SEAWATER DESALINATION BY FREEZE DESALINATION AND MEMBRANE DISTILLATION

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SEAWATER DESALINATION BY FREEZE DESALINATION AND MEMBRANE DISTILLATION

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DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

___________________________
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12 March 2018
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Summary

Effective and sustainable seawater desalination can be achieved by two consecutive processes of freeze desalination and membrane distillation.

Because the latent heat of ice fusion is only 1/7 of the latent heat of water vaporization, it is much more energy-efficient to harvest ice crystals from seawater than to produce potable water by means of evaporation. The major operating parameters of FD that were investigated are coolant temperature, freezing duration, supercooling, seeding, mixing, crystallizer material and subsequent washing procedure on ice production and water quality. It was found that the optimal freezing duration per batch was 1 h for an iron crystallizer and 1.5 h for a glass crystallizer. The optimal coolant temperature should be around -8 °C. The optimal amount of washing water to clean the raw ice was about 50 wt% of the raw ice. Over 50 wt% of the feed could be recovered as raw ice within 1 h, which means an overall ice recovery rate of higher than 25% (of the original seawater), considering the consumption of washing water. Both artificial and real seawater were tested under the optimized conditions. The total dissolved solid in the product ice was around 300 ppm, which met the World Health Organization (WHO) potable water salinity standard of 500 ppm. Therefore, the process parameters optimized can be directly used for the freeze desalination of seawater.

Subsequently, the concentrated brine could be treated by membrane distillation that is insensitive to high feed concentrations. While membrane technology continues to thrive in seawater desalination, it would defeat the very purpose of
saving the environment if toxic solvents are involved in membrane manufacture. As a paradigm of green chemistry, a non-toxic solvent, triethyl phosphate (TEP), was used for the first time to fabricate polyvinylidene fluoride (PVDF) hollow fiber membranes for direct contact membrane distillation (DCMD). The phase inversion kinetics of the PVDF/TEP system was closely investigated and compared with the conventional N-Methyl-2-pyrrolidone (NMP)/PVDF system. The former showed a less abrupt phase inversion rate and produced a more porous sponge-like structure than the latter. The 12/88 wt% PVDF/TEP binary solution produced fibers with promising performance. They not only possessed robust mechanical properties and a liquid entry pressure up to 2.0 bar but also exhibited an average flux of 20 kg/m²·h at 60 °C and a NaCl rejection of 99.99%. In addition, hollow fiber membranes spun from this PVDF/TEP system had porosity of greater than 83% for all conditions studied. Since there were no additives or non-solvents in the dope solutions and no post-treatments involved, the use of TEP as a green solvent could significantly reduce the complexity of membrane fabrication, scale up and commercialization. Clearly, the much safer solvent TEP is able to replace toxic solvents commonly used in membrane manufacture and to produce membranes with highly competitive performance.
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List of Symbols and Abbreviations

A = effective membrane area

$C_p$ = NaCl concentrations of the permeate

$C_f$ = NaCl concentrations of the feed

$K_{FP}$ = cryoscopic constant

$L_f$ = latent heat of fusion

$m$ = molality (mol solute/1000 g solvent)

$m'$ = mass of the membrane

$M_0$ = mass of feed solution

$M_i$ = mass of raw ice

$M_{pi}$ = mass of product ice

$M_s$ = mass of seed ice

$r^*$ = critical radius

$t$ = corresponding duration

$T_f$ = freezing temperature

$\Delta T$ = temperature difference departed from freezing point

$\Delta T_f$ = freezing point depression

$V_{\text{void}}$ = void volume

$V_{\text{membrane}}$ = hollow fiber membrane volume

$V_{\text{polymer}}$ = volume of polymer skeleton

$\Delta W$ = increase of the permeate mass

Greek symbols

$\varepsilon$ = membrane porosity

$\eta$ = percentage of washing water’s mass relative to raw ice
\( \rho_{\text{polymer}} = \) polymer density

\( \sigma = \) interfacial tension between water and ice

\( \varphi = \) ice recovery rate

DCMD: direct contact membrane distillation

DMAc: dimethylacetamide

DMF: dimethylformamide

FD: freeze desalination

FESEM: field emission scanning electron microscopy

IPA: isopropanol

LEP: liquid entry pressure

LNG: liquefied natural gas

MD: membrane distillation

MED: multi-effect distillation

MSD: mean squared displacement

NMP: N-Methyl-2-pyrrolidone

NPT: isobaric-isothermal

PME: particle mesh Ewald

PVDF: polyvinylidene fluoride

RO: reverse osmosis

TDS: total dissolved solid

TEP: triethyl phosphate

WHO: world health organization
1. Introduction

1.1 Water Scarcity

Although water is one of the most abundant substances on earth, only 3% of it is fresh water. And almost 2.5% exists in glaciers and atmosphere. Hence, only 0.5% of water is suitable for and accessible to humans, plants and animals [1]. Currently around 30% of the world population do not have sufficient water sources for basic sanitation needs, and 60-70% will have to live with severe water shortage [2]. Many countries including the U.S., Middle Eastern and North African countries (MENA region) and southeastern European countries, Southern India, Pakistan, Mongolia, Afghanistan, Kazakhstan, Turkmenistan, Uzbekistan, Tajikistan and western Australia are facing physical water scarcity. Besides physical water scarcity, there is also economic water scarcity where people lack proper mechanisms to acquire access to the available water sources in the local area. Economic water scarcity is experienced in Central and Latin America including Caribbean region, South and Central Africa, North India, some parts of China and some other Asian countries. The water shortage phenomenon is shown more clearly in Fig. 1 [3].

With the understanding of water scarcity, the need for desalination technologies becomes more and more critical. When efficient and cost-effective desalination technologies are developed, the water shortage problem can be easily solved considering the vast quantity of seawater on earth.
1.2 Desalination Processes

The most common desalination technologies are membrane based and thermal based [4]. Membrane processes use a physical barrier to separate the dissolved salts from the feed by mechanical, chemical or electrical means. Thermal processes consist of an evaporator and a condenser to vaporize water from the feed. Common membrane desalination technologies include reverse osmosis, forward osmosis, electrodialysis, etc. Thermal desalination technologies are multi-effect evaporation/distillation (MED), multi-stage flash distillation (MSF), thermal vapor compression (TVC) and mechanical vapor compression (MVC). There are also hybrid systems that thermal device and membrane are
both utilized in a single unit or in sequential steps, such as membrane distillation (MD) and reverse osmosis combined with MSF or MED processes.

In year 2005, thermal desalination technologies dominated the desalination share by up to 60%. The membrane desalination technologies accounted to 40% [4]. Nonetheless, more and more membrane based desalination plants were built thereafter. In the last decade, most of the desalination plants installed were membrane desalination plants [5].

1.3 Freeze Desalination

Freeze desalination (FD) is an emerging desalination technology because of its insensitivities to fouling problems and the provision of cold energy from processes such as regasification of liquefied natural gas (LNG) in recent years [6-8]. The cold energy is the heat absorbed from ambient surrounding when converting LNG (-162 °C) back to natural gas at LNG terminals [8-9]. It is one of high quality energy sources to cool other media, but most cold energy during LNG regasification has been wasted until today. Because the latent heat of ice fusion is only 1/7 of the latent heat of water vaporization [10], it is much easier and more cost-effective to induce and harvest ice crystals from seawater by the cold energy in FD than to produce potable water by means of evaporation in many distillation processes [8,11].

There are two categories of freezing processes in FD; namely, direct and indirect contact freezing [12]. The former mixes seawater with a liquid refrigerant directly. The refrigerant vaporizes and escapes from the top of the freezer. At
the same time, seawater is cooled and then freezes. This process has a high production rate, but the requirements of the refrigerant are stringent. It should be nontoxic, chemically inactive, immiscible in water, and resistant to forming hydrates [10]. In contrast, indirect freezing uses walls to isolate the refrigerant from seawater [13]. Heat exchange happens through the crystallizer walls with adjustable cooling conditions [8,14]. An intermediate coolant may be utilized to pass the cold energy from LNG to seawater at an appropriate temperature to facilitate ice production without incurring salts. Some previous studies used -10 °C or -15 °C for simplicity [8,15-16], while this work will find the optimal coolant temperature.

Various crystallizer configurations such as static layer crystallizer [17], progressive crystallizer [18], dynamic layer crystallizer [19], have been employed to investigate the ice formation in FD. In a static layer growth system, the seawater stays stagnant on a surface, the driving forces for heat and mass transfers are free convection and gravity. Thus, it would take a long time, usually more than 10 h per batch, to form a reasonable amount of ice crystals. In a progressive crystallizer, only one single ice crystal is present, which is at one end of the vessel. The ice-solution interface gradually moves towards the other end. However, the speed of the freezing front is highly constrained. A fast moving freezing front would inevitably cause concentration polarization. In a dynamic growth system, seawater flows down along a cold surface and ice crystals form underneath the flowing film. One of the major obstacles in this process is the salt entrainment [20]. The brine tends to be trapped in the interstices of ice crystals due to capillary force. Different from aforementioned
approaches, the current study uses a simple batch reactor. We aim to have a
deeper understanding of each basic parameter that would benefit FD
development in years to come.

There are two major challenges in the FD technology. One is the amount of salts
adsorbed on the ice crystals, while the other is the amount of washing water to
remove these salts. Since ice crystals generated in FD have very small sizes,
they have an enormous specific surface area. Their surfaces are usually covered
by a slew of salts due to the strong adhesive force between ice and brine.
Therefore, one must wash ice crystals to remove these salts. The amount of
washing water has been overlooked in most of past studies, but this study would
revisit this crucial issue and optimize the amount of washing water. Therefore,
this study may provide useful insights and operational data for the entire FD
process. In addition to these challenges, FD also faces the difficulties of being
accepted as a new technology from industries, especially when it is perceived
as costly and mechanically complex [21].

