

CRANFIELD UNIVERSITY

APHIWE JIKAZANA

SUPERSATURATION CONTROL IN MEMBRANE
DISTILLATION CRYSTALLISATION

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Cranfield Water Science Institute

PhD

Academic Year: 2018 - 2022

Supervisor: Prof. Ewan McAdam
Associate Supervisor: Dr Pablo Campo Moreno
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Abstract

Membrane distillation crystallisation (MDC) has emerged as a potential alternative to conventional industrial crystallisers. MDC provides controlled hydrodynamics and uniform supersaturation conditions for crystallisation, thereby enhancing scalability, which is desperately lacking in conventional crystallisation systems. Unfortunately, crystallisation near the membrane surface is also associated with inorganic fouling (scaling), which can ultimately lead to process failure. As such, the viability of the technology is dependent on scale-free bulk crystallisation. To date however, scaling mitigation strategies have been based on empirical observations with contradictory postulations regarding the governing crystallisation mechanism(s). In this work, the distinct mechanisms of scaling and bulk crystallisation have been elucidated for the first time. The application of novel inline and online experimental techniques facilitated the development of a mechanistic framework which is able to predict the likelihood of scaling in addition to mediating bulk nucleation kinetics. As such, scale-free operation was achieved at temperatures and hydrodynamic conditions which were previously associated with scaling. This study has therefore broadened the perceived range of kinetic trajectories achievable with MDC and evidenced its applicability to multi-component systems, polymorph selection, and a variety of product specifications. Furthermore, the use of hydrodynamics to decouple nucleation and growth kinetics revealed the potential of MDC to minimise the usual trade-off between product quality and yield in crystallisation systems. While existing scaling mitigation strategies are largely hydrodynamic and thermodynamic in nature, this study has shown that the contribution of crystallisation kinetics (supersaturation rate) to scaling propensity cannot be underestimated. Hence, application of the kinetic framework developed could provide more targeted strategies for scaling prevention in various applications such as heat exchangers and reverse osmosis/nanofiltration (RO/NF), where polarisation phenomena are prevalent.

Keywords: Scaling, classical nucleation theory, crystal growth, metastable zone width (MSZW), diffusion

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To God be the glory, honour and praise. I thank Him for blessing me with this opportunity and empowering me through the journey. I dedicate this to my dad who passed away during this journey. Then to my supervisor, Professor Ewan McAdam, I am truly grateful for your unwavering support, time and patience. Thank you also to Dr Pablo Campo Moreno for your contributions at various stages of the project, Dr Kristell Le Corre Pidou, as well as the laboratory technicians at the Cranfield Water Science Institute. Lastly, I would like to thank my loved ones, especially my mother and sister, for their never-ending prayers, love and support.

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Nomenclature

Roman symbols

A	Pre-exponential factor	$\text{m}^{-3} \text{s}^{-1}$
A_m	Membrane surface area	m^2
B	Thermodynamic parameter	-
B_m	Nucleation rate (mass basis)	$\text{kg m}^{-3} \text{s}^{-1}$
B_n	Nucleation rate (number basis)	$\text{m}^{-3} \text{s}^{-1}$
C	Concentration	kg m^{-3}
cp	Specific heat capacity	$\text{J kg}^{-1} \text{K}^{-1}$
D	Molecular diffusivity/diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
dC	Concentration gradient	mol
dh	Hydraulic diameter	m
dx	Boundary-layer thickness	m
G	Growth rate	m s^{-1}
h	Heat transfer coefficient	$\text{W m}^{-2} \text{K}^{-1}$
J	Flux	$\text{kg m}^{-2} \text{s}^{-2}$
K	Mass transfer coefficient	m s^{-1}
k	Thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
k_B	Boltzmann constant	-
L	Length	m
L_{50}	Median size	m
N	Crystalliser agitation rate	rps
Nu	Nusselt number	-
Pr	Prandtl number	-
R'	Interfacial supersaturation rate	$\text{kg m}^{-3} \text{s}^{-1}$
Re	Reynolds number	-
Re_N	Agitator Reynolds number	-
S	Supersaturation level	-
t	Time	s
T	Temperature	$^{\circ}\text{C/K}$
V	Velocity	m s^{-1}
V_c	Volume of crystals in suspension	m^3
V_{susp}	Volume of suspension	m^3

V_{sol}	Volume of solution	m^3
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Greek symbols

δ_m	Membrane thickness	m
ΔT	Temperature difference	$^{\circ}C/K$
ΔG_{hom}^*	Critical Gibbs free energy	J
ΔH_v	Heat of vaporisation	$J\ kg^{-1}$
Δm	Change in permeate mass	kg
Δt	Change in time	s
ΔC	Change in concentration	$kg\ m^{-3}$
ΔG	Gibbs free energy	J
$\Delta \mu$	Chemical potential difference	J
v	Volume of solute molecule	m^3
α	Volume shape factor	-
γ	Interfacial energy	$J\ m^{-2}$
θ	Contact angle	$^{\circ}$
μ	Dynamic viscosity	Pa s
μ_c	Chemical potential of crystal	J
μ_{sol}	Chemical potential of solution	J
ρ	Density	$kg\ m^{-3}$
φ	Volumetric hold up of crystals	-
ε	Membrane porosity	-

Subscripts

0	Initial
b	Bulk
c	Crystal
eff	Effective
f	Feed
het	Heterogeneous nucleation
hom	Homogeneous nucleation
ind	Induction
int	Interface
m	Membrane

max	Maximum
nucl	Nucleation
p	Permeate
sat	Saturation
sol	Solution

Abbreviations

CFD	Computational fluid dynamics
CNT	Classical nucleation theory
CPC	Concentration polarisation coefficient
CSD	Crystal size distribution
DT	Draft tube
DTB	Draft tube baffle
ECSN	Embryo coagulation secondary nucleation
ePTFE	Expanded polytetrafluoroethylene
FC	Forced convection
GOR	Gained output ratio
MD	Membrane distillation
MDC	Membrane distillation crystallisation
MSZ	Metastable zone
MSZW	Metastable zone width
NF	Nanofiltration
PP	Polypropylene
PVDF	Polyvinylidene difluoride
RO	Reverse osmosis
SNM	Secondary nucleation mechanism
SNT	Secondary nucleation threshold
TPC	Temperature polarisation coefficients
UK	United Kingdom
ZLD	Zero-liquid discharge

1. Introduction

1.1 Crystallisation control

The crystallisation process is applied in a wide range of industries for the production, separation and/or purification of solid compounds from liquid solutions [1]. Typical industrial examples include pharmaceuticals, bulk chemicals, and more recently, resource recovery from wastewater [2, 3]. Highly-pure crystal products with uniform morphologies and narrow crystal size distributions (CSDs) are usually preferred [4, 5]. These characteristics are not only beneficial for their final applications but also enable the efficiency of downstream processes such as filtration and drying [4, 6, 7].

For crystallisation to occur, the concentration of a solution is increased until the solubility of the solute in the solvent is exceeded and the solution becomes supersaturated [8]. Since a supersaturated solution is not in equilibrium, the system works to return to equilibrium by removing the excess solutes in solution through the formation (nucleation) and growth of crystals, i.e., through crystallisation [9]. Supersaturation is therefore the driving force of crystal nucleation and growth [8]. While thermodynamic parameters (such as solubility) outline the physical limits of a crystallising system, the crystal product characteristics are determined by the kinetic metastability as outlined by the metastable zone width (MSZW) [8, 10, 11].

