Nano-Enhanced Composite Membranes for Water Desalination

A Senior Project

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By

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ABSTRACT

In theory single walled carbon nanotubes (SWCNT) will aid in ion rejection due hydrophobicity and smoothness of the SWCNT. An efficient means of water desalination utilizing SWCNT in a membrane seems plausible. A lyotropic liquid crystal (LLC) solution was made with a synthesized polymerizable surfactant methacryloxy ethyl hexadecyl dimethyl ammonium bromide (C16MA) to help with vertical alignment of SWCNT. Due to SWCNT lack of solubility and tendency to agglomerate in water, a dispersion performed using an inert surfactant centrimonium bromide (CTAB) to make sure that the SWCNT were homogeneously dispersed in the solution without altering the hexagonal packing factor of the LLC, while keeping the viscosity of the solution low. To make sure that the right viscosity was achieved, viscometer testing indicating the solution of 52 wt-% had the optimal viscosity. Moreover, polarized optical microscopy indicated that the 52 wt-% LLC was the critical concentration for the LLC to enter the hexagonal liquid crystal phase. The ultimate goal was then to lock the SWCNT into the hexagonal phase of the LLC by UV-curing the solution unto a polyether sulfone membrane to produce a nano-enhanced composite membrane. Desalination efficiency testing was then performed to determine the ion rejection rate of the membranes, however results were indicative that further improvements are necessary for the solution to properly adhere to the membrane.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

Table of Figures

1. INTRODUCTION

The problem being addressed in this project is building up the desalination project together with other students in the chemistry department by synthesizing polymer scaffold to be used to produce the nano-composite.

1.1 Stakeholders

The stakeholders for this project are primarily the people affected by water shortage that will be able to benefit from this technology. Moreover, one of the primary goals of the project is to produce a technology that is more efficient and environmentally friendly than current ones. Therefore, considering the current environmental conundrum that humanity is facing, producing a more green technology seeks to benefit the environment as well. However, one should use caution dealing with nano materials, as their health impacts are relatively unknown, even though carbon nanotubes are inert. Moreover, desalination technology possesses potential risk of altering the environment if this technology is used to change the salinity around the areas of water desalination plants. Other stake holders include National Science Foundation who is sponsoring this project, and the students and faculty involved.

1.2 Broader Impact

Purification of water is quickly becoming one of the most pressing issues in environmental engineering and science. Predictions state that by 2030 one third of the world population will be living in river basins of developing countries facing significant water stress. According to the UN 7 billion people in 60 countries will be facing water scarcity by 2050 [1]. As a result intensive effort is underway to develop more efficient and reliable water purification technology to avert this impending disaster. Different approaches have been made to try and solve this dilemma, however, seawater and brackish water seem to hold the most promise since they account for approximately 98% of all the water on earth [1].

The use of membranes could offers a more advanced and environmentally friendly approach to water desalination process; conventional separation technologies such as distillation and evaporation typically suffer from high cost and the need for chemical treatment [2]. Current membranes for separation are based on reverse osmosis (RO), where the advantages are low operating temperature, low energy consumption, and high filtration capacity. The drawback of osmosis membranes by themselves is that their energy consumption is still not low enough to make the technology feasible. Furthermore, the membranes suffer from low chlorine resistance and low antifouling, which shortens the lifetime of the membranes and decreases its overall performance. However, nano-technology, specifically carbon nanotubes (CNT) shows great promise at alleviating this issue by offering ultrahigh water flux, as well as mechanical stability for the membranes. This project will primarily dealing with building up the desalination system, manufacture the membranes as well as optimizing the polymerization condition.

2. BACKGROUND

2.1 Introduction

Purification of water is quickly becoming one of the most pressing issues in environmental engineering and science. As previously mentioned predictions state that by 2030 one third of the world population in will be living in river basins of developing countries facing significant water stress, and according to the UN 7 billion people in 60 countries will be facing water scarcity by 2050 [1]. However, even now many arid regions are suffering from water shortage due to lack of direct access to any surface water source such as a lake or river basins. As a result intensive effort is underway to develop more efficient and reliable water purification technology to avert this impending disaster. Different approaches have been made to try and solve this dilemma, where the technology needs to be sufficient enough to filter seawater since it account for approximately 97.2% of all the water on earth [1].

Desalination or distillation of water is perhaps one of the earliest forms of water treatment and is still frequently used today. Desalinated water is produced by either using brackish water, which has salinity around 10,000 mg salt/L, or seawater, which have a salinity ranging from 30,000 to 44,000 mg/L [3]. Normal drinking water should have a salinity less than 1000 mg/L to be safe to drink, however this is considered a maximum and in most metropolitan areas the range is typically between 100-400 mg/L. While brackish water allows for cheaper desalination, it's unlikely to be a main source of desalinated water as it makes up less than 1% of the world's water. The world's ocean makes up 97.2% of the planets water, but the high salinity of makes it expensive to desalinate [1]. However, climate change and pollution increases demands for sustainable, long-term water demand, thus the necessity for more sophisticated water desalination technology.

Currently two main methods for desalinating water are being employed: thermal evaporation and membrane separation. In the past decade reverse osmosis (RO) membranes have come to dominate the desalination market outside of the Middle East. While RO membranes have gained some traction in the Middle East, thermal evaporation is still the dominant technology due to access to cheap fuel [4]. There are a variety of factors that come into play when selecting the appropriate solution — quality of the source water, the desired quality and quantity of the desalinated water, pretreatment, energy requirement and disposal of concentrate.

