A comprehensive understanding of co-solvent effects on interfacial polymerization : interaction with trimesoyl chloride

Lee, Jaewoo; Wang, Rong; Bae, Tae-Hyun

2019

Lee, J., Wang, R., & Bae, T.-H. (2019). A comprehensive understanding of co-solvent effects on interfacial polymerization : interaction with trimesoyl chloride. *Journal of Membrane Science*, 58370-80. doi:10.1016/j.memsci.2019.04.038

<https://hdl.handle.net/10356/103412>

<https://doi.org/212518>;

<https://doi.org/10.1016/j.memsci.2019.04.038>;

<https://doi.org/212518>

© 2019 Elsevier. All rights reserved. This paper was published in *Journal of Membrane Science* and is made available with permission of Elsevier.

Downloaded on 26 Apr 2023 19:49:30 SGT

Accepted Manuscript

A comprehensive understanding of co-solvent effects on interfacial polymerization:
Interaction with trimesoyl chloride

Jaewoo Lee, Rong Wang, Tae-Hyun Bae

PII: S0376-7388(18)32555-9

DOI: <https://doi.org/10.1016/j.memsci.2019.04.038>

Reference: MEMSCI 17034

To appear in: *Journal of Membrane Science*

Received Date: 12 September 2018

Revised Date: 22 January 2019

Accepted Date: 17 April 2019

Please cite this article as: J. Lee, R. Wang, T.-H. Bae, A comprehensive understanding of co-solvent effects on interfacial polymerization: Interaction with trimesoyl chloride, *Journal of Membrane Science* (2019), doi: <https://doi.org/10.1016/j.memsci.2019.04.038>.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**A comprehensive understanding of co-solvent effects on interfacial
polymerization: Interaction with trimesoyl chloride**

Jaewoo Lee^a, Rong Wang^{a,b}, Tae-Hyun Bae^{a,c,*}

^a Singapore Membrane Technology Center, Nanyang Environment and Water Research Institute, Nanyang Technological University, 637141, Singapore

^b School of Civil and Environmental Engineering, Nanyang Technological University, 639798, Singapore

^c School of Chemical and Biomedical Engineering, Nanyang Technological University, 637459, Singapore

*E-MAIL: thbae@ntu.edu.sg

ABSTRACT

Co-solvent assisted interfacial polymerization (CAIP) has been widely used to increase the water permeability of thin-film composite (TFC) reverse osmosis (RO) membranes. However, its outcomes are often poorly understood or unpredictable. To bridge the gap between conventional wisdom and the real effects of the co-solvent, we report—for the first time, to the best of our knowledge—empirical evidence in terms of the actual interfacial tension between two immiscible solutions used in CAIP. According to our results, dimethyl sulfoxide (DMSO), which is frequently used as a co-solvent, influences IP by interacting with trimesoyl chloride (TMC). The dipole-dipole interaction between DMSO and TMC was estimated to increase the TMC concentration at the interface and, thereby, the reaction rate. Due to the fast reaction, the diffusion barrier forms quickly, reducing the thickness and roughness of the active layer. The cross-linking degree was also determined to decrease due to the incomplete reaction that occurs when one of three acyl chloride groups interacts with $S^{\delta+}-O^{\delta-}$ electrostatic dipoles of DMSO at the interface, as evidenced by the variation in unreacted acyl chloride groups in the active layer and by the nitrogen/oxygen ratio. Such morphological changes were consistent with the trend in the performances of the RO membranes prepared with different amounts of DMSO, and were used to interpret the possible transport phenomena.

Keywords: Interfacial polymerization, Thin-film composite, Co-solvent, Polyamide, Interfacial tension

1. Introduction

Interfacial polymerization (IP), which has been widely used to produce thin-film composite (TFC) membranes for desalination, has been improved substantially over the past few decades [1]. As a result, the water permeability of TFC membranes prepared via IP has become high enough that hydraulic overpressures are not excessive, making reverse osmosis (RO) using the TFC membranes energy-efficient [2]. Instead, the TFC membranes demand high selectivity, not only to improve treated water quality but also to reduce the costs of the pre- and post-treatments [3].

However, it does not necessarily mean that maximizing salt rejection always assures more benefits. For example, a TFC membrane with extremely high selectivity would inevitably have too low water permeability due to the constraint imposed by the trade-off between water permeability and water/salt permselectivity. Low water permeability can entail great expense in terms of a large footprint and membrane area to produce the same amount of fresh water per unit area and time, which could cause additional costs due to greater demand for membrane replacement and chemical cleaning agents [4]. Therefore, to achieve both high-quality treated water and high productivity at a minimum cost, a TFC membrane must be optimized to balance water permeability and water/salt permselectivity.

For a fine modulation of these two parameters, it is necessary to comprehensively understand the formation mechanism of TFC membranes. However, it is challenging to fully determine the detailed IP mechanism because the reaction is not only too fast to observe but is also affected by many factors (e.g., the organic solution temperature [5]) simultaneously. Especially, it becomes much more complicated in IP where additives are used. For instance, Tang et al.[6] reported that lithium cation (Li^+) appeared to induce a dense skin layer by interacting with alcohol amines and thereby increasing the density and reactivity of their

hydroxyl group while it also seemed to form a hydrophilic and loose surface by making acyl halides prone to the hydrolysis via complexation. It is also true for co-solvent assisted IP (CAIP). For this reason, CAIP has mainly been investigated based on the characteristics of the films obtained after the reaction, and the phenomena have been interpreted with ex-post information such as morphology and surface chemistry. In many cases, however, such an interpretation is limited, as it is strongly dependent on the point of view of the observer due to limited information about the reaction process compared to direct observation and can result in analysis based on only fragmentary evidence.

To better understand the mechanism underlying CAIP, several studies have put forth the idea that a co-solvent is likely to promote *m*-phenylenediamine (MPD) diffusion because it can reduce the solubility difference or interfacial tension between the two immiscible solutions [7-13]. However, although the co-solvents reported in the literature were known to play a similar role, CAIP has shown different morphological features. As such, the complex system leaves a great deal of room for the interpretation of the phenomena occurring during IP. This matter can be addressed through an analysis of several aspects of the phenomena and a broader view.

As part of an effort to grasp the complex system in which CAIP occurs, we scrutinized the measurable parameters known to affect CAIP in the literature. We chose dimethyl sulfoxide (DMSO) as a co-solvent and examined how DMSO influences the surface tension of an MPD aqueous solution, the interfacial tension between the two immiscible solutions used in IP, and the MPD diffusion rate by measuring them directly. We also tried to clarify the mechanism underlying IP carried out with DMSO by comprehensively factoring in several aspects of the DMSO effect. Through our parametric study, we identified another

previously unknown parameter dictating CAIP and sought to establish a new mechanism underlying the co-solvent effect based on empirical evidence.

2. Materials and methods

2.1. Preparation of support membranes

Unless specified otherwise, all chemicals were used as they were received from Sigma-Aldrich. Polymer solutions to fabricate polysulfone (PSf; Udel® P 3500 MB7, Solvay Korea, Seoul) support membranes were prepared based on the condition recently optimized by our group [4]. This support membrane features large surface pores, negligible sublayer resistance, and excellent mechanical strength, which fits the requirements for the support membrane to prepare high-performance RO membranes [14]. PSf beads (10 wt%) were added and dissolved in a solvent mixture at a ratio of 1:7 for N-methyl-2-pyrrolidinone (NMP) and N,N-dimethylformamide (DMF). The dissolved polymer solution was confirmed to have the viscosity of 5.7×10^{-2} ($\pm 0.5 \times 10^{-2}$; n=3) Pa.s (Physica MCR 101, Anton Paar, Austria). Except for the composition of the solvent mixture, all of the procedures to prepare support membranes via non-solvent-induced phase separation (NIPS) were carried out as reported previously [15]. The polymer solution was manually coated on a non-woven fabric using a casting knife with a gate height of 200 μ m and subsequently immersed in tap water at room temperature for solidification via NIPS. The as-prepared support membrane was stored in a water bath overnight before use.