The MSZW is the maximum supersaturation level achieved by a system at a specific set of operating conditions [11]. In unseeded crystallisation systems (without pre-existing crystals), the MSZW determines the primary nucleation rate [9, 11]. According to classical nucleation theory (CNT), primary nucleation can occur either homogeneously in pure solutions (containing only the solvent and crystallising solute) or heterogeneously in the presence of external surfaces [8]. The homogeneous metastable limit denotes the supersaturation level above which homogeneous nucleation occurs (Figure 1.1). At this supersaturation level, the system has sufficient energy (ΔG^*) to create a stable nucleus which can continue to grow into a crystal [9]. The activation energy barrier or critical Gibbs free energy for homogeneous nucleation (ΔG_{hom}^*) can be described as follows:

$$\Delta G_{hom}^* = \frac{16\pi\gamma^3 v^2}{3(k_B T)^2 \ln^2 S} \quad (1-1)$$

where k_B is the Boltzmann constant, T is the nucleation temperature v is the volume of the solute molecule, γ is the cluster-solution interfacial energy, and S is the supersaturation level. In the presence of a foreign surface, the activation energy for nucleation is reduced due to a decrease in excess surface energy [7, 9]. Since,

$$\Delta G_{het}^*(\gamma_{eff}) < \Delta G_{hom}^*(\gamma) \quad (1-2)$$

where ΔG_{het}^* and γ_{eff} are critical Gibbs free energy and effective interfacial energy for heterogeneous nucleation, respectively, lower supersaturation levels are required for heterogeneous nucleation. As a result, the heterogeneous nucleation metastable limit is below that of homogeneous nucleation [9].

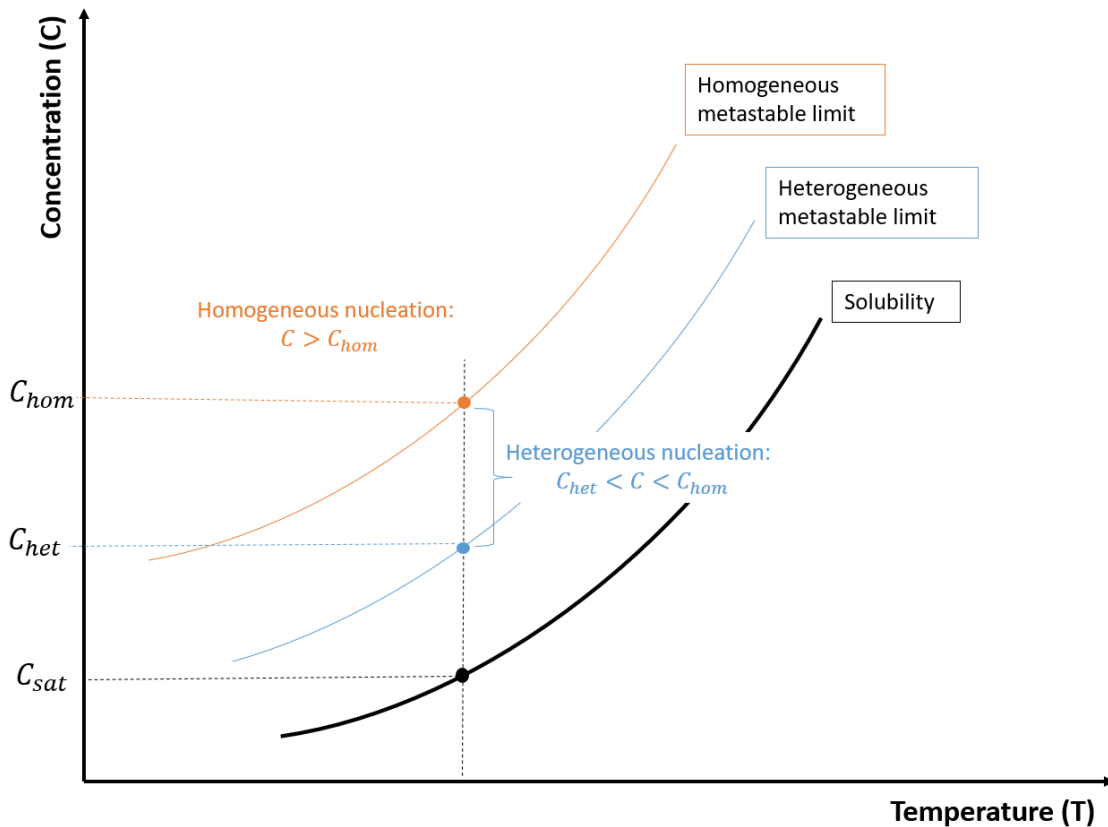


Figure 1.1. Description of how metastable zone width (MSZW, $C - C_{sat}$) determines the primary nucleation mechanism. Homogeneous or heterogeneous nucleation occurs based on C achieved relative to respective metastable limits (C_{hom} and C_{het} , respectively).

The excessively high nucleation rates associated with homogeneous nucleation and wide MSZWs are not usually preferred as they result in a large number of small crystals [7, 9, 11, 12]. This is due to the high consumption of supersaturation by crystal formation which reduces the supersaturation (driving force) for crystal growth [12]. Furthermore, high supersaturation levels and nucleation rates exacerbate agglomeration, which is an undesirable crystallisation phenomenon [13–15]. It involves the aggregation and cementation of small crystals which grow into polycrystalline particles (agglomerates) [15, 16]. Agglomeration results in non-uniform CSDs and reduces product purity by entrapping impurities and/or the mother liquor. It also has a negative effect on downstream processes and transportation due to enhanced breakage and fines production as well as slower rates of dissolution due to the large, irregularly shaped crystals formed [13, 17]. Reduced nucleation rates at narrower MSZWs are therefore more likely to produce larger crystals and more uniform CSDs. Hence, the MSZW plays an integral role in controlling both crystal nucleation and growth rates. It can be regulated by varying operating conditions such as supersaturation rate, temperature, and agitating rate [11, 18–20]. Higher rates of supersaturation result in wider MSZWs as the system has insufficient time to respond to the intermediate changes in supersaturation level. As a result, higher supersaturation levels can be reached prior to nucleation taking place [21, 22]. In contrast, higher temperatures narrow the MSZW by reducing the activation energy required for nucleation while also increasing the kinetic energy of the molecules which enhances the likelihood of molecular collisions [8, 23]. Similarly, increased agitation narrows the MSZW by promoting diffusive mass transfer and increasing molecular interactions [19, 21, 24, 25].

Once crystals are present in solution, supersaturation can be consumed by either secondary nucleation (further formation of new crystals) or crystal growth [26]. These phenomena describe the two regions of the metastable zone (MSZ) (Figure 1.2). According to Threlfall and Coles [27], a secondary nucleation threshold (SNT) exists within the MSZW. The regions below and above the SNT were termed “growth-only” and crystal “proliferation” zones, respectively [26, 27].