1.4 Membrane Distillation
To overcome water scarcity, many emerging desalination technologies have
been proposed. One of them is the membrane distillation (MD) where it harvests
the condensed water vapor across a porous hydrophobic membrane [22-23]. The
driving force for water transport is the difference of its partial vapor pressures
across the membrane between the hot seawater and the cold distillate stream.
Since MD is commonly operated below 80 °C, it could utilize low grade or
renewable heat sources, such as industrial waste heat or solar panels to lower its
overall cost. MD has other advantages including 1) nearly 100% rejection of inorganic ions, macromolecules and other non-volatile compounds; 2) less pressure requirement than conventional pressure-driven membrane separation processes; 3) insensitive to feed concentration and heterogeneity of components; and 4) relatively lower requirements on membranes’ mechanical strengths [22-26].

Direct contact membrane distillation (DCMD) is the simplest MD configuration and the easiest to operate. Many efforts have been devoted to fabricating DCMD membranes and modules with extraordinary performances such as high flux, strong anti-fouling, super hydrophobic and so on [27-35]. However, most previous studies used toxic solvents in many steps of membrane fabrication. Although these solvents pose threat to human health and the environment, it is hard to replace them because of their broadly satisfactory properties such as solubility, viscosity, polarity and boiling points [36-37]. Common solvents to prepare PVDF membranes for DCMD are dimethylformamide (DMF), dimethylacetamide (DMAc) and N-Methyl-2-pyrrolidone (NMP). For example, Tomaszewska used DMF and DMAc to cast flat sheet membranes with a permeation flux of about 10 kg/m²·h [38]. Hou et al. employed DMAc to fabricate single-layer hollow fiber membranes with a permeation flux of about 20 kg/m²·h [39]. Wang et al. utilized NMP to produce dual-layer hollow fiber membranes with a permeation flux over 40 kg/m²·h [40]. However, all these three solvents are very toxic and can cause many diseases. Table 1 briefly summarizes their hazard statements and linked diseases [41-42]. In contrast, triethyl phosphate (TEP) is a much safer solvent [43-44]. It is only harmful
when being swallowed. In this case, not only can workers be better protected, the treatment of waste effluent can also be simplified.

Table 1: The hazard statements and toxicology of common organic solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Hazard codes</th>
<th>Hazard statements</th>
<th>(a) Regulation (EC) No 1272/2008 [41]</th>
<th>(b) Casarett and Doull's toxicology [42]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>H350D</td>
<td>May damage the unborn child</td>
<td>Strong Evidence</td>
<td>Acute hepatocellular injury (hepatitis), Steatosis (fatty liver)</td>
</tr>
<tr>
<td></td>
<td>H332</td>
<td>Harmful if inhaled</td>
<td>Good Evidence</td>
<td>Pancreatitis</td>
</tr>
<tr>
<td></td>
<td>H312</td>
<td>Harmful in contact with skin</td>
<td>Limited Evidence</td>
<td>Testicular cancer</td>
</tr>
<tr>
<td></td>
<td>H319</td>
<td>Causes serious eye irritation</td>
<td></td>
<td>Acute hepatocellular injury (hepatitis)</td>
</tr>
<tr>
<td>DMAC</td>
<td>H350D</td>
<td>May damage the unborn child</td>
<td>Limited Evidence</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H332</td>
<td>Harmful if inhaled</td>
<td></td>
<td>Acute hepatocellular injury (hepatitis)</td>
</tr>
<tr>
<td>NMP</td>
<td>H319</td>
<td>Causes serious eye irritation</td>
<td>Good Evidence</td>
<td>Fetal toxicity (miscarriage / spontaneous abortion, stillbirth)</td>
</tr>
<tr>
<td>TEP</td>
<td>H302</td>
<td>Harmful if swallowed</td>
<td>Limited Evidence</td>
<td>Low birth weight / small for gestational age / intra-uterine growth retardation</td>
</tr>
</tbody>
</table>

The major challenge when replacing a common toxic solvent with a green solvent is the difficulty to achieve competitive product performance [36-37]. So far, there were only three papers using TEP for the fabrication of PVDF membranes for MD, albeit none was hollow fiber membrane. Nejati et al. produced flat sheet PVDF membranes with porosity below 75% [23]. Their super thin membrane had a flux up to 40 L/m2-hour (LMH). However, no quantitative mechanical properties were reported. Fadhil et al. fabricated a flat sheet membrane made of co-polymer PVDF-HFP. The membranes had relatively low fluxes even after the optimization of the co-polymer and additive concentrations to improve the overall performance [45]. Chang et al. also prepared flat sheet PVDF membranes with the highest flux below 13 LMH [46]. Since the benefits from a more sustainable and greener process are invaluable, the objectives of this work are to (1) conduct a fundamental study on membrane formation using TEP, (2) uncover the major difficulties when using TEP to replace common toxic solvents in hollow fiber fabrication for MD applications, and (3) demonstrate solutions to overcome the difficulties. As a result, one may
be able to pursue both the environmental and economic goals in membrane manufacture.

In order to meet our objectives, we would (1) investigate the phase inversion process of the PVDF/TEP system, (2) examine its hollow fiber formation and morphology and (3) study the DCMD performance. A PVDF/NMP system was also chosen as a benchmark for comparison. NMP was chosen over DMF and DMAc because the former is less toxic than the latter. To our best knowledge, this is the first attempt to fabricate MD hollow fiber membranes using TEP. It may provide useful insights to green membrane production for many years to come.
Chapter 2. Background and Theory of Freeze Desalination

2.1 Pivotal role of washing in FD

Freezing pure water and saline water are distinctly different. Without the disturbance of soluble ions, the ice crystals grow on top of one another. Their sizes can be very large. Visibly, the ice could form an entire chunk in the cylinder. However, water does not freeze in the same manner when many ions are present. Instead, dendritic ice crystals [47-48] will occupy the space and form a slurry.

Brine adheres to ice crystals considerably due to the massive interfacial tension [49]. A thorough separation of ice and brine require accessory procedures other than simply draining off or normal filtration. The design of washing columns has been actively investigated [49-50] and used in pilot plants [16]. The ice slurry is introduced to the bottom of the washing column that is filled with clean water. Ice crystals float up by the buoyancy force and the brine trapped in interstices would be displaced. Clean ice can then be harvested at the top of the washing column. However, there exists a serious dilemma regarding whether to use agitation and pulsing. Without them, the mass transfer would be extremely slow because the buoyant movement is severely inhibited by the adherence force between ice and water. If agitation and pulsing are adopted, their contributions to longitudinal mixing would disrupt the concentration gradient distribution [51]. Once the upper portion of the column contains a high amount of salts, the column is no longer able to purify ice. In contrast, washing ice crystals with the aid of vacuum filtration can drain out salty water within
seconds. Not only can it lower the salt impurity on the ice crystals to be almost negligible but also significantly reduce the energy consumption for the washing procedures.

2.2 Supercooling and nucleation

Supercooling is the process where a liquid is cooled below its freezing point without crystallizing. For instance, pure water has to be cooled below 0 °C to initiate freezing. Although 0 °C is widely understood as its freezing point, it is rather an equilibrium point during the freezing process. The real temperature for water to start freezing depends on when nucleation happens. According to crystallization kinetics, a trace amount of ice lattice larger than the critical size must be generated [52]. In other words, there is a minimum embryo-crystal size (i.e., the critical radius) for the embryo to grow spontaneously. In fact, for a given temperature there will be a critical radius. The relationship among them is reflected by the Kelvin equation [47]:

\[
r^* = \frac{2\sigma T_f}{L_f \Delta T}
\]

where \(r^*\) is the critical radius, \(T_f\) is the freezing temperature, \(L_f\) is the latent heat of fusion, \(\Delta T\) is the temperature difference departed from the freezing point, and \(\sigma\) is the interfacial tension between water and ice that is estimated to be 22 erg/cm\(^2\). The critical radius is then plotted relative to water temperature in Fig. 2 (a).
Once ice has the critical radius, nucleation may take place by either homogeneous or heterogeneous nucleation. Theoretically, a cluster of about 25 water molecules would form ice at -41 °C via homogeneous nucleation. In reality, it is difficult to cool the water down to near this temperature without forming ice because the nucleation barrier is largely reduced by the existence of impurities that lead to heterogeneous nucleation. As depicted in Fig. 2 (b), when water molecules wet an impurity surface, a small portion can actually correspond to a much larger radius [53]. As a result, this cluster of water molecules is likely to stabilize themselves at a much higher temperature and spontaneously set off the heterogeneous nucleation. The ice crystal would then grow irreversibly as long as the cooling condition is maintained.

Additionally, the supercooling condition can be interrupted when nucleation is triggered by external nucleus. If any seed ice is added into the supercooled solution, the status of supercooling would cease immediately and a large amount of ice crystals would form shortly. This process releases so much heat that the
system temperature would rise shortly to the equilibrium point, i.e., freezing point. In the absence of a seed, the temperature at which ice crystallization will occur is highly stochastic (random). Seeding helps to overcome this variability because ice crystallization will occur at the same temperature with seeding.

2.3 Freezing-point depression

Freezing-point depression is a phenomenon where the freezing point of a solvent is decreased by the presence of solutes [54-55]. Experimentally, it is noted that the lowering of the freezing point does not depend on the nature of the solutes. Instead, it is only proportional to the number of dissolved molecules and ions. The expression of freezing-point depression is generally given as:

\[ \Delta T_f = -K_{FP}m \]  

(2)

where \( \Delta T_f \) is the freezing point depression, \( K_{FP} \) is the cryoscopic constant which is 1.86 K·kg/mol for water, and \( m \) is the molality (mol solute/1000 g solvent). Although this simple relation assumes the solution to be an ideal solution, i.e. it does not include the nature of the solute, it is sufficiently effective for a diluted solution like seawater. Thus, for seawater with a salt concentration of 35 g/kg, the freezing point is depressed to \(-2.1 \sim -2.2 \degree C\). However, once the solution starts freezing, it gets more and more concentrated. The freezing point is therefore further depressed. Fig. 3 illustrates this process on a NaCl-water phase diagram. Route 1 stands for the cooling of saline water from room temperature to its freezing point. Route 2 is the process of supercooling explained in section 2.2. The temperature quickly jumps back to the freezing point in Route 3 when nucleation takes place. Then the entire system proceeds along the equilibrium curve as shown by Route 4. If seeding is applied at the point when seawater is
just cooled to the freezing point, supercooling would be forestalled and the process paths become 1 & 4 instead.