Thermal desalination mimics hydrological cycle of water by the movement of water above and below the surface of the earth — evaporation from the ocean causes the water to accumulate in the atmosphere, whereupon it condenses as rain or snow. As the name implies, heat is required for thermal desalination to function, hence the procedure is best implemented in power plants and other refineries that produce a lot of excess waste heat that can be recycled. As of now there are three main types of thermal desalination — vapor compression (VC), multi-effect distillation (MED), and multi-stage flash distillation (MSF) [5]. VC functions by delivering compressed vapor, water evaporates and is collected, while the heat is recycled back to the remaining feed water. In MED, water is boiled in successive stages, each stage at a lower temperature to reduce the energy needed, and the boiling/condensation process producing the clean water. This is the most energy efficient process, thus the cheapest, as does not require pretreatment as it can manage different quality of the initial seawater. In MSF seawater is evaporated by reducing the pressure of the water in multiple stages and flashing portions of the water into steam [5].

RO membranes have become increasingly popular due to a combination of factors. Transition to large capacity plants, on location power plant generation, and from Build-Own-Operate-Transfer (BOOT) method of project delivery, which all have resulted in a dramatic decrease in cost for water desalination [5]. However, the key factor to the decreasing cost is the advancement of the RO technology. Newer membranes are designed to optimize freshwater per membrane element, i.e. higher surface area and denser membrane packing. An increase in surface area allows for a higher desalination rate of the membrane while keeping the diameter constant. Furthermore, one of the primary benefits of the RO membranes is its ability to remove many types of molecules and ions, thus making it well suited for potable and industrial uses. Regular osmosis functions by a net movement of solvent molecules moving from area of low concentration through a selectively permeable membrane to an area of high concentration. The movement of solvent from low concentration to high reduces the free energy of the system by generating osmotic pressure. Generating pressure to reverse the natural flow of solvent is called reverse osmosis. To produce clean water using RO, seawater or brackish water is pressurized against one surface of a membrane causing pure water to exit on the low-pressure side.

2.2. Overview of Reverse Osmosis Water filtration

As of today more than half of all the desalination plants across the world utilizes RO technology due to relative simplicity and low cost compared to thermal distillation. Due to the steady advancement of RO technology in terms of improvement of material properties, and reduction of energy consumption the membrane industry is quickly becoming a multi-billion dollar industry [6].

RO fundamentals are based on semi-permeable membranes that preferentially allows for water molecules to pass through, while blocking the passage of salt ions by applying an external pressure (Figure 1). The solvent and solute permeate through the membrane by solution-diffusion transport mechanism. If the applied pressure is higher that osmotic pressure the solvent starts flowing to the area of lower concentration, which in the case of RO should be through the membrane. The flux through a membrane can be expressed by the following equation:

$$J = A(\Delta p - \Delta \pi) \hspace{4cm} \text{Eq. 1}$$

Where $\Delta \pi$ denotes the osmotic pressure difference between the feed and permeate, Δp denotes the pressure difference across the membrane, and A denotes the physical characteristics of the membrane. Membranes are characterized by their average pore size, which is typically smaller than 10nm, and the 80 bar pressure required to overcome the osmotic pressure of seawater, which is roughly 25 bar. The performance of these membranes are measured by the rate of water flux and the amount of salt rejection, where an ideal RO membrane should have a ion rejection rate of more than 99% [7].
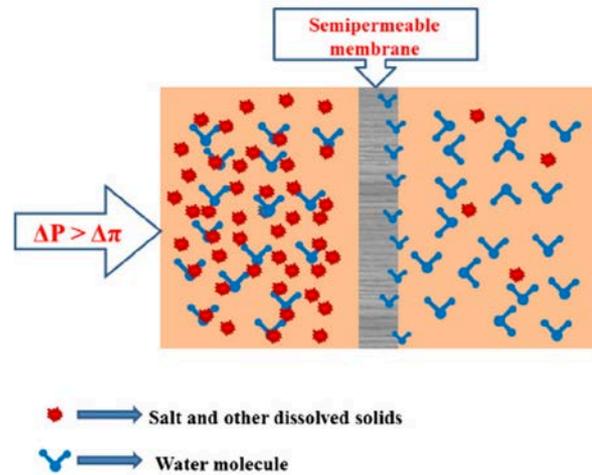
Figure 1. Displays a typical RO process where the applied pressure being greater than the osmotic pressure forces water through the membrane leaving salt behind [7].

A typical RO filtration plant typically consists of 4 stages: Pretreatment, high pressure pumping, salt separation and post treatment, where the salt separation, specifically the membrane itself is the most important component of the process. RO membranes have been used commercially since the 1960s when the cellulose diacetate (CA) asymmetric membrane was first synthesized [6]. However, these membranes have since long been replaced by other more sophisticated membranes, the most common being polyamide (PA) membranes, which have five times higher flux and water quality than CA membranes. In theory the minimum energy required for water separation should be 0.7 kWh/m^3, yet with current materials, and technology the energy consumption remains at between 2-5 kWh/m^3. Thus there is still a significant incentive to further improve on membrane technology.

2.3 Membranes for RO

As of today there exist a myriad of membranes types being used for water desalination, where the four major groups are: polymeric membranes, inorganic/ceramic membranes, mixed matrix membranes and biomimetic membranes. This review will focus primarily on polymeric membranes and biomimetic membranes.