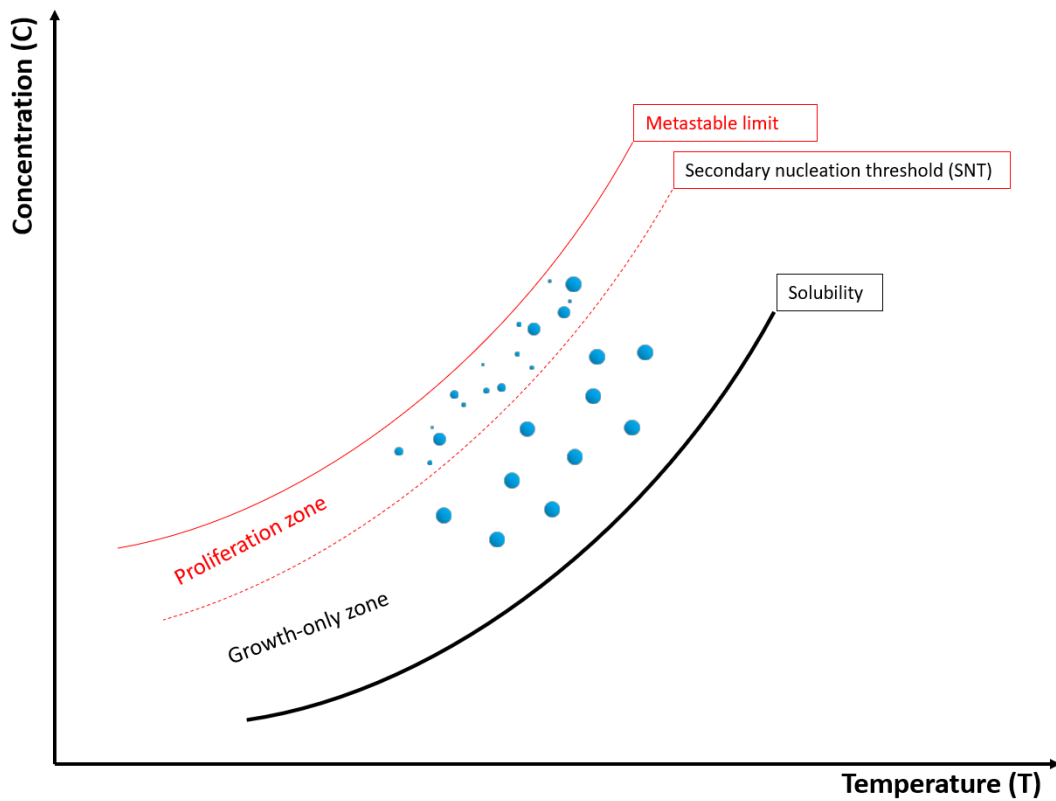


Figure 1.2. Characterisation of regions within an established metastable zone (MSZ), i.e., after primary nucleation. Secondary nucleation threshold (SNT) divides growth-only and proliferation zones [27].

At lower supersaturations (below the SNT), a smooth crystal growth mechanism dominates and the morphology of the crystals present in solution tends toward the thermodynamically favourable equilibrium shape with a minimum total surface energy [28]. In this region, secondary nucleation only occurs mechanically by the attrition (macro-abrasion/macro-attrition) of parent crystals due to collisions with other crystals, the stirrer, crystalliser walls and/or other process equipment [9, 29]. Above the SNT, rapid growth occurs [27]. As a result, nonequilibrium (kinetically-controlled) morphologies are prevalent [28] and phenomena such as dendrite formation from irregularities on the crystal surface are observed [27]. The detachment of these dendrites results in the formation of secondary nuclei and hence, the secondary nucleation mechanism (SNM) of dendritic or needle breeding occurs at high supersaturation levels [9, 26, 27, 29]. While secondary nucleation only occurs via macro-attrition below the SNT, micro-attrition is

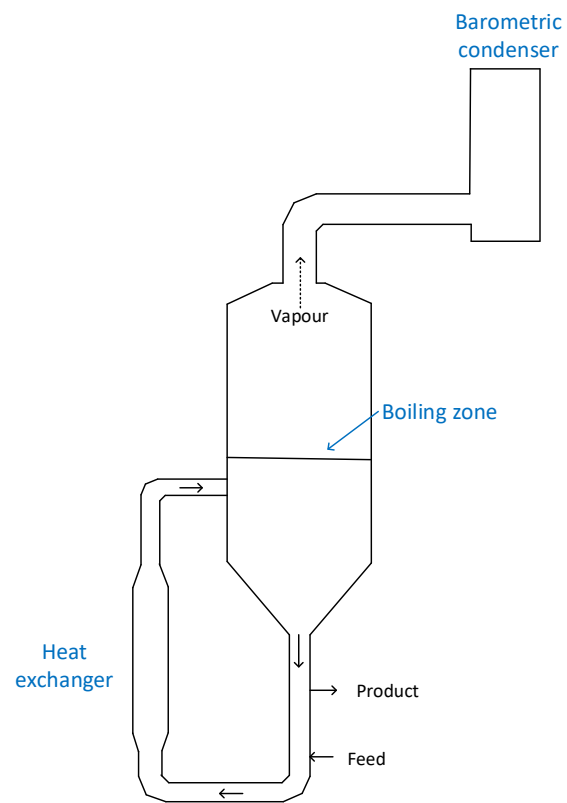
considered an important SNM above the SNT [29]. Micro-attrition involves the removal of solute clusters formed on the crystal surface, or in the boundary layer around the crystal, via collisions with the surrounding solids (contact nucleation) and/or by fluid shear (shear nucleation). This is explained by the embryo coagulation secondary nucleation (ECSN) theory which describes the solute clusters as embryos attracted to crystal surfaces by van der Waals forces. The embryos then coagulate to form nuclei which are removed by contact or shear nucleation and continue to grow into crystals in solution [26, 29]. High supersaturation levels favour this SNM because the concentration of solute clusters increases along with the thickness of the boundary layer around the crystal. The critical size of a stable nucleus is also smaller at higher supersaturation levels [9]. Hence, product quality is governed by the supersaturation trajectory of the solution as it transitions through the various regions of the MSZ. As such, an understanding of how operating conditions impact the supersaturation trajectory and resultant crystallisation rates and mechanisms is essential to achieve the desired product quality [10, 23]. Furthermore, it is critical to ensure uniform heat and mass transfer conditions throughout the system in order to obtain the uniform supersaturation levels required to produce a narrow CSD [7].

Hydrodynamics have a profound influence on supersaturation control [7]. Not only do they facilitate uniform supersaturation conditions [7, 30], but increased mixing also improves both nucleation [19, 21, 24, 25] and growth kinetics through enhanced diffusion [31, 32]. Excessive mixing however, increases the likelihood of secondary nucleation through both macro- and micro-attrition, potentially damaging the crystals through fragmentation and producing undesirably wide CSDs [31]. Precise control of hydrodynamics is therefore a fundamental requirement of crystallisation systems [6]. Failure to strictly regulate hydrodynamics causes inhomogeneous supersaturation conditions and limited control of the MSZW and crystallisation kinetics. This results in irreproducible crystal qualities and severely jeopardises the scalability of the crystallisation process [4, 7, 33, 34].

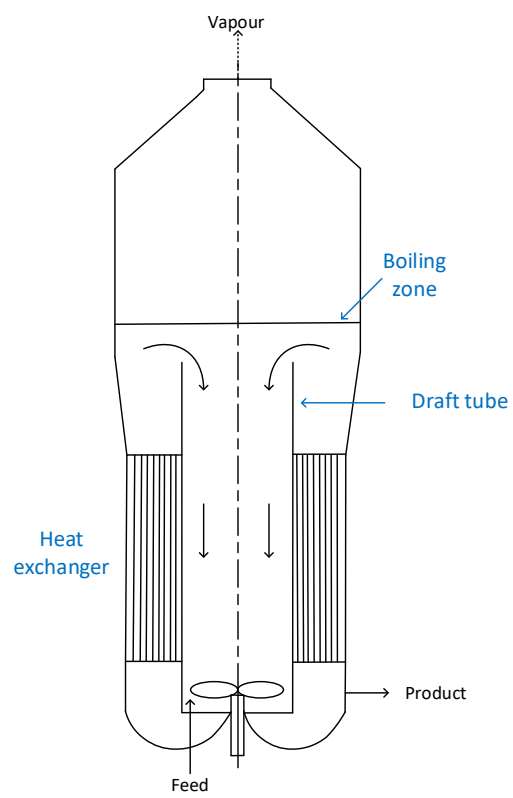
1.2 The need for improved crystallisation technology