2.2. Preparation of TFC membranes

To determine the effect of DMSO on IP and the performance of TFC membranes, we performed IP with the aqueous solution containing 2 wt% MPD and various concentrations of DMSO (0 to 3 wt%). The as-prepared MPD solutions were used to fabricate TFC membranes with an organic solution comprising 0.1 w/v% trimesoyl chloride (TMC) and hexane (Merck, Germany). To precisely weigh the mass of TMC, we first froze the original stock of TMC (liquid) at $-20\text{ }^{\circ}\text{C}$ and subsequently scraped TMC powder off a frozen solid lump of TMC. This manner allows us to accurately measure the TMC mass within the error range of $\pm 2\%$.

Other than the composition of the additives, all of the procedures were carried out as reported previously [2, 4]. In detail, the as-prepared support membranes were immersed in the MPD aqueous solutions for 1 min and were then subjected to the rolling process to remove the excess MPD solution. Subsequently, the MPD-soaked support membranes were immersed in a TMC solution for another 1 min. The as-prepared TFC membranes were washed with hexane to remove unreacted TMC monomers and then immediately cured at $60\text{ }^{\circ}\text{C}$ for 10 min. The TFC membranes prepared using 0, 1, 2, and 3 wt% DMSO were marked as TFC-D0 (control), TFC-D1, TFC-D2, and TFC-D3, respectively.

2.3. Determination of surface and interfacial tensions

The surface tension of aqueous MPD solutions with different DMSO concentrations was evaluated based on the Wilhelmy plate method using a tensiometer (DCAT11, Dataphysics, Germany) at $25\pm 0.5\text{ }^{\circ}\text{C}$. The aqueous mixture was stirred at 300 rpm for longer than 10 min at least to make it homogeneous once DMSO was added, and this procedure was also used when preparing the samples for the interfacial tension measurement. The used Wilhelmy

Fig. 1. Schematic diagram of the measurement of (a) the buoyancy of an organic solution, (b) the surface tension of an aqueous solution, and (c) the interfacial tension between organic and aqueous solutions. This figure shows the side view of the Wilhelmy plate, which is shown as larger than in reality.

platinum-iridium plate (length: 10 mm, width: 19.9 mm, thickness: 0.2 mm) was rinsed with isopropanol and burned with a Bunsen burner to thoroughly remove the residue in the parts wetted during the measurement. The test probe was reused to assess the surface tension after cooled down enough.

A tensiometer was also used to evaluate the interfacial tension between aqueous solutions (heavier test liquids) and organic solutions (lighter test liquids). The buoyancy force of an organic solution was first assessed by dipping the test probe in an organic solution (Fig. 1(a)). Note that an organic solution should be filled to at least the minimum filling height (13 mm) to ensure that the test probe is entirely submerged into an organic solution and the buoyancy is correctly measured (Fig. 1(a)). Next, the surface tension of an aqueous solution was measured as described above (Fig. 1(b)). The minimum filling height of an aqueous solution is also 13 mm. An organic solution was carefully poured on top of the aqueous solution along the wall of the vessel, and the weight was measured while the test probe moved back to the interface between air and the organic solution (Fig. 1(c)). The measured weight corresponds to the gravitational force of the interfacial layer and can be used to calculate the interfacial tension based on the Wilhelmy equation (Eq. (1)).

$$\sigma = \frac{F_G}{L \cdot \cos\theta_C} \quad (1)$$

where σ is the interfacial tension, F_G is the gravitational force, L is the wetted length of the plate, θ_C is the contact angle.

131

132 **2.4. Diffusion kinetics of MPD monomers**

133 Ultraviolet-visible (UV-vis) spectroscopy (UV-1800, Shimadzu, Japan) was used to
 134 examine how the diffusion rate of MPD changes with DMSO concentration, as described
 135 previously [9]. We first filled 0.5 mL of an aqueous MPD solution in a quartz cuvette to
 136 make sure the liquid-air interface to be placed below the light source, and then immediately
 137 added 1 mL of hexane on top of the aqueous solution. Then, the UV absorption spectra were
 138 recorded at 288 nm every 3 s for 4 min.

139

140 **2.5. Membrane characterization**

141 Electron microscope images of the polyamide active layers were taken using a field
 142 emission scanning electron microscope (FESEM; JSM-7600F, JEOL, Japan). Prior to
 143 acquiring the cross-sectional images, the TFC membranes were freeze-fractured in liquid
 144 nitrogen, dried in air overnight, and then coated with platinum by means of a sputter coater
 145 (JEC-1600, JEOL, Japan). The as-acquired cross-sectional images were used to measure the
 146 active layer thickness, as described previously [2, 4, 16-18]. The average thickness of an
 147 active layer was obtained at five arbitrary locations, and the five average thicknesses were
 148 used to determine the mean of the average thickness. The roughness and surface area of the

active layer were measured using an atomic force microscope (AFM; NX10, Park Systems, Korea).

Table 1. Peak assignments of the IR active vibrations of PSf or amide groups.

Polymer	Frequency (cm ⁻¹)	Assignment	Ref.
Polyamide	950	Stretching vibration of acyl chloride groups	[19]
	3250-3300	Amide A (N-H stretch in resonance with amide II overtone)	[20]
	3080	Amide B	[20]
	1663	Amide I (C=O stretching – dominant contributor, C–N stretching, and C–C–N deformation vibration in a secondary amide group)	[21]
	1541	Amide II (N–H in-plane bending and N–C stretching vibration of a –CO–NH– group)	[21]
	1230-1330	Amide III (N-H bend in plane and C-N stretch)	[20]
	625-770	Amide IV (Mainly O=C-N deformation)	[20]
	1609	Aromatic amide (N–H deformation vibration or C=C ring stretching vibration)	[21]
	~1395	COO- (C=O stretch)	[20]
PSf	1411	Carboxyl acid group (O-H deformation)	[22]
	1488, 1504 ~1587	Aromatic in-plane ring bend stretching vibration	[21]
	1365-1385	C–H symmetric deformation vibration of >C(CH ₃) ₂	[21]
	1280-1350	Asymmetric SO ₂ stretching vibration	[21]
	~1245	C–O–C asymmetric stretching vibration of the aryl–O–aryl group	[21]

The unreacted acyl chloride groups of as-prepared membranes were characterized using a Fourier transform infrared (FTIR) spectrometer (IR Prestige-21, Shimadzu, Japan) equipped with attenuated total reflection (ATR) right after the IP and curing process. An FTIR analysis was adopted to effectively distinguish the unreacted acyl chloride groups assigned to 950 cm^{-1} without superimposed interference from other groups because it is far from other peaks assigned to PSf or amide groups (see Table 1 for more details).