Figure 3: The operating process of freeze desalination (FD) illustrated on the phase diagram of sodium chloride solutions [53].
Chapter 3. Optimization of Freeze Desalination Parameters

3.1. Experimental setup and materials

To mimic the LNG regasification process in a LNG vaporizer, an environmentally friendly Freon® gas (R23, DuPont, boiling point: -82.1 °C) was used in this experiment because it possesses the closest vaporization behaviour as LNG and its vaporization can lower the temperature of the coolant (EG, >99.5%). A customized gas compressor and condenser unit (Yohokomo, Singapore) were used to compress Freon® gas into a liquid form and recycle the liquid, respectively. Fig. 4 shows the setup of the ice crystallization unit [8]. To ensure enough mixing in the cylinder, a mechanical stirrer with a 3-bladed impeller (MG-1, Li Yuan) was installed in the center with an adjustable rotation speed of 0 – 300 rpm. The cylinder wall of the crystallizer was made of either glass or iron in order to study their effects on ice formation.

Figure 4: Schematic design and images of the indirect contact freeze desalination unit [8].
Fig. 5 displays the schematic diagram and the image of the vacuum filtration unit. The vacuum pump (MAJP – 40V(L)) has a maximum vacuum of 80 torr (≈ 0.125 atm). Three types of seawater were employed in this study: (1) a NaCl (35 g/kg) solution was used to simulate seawater for most parts of the parameter studies; (2) an artificial seawater was made according to the formulation of Subow (Subow, 1931), as listed in Table 2 (a); and (3) a real seawater was obtained from the Public Utilities Board (PUB), Singapore (Qin et al., 2009) after pre-treatments to remove insoluble solids and organisms. Table 2 (b) tabulates its composition.

![Schematic design and images of the vacuum filtration set and the washing unit.](image-url)
Table 2: The compositions of artificial seawater & real seawater.

(a) Artificial seawater composition (Subow, 1931)

<table>
<thead>
<tr>
<th>Salt</th>
<th>NaCl</th>
<th>MgCl₂</th>
<th>MgSO₄</th>
<th>CaCl₂</th>
<th>KCl</th>
<th>NaHCO₃</th>
<th>NaBr</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/kg</td>
<td>26.518</td>
<td>2.447</td>
<td>3.305</td>
<td>1.141</td>
<td>0.725</td>
<td>0.202</td>
<td>0.083</td>
<td>34.421</td>
</tr>
</tbody>
</table>

(b) Real seawater composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Ba</th>
<th>Sr</th>
<th>CO₃</th>
<th>HCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/kg</td>
<td>396.15</td>
<td>1485.45</td>
<td>9895.1</td>
<td>791.35</td>
<td>0.099</td>
<td>7.9225</td>
<td>24.1</td>
<td>107.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>SO₄</th>
<th>Cl</th>
<th>F</th>
<th>NO₃</th>
<th>B</th>
<th>SiO₂</th>
<th>CO₂</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/kg</td>
<td>2872.25</td>
<td>19793.5</td>
<td>2</td>
<td>1</td>
<td>4.79</td>
<td>4.95</td>
<td>0</td>
<td>35386.05</td>
</tr>
</tbody>
</table>

3.2 Experimental procedures

The cooling medium EG was firstly cooled to a desired temperature. Meanwhile, a NaCl solution (35 g/kg) or seawater of M₀ (1 kg) was pre-cooled in a freezer to around 0°C before being poured into the crystallizing cylinder. A certain amount of seed ice (Mₛ) was used to trigger the nucleation at its freezing point (-2.1 °C) or a certain supercooled temperature. The seed ice was weighed and grinded by a bench-top mill (Cole-Parmer, Singapore). The process was timed starting from the onset of nucleation. After a specified freezing duration, the entire ice slurry was transferred to a washing unit which is a vacuum filtration unit consisting of a metal mesh with a wire diameter of 0.12 mm and an aperture of 0.198 mm. The brine was drained off from the slurry by applying vacuum filtration for 10 s to completely remove the brine. The raw ice was weighed (Mᵢ). Then, chilled tap water (0°C) was used to re-wash the raw ice. For each re-wash, a designated amount of tap water was used with aid of vacuum filtration for 10 - 20 s. Eventually, the product ice (Mₚᵢ) was transferred to a melting unit to melt naturally.
The mass of washing water was represented as a percentage ($\eta$) of the raw ice ($M_i$), i.e., $\eta \cdot M_i$. In this study, $\eta$ was studied in the range of 0 – 60 wt%. The recovery rate of the product ice and the ice salinity were used to quantify the performance of the FD process. The ice recovery rate ($\varphi$) was defined as following:

$$\varphi = \frac{M_{pi} - M_s - \eta M_i}{M_0} \times 100\% \tag{3}$$

$\eta \cdot M_i$ is included in the numerator because it is the amount of tap water used to wash the raw ice.

For NaCl solution tests, the ice salinity was measured by a conductivity meter (Lab960, SCHOOT instrument, Germany). For artificial seawater and real seawater tests, the ion composition was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES, Optima 7300DV, Perkin Elmer, USA).

To achieve the highest purity and productivity, the parameters that were optimized in this process are coolant temperature, process duration, supercooling, agitation and washing design. Each of them was investigated under ceteris paribus conditions. (i.e., with other conditions remaining the same). For comparison, a base case was established where a NaCl solution (35 g/kg) of 1kg was cooled for 1 h without supercooling, agitated by the stirrer at 100 rpm and a coolant temperature of -8 °C.
After optimizing the operation parameters using the NaCl solution, both artificial and real seawater were tested respectively under the optimal conditions. The artificial seawater contained all the major ions of seawater, so it served as a better simulation than the NaCl solution. After understanding the roles of Mg\(^+\), Ca\(^{2+}\) and K\(^+\), real seawater was finally tested. Compared to the artificial seawater, the real seawater contained a much more complicated composition. There were many other ions dissolved in it, although the quantity was minimum.

Each test was repeated at least 3 times to check reliability and the average values were reported.

3.3 Results and discussion

3.3.1 Determination of major parameters

The major process parameters that greatly affect the FD unit performance are washing procedure, coolant temperature, process duration, supercooling and agitation [10]. Among them, washing procedure outweighs other parameters because the product water must contain minimal impurities and the salts adhered onto the ice crystals’ surfaces actually account for most of the impurities [56].

3.3.2 Washing procedures

3.3.2.1 The amount of washing water without recycling

Fig. 6(a) shows the salinity of the product ice as a function of \(\eta\) (i.e., the mass ratio of chilled tap water to raw ice) with a stepwise increment of 10%. The salinity deceases after each step of washing. After six steps, the ice salinity
meets the WHO potable water standard (<0.5 g/kg). In other words, to meet this standard, the amount of washing water should be about 60 wt% of the raw ice. This translates to that about 40% of the raw ice can be delivered as the product ice, considering a portion of the clean ice will be consumed as washing water. To simplify the washing procedure, the $\eta$ value is increased in each step and the effects are depicted in Figs. 6(b)-(d). Two conclusions may be drawn from these results. Firstly, the required washing steps can be reduced with an increase in stepwise $\eta$ value and produce ice that meets the WHO standard. Secondly, regardless of the $\eta$ value, the total amount of washing water is all the same, which is 60 wt% of the raw ice. This proves the proposition that the total $\eta$ value has to be about 60 wt%. It may be noted that the simplest case of one-step washing with an $\eta$ value of 60 wt% is not included in the figure. That is because the resultant ice has a salinity of 1.101 g/kg. Therefore, at least a two-step washing should be applied.
Figure 6: The effect of different washing procedures on ice salinity as a function of \( \eta \) (the mass ratio of chilled tap water to raw ice).
It is worth noting that during washing, all measures were taken to minimize agglomeration of ice crystals. For instance, any compression or other external forces should be avoided on the ice bed. This is also part of the reasons why centrifugal separation is not chosen in this study to separate wastewater from the ice in the washing step.

3.3.2.2 The amount of washing water with recycling
To reduce the amount of tap water for ice washing, the used washing water is recycled to wash ice. A simple two-step washing is investigated. As illustrated in Fig. 7, the wastewater from the 1st step of ice washing has a high salinity close to the concentrated feed left in the reactor, whereas the one from the 2nd step of ice washing has a salinity of about 11.47 g/kg. The latter is about 80% lower in salinity than the former. It is because the porous ice bed exposes most of the crystal surfaces. After a full contact, the first stream of tap water is able to dissolve most of the surface impurities by the time when it flows away from the bed. Since there is a small amount of residues left, the wastewater from the second step is much less concentrated. Therefore, the wastewater from the 2nd step of ice washing (i.e., referred to as the wastewater 2) could be reused to wash the raw ice. To demonstrate the feasibility, experiments were conducted as presented in Fig. 8. The wastewater from the 2nd step of ice washing (i.e., wastewater 2) in batch A is reused to wash the raw ice in batch B. As a result, the tap water needed in batch B is only 40 wt% of the raw ice, which is a reduction of 20%. When combining these two batches together, one can expect
that the total amount of tap water for ice washing is reduced to about 50 wt% of the raw ice.

Figure 7: Salinities of brine and wastewater after the 1st and 2nd step washing from FD.
Figure 8: Flowchart of the FD operation with the recycling of low concentrated wastewater.

If the wastewater from the 3rd step of ice washing in batch B (i.e., referred to as the wastewater 3 in Fig. 8) is reused, then the amount of washing water may be further reduced to below 50 wt% of the raw ice. The reuse of washing water from more than two batches of ice washing will be studied in the future. In addition, the concentrated wastewater left from FD may be recyclable using membrane (MD) because it is less sensitive to the feed concentration [24-25].