The type of crystallisation method employed is largely dependent on the thermodynamics of the system [33, 35]. Crystallisation from a solution can be achieved by either evaporation, cooling, precipitation or the addition of an anti-solvent. In the case of salts with a relatively flat temperature versus solubility trend such as sodium chloride (NaCl), evaporative crystallisation is preferred [35]. In this method, supersaturation is achieved by solvent removal via boiling [10, 35, 36]. Forced convection (FC) crystallisers are the most commonly applied crystalliser configuration for the large-scale production of salts such as NaCl [10, 35] (Figure 1.3a). FC crystallisers comprise of a crystallisation vessel with a conical base attached to an external tubular heat exchanger. Circulation of the crystallisation suspension between the units is achieved by pumping [36]. The feed is inserted via a (usually) tangential inlet which must be positioned at a level that ensures the minimum boiling height is above the inlet from the heat exchanger to prevent scaling of the heat-exchanger tubes. The feed inlet level is therefore dependent on the temperature difference in the heat exchanger [35]. Since the temperature difference determines the rate of supersaturation, the extent and flexibility of the supersaturation rate (and therefore the MSZW) is limited in FC crystallisers. Although the hydrodynamics of this configuration are often considered to closely resemble those of a well-mixed process vessel, operation has been shown to deviate substantially from this assumption, leading to non-uniform supersaturation conditions and wide, irreproducible CSDs [33]. Other disadvantages include attrition (secondary nucleation) of the crystals caused by pumping and heat-exchanger tubing. Furthermore, crystal products achieved are also relatively small while high capital costs are required due to complicated mechanical and structural requirements [10, 35, 36]. A summary of the advantages and disadvantages of FC crystallisers is provided in Table 1.1 along with those of other common evaporative crystalliser configurations.

(a)



(b)



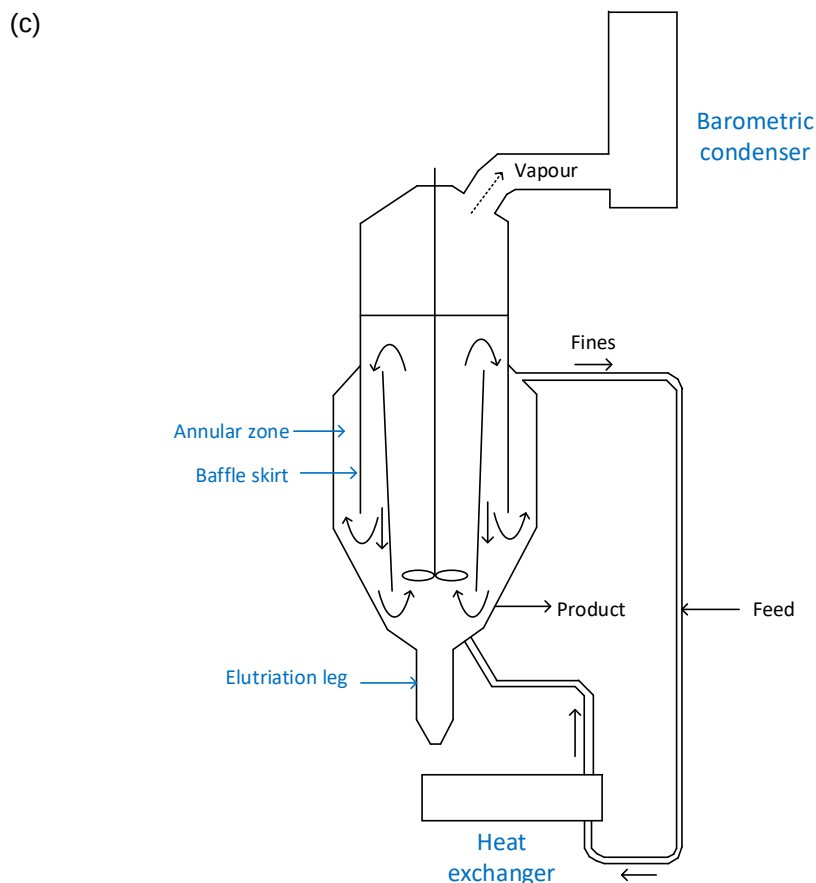


Figure 1.3. Conventional evaporative crystalliser configurations: (a) Forced convection (FC) crystalliser; (b) stirred draft tube (DT) crystalliser with internal heat exchanger; and (c) stirred draft tube baffle (DTB) crystalliser with external heat exchanger. Adapted from Kramer and Lakerveld [10].

The stirred draft tube (DT) crystalliser has the benefit of a simple, well-mixed configuration along with reduced attrition due to pumping when an internal heat exchanger is employed (Figure 1.3b) [10]. Mixing is achieved by a stirrer inserted at the bottom of the crystalliser next to the feed inlet. Unfortunately, the use of an internal heat exchanger limits the flexibility of the crystallisation process as well as the area available for heat transfer. Hence, the optimisation of the supersaturation rate is compromised. As a result, the reduced heat-transfer area means that it can only be used in applications with low heating requirements and/or small production volumes [10]. Furthermore, the introduction of an impeller results in an additional source of attrition [10, 35]. The addition of a baffle to the DT crystalliser results in the stirred draft tube baffle (DTB) crystalliser (Figure

1.3c) [10, 34]. The baffle skirt produces an annular zone for fines removal which enables the production of larger crystals [35]. The use of an external heat exchanger enhances process flexibility and the available heat transfer area although attrition due to pumping is re-introduced. This is likely to be lower than the pumping attrition observed in FC crystallisers, however, as only fines are pumped to the external heat exchanger [10]. Nevertheless, the DTB has a more complex design [37] which results in higher capital and operating costs. This is in addition to hydrodynamic problems such as non-uniform mixing environments [33] which are not only irreproducible during scale-up [34], but also impact the heat and mass transfer rates of the process which control crystallisation kinetics and the resultant crystal product quality [4, 34]. Crystallisation systems with more predictable and controllable hydrodynamics are therefore required for improved supersaturation control [7, 30].

Table 1.1. *Comparison of common-used evaporative crystalliser configurations*

Name	Advantages	Disadvantages
Forced circulation	Large production volumes [33]	Attrition of crystals due to pumping [35]
	Can be applied for salts with low dependence of solubility on temperature such as NaCl [10,35]	Operation deviates largely from well-mixed modelling assumptions [33]
		Encrustation in boiling zone [35]
		Relatively small crystal product [36]
		Possible heat exchanger tube scaling [10, 35]
		High capital costs due to complicated mechanical construction requirements [35]
Stirred draft tube (DT) with internal heat exchanger	Simple design [10]	Limited heat transfer area [10]
	Improved mixing due to stirrer [10]	Applicable for low heating requirements [10]
	No additional pumping required - reduced attrition of crystals [10]	Small production volumes [10]
		Attrition of crystals in heat exchanger and due to impeller [35]
		Inflexible operation due to internal heat exchanger [10, 35]
		Encrustation in boiling zone [35]
Stirred draft tube baffle (DTB) with external heat exchanger	Fines removal allows formation of coarser/larger product size [10, 35,36]	More complex process [37]
	Lower pumping attrition of crystals compared to FC (and DT with external heat exchanger) due to only fines pumped to external heat exchanger [10]	Higher capital and operating costs (due to complexities)
		Attrition of crystals due to impeller and pumping [35]
		Encrustation in boiling zone [35]

1.3 Membrane distillation crystallisation

Membrane distillation crystallisation (MDC) provides a potential solution for supersaturation regulation in crystallisation processes [3, 30]. During MDC, the supersaturation of the feed solution is achieved by applying a vapour-pressure gradient across a hydrophobic, microporous membrane contactor [7]. The rate of vapour transfer across the membrane from the feed to the permeate solution can be precisely controlled by adjusting operating conditions such as feed- and

permeate-side temperatures and flow rates [7, 30]. This enables strict control of the supersaturation trajectory along with lower energy requirements for solvent removal due to lower operating temperatures compared to conventional evaporative crystallisation processes [7, 38–40]. The membrane surface also provides additional benefits of inherent scalability; increased surface area for heat and mass transfer which maximises the achievable supersaturation rate; and nucleation promotion [1, 2, 7, 37, 39, 40]. In addition to the reduction in interfacial energy offered by the membrane surface, Di Profio et al. [7] proposed the following mechanism for the enhancement of nucleation facilitated by surface roughness induced by the membrane pores, leading to fluid stagnation and limited solute backtransport at the interface (Figure 1.4):