Meanwhile, the FTIR spectra of acyl chlorides could also be useful in simply approximating the degree of cross-linking, given that the cross-linked portion does not contain the functional groups theoretically. However, strictly speaking, it is not appropriate to quantitatively discriminate the cross-linking degree based on the relative intensity of acyl chlorides because their hydrolysis can occur even by water vapor in the air (Fig. S1). Instead, it is possible to estimate the cross-linking degree based on the density of carboxyl groups in that the linear portion comes to have carboxyl groups, which are not as variable as acyl chlorides, after full hydrolysis of acyl chlorides whereas the cross-linked one does not. Unfortunately, however, it is hard to differentiate the peak assigned to a carboxyl group from those of PSf because the relevant peaks are too close to each other (see Table 1 for more details). On the other hand, provided that PSf is removed with organic solvents to rule out the influence of PSf, it could be too difficult to keep a polyamide layer intact and to get reliable data on account of the possible deformation (e.g., swelling) of a polyamide layer. For this reason, the cross-linking degree of an active layer was investigated using X-ray photoelectron spectroscopy (XPS; Axis-HSI, Kratos Analytical, UK) by comparing the relative atomic concentrations of nitrogen and oxygen in an active layer as described previously [2, 7, 23-25]. To evaluate the average roughness and N/O ratio, five different samples of each TFC membrane were used to make sure to thoroughly assess the repeatability.

The mean pore diameter and molecular weight cut-off of the as-prepared TFC membranes were estimated based on the Stokes radii of ethylene glycol, diethylene glycol, and polyethylene glycol (PEG) with various molecular weights (PEG 200, PEG 400, PEG 1,000, and PEG 3,000) used in solute transport along with their rejection. The Stokes radii of ethylene glycol and diethylene glycol were calculated based on Eq. (2) [26].

$$r_s = 4.61 \times 10^{-2} M^{0.395} \quad (2)$$

where r_s is the Stokes radius (nm) and M is the molecular weight of used solutes.

The Stokes radii of PEG were calculated based on Eq. (3) [27].

$$r_s = 16.73 \times 10^{-3} M^{0.557} \quad (3)$$

The solute concentration was 1,000 ppm, and the filtration test was conducted at 500 rpm and 10 bar.

Lastly, the surface zeta potential of the as-prepared TFC membranes was measured with a Zetasizer Nano ZS (ZEN3600, Malvern, UK). Prior to the measurement, all of the TFC membranes were stored in deionized water for over 24 h for full hydrolysis of acyl chlorides and air-dried for another 24 h. An electrolyte solution was prepared using a moderate concentration of NaCl (1mM) to avoid excessive Joule heating. A 10% latex (300 nm) solution was used as a tracer solution after diluted 1:2000 with the electrolyte solution.

2.6. Membrane filtration test

The water flux ($\text{L m}^{-2} \text{ h}^{-1}$; LMH) and salt rejection ($R = 1 - \frac{C_p}{C_f}$, %) of three different samples of each TFC membrane were evaluated using a bench-scale cross-flow filtration system equipped with a permeation cell (CF042, Sterlitech, Kent, WA, USA) with the effective membrane area of 42 cm^2 . C_p and C_f are the salt concentrations of the permeate and feed solutions, respectively. The cross-flow system was stabilized with a 2,000 ppm NaCl solution at a hydraulic pressure of 25 bar and a cross-flow rate of 0.8 L min^{-1} for 30 min before the permeate solution was collected. The permeate solution was then collected for another 30 min at 15.5 bar. The volume and conductivity of the permeate solution were measured to calculate water flux and salt rejection, respectively, as reported previously [2, 4]. Based on the water flux and salt rejection, the following parameters were obtained:

$$A = \frac{J_v}{\Delta P - \Delta \pi} \quad (4)$$

$$B = \frac{(1 - R) \cdot A \cdot (\Delta P - \Delta \pi)}{R} \quad (5)$$

where A is the water permeability coefficient, B is the salt permeability coefficient, J_v is the volumetric water flux, ΔP is the pressure difference across the membrane, and $\Delta \pi$ is the osmotic pressure difference across the membrane. The water/salt permselectivity ($\alpha_{w/s}$) of the TFC membranes was acquired from the following relationship:

$$\alpha_{w/s} = \frac{P_w}{P_s} \quad (6)$$

$$P_w = \frac{R_g \cdot T \cdot L \cdot A}{M_w} \quad (7)$$

$$P_s = B \cdot L \quad (8)$$

where P_w is the water permeability, P_s is the salt permeability, R_g is the ideal gas constant, T is the absolute temperature, L is the active layer thickness, and M_w is the molecular weight of water.

2.7. Statistical analysis

All statistical analyses were carried out with Prism 6 Version 6.04 (GraphPad). One-way analysis of variance (ANOVA) with Dunnett's multiple comparison tests and Student t -test were used to assess the statistical significance of the differences between the surface or interfacial tensions, which were measured by changing the concentration of DMSO or co-solvent types. The adjusted P values (P_{adj}) were included to allow multiple comparisons.

3. Results and discussion

3.1. Does DMSO have a direct impact on the interfacial tension and MPD diffusion rate?

Table 2. Comparisons between phenomena observed or characteristics of the active layer formed from CAIP. This table shows only CAIP where MPD and TMC were used, for valid comparative studies. The co-solvents used in the literature are known to increase the miscibility between the two immiscible solutions, to reduce the solubility difference, to decrease the interfacial tension, or to enhance MPD diffusion.

Additive (Phase)	Active layer thickness	Active layer roughness	Cross-linking degree or pore size	Interfacial tension [†]	MPD diffusion	Ref.
DMSO (Aqueous)	Decrease	Decrease	Decrease (Cross-linking degree); Increase (Pore size)	Not significant	Not significant	This work
DMSO (Aqueous)	N.A.	Increase	Increase (Cross-linking degree; Pore size & number [‡])	N.A.	N.A.	[7]
DMSO (Aqueous)	Increase	Decrease	Increase (Cross-linking degree)	N.A.	N.A.	[8]
Hexamethyl phosphoramide (Aqueous)	Increase	Increase	Increase (Cross-linking degree)	N.A.	Increase	[9]
Acetone (Organic)	Decrease	Decrease	Increase (Pore size)	N.A.	Increase	[10]
Acetone (Aqueous)	Increase	N.A.	Increase (Cross-linking)	N.A.	N.A.	[11]
Propanone/ Butanone (Organic)	Decrease	Decrease	Increase (Pore size)	N.A.	N.A.	[12]
Ethanol/ Ethylene glycol/ Xylitol (Aqueous)	Increase	Variable [§]	Decrease (Cross-linking degree)	N.A.	N.A.	[13]

[†]Interfacial tension between aqueous solutions containing different concentrations of DMSO and hexane.

[‡]Aggregate pores (3.5 to 4.5 Å) increased in size but decreased in number, whereas network pores (2.1 to 2.4 Å) increased in both size and number.

[§]The roughness increased when the co-solvents of 1 wt% were added, but further addition (6 wt%) effectively reduced the roughness.

We investigated the characteristics of the active layer formed via the IP carried out with different concentrations (0 to 3 wt%) of DMSO. Our results demonstrated that the thickness, roughness, and cross-linking degree of the active layer decreased as DMSO loading increased (Figs. 2(a) to 2(c); see Table 2 for a comparison with the literature). These phenomena can probably be explained in a similar way to that introduced in the literature [7-13]. On the other hand, a simulation study [28] showed no significant change in the interfacial tension between water and hexane within the DMSO concentration range. According to the simulation study, the interfacial tension between water and hexane was reduced only from 53 to about 50 mN m⁻¹ as DMSO was added from 0 to 1 mole % (which translates to the variation in the concentration from 0 to 4.2 wt%). For this reason, we eliminated as much guesswork as possible and directly measured the surface tension of the MPD/DMSO mixtures and the interfacial tension between the mixtures and hexane to ascertain the DMSO effect from various perspectives. To the best of our knowledge, no study has measured the change in interfacial tension induced by co-solvents.