2.3.1 Types of Membranes

Amongst the polymeric membranes, polyamides are the most popular and widely used class of RO membranes, especially after the development of thin film composite (TFC) membrane. PA-TFC membranes consist of polyester material, which is reinforced by a porous substrate (usually polysulfone). The current challenge with polyamide (PA) membranes lies in the choice of substrate,

4

additives, and choice of monomer to optimize the thin film to enhance water flux, ion rejection, and fouling resistance [6]. The main role of the substrate is to provide mechanical support for the membrane since the membrane must be able to withstand the high-pressure demand for a RO procedure. As a result the right choice of substrate is essential to produce a defect free PA film — this is achieved by making the surface as smooth as possible [7].

Smoother and thicker surface of PA films have been reported by the addition of hydrophilic additives such as polyvinylpyrrolidone (PVP) or polyethylene glycol (PEG). Additionally, permanent hydrophilicity of the membrane can be imparted by plasma treatment, which has proven to improve both water permeability and chlorine resistance. Polysulfone (PS) is the most widely used support material for PA membranes due to its low cost, availability, as well as chemical, mechanical, and thermal resistance [6]. Further improvement of thin film barrier layer in PA membranes is required to improve water flux and ion rejection, in addition to improving fouling resistance. Fouling is the decrease in flux of the membrane, due to lifespan depletion as a result of chlorine atoms changing the hydrogen bonding of the membrane from intermolecular to intramolecular [6]. Therefore, to increase the lifecycle of the membranes it is necessary that they have high chlorine tolerance.

Selectivity and permeability of the membrane is mainly governed by the varying polymerization conditions, which includes choice of monomer, the concentration of said monomer, reaction time and curing condition. The permeability of the membranes has shown to be improved by the addition of solvents such as DMSO and DMF in aqueous amine solution [6][7]. This occurred due to an increase in miscibility of water and organic solvents [6][7]. Moreover, interaction with PA films with hydrofluoric acid (HF) or isopropyl alcohol (IPA) has was shown by Mukherjee et al to reduce the polymer chain entanglement, due to limited hydrolysis of the amide network, which results in an increased water flux [8]. Using IPA was also reported by H. J. Kim et al for their synthesis of PA membranes to have been used to enlarge the pores of the PA membranes [7].

2.3.2 Biomimetic membranes
Biomimetic as the name may imply refers to membranes that aim to mimic those of biological systems and that can be compared to biological channels flux that have the capability of transferring 10^7 ions per pore per second [6]. In living organism water is permeated through aquaporin's that are bound to the phospholipid bilayer in the cellular membranes (Figure 2). Zhao et al produced at TFC RO membrane by soaking a PS film substrate in m-phenylenediamine, which contained aquaporins based on proteoliposomes [8]. The substrate was cross-linked with trimesoyl chloride (TMC) to form a three dimensional polyamide layer. This corresponding membrane had a 40% increase in permeability compared to commercial brackish water RO membrane BW30, and one order of magnitude higher than seawater RO membranes [9].

Recently nanostructures that mimics biological transport channels have gained widespread popularity. Majumder et al have demonstrated that a polystyrene film composed of aligned carbon nanotubes (CNT) increased the water transport through the membrane by an order of 4-5 times faster than predicted based on conventional fluid-flow theory [10]. This dramatic increase in flux is due to the
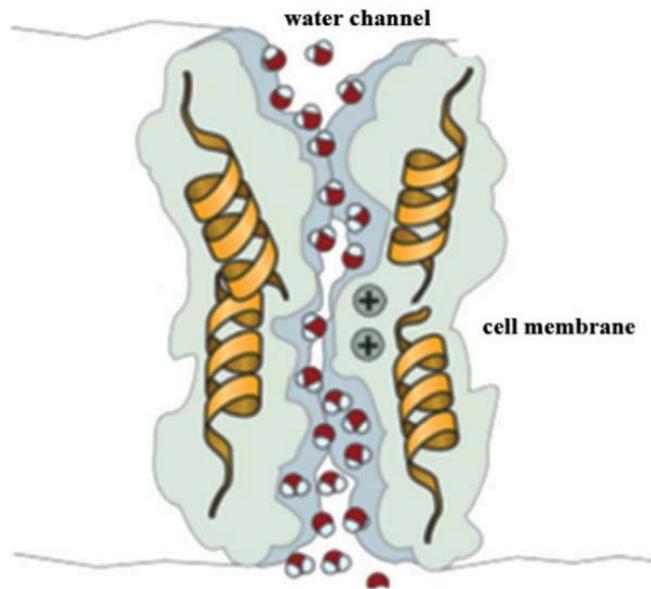

Figure 2. Typical aquaporin's that are present in most biological systems could be a valid model to base future RO systems on [8].

almost frictionless smoothness of the CNT. While Majumder et al clearly shows the significant benefits of adding CNTs to membranes, the challenge remains how to properly incorporate CNTs in more practical membranes such as PS that may be more useful in actual RO processes.

2.4 How is Water Flux and Ion Rejection is Affected by CNTs Composites

2.4.1 Overview

For the past decade nanomaterials have attracted considerable attention due to their unique mechanical, chemical, electrical, and thermal properties. The reason CNTs have been emerging in the water filtration systems is due to their large surface area, ease of functionalization, high aspect ratio, and particularly fast water transport [11]. The reason CNTs work so well for filtration is due the smoothness (frictionless) of the inner walls of the nanotubes. However, the narrow diameter of the nanotubes also plays an important role in improving water flux. This is due to facilitating chains of water molecules that are held together by their strong hydrogen bonds, thus CNTs act as a fast lane for water molecules. Furthermore, CNTs potential in membrane filtration application have been further reinforced due to having a longer lifetime compared to conventional polymeric RO membranes. This is a result of the improved cytotoxic properties of CNT membranes, due to decreasing the risk of biofouling by eliminating bacterial and viral pathogens [12]. While CNTs are harmful to the environment due to leaching, the toxicity depends largely on the physical state of the CNTs. Changing the dimensions, presence of impurities, and degree of dispersion in the sample can control the physical state, thus lower its toxicity.