- (i) molecular ions in solution (at the boundary layer) are attracted to and adsorb onto the membrane surface
- (ii) cavities of the membrane pores physically entrap solute molecules, thereby preventing the continual lateral movement of ions with the fluid
- (iii) localised areas of high supersaturation facilitate the intermolecular interactions required for cluster aggregation and nucleation

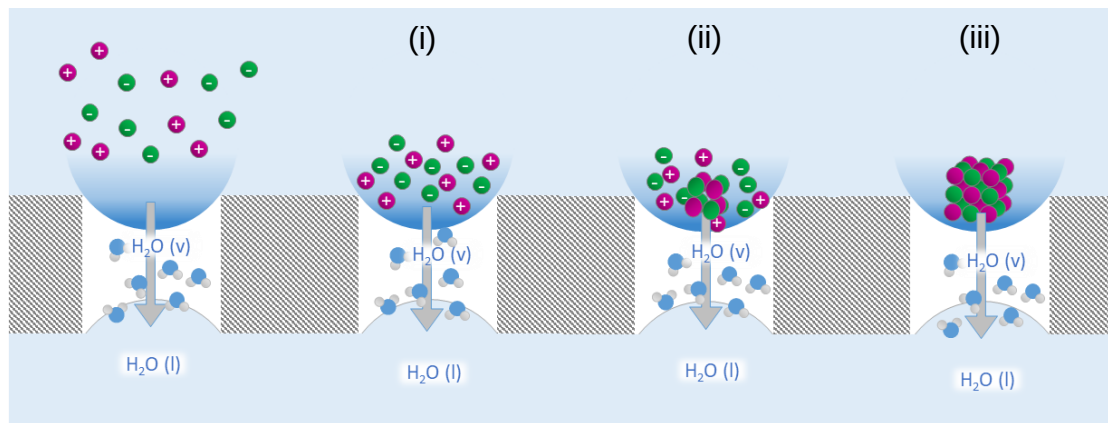


Figure 1.4. Proposed nucleation-promoting mechanism due to surface roughness created by membrane pores in MDC [7]. Mechanism describes (i) attraction; (ii) entrapment into pores/cavities; and (iii) interaction of positive (+) and negative (-) solute ions. $H_2O (v)$ and $H_2O (l)$ represent permeate vapour and condensed water vapour, respectively.

This mechanism has been validated by later studies evaluating the impact of physio-chemical properties of the membrane surface on the crystallisation of inorganic salts such as NaCl [41–44]. As such, hydrophobic membrane surfaces have been shown to reduce the induction time for crystal nucleation. Tsai et al. [44] demonstrated that the presence of polyvinylidene difluoride (PVDF) and polypropylene (PP) membranes resulted in faster formation of NaCl crystals compared to the bulk solution. This was further affirmed by molecular dynamic simulations which showed that the PP and PVDF membranes drastically improved the nucleation rate. The reduced induction time observed by Tsai et al. [44] was attributed to the repulsion of water molecules by the hydrophobic surface. The enhanced water removal near the hydrophobic surface therefore promoted the interaction of solute ions via Coulomb attractive forces, thereby reducing the time required for aggregation to take place [44, 45].

Unfortunately, the nucleation-promoting benefits of the membrane surface also make it susceptible to inorganic fouling (scaling). Inherently, mineral scaling is one of the major technical challenges for membrane distillation (MD) [46, 47]. Scaling is a result of the deposition and/or surface nucleation of bulk crystals which continue to grow on the surface and inside the membrane pores [46, 48]. This can lead to ultimate process failure by pore blockage and loss of vapour permeability; increased wettability and subsequent salt breakthrough; as well as potential structural damage of the membrane [2, 46–49]. Hence, the industrial application of MDC is dependent on process development which prevents scaling and enables the exploitation of the membrane as a nucleation promotor while ensuring a reproducibly high product quality.

1.4 Membrane surface modification for crystallisation and scaling control

Most recently, membrane surface modification has been at the centre of efforts to maximise product quality and mitigate scaling in MDC [50-51]. For the optimisation of crystal quality, the membrane surface characteristics are adjusted to control the crystallisation kinetics and thermodynamics which govern nucleation and growth [51]. Active surfaces have been used promote the rate of water exclusion from ion aggregates and catalyse supersaturation followed by

crystal formation. Macedonio et al. [43] showed an improvement in the growth rate and a lower coefficient of variation (i.e., narrower CSD) of NaCl when bismuth selenide (Bi_2Se_3) nanofillers were entrapped in PVDF membranes. The adsorption of water ions to vacancies and edges of Bi_2Se_3 in the polymer matrix enabled faster structural ordering of ions by reducing ion-water interactions. Similarly, Perrotta et al. [42] and Perrotta et al. [41] reported that the inclusion of graphene platelets in a PVDF membrane increased water removal, improved crystallisation kinetics, and a more cubic structure relative to an inert PVDF surface. These studies clearly show during MDC, the rate of water removal (i.e., supersaturation rate) and the interaction of ions near the membrane surface have a strong impact on the crystal products formed. The active surfaces therefore altered the mass transport and crystallisation kinetics the interfacial boundary layer.

For scaling mitigation, superhydrophobic membranes have proven effective at inhibiting scaling kinetics by delaying the onset of scaling and reducing the rate at which it occurs [46]. For example, superhydrophobic polyvinylidene fluoride (PVDF) membranes with micropillar arrays and CF_4 plasma treatment (PVDF-MP- CF_4) were shown to greatly reduce NaCl and CaSO_4 scale formation compared to conventional PVDF membranes used in MD [49-52]. Superhydrophobic membranes are said to reduce scaling via a combination of three mechanisms [50]. Firstly, an air layer between the membrane surface and feed solution reduces the contact area between the solute and membrane. Secondly, the air layer also reduces viscous drag, which decreases the residence time of the solute in the membrane module. The reduction in contact area and time available reduces the likelihood of crystal-solid interactions. Lastly, increased hydrophobicity enhances the contact angle between the solution and membrane surface, which thermodynamically reduces the likelihood of heterogeneous nucleation [46, 47, 50].

Although surface modification has shown some improvements to MDC process control, Su et al. [47] noted that the addition of fluorinated nanoparticles to produce superhydrophobic membranes from commercial PVDF membranes was problematic in that ensuring particle attachment usually required a

complicated process with multiple stages and often lead to reduced membrane permeability. This loss in permeability with the addition of membrane coatings was also observed in a study by Frappa et al. [53]. Nevertheless, these surface-modification investigations clearly indicate that molecular interactions (via mass transfer) and crystallisation kinetics at the membrane interface are integral considerations for the control of both crystal quality and scale formation in MDC. While thermodynamics play an important role, Xiao et al. [49] showed that even with the use of superhydrophobic membranes, the hydrodynamically influenced crystallisation kinetics have a profound impact on scaling propensity. Many MD and MDC studies have shown that operating conditions can be used to alter both interfacial hydrodynamics and crystallisation kinetics. This indicates that both scaling and crystallisation kinetics can be controlled without the need for surface modification. As it stands, however, there is no cohesive framework underpinning how operating conditions can be used for both scaling mitigation and optimisation of product quality.