Fig. 2. (a) The average thickness, (b) roughness, and (c) N/O ratio of the TFC membranes prepared with different concentrations of DMSO. See Figs. S2 and S3 for the average thickness and roughness, respectively. Error bars indicate the standard deviations of the mean (for (a)) and standard deviations (for (b) and (c)) obtained from five different samples. Note that the TFC-D0, TFC-D1, TFC-D2, and TFC-D3 stand for the TFC membranes prepared using 0, 1, 2, and 3 wt% DMSO, respectively.

Fig. 3. Surface and interfacial tensions measured using MPD aqueous solutions with different DMSO concentrations. Hexane was used as an organic solvent when the interfacial tension was measured. Error bars indicate the standard deviations obtained from three different samples. In Graph Pad Prism 6 software, a significant difference is indicated as follows: NS (not significant) $P > 0.05$ (see Tables S1 and S2 for more details).

We found no significant difference between the surface tension of the MPD solutions including different amounts of DMSO (Fig. 3). DMSO reduced the surface tension of the MPD solution from 70.3 to 68.9 mN m^{-1} even at 3 wt% (Fig. 3). This was also the case for the interfacial tension between aqueous MPD solutions containing different concentrations of DMSO and hexane (Fig. 3), which was consistent with the simulation study. Next, we

Fig. 4. The absorbance variations observed while MPD monomers diffuse into hexane from aqueous solutions containing different concentrations of DMSO. Error bars indicate the standard deviations obtained from five different samples.

attempted to ascertain whether DMSO would enhance MPD diffusion, given that DMSO probably increases the miscibility of the two immiscible solutions [7, 8, 11, 13]. However, it was difficult to find any significant difference in the MPD diffusion rates (Fig. 4). The similar MPD diffusion rates show that DMSO in the transitional zone (or reaction zone) at the interface is not key to facilitating MPD diffusion within the DMSO concentration (0 to 3 wt%), perhaps because the MPD diffusion rate is already fast enough due to the much higher concentration compared to that of TMC.

3.2. A new perspective on the role of DMSO in IP

The effect of DMSO on IP may possibly be associated with TMC rather than MPD. It is this second belief in the DMSO effect that we put into question in this work. However, it is quite challenging to predict or compare the behavior of TMC occurring in IP because TMC rarely diffuses toward an aqueous phase, unlike MPD, which can diffuse into an organic phase. Instead, we noted that MPD itself decreased the interfacial tension between water and hexane from 47.1 to 37.9 mN m⁻¹ (Fig. 3), while the surface tension did not show a significant difference before (72.1 mN m⁻¹) and after (70.3 mN m⁻¹) adding MPD to the water (Fig. 3). This phenomenon is attributed to the adsorption of solutes onto the interface. According to the literature [29, 30], if solutes are added and accumulate on the interface, the adsorption of solutes occurs on the interface and inhibits the coalescence of water droplets at the interface, while the solutes form larger numbers of hydrogen bonds (or other types of electrostatic forces such as induced dipole-dipole interaction) with water molecules. For this reason, the presence of solutes at the interface decreases interfacial tension, and this tendency becomes more pronounced with an increase in the concentration of solutes at the interface.

We can therefore estimate that the presence of MPD at the interface was accompanied by the observed reduction in interfacial tension.

The above observation suggests that the concentration of TMC at the interface could be indirectly assessed by monitoring the change in the interfacial tension with different DMSO loadings and could be a measure of the interaction between DMSO and TMC. To test the hypothesis, we measured the interfacial tension between the TMC solution and the aqueous solutions including different concentrations of DMSO and verified whether the concentration of TMC at the interface varies with the added DMSO. As shown in Fig. 5(a), the interfacial tension between aqueous solutions containing 0 to 3 wt% DMSO and the TMC solution was reduced to a statistically significant level (from 45.6 to 39.0 mN m⁻¹) with an increase in the DMSO concentration, which means that the concentration of TMC at the interface increased with DMSO loading.

Particularly, the above result piqued our interest in that other polar aprotic solvents (e.g., NMP, DMF, and acetone) considerably reduced the interfacial tension (Fig. 5(b)) once they were added in an aqueous solution regardless of the presence of TMC in an organic phase. This discrepancy results from the different dielectric constants. In detail, a dielectric constant relates to solvent polarity which indicates the sum of both specific and non-specific interactions between different molecular species [31, 32]. Accordingly, significantly different two solvents in the view of dielectric constant should possess quite different polarities, necessarily making them less miscible. In this context, it is noteworthy that DMSO has the dielectric constant of 48.9 whereas the others have relatively low values (e.g., 32.2, 36.7, and 20.6 for NMP, DMF, and acetone, respectively. See Table 3 for more details.). In short, the other polar aprotic solvents seemed more miscible with hexane owing to their lower dielectric

Fig. 5. (a) Interfacial tensions between water with different concentrations (0 to 3 wt%) of DMSO and hexane or a 0.1 w/v% TMC solution. One-way ANOVA with Dunnett's multiple comparison test was performed to compare interfacial tensions (see Tables S3 and S4 for more details). (b) Interfacial tensions between water containing 3 wt% of different co-solvents and hexane or a 0.1 w/v% TMC solution. Student's *t*-test was conducted to compare interfacial tensions (see Table S5 for more details). Error bars indicate the standard deviations obtained from three different samples. In Graph Pad Prism 6 software, a significant difference is indicated as follows: NS (not significant) $P > 0.05$, * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$, and **** $P < 0.0001$.

constants, such that they drastically reduced the interfacial tension between aqueous solutions and pure hexane. Due to the already lowered interfacial tension, the interfacial tension did not noticeably differ or slightly changed after TMC was added to hexane (Fig. 5(b)), making it hard to clearly determine whether the other co-solvents also increased the TMC partition at

the interface. In contrast, DMSO was estimated not to be intermingled with hexane as well as the aforementioned co-solvents on account of its high dielectric constant (Table 3), and thus, not to be able to effectively vary the interfacial tension for itself within the concentration range. Based on the above discussion, we could conclude that the reduction in the interfacial tension shown in Fig. 5(a) stems from the increase in the TMC concentration at the interface induced by DMSO, and it could be unambiguously discriminated since the dielectric constant of DMSO possibly lies above the threshold (which is assumed between 36.7 and 48.9) leading to a dramatic transition in the interfacial tension.

Table 3. Dielectric constant, dipole moment, and surface tension of different solvents at 20 °C [33].

Solvent		Dielectric constant	Dipole moment (D)	Surface tension (mN m ⁻¹)
Non-polar	Hexane	1.89	<0.1	18.4
	DMSO	48.9	4.00	43.7
Polar aprotic	NMP	32.2	4.09	40.8
	DMF	36.7	3.86	37.1
	Acetone	20.6	2.91	23.7

Next, we examine the probability that the increased TMC concentration at the interface and the resulting reduced interfacial tension arise from the interaction between DMSO and TMC as follows. TMC monomers are expected to be delocalized over a volume of a TMC solution at the beginning of IP. However, when DMSO exists in an aqueous phase, TMC monomers could interact with DMSO via the dipole-dipole interaction between the $S^{\delta+}-O^{\delta-}$ electrostatic dipoles of DMSO and carbonyl oxygens of TMC (Fig. 6) because the carbonyl oxygens can induce a dipole-dipole interaction [34, 35]. The interaction between DMSO and TMC can yield a relatively localized TMC distribution (i.e., an increase in the TMC concentration) at the interface. The accumulated TMC on the interface is assumed to hinder the coalescence of water molecules surrounding the DMSO at the interface via the interaction and to eventually decrease the interfacial tension, as shown in Fig. 5. Note that the decrease

Fig. 6. Schematic illustration of how DMSO affects IP via the dipole-dipole interaction between DMSO and TMC at the interface. Color scheme: N, black; C, grey; O, red; H, white; S, yellow; Cl, blue.

in the interfacial tension arises not from the addition of DMSO itself but from the increased TMC concentration due to the interaction between DMSO and TMC. As such, DMSO is thought to increase the TMC concentration at the interface by interacting with TMC rather than that it alone gives a direct contribution to IP.