CNT membranes can generally be split into two main categories: freestanding CNT membranes, and mixed (nanocomposite) CNT membranes. Freestanding consists of two main types vertically aligned CNT (VA-CNT) membranes and bucky-paper membranes [11]. In VA-CNT membranes, the CNTs are aligned such that they mimic cylindrical pores similar to those in biological systems previously mentioned. Bucky-paper the CNTs are randomly aligned in a large porous 3D network. Mixed-CNT membranes have structure similar to thin-film composite RO membrane with the top layer of the composite is mixed with CNT and polymer. Both types of membranes have their pros and cons. VA-CNT have a higher water flux due to a compact nanotube layup, and short nanochannel length, however, they are difficult to fabricate, especially for large-scale applications. Mixed CNT membranes on the other hand are simple to synthesize, albeit at the cost of significantly lower flux compared to VA-CNTs.

2.4.2 Modification of CNTs

While CNTs have a many properties that make them attractive for a myriad of applications, their lack of solubility and difficulty to process in many solvents has retarded their development. Dispersion of CNTs can be done in some solvents by utilizing ultrasonic energy, however this process usually results in precipitation once the ultra sonication is completed [11]. One solution to this problem is to attach polar functional groups to the surface of CNTs to overcome their lack of solubility and to improve dispersion in solution. Attachment of functional groups to CNTs can be done by standard chemistry reactions such as esterification, alkylation, or thiolation. Moreover, modified CNTs by functional groups can improve their interfacial bonding with many polymers, significantly improving the mechanical properties of the CNTs. However, adding functional groups to CNTs does not come without a cost; modification at the surface of the CNT changes the hybridization of the carbon atoms from sp^2 to sp^3—this results in a loss of electrical conductivity of the CNT due to a loss in π-conjugation [11]. Because of this, finding a dependable method to solubilize CNTs without affected their structure and properties are one of the greatest challenges concerning CNTs.

Non-covalent modification at the surface of CNTs typically involves the adsorption of a surfactant. This method is attractive, as it does not jeopardize the physical properties of the CNT. Dispersions of CNT in solution have been have been done creating supramolecular structures of polystyrene held together by van der Waals forces and π-π stacking between the CNT and aromatic rings of the polymer chains. This led to weakening of the intramolecular van der Waals forces, thus increasing the ability of CNT to properly disperse in the solution [12]. Certain proteins and carbohydrates have show to be particularly effective at forming stable dispersions of CNTs [11]. For example, DNA molecules were capable of dispersing CNT due the DNA bases binding to CNTs via π-π interactions. This resulted in the polar backbone of the DNA molecule being able to react with solvent molecules — hence successfully dispersing the CNTs [11].

2.4.3 Vertically Aligned CNTs

Hind's research groups was the first one to propose vertically aligned CNTs in 2004, where CNTs were produced using CVD in PS matrix [11]. As previously mentioned the vertically aligned CNT membranes mimic the properties of many aquaporin's in biological systems, due to the diameter of the tubes being perfectly fitted for water, as well as having selectivity due to functionalized polar groups at the end of the tubes to increase specificity [11]. There are several different methods for aligning CNTs, such as CVD, growing them directly onto a substrate, or utilizing scaffolding system

as demonstrated by Kasprzak et al [11][13]. What method used for alignment largely depends on the application and in what solvent the CNTs will be embedded.

2.5 Dispersion of CNT in polymer matrix

Surfactants due to being amphiphilic have proven to be extremely effective at dispersing CNTs. Surfactants with ionic, polar head groups such as sodium dodecylsulfate (SDS) can stabilize CNT dispersion by utilizing electrostatic repulsion mechanism [11]. Polyoxyethylene octylphenylether, a commonly used non-ionic surfactant on the other hand utilizes hydrophilic moiety to form solvation shells around the CNT, which aids in the dispersion of the CNT [11]. There exist a variety of different surfactants that can disperse CNTs in solution to varying degree. The main factor determining the dispersability of the CNT in water is the presence of long, branched, and disordered polar chain, e.g. poly (ethylene glycol) [12]. This follows a general trend of increasing in efficiency proportional with increasing molecular weight of the surfactant. Furthermore, the presence of unsaturated double bonds can provide additional advantage due to π-orbital affinity of the surfactants towards the π-system in the CNT. Surfactant molecules function by introducing small inclusions between the tubes in the bundle, thus preventing re-aggregation. It follows that surfactants with too bulky polar groups are less successful at penetrating into the inter-tube; therefore they exhibit reduced debundling capacity.

However, knowledge regarding surfactants for organic solvents is far more limited. While they exhibit same mechanism as those used for water, there is significant challenge with dispensability of CNT in organic solvents. Hydrophobic CNTs are expected to have good wetting in organic solvents and therefore should self-assemble in bundles. Nevertheless, CNT have shown to exhibit only limited dispensability in a few number of solvents, such as DMF, chloroform, and isopropanol [12].