1.5 Membrane surface nucleation mechanism

In line with the no-slip condition, the viscous flow of the feed solution across the membrane surface in MDC creates a boundary layer adjacent to the membrane wall where the fluid velocity declines to zero [54, 55]. Along with this velocity gradient, mass and heat transfer across the boundary layer result in concentration and temperature polarisation, respectively [7, 39, 56]. High concentrations and low temperatures at the membrane give rise to a supersaturation gradient which is exacerbated for positive temperature-solubility gradient salts such as NaCl [50, 57, 58]. Since high supersaturation levels promote the driving force for crystallisation [7], it is widely understood that along with scaling, bulk nucleation is induced near the membrane interface [39, 40, 50, 56]. The primary nucleation mechanism(s) responsible for these phenomena however, remain unresolved [50].

A sequential mechanism for scaling and bulk nucleation has been proposed [40]. It is suggested that scaling initially occurs via a heterogeneous (surface) nucleation mechanism assisted by the membrane lowering the interfacial energy

and activation energy barrier [40]. Bulk nucleation then occurs by the detachment of previously-adhered crystals by hydrodynamic forces at the interface [39, 40]. Thermodynamically however, the hydrophobicity of the membrane surfaces used in MDC reduces the likelihood of heterogeneous nucleation due to relatively high water contact angles ($\theta > 90^\circ$) and lower surface energy which decrease the probability of solute interactions with the membrane surface [9, 55]. This effect was observed by Warsinger et al. [59] who noted that crystallisation in MD was initiated in the bulk solution followed by the deposition of crystals on the membrane surface. Furthermore, high interfacial supersaturation levels are likely to encourage homogeneous (bulk) nucleation due to a greater likelihood of surpassing the homogeneous metastable limit [8, 9]. As such, the mechanism of nucleation in MDC is likely to be mediated by the MSZW of the system at various process conditions.

In past studies, high temperatures and temperature differences across the membrane have been associated with increased scaling propensity [48, 57, 58]. Warsinger et al. [55] observed that the scaling induction time (which is another indicator of system metastability) is reduced with increasing temperature. Their finding corroborates the results of Jiang et al. [23] who showed a narrowing of the MSZW at higher temperatures. This was because enhanced temperatures increase the energy of the molecules in solution which increases the probability of molecular collisions [9]. Operating at high temperature differences across the membrane increases the permeate flux which increases the supersaturation level at induction (i.e., widens the MSZW) by increasing the rate of supersaturation [23]. High levels of supersaturation at the membrane interface are considered to promote scaling [57, 58]. However, since two nucleation events occur in MDC, namely, scaling and bulk induction, two MSZWs are required to distinguish their mechanism(s). In the aforementioned MD studies, a single MSZW and/or induction time has been defined based on drastic decline in permeate flux [23, 55, 57, 60]. This is the point at which crystal growth on the membrane surface has a noticeable effect on membrane permeability. Since there is usually a lag time between the first appearance of crystals on the surface and substantial pore blockage [2], this point is neither an accurate indication of surface nucleation nor

bulk nucleation [50]. As such, the effect of operating conditions on crystallisation kinetics in MDC have yet to be accurately characterised. Precise examination of nucleation kinetics would require inline and online telemetry to observe the presence of both surface and bulk crystals. In so doing, the MSZWs of bulk nucleation and scaling can be determined at various operating conditions. This will enable the kinetic operating window, in which scaling does not occur in MDC, to be outlined.

1.6 Hydrodynamic control of crystallisation kinetics

For operational flexibility, a wide operating window is preferred. Existing MD studies have evidenced the potential benefits of high-shear hydrodynamic conditions for scaling mitigation [40, 48, 50, 55, 58]. Operation at elevated feed Reynolds numbers or flow velocities have often been recommended for a number of reasons. Firstly, high shear stress can be used to detach crystals adhered to the membrane surface [39, 40, 56]. Secondly, turbulence disrupts the formation of the boundary layer which reduces temperature and concentration polarisation and the risk of oversaturation [50, 58]. Warsinger et al. [55] also indicated that increasing the feed flow rate reduces the residence time of molecular ions at the interface which decreases the likelihood of scaling. However, increasing the feed flow rate has also been shown to improve the permeate flux [16, 58, 61, 62]. This is because higher velocities lead to enhanced feed-side and lower permeate-side outlet temperatures. This then increases the log-mean temperature difference (and therewith the vapour pressure difference) across the membrane which is the driving force for heat and mass transfer in MD [16, 61]. In addition, the improved mixing at the boundary layer increases the heat transfer coefficient which increases the rate of vapour transport across the membrane [58, 61, 62]. Therefore, although increasing the flow velocity is said to reduce particle adherence; boundary-layer thickness; and solute residence time, it can also increase the convection of solute ions and the resultant supersaturation level in the boundary-layer by enhancing the permeate flux. Since boundary-layer hydrodynamics affect molecular interactions and therefore crystallisation kinetics, their impact on the MSZW requires further investigation.

In conventional systems, crystalliser hydrodynamics are known to play an essential role in regulating the crystal growth rate and resultant morphology [31, 32]. While it is assumed that crystal growth in MDC occurs in the downstream crystalliser [39, 56], the growth rate is also heavily-dependent on the initial nucleation rate and residual supersaturation conditions [12]. This would indicate that growth kinetics cannot be considered independent of the conditions in the boundary-layer. Furthermore, hydrodynamics have been used in conventional crystallisation to promote diffusion and induce nucleation, resulting in shorter induction times and a narrower MSZW with increased mixing [19, 21, 24, 25]. The extent to which bulk hydrodynamics are able to influence the nucleation kinetics in MDC however, remains unknown. Although supersaturation is highest at the membrane interface, stagnant conditions drastically reduce the rate of solute diffusion. In contrast, greater fluid velocities in the bulk solution could promote bulk nucleation by increasing the likelihood of molecular collisions [63]. Hence, an understanding of the contributions of bulk and boundary-layer hydrodynamics to crystal nucleation and growth kinetics is fundamental for the development of appropriate operation and scale-up strategies.

1.7 Aims and objectives

The aim of this thesis is to exploit the ability of membrane distillation crystallisation to regulate crystallisation kinetics, via supersaturation control, by distinguishing the roles of supersaturation rate; boundary-layer hydrodynamics; and crystalliser mixing on crystal nucleation and growth kinetics as well as on the resultant product quality. The specific objectives are to:

- (i) Characterise the factors that inform supersaturation rate, with the use of inline crystallisation monitoring techniques, to create a kinetic framework that can independently relate supersaturation rate to the respective crystallisation kinetics, thereby distinguishing the mechanisms governing scaling and bulk crystallisation.
- (ii) Provide an analytical description of the boundary-layer to describe how hydrodynamics inform the nucleation and crystal growth kinetics for scaling and bulk crystallisation based on fundamental mass transfer and

classical nucleation theory. In so doing, the combined effects of supersaturation and hydrodynamics at the boundary layer will be ascertained.

- (iii) Delineate the role of mixing in membrane distillation crystallisation systems (i.e., boundary-layer hydrodynamics and crystalliser mixing) to provide a broader set of kinetic trajectories for the adjustment of crystal product quality.

1.8 Thesis structure

Three technical chapters (i.e., Chapters 2 to 4) are formatted as journal articles and address the aforementioned objectives (Figure 1.5). Chapter 2 develops “*A unifying kinetic framework for controlling scaling and crystal growth in membrane distillation crystallisation*” using novel experimental techniques to precisely map surface and bulk MSZWs at operating conditions which control the supersaturation rate, thereby elucidating the supersaturation conditions which govern the predominant nucleation mechanism(s) in the boundary layer. While the supersaturation driving force is changed explicitly through temperature and temperature difference in Chapter 2, Chapter 3 builds on the framework developed by comparing the explicit and implicit effects of temperature difference and Reynolds number on interfacial supersaturation conditions, respectively. Hence, by explaining the role of process driving force in mediating the supersaturation rate in relation to diffusive solute back transport which is influenced by hydrodynamic and supersaturation conditions in the boundary layer, Chapter 3 reveals that, “*Reynolds number establishes boundary-layer characteristics that determine nucleation and crystal growth kinetics (including scaling) in membrane distillation crystallisation*”. In Chapter 4, “*The role of mixing on the kinetics of nucleation and crystal growth in membrane crystallisation*”, is investigated by considering the independent contributions of boundary-layer and bulk hydrodynamics to crystallisation kinetics and resultant crystal product quality. As such, the effect of Reynolds number on crystallisation kinetics observed in Chapter 3 is further explored in Chapter 4. This is then followed by a

discussion of the overall thesis (Chapter 5) and the conclusions and proposals for future work in Chapter 6.