Lastly, we attempt to further explore the possibility of whether DMSO could also increase the TMC concentration at the interface via a dipole-dipole interaction even in the midst of the reaction between MPD and TMC. For verification, it is first required to examine if DMSO could encounter TMC at the interface prior to MPD. Here, we zero in on the phenomena occurring at the interface rather than embracing those over the reaction zone. In order to estimate the probability, the diffusivity in the aqueous phase and molar ratio at the interface are important factors to be considered. According to the literature, the diffusivity of DMSO ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [36]) in the aqueous phase is known to be similar to that of MPD ($8.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [37]). Therefore, DMSO is presumed to be able to diffuse to the interface at a similar rate to MPD, which means that the probability to meet TMC monomers at the interface would depend more on the DMSO/MPD molar ratio. Although it is hard to predict the exact molar ratio at the interface because it should be different from in the bulk (0.7, 1.4, and 2.1 for 1, 2, and 3 wt% DMSO/2 wt% MPD), we could at least estimate from the above discussion that a certain portion of TMC monomers could be exposed to DMSO even during CAIP and thereby dynamically delocalized at the interface via a dipole-dipole interaction.

3.3. Thin and smooth polyamide films resulting from the interaction between DMSO and TMC

We attempt to explain the phenomena observed in this study by correlating the obtained data in terms of the active layer characteristics with the interaction between DMSO and TMC. We think that the concentration of TMC at the interface increases due to the interaction between DMSO and TMC as more DMSO is added, which in turn leads to the faster reaction rate of IP given that the reaction rate has a positive correlation with the concentration of the reactant [38]. As a result of the fast IP reaction, the diffusion barrier can be formed more quickly before MPD diffuses deep into an organic phase, seemingly resulting in a thin and

Fig. 7. (a) The average thickness and (b) roughness of the TFC membranes prepared with different concentrations of TMC. An aqueous solution containing only 2 wt% MPD was used for IP. See Figs. S4 and S5 for the average thickness and roughness, respectively. Error bars indicate the standard deviations of the mean (for (a)) and standard deviations (for (b)) obtained from five different samples.

smooth active layer. This hypothesis is also in line with the assumption that the thickness of a reaction-diffusion boundary layer is inversely proportional to the square root of the initial TMC concentration [37]. To further verify how the variation in the TMC concentration induced by DMSO can impact the thickness and roughness of the active layer, we attempted to create a similar situation by intentionally adjusting the added amount of TMC in hexane and inquired into what happens during IP when the TMC concentration becomes higher as more TMC is added. It is evident in Figs. 7(a) and 7(b) that the thickness and roughness of the active layer gradually decrease as the TMC concentration increases with more TMC loading. These results support the hypothesis that the IP, which is accompanied by the interaction between DMSO and TMC, possibly forms a thin and smooth active layer as the TMC concentration at the reaction zone increases upon DMSO loading.

3.4. Empirical evidence suggesting that the interaction between DMSO and TMC alters the cross-linking degree

Also noteworthy is the change in the cross-linking degree. According to the literature [7], the ratio of nitrogen to oxygen (N/O ratio) of polyamide films prepared via IP using MPD and TMC can be used for the relative comparison of the cross-linking degree. The N/O ratio falls between 0.5 and 1, where values closer to 0.5 and 1 indicate lower and higher cross-linking degrees, respectively. Given the trend in the N/O ratio shown in Fig. 2(c), we can conclude that the cross-linking degree decreased with DMSO loading. The lowered cross-linking degree as the content of DMSO was increased can also be understood in relation to the interaction between DMSO and TMC. As indicated in Fig. 6, only two of three acyl chloride

groups of TMC are used to form the linear portion, whereas all the three groups should react with MPD to cross-link polyamide chains, which indicates that the cross-linking degree depends on the extent of the incomplete reaction between MPD and TMC. Based on this point, we investigated whether one of the acyl chloride groups was not used for the reaction with MPD but intercepted while interacting with the $S^{\delta+}-O^{\delta-}$ electrostatic dipoles of DMSO (Fig. 6). To obtain the empirical evidence of the incomplete reaction, we zeroed in on the

Fig. 8. FTIR spectra showing the change in the peak, which is assigned to acyl chloride groups, observed at 950 cm^{-1} (a) before and (b) after washing the TFC membranes prepared using different concentrations of DMSO with deionized water (i.e., before and after the hydrolysis of acyl chloride groups). Note that the TFC-D0, TFC-D1, TFC-D2, and TFC-D3 stand for the TFC membranes prepared using 0, 1, 2, and 3 wt% DMSO, respectively. FTIR spectra observed at 950 cm^{-1} (c) before and (d) after washing the prepared TFC membranes prepared using different concentrations of TMC with DI water. Note that the TFC-TMC0.1, TFC-TMC0.2, TFC-TMC0.4, and TFC-TMC0.8 stand for the TFC membranes prepared using 0.1, 0.2, 0.4, and 0.8 w/v% TMC, respectively.

FTIR peak at about 950 cm^{-1} . We noticed the peak for the following reasons: i) the peak appeared (Figs. 8(a) and 8(b)) only before the as-prepared membranes were washed with deionized water (i.e., Fig. 8(a) was obtained when the unreacted acyl chloride groups were left intact, whereas Fig. 8(b) was done after they were hydrolyzed) and ii) it is known from the literature to be assigned to the stretching vibration of acyl chloride groups [19]. Fig. 8(a) shows that the relative intensity of acyl chloride groups was higher in all of the TFC membranes prepared with DMSO as compared to the TFC-D0. Considering that more unreacted acyl chlorides stems from a more linear portion, Fig. 8(a) conversely accounts for that less cross-linking occurred as more DMSO was added. Overall, this result indicates that the interaction between DMSO and TMC leads to an incomplete reaction between MPD and TMC, thereby reducing the cross-linking degree. Although an accurate quantitative assessment could not be made regarding the cross-linking degree only with the trend in the FTIR peaks assigned to unreacted acyl chloride groups (observed at 950 cm^{-1}), we believe that the approach using FTIR spectra is likely to contribute to interpreting the phenomena during CAIP from various angles along with the N/O ratio data.

3.5. Second thoughts about whether the cross-linking degree could be affected by other factors than the interaction between DMSO and TMC

Meanwhile, we also tried to weigh the possibility of whether the cross-linking degree could be more affected by other factors than the interaction between MPD and TMC, to see the other side of the process where a polyamide layer is cross-linked and thereby to avoid the above interpretation being only half the story. According to Ghosh et al. [39], cross-linking was assumed to be negatively related to MPD solubility whereas it seemed to have a positive correlation with MPD diffusivity. Unfortunately, however, we could not attempt to interpret

the phenomena regarding the cross-linking degree based on the relevant characteristics of MPD because we verified that there was no significant distinction in both solubilities (Fig. 3) and diffusivities (Fig. 4) of MPD regardless of the addition amount of DMSO due to the already high concentration of MPD monomers. On the other hand, it may be possible that DMSO addition might enhance the solubility and diffusivity of TMC in the aqueous phase, which could change the MPD/TMC stoichiometry at the reaction zone and the cross-linking degree of a polyamide active layer. In this case, we cannot make light of the influences of DMSO on the TMC's solubility/diffusivity in discussing the cross-linking.