Recently lyotropic liquid crystalline (LLC) surfactants have received attention due to their spontaneous ordering in aqueous solutions. With an increasing concentration exceeding that of the critical value, the surfactants will spontaneously form an ordered mesosphere wherein CNTs are hosted. Hence, LLC not only helps dispersing CNT in aqueous solutions, but also aids in the orientation in the mesophase. Therefore, LLC aided CNT alignment provides a way to exploit the anisotropic properties of CNT. Moreover, recent advances in polymerizable LLC surfactants have been able to produce ordered nanostructures of CNT based polymer composites. Moreover, due to an inherent property of the LLC known as "tumbling", allows it to align itself in the direction of an applied shear force [13]. These structures not only self-organize into ordered mesophases, but in addition facilitates covalent bonding to their neighbors to form strong polymer nanostructures (Figure 3) [13]. Kasprzak et al tested the degree of alignment by utilizing polarized atomic force microscopy (Figure 4) [13].
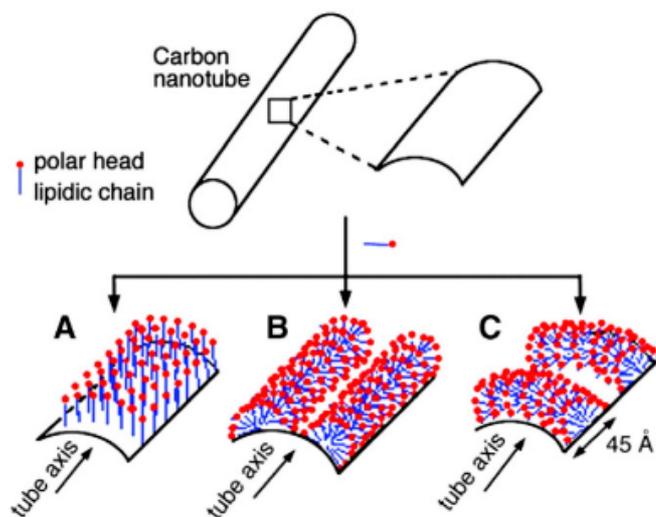
Figure 3. Different organization of SDS molecules depends on how they absorb on the surface of CNT [12].
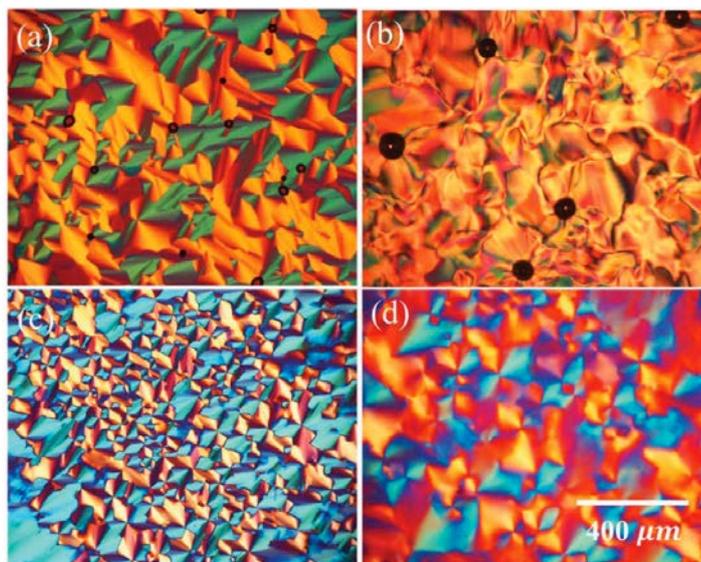

Figure 4. Displays the polarized optical image of the monomer surfactant $C_{16}MA$ in mesophase that shows promises as CNT scaffolding for membrane alignment [13].

2.6 RESEARCH QUESTION

How can I optimize the polymerization process and RO membrane manufacturing using single walled CNTs and the $C_{16}MA$ surfactant by varying the wt. % concentration of $C_{16}MA$, CTAB, and CNT to align the SWCNT, then dispersing these in a polyether sulfone (PES) membrane by ultra-sonication to achieve a homogeneous membrane with minimal agglomeration?

3. EXPERIMENTAL PROCEDURES

3.1 Design Project

The design criteria for the CNT composite for water desalination is being able to align carbon nanotube by polymerizing them together with a monomer surfactant to increase the ion rejection rate of the membrane as well increase the mechanical properties of the membrane. Variables that will be measured during the investigation are the amount of CNT, CTAB (by wt. %) and the amount of monomer incorporated with each other to figure out optimal ratio for perfect alignment. Once the previous step has been optimized successful incorporation of the CNT monomer with the membrane will be performed.

To measure alignment of CNT-monomer dispersed in membrane a polarized optical microscope will be utilized to observe agglomeration of CNT in membrane and to make sure there is alignment of the CNT. Level of success in this project will be measured by incorporation of aligned CNT in membrane If the alignment of CNT has been successful with the membrane there should be a significant increase in water permeability through the membrane as opposed to CNT membranes that does not have alignment of CNT.

3.2 Experiment and Design

Factors being studied in this experiment are if the alignment of CNT in a membrane will increase water permeability in a nanocomposite membrane, and if the alignment is possible with the liquid crystal surfactant being supplied by the project sponsor. Three different wt. % starting from 48wt% of $C_{16}MA$ increasing upward to max 52wt% with CNT diluted in nanopure DI water and a varying concentration of CTAB.

Response variable is the wt. % CNT in the membrane and the degree of alignment correlating to an increase in. Expected response is that water permeation will vary depending on wt. % of CNT and the degree of alignment. Therefore it should be possible to use statistical method to analyze the results (e.g. one way ANOVA, and possible two way ANOVA). Alignment of CNTs will be tested using polarized optical microscope, and possibly small angle x-ray diffraction (SAXS).

3.3 Experimentation

First stage of the project requires the optimization of the film/membrane and finding the right ratio of $C_{16}MA$ surfactant to other components to align the CNT in the membrane. How well aligned the CNTs are will be determined using polarized optical microscope. However, future studies might want to consider SAXS and TEM.