3.3.3 Effects of coolant temperature

As illustrated in Sections 2.2 and 2.3, the feed solution undergoes freezing process at equilibrium point (i.e., freezing point). Therefore, the driving force for freezing is the temperature difference between the feed solution and the
circulating coolant. A large temperature difference would facilitate a higher ice production rate. However, an excessive driving force would distort the freezing process. When coolant temperature is lower than -10 °C, a thick ice layer would quickly form on the cylinder wall within minutes. The fast agglomeration of ice may trap salts inside, which are difficult to be washed away. In addition, the dense ice layer is difficult to be peeled off from the cylinder wall. Thus, a very large temperature difference is not desirable. On the contrary, a very small temperature difference would prolong the ice production process. Hence, an optimal coolant temperature should be identified.

Fig. 9 shows the ice recovery rate and salinity as a function of coolant temperature. The experiments were conducted using seed ice of 1g at -2.1 °C with an agitation speed of 100 rpm for 1 h and then washed optimally using chilled tap water equal to 50 wt% of the raw ice with recycling. A sufficiently high coolant flow rate was used throughout the study so that the coolant temperature increased a negligible amount after passing the cooling jacket. The resultant ice salinity varies in the range of 0.3-0.4 g/kg when the coolant temperature is higher than or equal to -8 °C. However, the ice salinity increases to 0.81 g/kg at -9 °C, which is higher than the WHO purity standard, because the ice layer is formed on the cylinder wall. The trapped concentrated salt solution between the ice crystals cannot be easily removed.
Figure 9: Ice recovery rate and salinity as a function of coolant temperature. (freezing duration: 1 h; seed ice: 1 g at -2.1 °C; agitation: 100 rpm; optimized washing: chilled tap water = 50 wt% of the raw ice)

Fig. 9 also shows that the ice recovery rate increases from 8.1% to 23% when the coolant temperature drops from -5 °C to -9 °C. However, the ice recovery rate only increases 1.9% from -8 °C to -9 °C, whereas it increases around 4.3% per degree of temperature drop in the range of -5 °C to -8 °C. The former is due to the fact that the ice layer on the cylinder wall impairs the heat exchange between the brine and the coolant, while the latter arises from the fact that ice crystals can hardly form a layer on the wall when the coolant temperature is at -8 °C or above. The incorporation of a scraper to constantly remove the ice layer will be investigated in future studies. Thus, to maximize the ice production whilst maintaining high purity water, -8 °C should be the best coolant temperature.
3.3.4 Effects of freezing duration

Apart from coolant temperature, freezing duration also determines the amount of ice produced. Generally, a longer duration would yield a higher ice production, but the purity of product ice may be sacrificed at a very high yield. There is an optimal duration to achieve both high recovery and purity.

Fig. 10 shows the effect of freezing duration on ice recovery and salinity under the same condition as Fig. 9 except the coolant temperature was set at -8 °C for various durations. When the duration is shorter than 1.75 h, the ice recovery increases with time and the salinity remains in the acceptable range. Results of very long durations are not presented here because the resultant ice is very impure with a salinity higher than 1 g/kg.
When increasing the freezing duration, the ice appearance in the reactor changes sharply. When about 20 - 30% of the seawater freezes to ice, an ice bed can be easily seen floating on top of the brine. Unlike an iceberg that rises above the sea, the ice bed remains below the brine surface due to the strong capillary effect. When the ice amount increases to roughly 40 wt% of the feed, it fully occupies the brine volume and therefore only a uniform ice slurry can be observed. Based on experimental results, converting 55% of the seawater to ice would be close to its limit and any further cooling would increase the recovery in a much slower manner. Furthermore, when it is higher than 55%, all the remaining brine would be absorbed into the voids of the porous ice bed due to the strong capillary effect. As a result, the entire system loses its fluidity and causes severe difficulties in subsequent transferring steps. In other words, it is suggested to convert only up to 50 - 55% of the seawater to ice in a single stage FD, which corresponds to an ice recovery rate of 25 - 27.5% after considering the amount of washing water. Therefore, the optimal freezing duration is around 1.5 h.

3.3.5 Effects of seeding at different temperatures

Without seeding, the feed NaCl solution starts homogeneous nucleation at -9.8 °C. The metastable zone [57] is therefore between -9.8 °C and -2.1 °C. The seed could be introduced at any solution temperature in the metastable zone. Fig. 11 shows the effect of seeding temperature on ice recovery and salinity. A low seeding temperature increases the ice production almost linearly while maintaining a reasonable purity. When homogeneous nucleation happens at -9.8 °C, ice crystals form rapidly in a short time. Thus, the exclusion of salts
from ice is compromised. The ice formed at this temperature has a salinity above the acceptable range.

Figure 11: Ice recovery rate and salinity as a function of the degree of supercooling. (freezing duration: 1 h; seed ice: 1 g; agitation: 100 rpm; optimized washing: chilled tap water = 50 wt% of the raw ice)

Although a higher recovery rate can be achieved by seeding at a lower temperature, it is actually at the cost of more energy consumption. For instance, it took 42 min to cool the solution from -2.1 °C to -9.8 °C. Since the freezing duration lasted another 1 h, the entire duration was actually extended to nearly 1.75 h. However, its ice recovery rate of 27.2% is very comparable to that of 28.1% in Fig. 10, which was conducted at -8 °C for 1.75 h. In addition, the former has an ice salinity much higher than the latter (0.6 vs. 0.31 g/Kg) and the WHO standard (0.5 g/Kg). Therefore, the degree of supercooling should be smaller than 7 °C. In addition, cooling the solution below its freezing point becomes harder and harder because its heat capacity also increases
simultaneously [58]. One should not keep lowering the solution temperature when it is already able to produce ice. With a small amount of seed ice, it can easily eliminate the waiting period towards lower temperatures and induce a smooth transit between phase changes.

3.3.6 Effects of seeding amount

Fig. 12 shows the amount of ice production and its salinity as a function of the amount of seed ice ($M_s$) added into the feed at -2.1 °C. The more the seeds result in the more the ice ($M_p$). Surprisingly, after subtracting the mass of the seed ice, the net ice production decreases with an increase in the amount of seed ice because of the redundancy of excessive seeding.

Remarks: The error bars appear to be large because the scale of the vertical axis is enlarged. The magnitude of errors is in fact within 5%.

![Figure 12: Ice mass and salinity as a function of seeding amount. (coolant temperature: -8 °C; freezing duration: 1 h; seed ice: at -2.1 °C; agitation: 100 rpm; optimized washing: chilled tap water = 50 wt% of the raw ice)]
To understand why more seeding results in a lower net ice production, the role of seeding needs to be elaborated. Essentially, it is to trigger the onset of nucleation, so a fraction of seed ice is enough to serve the purpose. Assuming the minimum amount is $M_s_{-min}$, then the extra portion of the seed ice (i.e., $M_s - M_s_{-min}$) is redundant to activate the nucleation. In addition, it occupies the space for the ice formation from the feed. Therefore, as shown in Fig. 12, 1 g of seed ice is enough in the current case. This amount can be further reduced. Nonetheless, it is needless in this study because 1 g is already reasonably minuscule. The ice-seeding amount is thus recommended to be 0.1 wt% of the feed solution, which should be practical and economical.

3.3.7 Effects of agitation

Freezing is a highly heat sensitive process where a large amount of heat has to be exchanged between the cylinder and the seawater crystallizer instantaneously. Apart from the thermal conductivity of the cylinder wall, mixing in the system also plays a crucial role.

As shown in Fig. 13, the ice recovery rate improves from 18.7% to 21.4% when speeding up the stirrer from 50 rpm to 100 rpm. This is because a better agitation increases the heat transfer rate and reduces the concentration polarization. When a freezing process starts, water molecules are integrated into ice crystal lattices and the adjacent salt concentration rises (Gay et al., 2003). Without enough mixing, concentration polarization takes place and makes the crystal growth difficult. Therefore, increasing agitation improves the ice recovery. Meanwhile, the ice salinity drops from 0.52 g/kg to 0.33 g/kg because the crystal surfaces
are no longer contiguous with locally concentrated brine. However, the ice recovery rate remains nearly the same (21.4%) if a further increase in agitation to 150 rpm. This indicates that 100 rpm is sufficient to mitigate the localized concentration polarization. Hence, a moderate amount of agitation, such as 100 rpm, would be feasible and advisable.

Figure 13: Ice recovery rate and salinity as a function of agitation. (coolant temperature: -8 °C; freezing duration: 1 h; seed ice: 1 g at -2.1 °C; optimized washing: chilled tap water = 50 wt% of the raw ice)

3.3.8 Morphology of ice crystals

Fig. 14 shows that ice crystals obtained from various conditions appear in clusters of amorphous shapes. Their sizes vary widely, but most of them are in the range of 0.3 – 1 mm. The formation of amorphous ice crystals can be comprehended according to the Kossel (1934) model of crystal growth [59], as illustrated in Fig. 15. Crystals grow the fastest at kinks and gradually complete
the surface. A fresh crystal could commence on the surface or at the corners, but its growth rate is much slower than those at kinks. Therefore, the maximum growth rate takes place theoretically when the surface is full of kinks. Since collisions among crystals in turbulent freezing conditions should be able to keep generating numerous kinks, it produces the ice crystals with irregular surfaces and amorphous morphologies very fast in this study. The irregular shapes shown in Fig. 14 also proves that such collisions are vigorous. Hence, kinks will be constantly created.

Figure 14: The morphologies of ice crystals. (Feed: 35 g/kg NaCl solution; Coolant temperature: -8 °C; freezing duration: 1 h; agitation: 100 rpm; seed ice: 1 g at -2.1 °C; optimized washing: chilled tap water = 50 wt% of the raw ice)
Figure 15: Kossel’s model of a growing crystal surface, (A) flat surfaces, (B) steps, (C) kinks, (D) surface-adsorbed growth units, (E) edge vacancies, and (F) surface vacancies [59].

*Remarks: Edge vacancies are different from kinks in that they can close up from two directions. Kinks, on the other hand, only grows from one side to the other.