First, we performed an FTIR analysis for the TFC membranes prepared using different concentrations (0.1, 0.2, 0.4, and 0.8 w/v%) of TMC at 950 cm^{-1} in order to determine whether the incomplete reaction between MPD and TMC monomers and the consequent cross-linking degree can be altered simply by the MPD/TMC stoichiometry at the reaction zone as the cases of the thickness and roughness. According to the FTIR spectra (Fig. 8(c)), there was no noticeable change in the FTIR peaks although the peaks were observed before the unreacted acyl chloride groups were hydrolyzed. This result implies that all of the as-prepared TFC membranes possessed unreacted acyl chloride groups at a similar level to one another regardless of the used TMC concentration, and furthermore, the incomplete reaction between MPD and TMC was not governed single-handedly by the MPD/TMC stoichiometry at the reaction zone. This fact corroborates that DMSO did more (e.g., the interaction with TMC at the interface) during CAIP than changed only the MPD/TMC stoichiometry at the reaction zone. From the above case, we could rule out the possibility that the MPD/TMC stoichiometry at the reaction zone for itself may dominate the incomplete reaction between MDP and TMC and thereby the cross-linking degree in explaining how DMSO affects the cross-linking degree.

It is also important in the context of the DMSO effect to consider the possibility of whether the solubility and diffusivity of TMC in the aqueous phase could be improved by DMSO. When it comes to the solubility, it is known that polar solvent molecules can attract the oppositely charged ends of solute molecules via electrostatic dipole-dipole interaction, thereby taking a chance to solvate the solute molecules [40]. Given that the $S^{\delta+}-O^{\delta-}$ electrostatic dipoles of DMSO and carbonyl oxygens of TMC can interact via the dipole-dipole interaction [34, 35], it is in the realm of possibility that DMSO probably increases the solubility of TMC in the aqueous phase (However, it is true that the solubility of TMC in the aqueous phase has never been characterized experimentally). On the other hand, the diffusivity is debatable since it could vary with kinds of solutes. For instance, ions are known to deform the interface to minimize the free energy of the system, facilitating ion's transport [28]. On the contrary, surfactant molecules tend to aggregate at the interface because they increase the free energy barrier while moving from one phase to another, making the diffusion of solutes quite tricky [28]. As such, the diffusivity of TMC in the aqueous phase remains a toss-up. Given the above facts, it is *de rigueur* to experimentally address the solubility and diffusivity of TMC in the aqueous phase before we jump to conclusions without adequate factual basis. Unfortunately, however, it is unachievable in the aqueous phase to directly observe the TMC's behavior to evaluate its solubility and diffusivity due to the diffusion resistance of TMC (Note that TMC is almost insoluble not only in the aqueous phase [41-43] but also in the formed polymer film [44]). To the best of our knowledge, there is no way to estimate the two indeterminate properties of TMC in the aqueous solution on account of the lack of the available technologies as of now, unlike MPD of which the diffusivity in an organic phase can be measured [37]. Alternatively, we attempt to establish a possible mechanism to describe how DMSO affects the active layer formation solely based on the interaction between DMSO and TMC rather than expanding the interpretation of the

DMSO effect with keeping its influence on the solubility and diffusivity of TMC in the aqueous phase on the table. What we have discussed about the effect of the interaction between DMSO and TMC on cross-linking thus far could be summarized as follows.

- (1) When DMSO exists in the aqueous phase, it can interact with carbonyl oxygens of TMC via a dipole-dipole interaction near the interface, which was verified by the change in the interfacial tension (Fig. 5(a)).
- (2) Some of the carbonyl oxygens could be intercepted near the interface during CAIP while interacting with DMSO for a short period of time.
- (3) Since the interaction is not strong enough to keep the products with unreacted acyl chloride groups at the interface, the products would be transported into an MPD-lean organic phase along with other products moving away from the interface.
- (4) Given that the probability of the collision and reaction between amines and the unreacted acyl chlorides of the products would be much lower in an MPD-lean organic phase compared to at the interface, the acyl chlorides left intact are assumed to remain unused for cross-linking at a relatively high rate. This assumption is supported by the acyl chloride peaks observed in the FTIR analysis (Fig. 8(a)).

3.6. Filtration performance of the TFC membranes prepared via IP carried out with DMSO

Lastly, we examined how the structural transition induced by DMSO alters the permselectivity of the TFC membranes (Figs. 9(a) to 9(c)). Considering that the IP using DMSO creates a thinner and looser active layer, DMSO loading was expected to induce a synergistic effect on enhancing the water flux of the as-prepared TFC membranes although

the active layer roughness was gradually reduced. As expected, all of the TFC membranes prepared with DMSO were superior to the control membrane (TFC-D0) in terms of water flux (Fig. 9(a)). However, the TFC membranes prepared with DMSO also showed an obvious trade-off between water flux and salt rejection. The relationship between the cross-linking degree and water/salt permselectivity is of utmost importance to determine where the behavior of the as-prepared TFC membranes comes from. Indeed, the trend seen in salt rejection (Fig. 9(a)) bears a striking resemblance to that of the N/O ratio (Fig. 2(c)).

Table 4. Comparisons of parameters determined from solute transport data of ethylene glycol, diethylene glycol, and PEG.

Membrane	Mean pore diameter (Å)	MWCO (nm)	Proportion of pores smaller than (< 7.2 Å) hydrated Na^+ ion (%)	Proportion of pores smaller than (< 6.6 Å) hydrated Cl^- ion (%)
TFC-D0	4.00	1.12	76	74
TFC-D1	4.76	1.44	67	64
TFC-D2	5.68	1.41	63	58
TFC-D3	6.68	2.44	53	49
TFC-D5	8.70	2.87	41	38

A small amount of DMSO (e.g., 1 wt%) appeared to reduce the cross-linking degree to a moderate extent, increasing both water and salt permeability coefficients with balance (Fig. 9(b)). The balance between water and salt permeability coefficients is highly likely due to the fact that the pore size became larger, but a considerable portion of pores was still smaller than hydrated ions (Fig. 9(d) and Table 4). As a result of the balance, the observed salt rejection

Fig. 9. (a) Water flux and salt rejection, (b) water and salt permeability coefficients, and (c) water/salt permselectivity of the TFC membranes prepared with different concentrations of DMSO. Note that the TFC-D0, TFC-D1, TFC-D2, TFC-D3, and TFC-D5 stand for the TFC membranes prepared using 0, 1, 2, 3 and 5 wt% DMSO, respectively. The TFC-D5 was additionally tested to show a clearer trend of the flux and rejection. (d) Plots between the Stokes radii of solutes (ethylene glycol, diethylene glycol, and PEG) with different molecular weights and their rejection by the TFC membranes prepared with different concentrations of DMSO. (e) Surface zeta potential and surface area of the as-prepared TFC membranes. The scanning area is 9 μm². Error bars indicate the standard deviations obtained from three different samples except for those of the surface area obtained from five different samples.

could be maintained while the water flux increased. Furthermore, provided that more carboxyl groups are formed by the hydrolysis of unreacted acyl chlorides (Fig. 9(e)), the water/salt permselectivity may even increase in some cases by effectively separating hydrated ions by electrostatic repulsion although the pore size slightly increases with a decrease in the cross-linking degree. We think that this explanation can account for how the TFC-D1 could exhibit a higher water/salt permselectivity (Fig. 9(c)) than TFC-D0, even though it was less cross-linked (Fig. 2(c)). However, excess DMSO tips the balance against permselectivity (Fig. 9(c)), as it causes too little cross-linking to separate ions properly (Fig. 2(c)). Also, the imbalance against permselectivity is thought to become more pronounced due to the reduced surface area accompanied by the effect of cancelling out the increased density of carboxyl groups with DMSO loading, which is evidenced by the negative zeta potential and surface

area that did not significantly change since they reached a certain value at the TFC-D2 (Fig. 9(e)). We guess that such changes exponentially raised the salt permeability coefficient (Fig. 9(b)), and the salt rejection drastically dropped as DMSO content exceeded 2 wt% (Fig. 9(a)). These results imply that it is necessary to carefully modulate the formulation of the additive system to obtain the best performance.