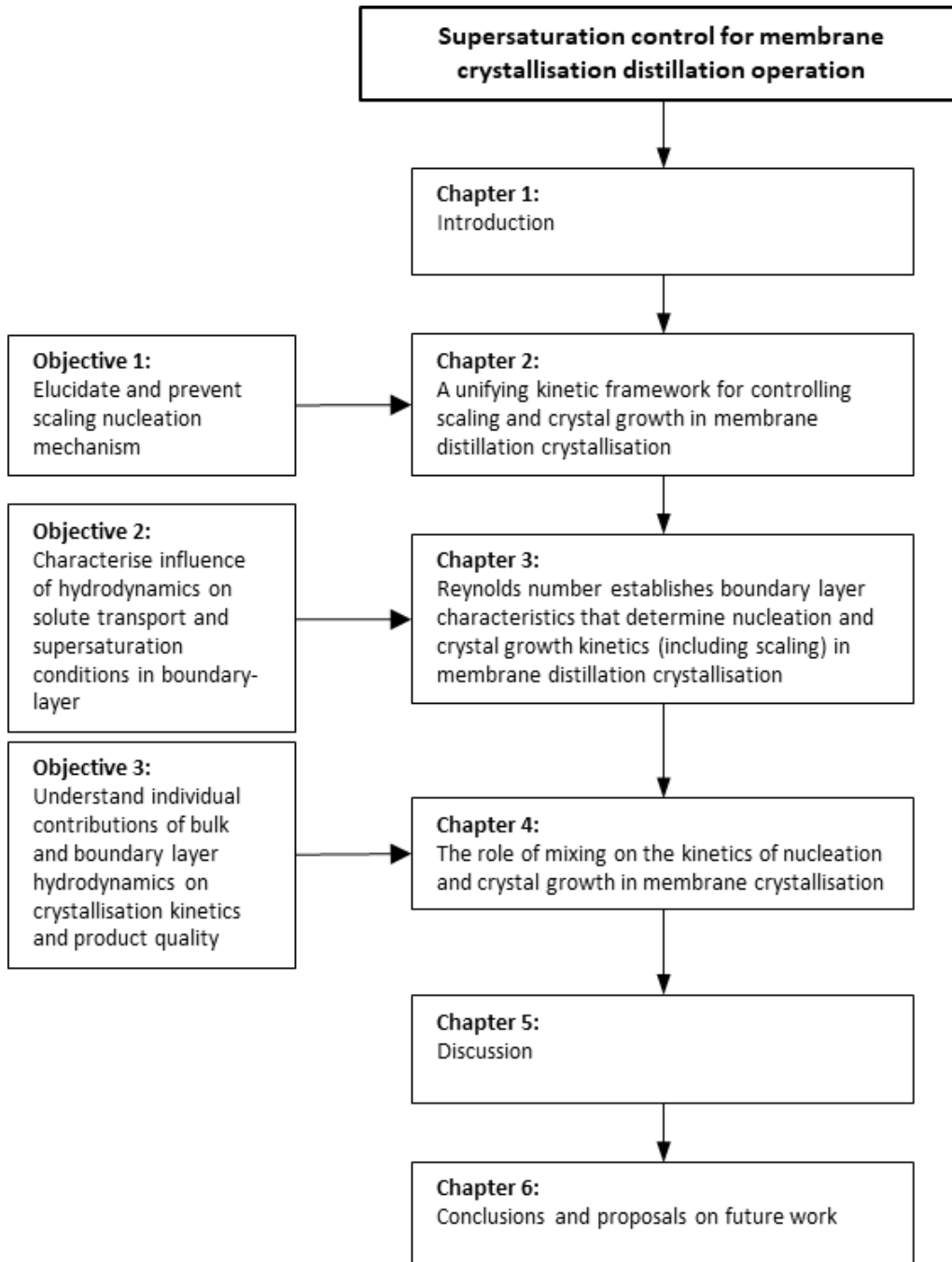


Figure 1.5. Outline of thesis structure including main objectives of technical chapters 2 to 4.

References

- [1] E. Chabanon, D. Mangin, and C. Charcosset, "Membranes and crystallization processes: State of the art and prospects," *J. Memb. Sci.*, vol. 509, pp. 57–67, 2016.
- [2] I. Ruiz Salmón and P. Luis, "Membrane crystallization via membrane distillation," *Chem. Eng. Process. Process Intensif.*, vol. 123, pp. 258–271, 2018.
- [3] Y. Choi, G. Naidu, L. D. Nghiem, S. Lee, and S. Vigneswaran, "Membrane distillation crystallization for brine mining and zero liquid discharge: Opportunities, challenges, and recent progress," *Environ. Sci. Water Res. Technol.*, vol. 5, pp. 1202–1221, 2019.
- [4] S. K. Jha, S. Karthika, and T. K. Radhakrishnan, "Modelling and control of crystallization process," *Resour. Technol.*, vol. 3, pp. 94–100, 2017.
- [5] X. Jiang, D. Lu, W. Xiao, X. Ruan, J. Fang, and G. He, "Membrane assisted cooling crystallization: Process model, nucleation, metastable zone, and crystal size distribution," *AIChE J.*, vol. 62, pp. 829–841, 2016.
- [6] J. Ulrich and P. Froberg, "Problems, potentials and future of industrial crystallization," *Front. Chem. Sci. Eng.*, vol. 7, pp. 1–8, 2013.
- [7] G. Di Profio, E. Curcio, and E. Drioli, "Supersaturation control and heterogeneous nucleation in membrane crystallizers: Facts and perspectives," *Ind. Eng. Chem. Res.*, vol. 49, pp. 11878–11889, 2010.
- [8] D. Kashchiev and G. M. Van Rosmalen, "Review: Nucleation in solutions revisited," *Cryst. Res. Technol.*, vol. 38, pp. 555–574, 2003.
- [9] A. S. Myerson, D. Erdemir, and A. Y. Lee, *Crystal nucleation*. 2019.
- [10] H. J. M. Kramer and R. Lakerveld, "Selection and design of industrial crystallizers," *Handb. Ind. Cryst.*, pp. 197–215, 2019.
- [11] J. Ulrich and C. Strege, "Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers," *J. Cryst. Growth*, vol. 237–239, pp. 2130–2135, 2002.
- [12] A. Mersmann, "Crystallization and precipitation," *KONA Powder Part. J.*, vol. 16, pp. 60–67, 1998.