Many studies in literatures preferred a much slower ice production because they aimed to form larger ice crystals with an easier washing step. As a result, their ice crystals must grow very slowly in static environments [10,60] and took hours or even days for freezing duration [15, 60,61]. The speedy ice growth in this study comes partially from the smaller crystal sizes. It might appear harder to be washed, but the dilemma is alleviated since the proposed vacuum-filtration washing is highly efficacious. Besides, small ice crystals add a bonus to the melting step as they melt faster.
3.3.9 Iron crystallizer

The aforementioned studies were conducted using a crystallizer consisting of a glass cylinder wall. A metal one with the same dimension was also studied for comparison. Since the thermal conductivity of iron is around 50 - 80 times of glass \[62\], it was expected to expedite the freezing process. As shown in Table 2, the iron cylinder generally raises the ice recovery rate by 1.2 – 1.8 times. Surprisingly, the lowest possible coolant temperature ensuring an acceptable purity is found to be around -8 °C, which is the same as that for the glass crystallizer. Similarly, a thick ice layer with a higher salinity was formed at -9 °C or below. Even though the iron cylinder facilitates heat transfer towards the seawater, it does not exacerbate the formation of a thick ice layer on its wall. This suggests temperature difference plays a more important role than cylinder material on the formation of the thick ice layer. Since a metal cylinder wall is a more practical choice than a glass one when scaling up the FD process, the above finding is encouraging because the formation of a thick ice layer on the iron cylinder is just as manageable as on a glass one.

Table 3: A comparison of the effects of cylinder materials on ice recovery and salinity*.

<table>
<thead>
<tr>
<th>Run</th>
<th>Cylinder material</th>
<th>Coolant temperature (°C)</th>
<th>Process duration (h)</th>
<th>Ice recovery rate (%)</th>
<th>Ice salinity (after washing) (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Glass</td>
<td>-8</td>
<td>0.5</td>
<td>11</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>Iron</td>
<td>-8</td>
<td>0.5</td>
<td>20</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>Glass</td>
<td>-8</td>
<td>1</td>
<td>21</td>
<td>0.33</td>
</tr>
<tr>
<td>4</td>
<td>Iron</td>
<td>-8</td>
<td>1</td>
<td>27</td>
<td>0.32</td>
</tr>
<tr>
<td>5</td>
<td>Glass</td>
<td>-9</td>
<td>1</td>
<td>23</td>
<td>0.81</td>
</tr>
<tr>
<td>6</td>
<td>Iron</td>
<td>-9</td>
<td>1</td>
<td>30</td>
<td>0.65</td>
</tr>
</tbody>
</table>

*Feeds: 1 kg NaCl solution (35 g/kg); seed ice: 1 g at -2.1 °C; agitation: 100rpm; optimized washing: chilled tap water = 50 wt% of the raw ice.
3.3.10 Artificial seawater and real seawater tests

After understanding the key operating parameters for the freeze desalination of the 3.5wt% NaCl solution, both artificial and real seawater were tested under the optimum conditions using an iron cylinder. 520 ~ 525 g of raw ice was formed from a 1 kg feed solution within 1 h. After deducting the mass of seed and washing water, it translates to a recovery rate of about 26%. This value agrees with the result of 26.7% obtained from the NaCl solution. Table 4 lists the compositions of the melted ice. They have the total dissolved solid (TDS) of 310 ppm to 320 ppm, these values are very close to the ice made from the NaCl solution (i.e., 0.33 g/kg or 330 ppm). Thus, it affirms that FD technology is promising to desalinate real seawater.

Table 4: Ice compositions, after washing ice made from artificial seawater & real seawater*.

<table>
<thead>
<tr>
<th>Component</th>
<th>Na⁺ (ppm)</th>
<th>Mg²⁺ (ppm)</th>
<th>Ca²⁺ (ppm)</th>
<th>K⁺ (ppm)</th>
<th>TDS (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>92.96 ±7.92</td>
<td>11.8 ±0.99</td>
<td>5.56 ±0.45</td>
<td>5.6 ±1.1</td>
<td>315.52 ±23.86</td>
</tr>
</tbody>
</table>

(b) Ice salinity of real seawater tests

<table>
<thead>
<tr>
<th>Component</th>
<th>Na⁺ (ppm)</th>
<th>Mg²⁺ (ppm)</th>
<th>Ca²⁺ (ppm)</th>
<th>K⁺ (ppm)</th>
<th>TDS (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>94.57 ±15.74</td>
<td>12.2 ±1.94</td>
<td>6.99 ±0.80</td>
<td>3.58 ±2.11</td>
<td>321.45 ±52.74</td>
</tr>
</tbody>
</table>

*Feeds: 1 kg artificial seawater or real seawater; freeze duration: 1 h using an iron cylinder; coolant temperature: -8 °C; seed ice: 1 g at -2.1 °C; optimized washing: chilled tap water = 50 wt% of the raw ice.

**Fig. 16** compares the relative percentages of major ions Mg⁺, Ca²⁺ and K⁺ in feeds and product ice in details. Interestingly, the relative percentage of each
ion is similar in both the feed and product ice. This suggests that none of these ions preferentially remains in the product ice because salt ions in the solution mainly adhere onto the ice surfaces and they are not trapped in the ice lattices. The non-trapping behaviors are important and desirable for freeze desalination of real seawater, especially in the washing process. Therefore, the process parameters optimized in this study provide good guidelines for the further development of the FD process.

![Figure 16](image)

**Figure 16:** Compositions of (a) artificial seawater, (b) ice produced from artificial seawater, (c) real seawater, (d) ice produced from real seawater.

### 3.4 Conclusion

In this chapter, the operating parameters and washing procedure of indirect contact FD using LNG were systematically investigated and optimized. The following conclusions can be drawn:
1) The importance of an effective washing procedure outweighs many other operating parameters. Vacuum filtration was found to effectively separate ice from the washing water. The amount of washing water needed was optimized to be 50 wt% of the raw ice.

2) While LNG is the source of cold energy, an intermediate coolant would be used to cool the seawater. The optimal coolant temperature should be around -8 °C. When using a colder coolant, a thick ice layer would likely form on the cylinder wall and thus reduce the purity of the product ice.

3) The optimal freezing duration was found to be 1 h for an iron crystallizer and 1.5 h for a glass crystallizer. With a longer duration, the amount of ice would significantly reduce the solution’s fluidity. Heat and mass transfer would then be greatly impaired.

4) Seed ice should be added to the feed seawater when it reaches freezing the point. It would trigger nucleation and ensure a smooth transit to freezing. The amount of seed ice was optimized to be 0.1 wt% of the feed solution. An excess amount of seed ice would actually decrease the net ice production.

5) Homogeneous mixing was also indispensable in this process. A moderate stirrer speed of 100 rpm was found to be practical and economical. Insufficient agitation would impede heat and mass transfer, while excessive agitation would waste energy.

6) Both artificial seawater and real seawater were tested under the optimized conditions. The product ice’s amount and salinity were both very close to those obtained from the 3.5 wt% NaCl solution. Raw ice of 520 ~ 525 g was formed from a 1 kg feed solution within 1 h, which corresponds to a recovery rate of about 26%. Thus, the process parameters optimized in this study can be directly
used for the freeze desalination of seawater. In the event of scaling up, the operating parameters will have to be adjusted to suit the greater capacity. A larger scale study of freeze desalination experiments should be conducted in the future accordingly.
Chapter 4. Use of Triethyl Phosphate in Membrane Fabrication

4.1. Experimental materials

A commercial PVDF polymer, Kynar® HSV 900 resin (specific gravity: 1.775), was kindly supplied by Arkema Inc. N-methyl-2-pyrrolidone (NMP), triethyl phosphate (TEP), isopropanol (IPA) and sodium chloride (NaCl) were purchased from Merck. Deionized water was produced by a Milli-Q unit from MilliPore with the resistivity of 18 MΩ·cm. All chemicals were used as received.

4.2 Experimental procedures

4.2.1 Preparation of PVDF hollow fiber membranes

The dope solutions were prepared by adding the dry PVDF powder into the solvents with a weight ratio of 12/88. Three solvent systems were studied: D1) NMP 88 wt%; D2) NMP/TEP 44/44 wt% and D3) TEP 88 wt%. The polymer solutions were mechanically stirred at 60 °C for 24 h to ensure reaching a homogeneous state. They were then degassed overnight before being transferred into ISCO syringe pumps. All hollow fibers were fabricated by a dry-jet wet-spinning process. Mixtures of water with IPA or TEP were used as the external coagulants. The specific spinning conditions are tabulated in Table 5, and the resultant fibers are named as M1-M9, respectively. After spinning, the as-spun fibers were immersed in water for 3 days. The water was changed daily to remove the residual solvents and IPA. Thereafter, the membranes were dried in a freeze drier (S61-Modulyo-D, Thermo Electron Corp.) before tests.
Table 5: Spinning conditions for PVDF hollow fiber membranes$^a$.

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>M7</th>
<th>M8</th>
<th>M9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope composition (PVDF/NMP/TEP wt%)</td>
<td>12/88/0</td>
<td>12/44/44</td>
<td></td>
<td></td>
<td></td>
<td>12/0/88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bore fluid composition (wt%)</td>
<td>NMP/water 40/60</td>
<td>TEP/water 40/60</td>
<td>TEP/water 30/70</td>
<td>TEP/water 20/80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>External coagulant (wt%)</td>
<td>IPA/water 30/70</td>
<td>water 100</td>
<td>TEP/water 30/70</td>
<td>TEP/water 60/40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Dope flow rate: 1.5 ml/min; bore fluid flow rate: 1.6 ml/min; air gap: 3 cm; Take up speed: 1.76 m/min; Spinneret dimension: OD/ID 1.6/1.05 mm; Coagulant bath and spinneret temperature: 25 °C.

4.2.2 Membrane characterizations

4.2.2.1 Membrane morphology, contact angle and porosity

Membrane morphologies were observed by Field Emission Scanning Electron Microscopy (FESEM JEOL JSM-6700LV). All samples were coated with platinum using a JEOL JFC-1200 ion sputtering device. Specifically, the cross-section samples were fractured in liquid nitrogen. An ImageJ software (NIH) was employed to analyze the surface porosity and pore size distribution using FESEM images.

The dynamic water contact angles of hollow fibers were measured by a KSV Sigma 701 tensiometer (± 0.01°, KSV Instruments Ltd., Finland). When the hollow fiber sample touched water, the change of the interfacial force would be detected by an extremely sensitive micro-balance. Each reported value was the average of 3 – 5 measurements.