4. Concluding remarks

We performed systematic studies to consider CAIP in depth and made efforts to draw a solid conclusion with empirical evidence. We obtained data to determine what happens to the interface during IP using DMSO and attempted to establish the influence mechanism of DMSO on IP based on experimentally measured data that are consistent with one another. According to our results, the thickness, roughness, and cross-linking degree of the active layer were reduced when the active layer was formed via the IP where DMSO was used as a co-solvent; this was ultimately due to the dipole-dipole interaction between DMSO and TMC. Due to the interaction, the TMC concentration at the interface increased as more DMSO was added, as evidenced by the decreased interfacial tension between DMSO and TMC solutions with DMSO loading. As the TMC concentration at the interface increased, the reaction rate became more rapid, such that the diffusion barrier formed faster. A series of the above-mentioned phenomena gave rise to a thinner and smoother active layer. The interaction between DMSO and TMC was also confirmed to reduce the cross-linking degree by inducing incomplete reaction between MPD and TMC, which was supported by the FTIR data showing the transition in the peak with regard to acyl chloride groups and the N/O ratio. Such morphological variances induced by DMSO improved the water flux remarkably. However, excess DMSO impaired the membrane performance by substantially lowering the cross-

linking degree and thereby upsetting the balance between the water and salt permeabilities.

Therefore, it is necessary to find the optimal balance between the two parameters.

We also think that an increase in TMC concentration at the interface could be found in IP with the assistance of other kinds of additives, which are also likely to interact with TMC and thereby increase the partition of TMC at the interface. Therefore, we suggest examining the change in TMC concentration at the interface based on the interfacial tension between an aqueous solution and a TMC solution for future work for a more comprehensive understanding of additive-assisted IP. Meanwhile, it is also worth noting that CAIP led to a smoother surface which is known to have a lower fouling tendency [45] in that it could offer a successful strategy to develop antifouling membranes. Lastly, it is still early to draw general conclusions on the effect of a co-solvent due to the lack of relevant research as shown in Table 1. Accordingly, more researches are encouraged to collate related data/information and thereby to get definitive conclusions. We hope that our findings will contribute to a greater understanding of the CAIP and provide insights into how to make full use of co-solvents to prepare high-performance TFC membranes with high productivity.

Acknowledgements

This work was supported by the Singapore National Research Foundation under its Environmental & Water Industry Programme (grant number: 1501-IRIS-04) and administered by PUB, Singapore's National Water Agency.

References

- [1] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—development to date and future potential, *J. Membr. Sci.*, 370 (2011) 1-22.

- [2] J. Lee, J.H. Jang, H.-R. Chae, S.H. Lee, C.-H. Lee, P.-K. Park, Y.-J. Won, I.-C. Kim, A facile route to enhance the water flux of a thin-film composite reverse osmosis membrane: incorporating thickness-controlled graphene oxide into a highly porous support layer, *Journal of Materials Chemistry A*, 3 (2015) 22053-22060.
- [3] J.R. Werber, A. Deshmukh, M. Elimelech, The critical need for increased selectivity, not increased water permeability, for desalination membranes, *Environmental Science & Technology Letters*, 3 (2016) 112-120.
- [4] J. Lee, R. Wang, T.-H. Bae, High-performance reverse osmosis membranes fabricated on highly porous microstructured supports, *Desalination*, 436 (2018) 48-55.
- [5] B. Khorshidi, T. Thundat, B.A. Fleck, M. Sadrzadeh, A novel approach toward fabrication of high performance thin film composite polyamide membranes, *Sci. Rep.*, 6 (2016) 22069.
- [6] B. Tang, C. Zou, P. Wu, Study on a novel polyester composite nanofiltration membrane by interfacial polymerization. II. The role of lithium bromide in the performance and formation of composite membrane, *J. Membr. Sci.*, 365 (2010) 276-285.
- [7] S.H. Kim, S.-Y. Kwak, T. Suzuki, Positron annihilation spectroscopic evidence to demonstrate the flux-enhancement mechanism in morphology-controlled thin-film-composite (TFC) membrane, *Environ. Sci. Technol.*, 39 (2005) 1764-1770.
- [8] B. Khorshidi, T. Thundat, D. Pernitsky, M. Sadrzadeh, A parametric study on the synergistic impacts of chemical additives on permeation properties of thin film composite polyamide membrane, *J. Membr. Sci.*, 535 (2017) 248-257.
- [9] M. Duan, Z. Wang, J. Xu, J. Wang, S. Wang, Influence of hexamethyl phosphoramidate on polyamide composite reverse osmosis membrane performance, *Sep. Purif. Technol.*, 75 (2010) 145-155.
- [10] C. Kong, T. Shintani, T. Kamada, V. Freger, T. Tsuru, Co-solvent-mediated synthesis of thin polyamide membranes, *J. Membr. Sci.*, 384 (2011) 10-16.
- [11] J.A.D. Marquez, M.B.M.Y. Ang, B.T. Doma Jr, S.-H. Huang, H.-A. Tsai, K.-R. Lee, J.-Y. Lai, Application of cosolvent-assisted interfacial polymerization technique to fabricate thin-film composite polyamide pervaporation membranes with PVDF hollow fiber as support, *J. Membr. Sci.*, (2018).
- [12] F. Esfandian, M. Peyravi, A.A. Ghoreyshi, M. Jahanshahi, A.S. Rad, Fabrication of TFC nanofiltration membranes via co-solvent assisted interfacial polymerization for lactose recovery, *Arabian Journal of Chemistry*, (2017).
- [13] B. Khorshidi, B. Soltannia, T. Thundat, M. Sadrzadeh, Synthesis of thin film composite polyamide membranes: Effect of monohydric and polyhydric alcohol additives in aqueous solution, *J. Membr. Sci.*, 523 (2017) 336-345.
- [14] J. Lee, H. Yoon, J.H. Yoo, D.-C. Choi, C.H. Nahm, S.H. Lee, H.-R. Chae, Y.H. Kim, C.-H. Lee, P.-K. Park, Influence of the sublayer structure of thin-film composite reverse osmosis membranes on the overall water flux, *Environmental Science: Water Research & Technology*, (2018).
- [15] J. Lee, H.-R. Chae, Y.J. Won, K. Lee, C.-H. Lee, H.H. Lee, I.-C. Kim, J.-m. Lee, Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment, *J. Membr. Sci.*, 448 (2013) 223-230.
- [16] T.H. Lee, M.Y. Lee, H.D. Lee, J.S. Roh, H.W. Kim, H.B. Park, Highly porous carbon nanotube/polysulfone nanocomposite supports for high-flux polyamide reverse osmosis membranes, *J. Membr. Sci.*, (2017).
- [17] X. Song, Z. Liu, D.D. Sun, Nano gives the answer: breaking the bottleneck of internal concentration polarization with a nanofiber composite forward osmosis membrane for a high water production rate, *Adv. Mater.*, 23 (2011) 3256-3260.
- [18] J. Xu, H. Yan, Y. Zhang, G. Pan, Y. Liu, The morphology of fully-aromatic polyamide separation layer and its relationship with separation performance of TFC membranes, *J. Membr. Sci.*, 541 (2017) 174-188.
- [19] X.F. Li, S.X. Peng, H. Yan, Microtribological Behavior of Polymer-Nanoparticle Thin Film with AFM, in: *Scanning Probe Microscopy-Physical Property Characterization at Nanoscale*, InTech, 2012.