Once manufacturing of film membrane has been optimized, testing will move onto second stage, which will be conducting water flux and ion rejection testing. Based on previous studies, a high degree of alignment should result in a higher water flux for the membranes, however, the ion rejection may not follow the same trend and needs to be determined.

4. METHODS

4.1 Synthesis of Monomer

The monomer surfactant $C_{16}MA$ is synthesized via a quarternization reaction using 1-bromohexadecane and 2-(dimethyl amino) ethyl methacrylate (DEMA) (Figure 5). This is performed by adding 0.10 mol 1-bromhexadecane, 0.12 mol of DEMA, and roughly 520 mL of acetone to 2L round bottom flask. Additionally, 0.006 mol of hydroquinone is added to act as a radical scavenger. The round bottom flask is attached to a west-condenser, placed in a silicon oil bath and refluxed at 55°C for 7 days. Upon completion the acetone is removed using a rotary evaporator (BUCHI Rotavapor RII). To isolate the $C_{16}MA$ the precipitate is added to diethyl ether, and recrystallized using vacuum filtration to yield a white powder, with a slight rouge nuance.
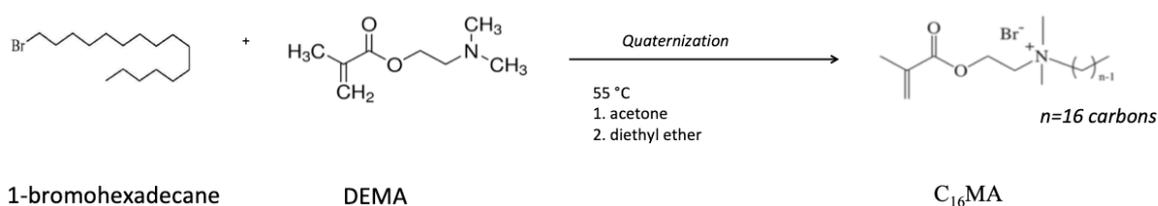

Figure 5. Molecular structure of the reactants and product; in addition of the reaction conditions.

4.2 Production of CNT-Solution

Aqueous homogeneous dispersion of SWNTs at 0.10 wt. % (of monomer concentration) is prepared with the aid of 4.0 wt. % (of monomer concentration) CTAB in DI water under micro-tip sonication (Figure 6). A calculated amount of monomer surfactants $C_{16}MA$ at 48-52% wt. %, and corresponding amount of DI water is added to SWNT dispersion and the mixture is then homogenized by a combination of both bath sonication at 50°C for 30 min and stirring by hand using a small spatula for roughly 2 minutes. This is then followed by micro-tip sonication for 30 min with 60% amplitude, with 15s pulses and 10s of rest.

Ladder Study To Activate LLC Phase

48-52 wt% $C_{16}MA$
48-52 wt% DI Water
0.1 wt%CNT (By monomer)
1-5 wt% Cetyl Trimethyl Ammonium Bromide (CTAB)

1. Mechanical mixing
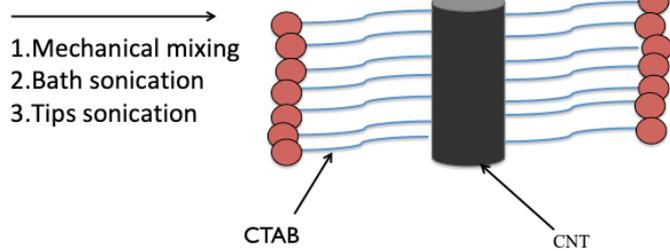2. Bath sonication
3. Tips sonication

CTAB

CNT

Figure 6. The ladder study was performed to determine the right ratio of regents in the solution, and the proper preparation parameters. The CTAB was used to reduce agglomeration of the CNT, while also aid in interfacing with the $C_{16}MA$.

To find the optimal solution make up three individual ladder studies were conducted. $C_{16}MA$ was varied between 48-52 wt.% concentrations to determine the solution that would yield the lowest viscosity and exhibit the hexagonal mesophase. The CTAB concentration was the varied between 1 and 5 wt.%, and the photo initiator was varied between 1 and 4 wt%.

4.3 Production of Nanocomposite

The initiator 2,2-dimethoxy- 2-phenylacetophenone (2 wt.%) and cross-linker N,N-methylenebisacrylamide (4 mol%) is added to the system and allowed to diffuse for 1-2 days to produce a homogeneous solution and to allow air to diffuse out of the solution mixture. To fabricate the solid nanocomposites, the solution was deposited onto a custom-made drawdown template, which
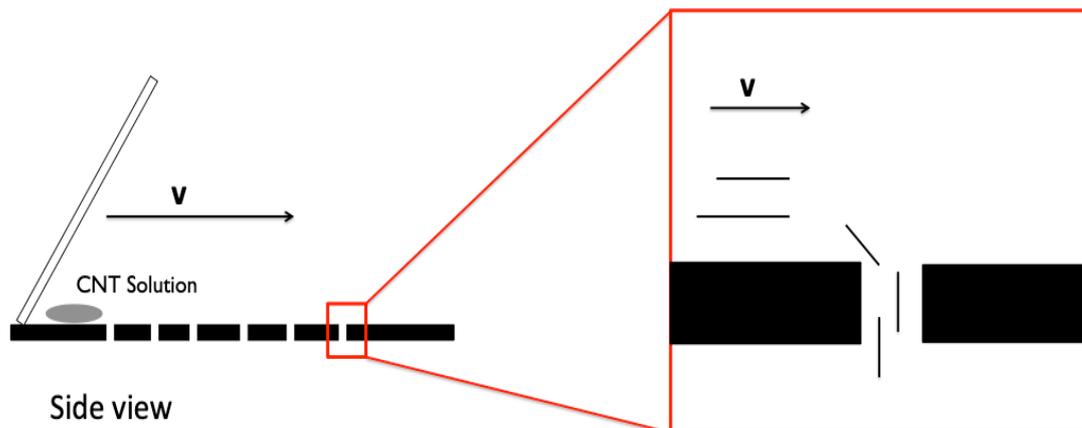

