aim to
answer.

Proposed experiments with a new DOTM system capable of high pressures needed for NF	Questions the experiments aim to answer
Redo our earlier studies with oil- water emulsions and PEM-coated Anopore membranes (or test those proposed above for the current DOTM system)	Our earlier studies in the absence of permeate flux showed that both highly favorable and highly unfavorable droplet- membrane interactions prevent coalescence and that the intermediate affinity encourages surface coalescence. Is this statement valid in the presence of permeate flux?
Model oil-water emulsion with MgSO ₄ and SDS	Does the actual concentration polarization layer affect the oil fouling behavior in the same way as the DOTM tests with simulated concentration polarization revealed?
Separation tests with model oil-water emulsions using crossflow rates > 0.1m/s for MF, UF and NF membranes	What is the role of the crossflow rate in limiting the attachment of oil droplets to the membrane surface relative to the roles of other factors (oil-membrane affinity, electrical charge, droplet stability)?

6.3 Proposed design for a DOTM system capable of imaging nano-emulsions

Design a DOTM cell/microscope setup capable of visualization work with nanoemulsions either using higher powered objective lens or fluorescent markers. A higher powered objective lens will have a different focus plane than the objective lenses currently employed in the DOTM system. This new focus plane might not be able to visualize the fouling layer, so an alternative visualization technique would be to use fluorescent markers for the oil droplets in an emulsion. Nano-emulsions are not visible with the current DOTM system, but the interactions of these small droplets might be more important than the interactions between micron-sized droplets. Proposed experiments with nano-emulsions could provide the possibility to observe the following:

- details of droplet behavior on the verge of coalescence (e.g. drainage of the water film between coalescing droplets)
- droplet break-up within a pore where a portion of the droplet permeates the membrane while another portion of the droplet is swept off by the shear of the crossflow
- details of droplet permeation through a membrane pore

6.4 Proposed membrane cleaning mechanisms

This work has helped to elucidate the mechanisms of membrane fouling by oil-water emulsions and recommend alternatives to modify the properties of either the emulsion or the membrane to limit the egregious forms of membrane fouling. There are two approaches that limit the membrane fouling and sustain the water throughput. The first approach involves modifying either the emulsion or the membrane to produce a situation where both the droplets and the membrane are highly charged (both positive or both negative) so that the affinity between the droplets and the membrane is very weak. This approach will limit droplet attachment to the membrane due to the repulsive forces, thus allowing for sustained flux rates. The second approach involves modifying either the emulsion or the membrane to ensure a moderate affinity between the droplets and the membrane; thus allowing for droplets to attach to the membrane; if the dropletdroplet interaction is favorable, the droplets will coalesce until they reach a critical droplet size, at which point they will be removed from the membrane surface by the crossflow shear. These two approaches should limit the egregious forms of membrane fouling by emulsified oil, but there will still be some oil that attaches to the membrane. Table 9 proposes possible membrane cleaning mechanisms that could help to further minimize fouling. The DOTM system could be used to visualize the effectiveness of the membrane cleaning mechanisms in real time.

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Table 9:Proposed experiments to test membrane cleaning mechanisms to further
minimize membrane fouling, and questions that the experiments aim to
answer.

Proposed experiments to test	Questions the experiments
membrane cleaning mechanisms to	aim to answer
further minimize membrane fouling	
Pulsating crossflow through the	Would the constantly changing flow patterns
filtration cell	cause the oil droplets attached to the
	membrane surface to become destabilized
	and eventually detach? Would the disruption
	of droplet-membrane interactions be more
	pronounced for superoleophobic
	membranes?
Separation tests with model oil-water	Do increased crossflow rates limit the
emulsions using crossflow rates >	attachment of oil droplets to the membrane
0.1m/s for MF, UF and NF	surface during the filtration due to the
membranes	increased shear? Do higher crossflow rates
	allow for droplet coalescence on the
	membrane surface?
Periodic membrane flushes with	Can Osorb Media (or other absorbent media)
Osorb Media or other absorbent	be added to the water used during periodic
media	membrane cleanings to absorb the oil both
	on the membrane surface and within the
	membrane pores, or does the media remain
	on the membrane surface creating a
	secondary fouling issue?