- [20] P. Garidel, H. Schott, Fourier-transform midinfrared spectroscopy for analysis and screening of liquid protein formulations, *Bioprocess international*, 4 (2006) 48-55.
- [21] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes: I. FTIR and XPS characterization of polyamide and coating layer chemistry, *Desalination*, 242 (2009) 149-167.
- [22] X. Tian, J. Wang, H. Zhang, Z. Cao, M. Zhao, Y. Guan, Y. Zhang, Establishment of transport channels with carriers for water in reverse osmosis membrane by incorporating hydrotalcite into the polyamide layer, *RSC Advances*, 8 (2018) 12439-12448.
- [23] W. Yan, Z. Wang, J. Wu, S. Zhao, J. Wang, S. Wang, Enhancing the flux of brackish water TFC RO membrane by improving support surface porosity via a secondary pore-forming method, *J. Membr. Sci.*, 498 (2016) 227-241.
- [24] M. Shi, Z. Wang, S. Zhao, J. Wang, S. Wang, A support surface pore structure re-construction method to enhance the flux of TFC RO membrane, *J. Membr. Sci.*, 541 (2017) 39-52.
- [25] S.-Y. Kwak, S.G. Jung, S.H. Kim, Structure-motion-performance relationship of flux-enhanced reverse osmosis (RO) membranes composed of aromatic polyamide thin films, *Environ. Sci. Technol.*, 35 (2001) 4334-4340.
- [26] T. Ni, Q. Ge, Highly hydrophilic thin-film composition forward osmosis (FO) membranes functionalized with aniline sulfonate/bisulfonate for desalination, *J. Membr. Sci.*, 564 (2018) 732-741.
- [27] S. Singh, K. Khulbe, T. Matsuura, P. Ramamurthy, Membrane characterization by solute transport and atomic force microscopy, *J. Membr. Sci.*, 142 (1998) 111-127.
- [28] Y.-F. Hu, W.-J. Lv, Y.-Z. Shang, H.-L. Liu, H.-L. Wang, S.-H. Suh, DMSO transport across water/hexane interface by molecular dynamics simulation, *Ind. Eng. Chem. Res.*, 52 (2013) 6550-6558.
- [29] C. Jian, M.R. Poopari, Q. Liu, N. Zerpa, H. Zeng, T. Tang, Reduction of water/oil interfacial tension by model asphaltene: the governing role of surface concentration, *The Journal of Physical Chemistry B*, 120 (2016) 5646-5654.
- [30] S. Gao, K. Moran, Z. Xu, J. Masliyah, Role of naphthenic acids in stabilizing water-in-diluted model oil emulsions, *The Journal of Physical Chemistry B*, 114 (2010) 7710-7718.
- [31] J.C. Duarte, Bioconversions in organic solvents, in: *Perspectives in Biotechnology*, Springer, 1987, pp. 23-41.
- [32] F. Derwenskus, F. Metz, A. Gille, U. Schmid- Staiger, K. Briviba, U. Schließmann, T. Hirth, Pressurized extraction of unsaturated fatty acids and carotenoids from wet *Chlorella vulgaris* and *Phaeodactylum tricornutum* biomass using subcritical liquids, *GCB Bioenergy*.
- [33] S. Li, X. Zhang, J. Zhao, F. Meng, G. Xu, Z. Yong, J. Jia, Z. Zhang, Q. Li, Enhancement of carbon nanotube fibres using different solvents and polymers, *Composites Sci. Technol.*, 72 (2012) 1402-1407.
- [34] I.-C. Kim, B.-R. Jeong, S.-J. Kim, K.-H. Lee, Preparation of high flux thin film composite polyamide membrane: the effect of alkyl phosphate additives during interfacial polymerization, *Desalination*, 308 (2013) 111-114.
- [35] S.B. Undre, M. Singh, R. Kale, Interaction behaviour of trimesoyl chloride derived 1st tier dendrimers determined with structural and physicochemical properties required for drug designing, *J. Mol. Liq.*, 182 (2013) 106-120.
- [36] C. Mata, E.K. Longmire, D.H. McKenna, K.K. Glass, A. Hubel, Experimental study of diffusion-based extraction from a cell suspension, *Microfluid. Nanofluid.*, 5 (2008) 529-540.
- [37] A. Nowbahar, V. Mansard, J.M. Mecca, M. Paul, T. Arrowood, T.M. Squires, Measuring Interfacial Polymerization Kinetics Using Microfluidic Interferometry, *J. Am. Chem. Soc.*, 140 (2018) 3173-3176.
- [38] C. Bravo- Díaz, L.S. Romsted, S. Losada- Barreiro, F. Paiva- Martins, Using a pseudophase model to determine AO distributions in emulsions: Why dynamic equilibrium matters, *Eur. J. Lipid Sci. Technol.*, 119 (2017) 1600277.
- [39] A.K. Ghosh, B.-H. Jeong, X. Huang, E.M. Hoek, Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties, *J. Membr. Sci.*, 311 (2008) 34-45.

- 660 [40] S. Kolhe, M. Chipade, P. Chaudhari, Solubility and Solubilization Techniques-A Review,
661 International journal of pharmaceutical and chemical sciences, 1 (2012).
- 662 [41] I.J. Roh, Influence of rupture strength of interfacially polymerized thin-film structure on the
663 performance of polyamide composite membranes, J. Membr. Sci., 198 (2002) 63-74.
- 664 [42] F. Foglia, S. Karan, M. Nania, Z. Jiang, A.E. Porter, R. Barker, A.G. Livingston, J.T. Cabral,
665 Neutron Reflectivity and Performance of Polyamide Nanofilms for Water Desalination, Adv. Funct.
666 Mater., 27 (2017) 1701738.
- 667 [43] S. Zhang, M.H. Peh, Z. Thong, T.-S. Chung, Thin film interfacial cross-linking approach to
668 fabricate a chitosan rejecting layer over poly (ether sulfone) support for heavy metal removal, Ind.
669 Eng. Chem. Res., 54 (2014) 472-479.
- 670 [44] V. Freger, Kinetics of film formation by interfacial polycondensation, Langmuir, 21 (2005)
671 1884-1894.
- 672 [45] H.-R. Chae, J. Lee, C.-H. Lee, I.-C. Kim, P.-K. Park, Graphene oxide-embedded thin-film
673 composite reverse osmosis membrane with high flux, anti-biofouling, and chlorine resistance, J.
674 Membr. Sci., 483 (2015) 128-135.

Highlights

- The interaction between DMSO and TMC was considered as a parameter dictating IP.
- DMSO increased the TMC concentration at the interface during IP.
- The increase in the TMC concentration led to a faster but incomplete IP reaction.
- The faster and incomplete IP changed the morphological features of polyamide films.
- A new mechanism was proposed to clarify the DMSO effect based on empirical evidence.

Highlights

- The interaction between DMSO and TMC was considered as a parameter dictating IP.
- DMSO increased the TMC concentration at the interface during IP.
- The increase in the TMC concentration led to a faster but incomplete IP reaction.
- The faster and incomplete IP changed the morphological features of polyamide films.
- A new mechanism was proposed to clarify the DMSO effect based on empirical evidence.