Figure 7 Illustration of how the screen-printing template takes advantage of the tumbling mechanic of the LLC solution, where the shear force should in theory cause alignment of the CNT due to being locked into the hexagonal mesophase.

is placed upon a PES membrane. A drop of the solution is then placed on the stencil and a drawdown card is used to shear the solution into the gaps of the template (Figure 7).

The membrane is subsequently polymerized, on a LC6 Benchtop UV Conveyor (Fusion F300 System) with I300 MB irradiator and D-type UV lamp (λ = 350–400 nm, 120 W cm^{-1}). The samples were run through the conveyor for 5 min at a conveyor belt speed of 20 fpm to ensure that the solution is properly locked into the membrane, as failure to do so may cause the solution to leak when ion rejection testing is done, yielding a higher conductivity measurement. Hence, a method to test whether the CNT solution has been properly photopolymerized, the membranes can be placed in DI water and test for potential changes in conductivity; if the conductivity increases it would imply that the CNTs have not been properly locked into the $C_{16}MA$, and due to the conductive properties of the CTN the conductivity of the DI water increases.

To perform for ion rejection testing a 0.17 M saline solution was prepared. The conductivity of this solution was tested using a Direct Soil EC probe. The nanocomposite membrane was then placed in a glass-sintered funnel attached to a vacuum flask with an applied vacuum, and the saline solution was poured through the membrane and conductivity measurement was performed on the solution that passed through the membrane.

5. RESULTS

5.1 Viscosity and Polarized Optical Microscopy

From the ladder study performed on the $C_{16}MA$ concentration it was found that the 52wt% and the 48wt% had optimal viscosities (Figure 1). Parallel to this ladder study the one testing for the optimal CTAB concentration resulted in 4wt% being the optimal concentration (Figure 8). The ladder study performed on the CTAB indicated that 4wt% exhibited optimal viscosity, with 2 and 3 being the worst (Figure 9). All the solution experienced non-Newtonian shear thinning behavior. However, while the 48wt% might seem slightly better than 52wt%, the 48wt% did not exhibit the hexagonal mesophase that is required for the $C_{16}MA$ to properly be photopolymerized to lock in the CNTs in the structure (Figure 10a-b).
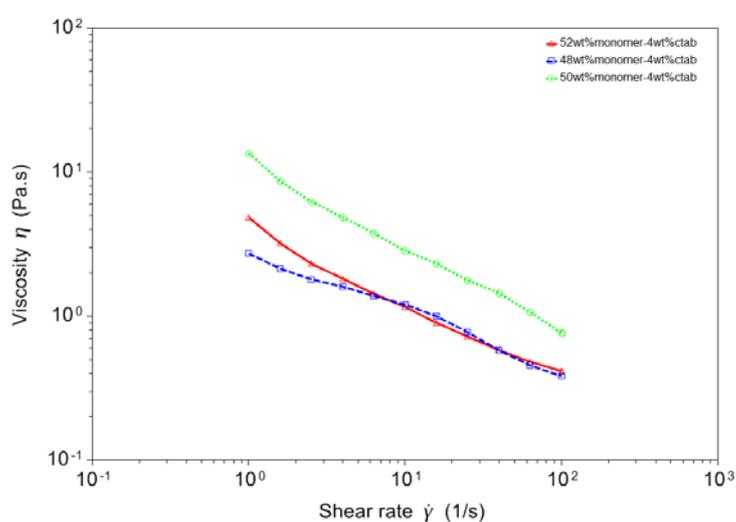

Figure 9. The viscosity testing performed on $C_{16}MA$ shows clear signs of shear thinning behavior.
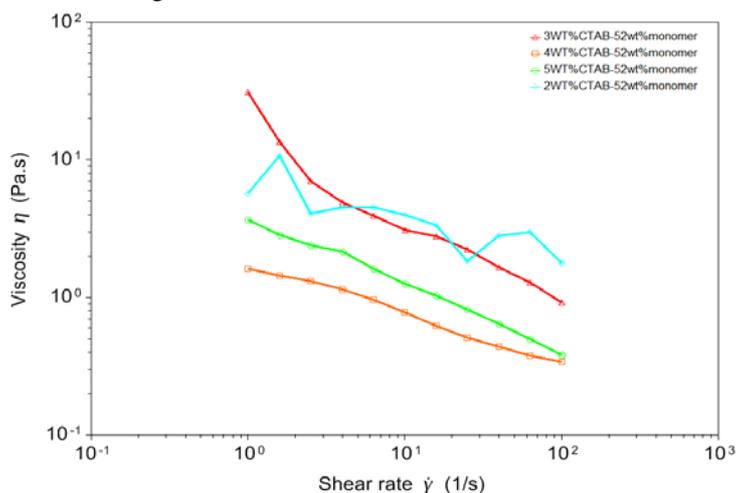