The overall membrane porosity was calculated by:

$$
\varepsilon = \frac{V_{\text{void}}}{V_{\text{membrane}}} = \frac{V_{\text{membrane}} - V_{\text{polymer}}}{V_{\text{membrane}}} = 1 - \frac{V_{\text{polymer}}}{V_{\text{membrane}}} = 1 - \frac{m/p_{\text{polymer}}}{V_{\text{membrane}}} \quad (4)
$$

where $V_{\text{void}}$ is the void volume, $V_{\text{membrane}}$ is the hollow fiber membrane volume, $V_{\text{polymer}}$ is the volume of the polymer skeleton, $m$ is the membrane mass and
\( \rho_{\text{polymer}} \) is the polymer density. The membrane mass was measured by a highly accurate beam balance (A&D, GR-200). \( V_{\text{membrane}} \) was calculated by multiplying the cross sectional area and the fiber length.

4.2.2.2 Rheological and mechanical properties

The viscosity of dope solutions was measured at 25°C by a digital rotary viscometer (Rotating viscometer B-One TOUCH, Lamy Rheology, France) using spindle No. 4 at a rotating speed of 150 rpm.

The maximum tensile stress, Young's modulus and elongation at break were measured by an Instron tensiometer (Model 5542, Instron Corp.). The starting gauge length was 50 mm, and the elongation rate was 10 mm/min.

4.2.2.3 Liquid entry pressure (LEP)

The LEP value of hollow fiber membranes was measured by a setup as shown in Fig. 17. One end of the hollow fiber module was sealed and immersed in a beaker full of DI water. The other end of the module was open with its lumen connected to a stainless steel cylinder cell filled with 3.5 wt% saline water. The cell pressure was controlled by a pressure gauge (Range: 0–4 bar ±0.001 bar, Wika) with the aid of a compressed nitrogen cylinder. The DI water in the beaker was constantly stirred and its conductivity was monitored by a conductivity meter (Lab960, SCHOOT instrument, Germany). Then the cell pressure was raised at 0.1 bar every 5 min. Once the reading of the conductivity meter began to increase, the pressure at that moment was recorded as the LEP.
4.2.3 Phase inversion studies of dope solutions

4.2.3.1 Ternary phase diagram (PVDF/solvent/water)

The PVDF polymer was dissolved in TEP and NMP at different concentrations (4% - 14%) at room temperature (25 °C). Water was slowly added into these solutions with a minuscule amount (<0.02 g) each time. A local precipitation would form immediately where the water droplet was added. The solution was then mechanically stirred until it reached a homogeneous state again. Afterwards, another water droplet would be added. When the precipitation in the mixture could no longer be dissolved within 3 days, the composition at this point would be recorded as a cloud point. The binodal curves were plotted based on two sets of cloud points.

4.2.3.2 Light transmittance tests and precipitation studies

The dope solution was cast on a glass slide by a casting knife with a gap of 150 μm. The slide was immediately placed into a plastic cuvette filled with an IPA/water 30/70 wt% solution. The cuvette was then positioned in a UV-vis...
scanning spectrophotometer (Pharo 300, Merck) where the light transmittance at 525 nm was recorded as a function of time by its inbuilt software.

The precipitation of dope solutions was also analyzed by a polarized light microscope (PLM, Olympus BX50) [63-65]. One drop of dope solutions was sandwiched between two microscopic glass slides. Then one drop of water was added to the edge of the slides as a coagulant. The water would be drawn into the glass gap automatically because of the capillary effect. The precipitation front was observed and video-recorded by an inbuilt software.

4.2.4 Direct contact membrane distillation (DCMD) tests
A hot model 3.5 wt% NaCl solution was used as the feed for DCMD tests. It was heated to 60 °C by a heating circulator (F12,Julabo) and circulated along the shell side of the hollow fiber modules. Cold DI water at 15 °C was circulated along the lumen side of the hollow fiber module with the aid of a refrigerated circulator (RT7,Thermo Scientific). The flow rates of the feed and permeate were 0.5 L/min and 0.1 L/min, respectively. The conductivity of the permeate solution was measured by a conductivity meter (Lab960, SCHOOT instrument, Germany). The permeation flux and salt rejection were calculated by the following equations:

\[
Permeation \text{ flux (} kg/m^2 \cdot h) = \frac{\Delta W}{A \times t} \tag{5}
\]

\[
Rejection (\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100 \tag{6}
\]
where $\Delta W$ (kg) is the increase of the permeate mass, $t$ (h) is the corresponding duration, $A$ ($m^2$) is the effective membrane area, $C_p$ and $C_f$ are the NaCl concentrations of the permeate and feed, respectively.

4.2.5 Molecular simulation

Atomistic simulations were carried out for PVDF polymer chains in NMP and TEP solvents. BIOVIA Materials Studio 2017 was used to build the models. The PVDF models were simulated based on OPLS-AA (All-atom) force field, which is a commonly used force field for polymer and biological systems. It includes the equilibrium bond lengths, angles and torsion angles, force constants, Lennard Jones parameters and partial charges, which are derived from quantum mechanical calculations [66]. 100 repeat units were constructed for the PVDF polymer. Considering the possible entanglement among polymer chains, two polymer chains were inserted in the periodic simulation box and the mass ratio between the polymer chains and solvents is 12/88. The model systems with around 15000 atoms were then imported as input and all the molecular dynamics simulations and data analysis were carried out with GROMACS package [67]. Each model was equilibrated for 10 ns, followed by 25 ns for data collection. The isobaric-isothermal (NPT) ensemble was performed with a Berendsen pressure control and V-rescale temperature control. The temperature was set as 298 K and the reference pressure as 1 bar. Particle mesh Ewald (PME) was used to calculate the electrostatic interactions with a direct-space cutoff of 1.5 nm and a grid spacing of 0.12 nm. The OPLS-AA force field [66] was employed for both PVDF polymer and solvents, which has been tested for NMP and similar organic solvents [68]. Water was simulated with the SPC/E model,
where water is represented as a triatomic molecule with rigid bonds and a single Lennard-Jones site centered on the oxygen atoms and point charges centered on each atom.

The motion of polymer chains and solvents can be characterized by mean squared displacement (MSD) as

\[
MSD (t) = \frac{1}{N} \sum_{i=1}^{N} \langle |r_i(t) - r_i(0)|^2 \rangle
\]

where \(N\) is the number of particles and \(r_i(t)\) and \(r_i(0)\) are the final and initial positions of particle \(i\) over the time interval \(t\). Here particles refer to all the non-hydrogen atoms on the backbone of polymer chains or in solvent molecules, respectively.

4.3 Results and discussion

4.3.1 Phase separation behavior of PVDF/solvent systems

Fig. 18 shows the ternary phase diagram of PVDF/solvent/water systems at 25 °C. The binodal curves denote the limit of the homogenous phase. When the solution is brought across the binodal curve, liquid-liquid demixing takes place [69-70]. Therefore, the binodal curve is essentially a liquid-liquid demixing boundary where the stable region is on its left and the unstable region is on its right. The binodal curve of TEP is on the left side of NMP’s, which means the PVDF/TEP system requires a less non-solvent to induce phase inversion. This could be because TEP is a slightly weaker solvent for PVDF compared to NMP [71-72]. This is also supported by a comparison of their solubility parameters shown in Table 6(a) [73-74]. TEP has a slightly more different solubility parameter (22.2 MPa\(^{1/2}\)) from PVDF (23.2 MPa\(^{1/2}\)) than NMP (22.9 MPa\(^{1/2}\)).
a result, TEP is slightly less compatible with PVDF. This could potentially favor a more porous structure as the polymer chains may exist in a more coiled state and leave more space among them. Previous studies also suggested that PVDF membranes made from a weak solvent like TEP tended to have a sponge structure [75-76] or a honeycomb structure [77].

Figure 18: Phase diagram of PVDF/solvent/water systems.

*Remarks: To read the composition of a specific point on the diagram, one can draw lines towards the individual axis. For instance, to read the PVDF composition, a horizontal line can be drawn to the right and the value can be read from where the line intersects the right axis. To read the water composition, a line that parallels the left axis can be drawn and the value can be read at where it crosses the horizontal axis.
Table 6: a) Hansen solubility parameters at 25 °C [73-74]. b) Molecular simulation results of the PVDF/solvent systems. c) Dynamic (shear) viscosity of the dope solutions for hollow fiber spinning.

(a)

<table>
<thead>
<tr>
<th>Solvent/Polymer</th>
<th>Water</th>
<th>NMP</th>
<th>TEP</th>
<th>IPA</th>
<th>PVDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_\text{e}$ (dispersion force)</td>
<td>15.6</td>
<td>18.0</td>
<td>16.8</td>
<td>15.8</td>
<td>17.0</td>
</tr>
<tr>
<td>$\delta_\text{p}$ (dipole force)</td>
<td>16.0</td>
<td>12.3</td>
<td>11.5</td>
<td>6.1</td>
<td>12.1</td>
</tr>
<tr>
<td>$\delta_\text{b}$ (hydrogen bonding force)</td>
<td>42.3</td>
<td>7.2</td>
<td>9.2</td>
<td>16.4</td>
<td>10.2</td>
</tr>
<tr>
<td>$\delta_{sp}$ (solubility parameter)</td>
<td>47.8</td>
<td>22.9</td>
<td>22.2</td>
<td>23.5</td>
<td>23.2</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th></th>
<th>12/88 PVDF/NMP</th>
<th>12/88 PVDF/TEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular size of solvent (Å²)</td>
<td>104.7</td>
<td>183.2</td>
</tr>
<tr>
<td>Radius of gyration of polymer (Å)</td>
<td>25.7 ± 1.9</td>
<td>18.9 ± 1.7</td>
</tr>
<tr>
<td>Self-diffusivity of solvent (cm²/s)</td>
<td>8.02 ± 0.17 (×10⁻⁷)</td>
<td>1.43 ± 0.21 (×10⁻⁷)</td>
</tr>
<tr>
<td>Interactions between polymer and solvent (kJ/mol)</td>
<td>-23.71 ± 0.68</td>
<td>-21.72 ± 0.71</td>
</tr>
</tbody>
</table>

(c)

<table>
<thead>
<tr>
<th>Dope solution</th>
<th>D₁ (12/88 PVDF/NMP)</th>
<th>D₂ (12/44/44 PVDF/NMP/TEP)</th>
<th>D₃ (12/88 PVDF/TEP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic viscosity (Pa·s)</td>
<td>10.9 ± 0.04</td>
<td>12.7 ± 0.05</td>
<td>15.0 ± 0.02</td>
</tr>
</tbody>
</table>

The weak solvent power of TEP is also supported by the molecular simulation results of the two PVDF/solvent systems. It is clear in Fig. 19(a) that PVDF polymer chains are more curled in TEP, with a smaller radius of gyration (18.9 Å vs. 25.7 Å) as shown in Table 6(b), which may be attributed to the larger molecular size of TEP and its slightly weaker interactions with PVDF polymer chains (-21.72 kJ/mol vs. -23.71 kJ/mol) for each PVDF repeat unit. In addition, the polymer chains display a smaller mean squared displacement (MSD) in TEP than in NMP as shown in Fig. 19(b), which also proves the weak solvent power of TEP.

*Remarks: Although the radius of gyration of PVDF in TEP is smaller, it does not result in a higher diffusivity for PVDF in TEP. The weaker interaction
between PVDF and TEP overwrites the effect of smaller radius of gyration, so it leads to a lower diffusivity for PVDF in TEP.

Figure 19: a) Snapshots from the molecular dynamics simulations showing the PVDF chain conformation in NMP (left) and TEP (right) solvents. b) Mean squared displacement (MSD) for the PVDF polymer chains in NMP and TEP solvents.

The kinetics of phase inversion behavior is shown in Fig. 20. The camera captures the exact position of the precipitation front when time elapses. It is clear that water intrudes much slower in the TEP solution. This may arise from a higher dope solution viscosity and a lower water affinity. In terms of water-
solvent affinity, Table 6(a) compares their Hansen solubility parameters and individual components. NMP and TEP have very comparable solubility parameters. Since the solubility parameter difference between TEP and water (22.2 vs. 47.8 MPa$^{1/2}$) is slightly more than that between NMP and water (22.9 vs. 47.8 MPa$^{1/2}$), TEP might have a slightly lower affinity to water and thus retard water from intrusion. Additionally, the harmonic mean value of diffusivity for the TEP and water pair ($8.7 \times 10^{-6}$ cm$^2$/s) is slightly less than that for the NMP and water pair ($9.1 \times 10^{-6}$ cm$^2$/s) [77]. This may also lead to a slower solvent exchange rate between TEP and water. In terms of viscosity, Table 6(c) presents the measured viscosity of each dope. D3 (PVDF/TEP 12/88 wt%) has the highest viscosity of 15.0 Pa·s, while D1 (PVDF/NMP 12/88 wt%) has the lowest viscosity of 10.9 Pa·s. The higher viscosity of PVDF/TEP may arise from a greater polymer entanglement, which can be observed from Fig. 19 as well as supported by an analysis of radial distribution function (RDF). RDF measures the probability of finding one atom located at a distance from the reference atom. Fig. 21 illustrates the RDF between the backbone C atoms in the first polymer chain and the second polymer chain. The peaks indicate the binding interaction between the selected atoms and the reference atoms. The sharp peaks at 0.56 nm reflect the strong close entanglement between two chains for both solvent environments. Interestingly, there is a broad hump located from 1.5 to 2.5 nm only for TEP, which signifies a larger degree of entanglement for PVDF in TEP. Consequently, the high viscosity may be the dominating factor to hinder the water intrusion into the PVDF/TEP dope solution.
Figure 20: Phase inversion phenomena of PVDF/solvent systems in water.

Figure 21: Radial distribution functions (RDFs) between the C atoms in different polymer chains.

The phase inversion kinetics studied by means of light transmission through cast membranes also confirm the above observation. When phase inversion progresses, the thin nascent membrane gradually loses its translucency
measured by a spectrophotometer. The decline rate of light intensity is usually proportional to the speed of phase inversion [65,78]. As shown in Fig. 22, the TEP solution shows a tardier decay of light transmittance, indicating that the PVDF/TEP solution has a slower phase inversion kinetics than the PVDF/NMP solution. As a result, the former favors to form a porous sponge-like membrane structure than the latter.

Figure 22: The decline of light transmittance through flat-sheet membrane films cast from NMP and TEP dope solutions and then immediately immersed in IPA/water 30/70 wt%.

4.3.2 Effects of solvent composition in dope solutions

Fig. 23 shows the FESEM morphology of hollow fibers spun from dopes with different solvent compositions. From M1 to M3, the spinning conditions are the
same except the solvent composition in dopes changes from NMP 88 wt% to NMP/TEP 44/44 wt% and then to TEP 88 wt%, respectively. A clear transition of porosity can be observed. M1 has the most dense outer and inner surfaces and cross-section, while M3 is the most porous. Fig. 24 shows that the overall porosity follows the order of M3 (89.7%) > M2 (79.5%) > M1 (72.4%). In addition, as shown in Table 7, the surface porosity of M3 is 20–30 times higher than that of M1. The disparity of porosity may result from the effects of a weaker solvent and a higher viscosity of the PVDF/TEP solution, as discussed previously. Moreover, the diffusivity of TEP in water ($6.3 \times 10^{-6}$ cm$^2$/s) is much less than water in TEP ($13.7 \times 10^{-6}$ cm$^2$/s) [77], which favors a water induced spinodal decomposition and a more porous structure. Table 7 tabulates their DCMD performance at 60 °C, all three hollow fibers have good salt rejections of about 99.99%, but the water vapor flux rises considerably from M1 (<1 kg/m$^2$·h) to M3 (22 kg/m$^2$·h) because of the increased porosity. Clearly, TEP can be a very effective solvent to fabricate PVDF membranes with a high flux.
Figure 23: Cross-section and outer/inner surface morphologies of hollow fiber membranes spun with different solvent composition. (Bore fluid: NMP/water 40/60 wt%; external coagulant: IPA/water 30/70 wt%).

Figure 24: Comparison of porosity among the as-spun hollow fiber membranes.
Table 7: Comparison of hollow fibers spun using different solvent composition

<table>
<thead>
<tr>
<th>Flux (kg/m²·h)</th>
<th>Rejection Overall (%), porosity (%)</th>
<th>Outer surface porosity (%)</th>
<th>Inner surface porosity (%)</th>
<th>Contact Angle (°)</th>
<th>Elongation at Break (%)</th>
<th>Max Tensile Stress (Mpa)</th>
<th>Young's Modulus (Mpa)</th>
<th>LEP (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>&lt;1</td>
<td>99.99</td>
<td>72.4 ± 1.2</td>
<td>0.49 ± 0.05</td>
<td>2.67 ± 0.3</td>
<td>95.42 ± 9.6</td>
<td>306 ± 6.3</td>
<td>6.29 ± 0.08</td>
</tr>
<tr>
<td>M2</td>
<td>15.1 ± 0.2</td>
<td>99.99</td>
<td>79.5 ± 1.4</td>
<td>0.50 ± 0.04</td>
<td>7.75 ± 0.3</td>
<td>102.8 ± 1.3</td>
<td>153 ± 9.4</td>
<td>2.72 ± 0.10</td>
</tr>
<tr>
<td>M3</td>
<td>21.8 ± 0.4</td>
<td>99.99</td>
<td>89.7 ± 0.9</td>
<td>16.9 ± 0.16</td>
<td>57.1 ± 0.9</td>
<td>313.6 ± 6.9</td>
<td>106 ± 7.6</td>
<td>0.76 ± 0.01</td>
</tr>
<tr>
<td>M4</td>
<td>23.5 ± 0.2</td>
<td>99.99</td>
<td>88.8 ± 1.1</td>
<td>13.4 ± 0.19</td>
<td>25.1 ± 0.5</td>
<td>113.6 ± 4.8</td>
<td>96.2 ± 10</td>
<td>0.87 ± 0.08</td>
</tr>
<tr>
<td>M5</td>
<td>10.7 ± 0.6</td>
<td>99.99</td>
<td>84.3 ± 0.9</td>
<td>0.88 ± 0.06</td>
<td>17.4 ± 0.2</td>
<td>89.89 ± 2.1</td>
<td>174 ± 5.4</td>
<td>1.78 ± 0.04</td>
</tr>
<tr>
<td>M6</td>
<td>19.9 ± 0.5</td>
<td>99.99</td>
<td>85.3 ± 0.4</td>
<td>3.18 ± 0.04</td>
<td>38.7 ± 0.4</td>
<td>102.4 ± 4.1</td>
<td>152 ± 6.5</td>
<td>1.35 ± 0.06</td>
</tr>
<tr>
<td>M7</td>
<td>18.4 ± 0.8</td>
<td>99.99</td>
<td>92.7 ± 0.5</td>
<td>3.05 ± 0.08</td>
<td>11.5 ± 0.2</td>
<td>143.0 ± 2.8</td>
<td>98.7 ± 5.2</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td>M8</td>
<td>19.3 ± 0.3</td>
<td>99.99</td>
<td>83.8 ± 0.8</td>
<td>2.14 ± 0.05</td>
<td>35.5 ± 0.6</td>
<td>103.8 ± 3.5</td>
<td>127 ± 3.3</td>
<td>1.60 ± 0.06</td>
</tr>
<tr>
<td>M9</td>
<td>18.0 ± 0.5</td>
<td>99.99</td>
<td>83.2 ± 0.6</td>
<td>1.63 ± 0.09</td>
<td>9.69 ± 0.3</td>
<td>99.12 ± 4.0</td>
<td>173 ± 4.3</td>
<td>2.08 ± 0.04</td>
</tr>
</tbody>
</table>

Table 7 also shows that the contact angle increases from M1 to M3 due to the effect of increased surface roughness [35,79]. However, a dramatic drop in LEP is also observed. The LEP value of M1 is 3.1 bar, but it decreases to 0.2 bar in M3. In addition, the mechanical properties in terms of the maximum tensile stress, Young’s modulus and elongation at break all drop substantially from M1 to M3, as shown in Table 7, due to the overly large pore size and macrovoids. Therefore, more efforts are needed to remedy the low LEP value and mechanical weakness in order to produce useful PVDF membranes using TEP for MD.