Figure 9. The ladder study of CTAB exhibiting shear-thinning behavior, with 4wt% having the lowest.
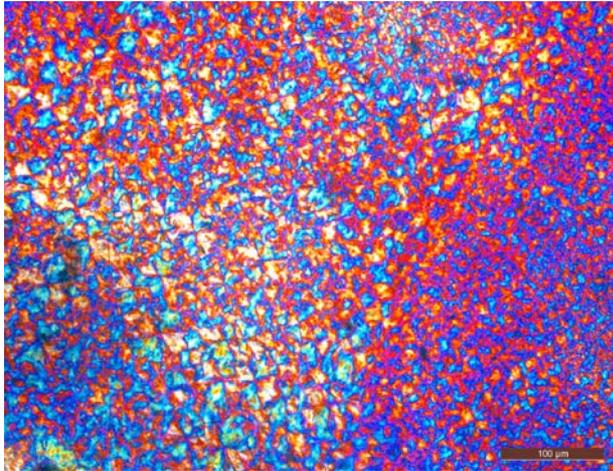
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Figure 11. The hexagonal mesophase exhibited from lyotropic liquid crystals, denoted by the has a kaleidoscope
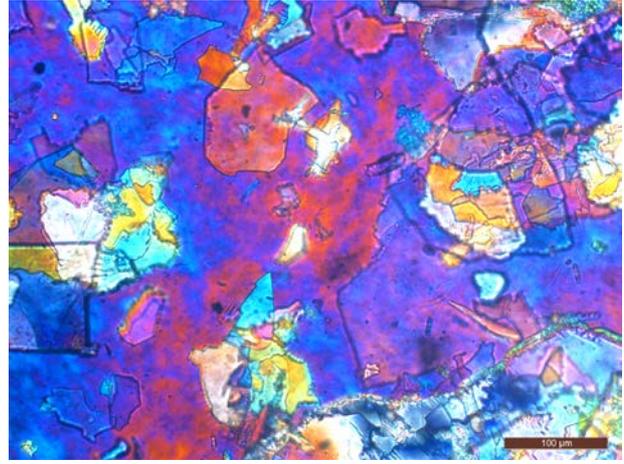
Figure 10. The 48wt% did not experience the hexagonal mesophase, instead forming annealed-like microstructure commonly seen in metals.

5.2 Ion rejection testing

The ion rejection testing did not result in any significant ion rejection results. This is potentially due to the pores sizes of the PES membranes are 30nm diameter; hence there is nothing that is forcing the NaCl particles through the CNT solution part of the membrane. To solve this problem a polyimide coating was proposed to use to try and selectively force the saline solution through the CNT solution, however, this ended up clogging the pores completely and no flux through the membrane occurred.

6. CONCLUSION

1. Synthesis and procedure parameters for the making of the CNT solution was established were it was found that mechanical mixing followed by bath sonication, and micro tip sonication yielded a solution with best dispersion.
2. 52 wt. % monomer with 4wt. % CTAB had the optimal viscosity, and exhibited the LLC phase.
3. The screen-printing apparatus did not work with the PES membranes as it did not cover the entire membrane, and no coating was found that could selectively allow diffusion to happen exclusively through the CNT solution in the membrane.

7. FUTURE WORKS

The requirement and critical issue for this project to be successful is the inherent property of the LLC that allows it to be vertically aligned when a shear force is applied. Hence, for this property to be optimized a few critical conditions needs to be meet.

First, the LLC-solution needs to have a viscosity that is low enough such that the shear force applied to the solution is enough to initiate the tumbling mechanic that aligns the solution, without jeopardizing the integrity of the constituents of solution. While there is some evidence that this was achieved from the POM images taken, further investigation would require SAXS, and TEM to certify the validity of this claim. However, for tumbling property to be able to activate properly it is of paramount importance that a sophisticated screen printing system and procedure is developed that will allow the shearing of the solution to be done onto a membrane in a way that allow for proper shear to be performed on the solution. It is important to note, should the viscosity be to high the tumbling property of the LLC will not activate, and as result no alignment will be achieved, but rather the solution will just fall into the pores of the membrane. Furthermore, it would advantageous if this screen-printing apparatus would be either able to interface with the entire membrane, or otherwise a coating is developed that can selectively restricts the saline solution to only pass through the CNT solution. Perhaps the main reason the ion rejection failed in this project is due to the screen printing method did not limit the saline solution to the CNT-solution of the membrane, hence the saline could take the path of least resistance, which was the large pores of the PES membrane. Thus, development of proper screen-printing is critical for this project be successful.

Second, findings from H. J. Kim et al indicate there was only a marginal increase in ion rejection based on their randomly oriented CNT membrane composite, however they did find an increase in water flux of these membranes [2]. Hence, another important parameter to test would be the change in water flux of vertical alignment of CNT in a host membrane. Because in the case that this project would result in zero increase in ion rejection compared to a conventional membrane would not imply that the LLC-solution does not work, as increase in water flux would mean more efficient membranes could be produced using the LLC-CNT solution to manufacture membranes that allows for faster water flux, and as a result more efficient water desalination.

Lastly, investigating possible means to reduce viscosity of the solution might be appropriate. This would entail seeing if there is an alternative surfactant to CTAB, specifically if there is one with a shorter hydrophobic tail, as this could possibly function to make the solution less viscous. Moreover, seeing if an alternative LLC surfactant is available might also be relevant. $C_{16}MA$ could potentially be synthesized as C_nMA, where n would denote a shorter hydrophobic tail. This would be synthesized as previously described, however, using a shorter chain 1-bromoalkanes, as this could potentially lead to a decrease in viscosity. While previous studies performed by Kasprzak et al investigated chain lengths of 1-bromoalkanes with n=12,14,16, and 18, found that n=16 had optimal properties, shorter chain lengths might still be viable [13].

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