To further apply the principle of green chemistry, the bore fluid of M3 is changed from a NMP/water mixture to a TEP/water mixture in M4. Fig. 23 and Table 7 compare their morphology and physicochemical properties. They have similar mechanical properties and overall morphologies. However, an obvious change lies at the inner surface morphology of M4, which becomes less porous. Because TEP is a weaker solvent than NMP, this leads to a faster phase inversion at the inner surface and results in a less porous surface in M4. In short, TEP favors to produce membranes with a more porous structure and a higher vapor flux. However, the mechanical integrity is greatly compromised. The next few sections attempt to solve this dilemma.
4.3.3 Effects of TEP concentration in the external coagulant

The addition of IPA into the external water coagulant is a common practice to induce the delay-deming process [44,45,80]. It often leads to a more porous membrane structure suitable for MD applications. While it can improve the permeation flux, the mechanical properties of the resultant membranes are often weakened. To overcome it, one may change the external coagulant to water or a TEP/water mixture. As a result, the phase inversion process is expedited so that the nascent porous membrane is rapidly solidified with reasonably good mechanical properties. According to Fadhil et al. [45], the TEP/water mixture has a milder effect of delay demixing than the IPA/water mixture. An additional benefit of replacing IPA by TEP in the external coagulant is to simplify the downstream wastewater treatment. Since the wastewater only comprises TEP and water, it would be easier to treat it than to treat that containing three components (i.e., water, TEP and IPA).

To search for an appropriate TEP concentration in the external coagulant, a range of 0 to 60 wt% TEP in water is studied. Fig. 25 shows the morphology of the hollow fiber membranes when the coagulant changes from water to 30/70 TEP/H₂O and 60/40 TEP/H₂O. Firstly, the outer surface pore size becomes larger from membranes M5 to M7 because a softer coagulant tends to induce more delay demixing and result in a more porous outer surface. Secondly, the cross sections turn out to be largely distinct. Large macrovoids gradually evolve with an increase in TEP concentration. Since almost all macrovoids are inward pointed [81], the macrovoids observed in M7 are formed because of the bore fluid intrusion. The cause of this phenomenon is probably due to the fact that
the much stronger delay demixing at the outer surface allows the bore fluid to intrude deep into the cross-section. In contrast, the external coagulants of M5 and M6 are relatively stronger so that the membranes solidify faster enough to counter the bore fluid intrusion. The porosity measurements shown in Fig. 24 and Table 7 also reflect the increasing trend of porosity from M5 to M7.

Figure 25: Cross-section and outer/inner surface morphologies of hollow fiber membranes spun with different external coagulants. (Dope solution: PVDF/TEP 12/88 wt%; bore fluid: TEP/water 40/60 wt%).

Fig. 26 displays the variations of mechanical properties and permeation flux under DCMD tests as a function of external coagulant composition, while Table 7 gives the detailed quantitative values. All three aspects of mechanical
properties decrease from M5 to M7 when the external coagulant becomes weaker. Especially for M7 where 60/40 TEP/H₂O is used as the coagulant, the maximum tensile stress and Young’s modulus drop by nearly 75% compared to M5 where water is employed as the coagulant. Since the membrane structure becomes overly porous, it actually impairs the mechanical integrity. On the other hand, the permeation flux shows a different trend. It increases from M5 to M6 but decreases from M6 to M7. With a higher porosity, the permeation flux is expected to increase from M5 to M6. However, the huge macrovoids in M7 actually widen the cross-section thickness (M7, 324 μm; M6, 166 μm) and thus prolong the vapor traveling distance. As a result, the permeate flux dips slightly.

Figure 26: Effects of external coagulant on MD water vapor permeation flux, elongation at break, maximum tensile stress and Young’s modulus.

Among these three membranes (i.e., M5 to M7), M6 has most balanced MD performance. It has the highest flux but slightly lower mechanical properties
compared to M5. Therefore, the 30/70 TEP/H₂O is used as the external coagulant in the subsequent studies in order to search for the optimal bore fluid composition.

4.3.4 Effects of TEP concentration in the bore fluid

The TEP concentration in the bore fluid is 40 wt% for M6. It is further varied from 20 to 60 wt% in the following investigation. However, hollow fibers spun from bore fluids containing 50 and 60 wt% TEP are not reported here because the spinning process is not stable. This is because when the bore fluid is too soft, it is hard to form the nascent membrane. The dope solution flows through the spinneret in a very fluidic state due to the extra-low degree of solidification. The spinning process is frequently discontinued due to the fiber breakage.

The range of TEP concentration in the bore fluid is therefore focused on 20, 30 and 40 wt%. Fig. 27 illustrates their hollow fiber morphology. From M6 to M8 and M9, the TEP concentration decreases. As expected and consistent with the observation in Figure 25, the inner surfaces become denser and the outer surfaces remain nearly the same. However, the morphological change in the cross section is interesting. When the TEP concentration deceases to 20 wt%, a macrovoid-free membrane structure is formed. This is because when the coagulation strength becomes higher with a lower TEP concentration in the bore fluid, the membrane precipitates faster. The rapid solidification prevents a large amount of bore fluid from penetrating into the cross-section during phase inversion. Thus, macrovoids are not readily formed. A macrovoid-free membrane should further improve the mechanical properties and make the
membranes longer-lasting. Fig. 28 confirms the enhancement in mechanical properties from M6 to M8 and M9. Comparing M8 to M9, the maximum tensile stress is improved by over 50% to 2.08 MPa, while the Young’s modulus is also improved to be greater than 40 MPa.

Figure 27: Cross-section and outer/inner surface morphologies of hollow fiber membranes spun with different bore fluids. (Dope solution: PVDF/TEP 12/88 wt%; external coagulant: TEP/water 30/70 wt%).
Figure 28: Effects of bore fluid on MD water vapor permeation flux, elongation at break, Maximum tensile stress and Young’s modulus.

As illustrated in Fig. 28, the permeation fluxes of M6, M8 and M9 vary between 18 and 20 kg/m²·h. The flux reduction from M6 to M8 and M9 can be attributed to the slightly denser inner surfaces and fewer macrovoids. Fig. 24 also shows that the membrane porosity drops slightly from 85.3% to 83.8% and 83.2%, respectively, indicating the vapor permeation resistance across the membranes is mildly increased from M6 to M8 and M9. However, the wetting resistance of M8 and M9 are encouraging. As presented in Table 7 and Fig. 29, the LEP values are much improved from M6 to M8 and M9 owing to the denser inner surfaces. Despite of a slightly lower MD flux in the resultant membranes, a higher LEP value is greatly important for real MD operations [82].
Considering the overall effects of TEP concentration on permeation flux, mechanical strength and LEP, a concentration of 30 wt% TEP might be an optimum choice for the bore fluid. Therefore, the hollow fiber membrane M8 fabricated from the optimal conditions, external coagulation of TEP/water 30/70 wt% and bore fluid of TEP/water 30/70 wt%, shows the most balanced flux of 19.3 kg/m²h, tensile strength of 1.6 MPa and LEP of 1.8 bar.

4.4 Conclusion
This study has attempted to plow the way through a green path to replace toxic solvents by using a non-toxic solvent, TEP, to fabricate highly porous PVDF hollow fiber membranes for MD applications. By comparing to one of the most common solvents, NMP, the phase inversion thermodynamics and kinetics of
the PVDF/TEP system are closely investigated. It is found that PVDF/TEP dope solutions naturally promote a more porous membrane structure. All membranes fabricated in this study have porosity higher than 80%, with the highest value of 92.7%. This advantage is attributed to a higher viscosity and a lower water affinity. The dope viscosity tends to be higher as TEP is a weak solvent for PVDF. The lower affinity to water is confirmed by the comparison of solubility parameters.

To avoid unsatisfactory compromises on mechanical strength and LEP values, caused by the use of TEP. The chemical compositions of external coagulant and bore fluid are further optimized. When both the external coagulant and bore fluid contain 30 wt% TEP in water, the resultant hollow fiber membranes have a promising permeation flux of about 20 kg/m²·h and an LEP of 1.8 bar. Clearly, the newly developed PVDF hollow fiber membranes spun from the green solvent of TEP at optimal conditions have achieved high MD performance in terms of permeation flux, robust mechanical strength and strong anti-wetting property.

In addition, all dope solutions investigated in this study are simply PVDF/solvent binary systems. No additive or post-treatment is involved. The simple fabrication method would smoothen out the complexity in scale-up and ensure favorable for commercialization.
Chapter 5. Conclusions and Future Work

Seawater desalination by freeze desalination and membrane distillation was studied. Freeze desalination is less energy-intensive but sensitive to high feed concentration, so it has to be the first step. On the contrary, membrane distillation is insensitive to high feed concentration but more energy-intensive, so it can be placed as the second step.

While pure ice is produced by the freeze desalination step, it is not recommended to concentrate the seawater to higher than 50 g/kg. Otherwise, the high salinity will seriously compromise the ice purity. When this concentrated brine is passed to the membrane distillation system, the flux will barely be affected by the raised feed concentration. The vapor pressure of the feed solution, according to Raoult's law, is almost unchanged unless the concentration goes significantly higher.

Although membrane distillation can run as a sustainable process, the membrane fabrication process usually involves a large amount of toxic solvents. The use of a green solvent, triethyl phosphate, to replace common toxic solvents was studied. It was for the first time used to fabricate hollow fiber membranes in membrane distillation. With the fundamental understanding of the solvent, highly porous membranes can be successfully made. The flux is as high as 20 LMH and it has a robust anti-wetting property.

In the future, there needs to be more detailed energy calculation for this hybrid process. While the cold energy from LNG regasification can be used for the freeze desalination process, solar panels may be used to power the membrane
distillation process. With accurate calculation, the footprint of this two-step system can be easily determined. Then it will be ready to be considered for commercialization.
References


[53] K. Muldrew, L.E. McGann, Physical Aspects of Freezing, University of Alberta, Cryobiology - A Short Course. Available from:


Publications