- [13] B. Gielen, J. Jordens, L. C. J. Thomassen, L. Braeken, and T. Van Gerven, "Agglomeration control during ultrasonic crystallization of an active pharmaceutical ingredient," *Crystals*, vol. 7, no. 2, pp. 1–20, 2017.
- [14] A. A. Fytopoulos, M. E. Kavousanakis, T. Van Gerven, A. G. Boudouvis, G. D. Stefanidis, and C. Xiouras, "Crystal Growth, Dissolution, and Agglomeration Kinetics of Sodium Chlorate," *Ind. Eng. Chem. Res.*, vol. 60, pp. 7367–7384, 2021.
- [15] M. Brunsteiner, A. G. Jones, F. Pratola, S. L. Price, and S. J. R. Simons, "Toward a Molecular Understanding of Crystal Agglomeration," *Cryst. Growth Des.*, vol. 5, pp. 3–16, Jan. 2005.
- [16] Y. N. Nariyoshi, C. E. Pantoja, M. M. Seckler, Y. N. Nariyoshi, C. E. Pantoja, and M. M. Seckler, "Evaluation of sodium chloride crystallization in membrane distillation crystallization applied to water desalination," *Brazilian J. Chem. Eng.*, vol. 33, pp. 675–690, 2016.
- [17] Z. Q. Yu, R. B. H. Tan, and P. S. Chow, "Effects of operating conditions on agglomeration and habit of paracetamol crystals in anti-solvent crystallization," *J. Cryst. Growth*, vol. 279, no. 3–4, pp. 477–488, 2005, doi: 10.1016/j.jcrysgro.2005.02.050.
- [18] S. Wang, M. Feng, H. Du, J. J. Weigand, Y. Zhang, and X. Wang, "Determination of metastable zone width, induction time and primary nucleation kinetics for cooling crystallization of sodium orthovanadate from NaOH solution," *J. Cryst. Growth*, vol. 545, p. 125721, 2020.
- [19] G. Zeng, H. Li, S. Huang, X. Wang, and J. Chen, "Determination of metastable zone width and the primary nucleation kinetics of sodium sulfate," *Theor. Found. Chem. Eng.*, vol. 49, pp. 869–876, 2015.
- [20] K. Sangwal, "A novel self-consistent Nývlt-like equation for metastable zone width determined by the polythermal method," *Cryst. Res. Technol.*, vol. 44, pp. 231–247, 2009.
- [21] C. Bian, H. Chen, X. Song, and J. Yu, "Metastable zone width and the primary nucleation kinetics for cooling crystallization of NaNO₃ from NaCl-NaNO₃-H₂O system," *J. Cryst. Growth*, vol. 518, pp. 5–13, 2019.

- [22] S. A. Kulkarni, S. S. Kadam, H. Meekes, A. I. Stankiewicz, and J. H. Ter Horst, "Crystal nucleation kinetics from induction times and metastable zone widths," *Cryst. Growth Des.*, vol. 13, pp. 2435–2440, 2013.
- [23] X. Jiang, X. Ruan, W. Xiao, D. Lu, and G. He, "A novel membrane distillation response technology for nucleation detection, metastable zone width measurement and analysis," *Chem. Eng. Sci.*, vol. 134, pp. 671–680, 2015.
- [24] K. Liang, G. White, D. Wilkinson, L. J. Ford, K. J. Roberts, and W. M. L. Wood, "Examination of the Process Scale Dependence of L-Glutamic Acid Batch Crystallized from Supersaturated Aqueous Solutions in Relation to Reactor Hydrodynamics," *Ind. Eng. Chem. Res.*, vol. 43, pp. 1227–1234, 2004.
- [25] L. Wang, H. Feng, J. Peng, N. Dong, W. Li, and Y. Dong, "Solubility, metastable zone width, and nucleation kinetics of sodium dichromate dihydrate," *J. Chem. Eng. Data*, vol. 60, pp. 185–191, 2015.
- [26] S. Xu, Y. Wang, Z. Hou, and X. Chuai, "Overview of secondary nucleation: From fundamentals to application," *Ind. Eng. Chem. Res.*, vol. 59, pp. 18335–18356, 2020.
- [27] T. L. Threlfall and S. J. Coles, "A perspective on the growth-only zone, the secondary nucleation threshold and crystal size distribution in solution crystallisation," *CrystEngComm*, vol. 18, pp. 369–378, 2016.
- [28] J. A. Dirksen and T. A. Ring, "Crystallization review," *Chemical Engineering Science*, vol. 46, no. 10, pp. 2389–2427, 1991.
- [29] S. G. Agrawal and A. H. J. Paterson, "Secondary Nucleation: Mechanisms and Models," *Chem. Eng. Commun.*, vol. 202, pp. 698–706, 2015.
- [30] C. Charcosset, R. Kieffer, D. Mangin, and F. Puel, "Coupling between membrane processes and crystallization operations," *Ind. Eng. Chem. Res.*, vol. 49, pp. 5489–5495, 2010.
- [31] M. Akrap, N. Kuzmanić, and J. Prlić-Kardum, "Effect of mixing on the crystal size distribution of borax decahydrate in a batch cooling crystallizer," *J. Cryst. Growth*, vol. 312, pp. 3603–3608, 2010.

- [32] W. R. Wilcox, "Transport phenomena in crystal growth from solution," *Prog. Cryst. Growth Charact. Mater.*, vol. 26, pp. 153–194, 1993.
- [33] H. J. M. Kramer, J. W. Dijkstra, P. J. T. Verheijen, and G. M. Van Rosmalen, "Modeling of industrial crystallizers for control and design purposes," *Powder Technol.*, vol. 108, pp. 185–191, 2000.
- [34] H. Y. Wei, "Computer-aided design and scale-up of crystallization processes: Integrating approaches and case studies," *Chem. Eng. Res. Des.*, vol. 88, pp. 1377–1380, 2010.
- [35] A. Lewis, M. M. Seckler, H. Kramer, and G. van Rosmalen, *Industrial Crystallization*. Cambridge: Cambridge University Press, 2015.
- [36] J. W. Mullin, *Crystallisation* (4th Edition). 2001.
- [37] M. Stoller, M. Bravi, and A. Chianese, "The effect of scaling on the performances of a DTB crystallizer by means of a compartmental simulation model," *Chem. Eng. Res. Des.*, vol. 83, pp. 126–132, 2005.
- [38] M. Brito Martínez, N. Jullok, Z. Rodríguez Negrín, B. Van der Bruggen, and P. Luis, "Membrane crystallization for the recovery of a pharmaceutical compound from waste streams," *Chem. Eng. Res. Des.*, vol. 92, pp. 264–272, 2014.
- [39] M. C. Sparenberg, S. Chergaoui, V. Sang Sefidi, and P. Luis, "Crystallization control via membrane distillation-crystallization: A review," *Desalination*, vol. 519, p. 115315, 2022.
- [40] X. Jiang et al., "Interface-based crystal particle autoselection via membrane crystallization: From scaling to process control," *AIChE J.*, vol. 65, pp. 723–733, 2019.
- [41] M. L. Perrotta, F. Macedonio, E. Tocci, L. Giorno, E. Drioli, and A. Gugliuzza, "Environmental Science Water Research & Technology Graphene stimulates the nucleation and growth rate of NaCl crystals from hypersaline solution via membrane crystallization †," *Cite this Environ. Sci. Water Res. Technol*, vol. 6, p. 1723, 2020.
- [42] M. L. Perrotta et al., "Molecular insights on NaCl crystal formation approaching PVDF membranes functionalized with graphene," *Phys. Chem. Chem. Phys*, vol. 22, p. 7817, 2020.

- [43] F. Macedonio, A. Politano, E. Drioli, and A. Gugliuzza, "Bi₂Se₃-assisted membrane crystallization," *Mater. Horizons*, vol. 5, pp. 912–919, 2018.
- [44] J.-H. H. Tsai et al., "Membrane-Assisted Crystallization: A Molecular View of NaCl Nucleation and Growth," *Appl. Sci.*, vol. 8, p. 2145, 2018.
- [45] D. Chakraborty and G. N. Patey, "Evidence that crystal nucleation in aqueous NaCl solution Occurs by the two-step mechanism," *Chem. Phys. Lett.*, vol. 587, pp. 25–29, 2013.
- [46] T. Horseman, C. Su, K. S. S. Christie, and S. Lin, "Highly effective scaling mitigation in membrane distillation using a superhydrophobic membrane with gas purging," *Environ. Sci. Technol. Lett.*, vol. 6, pp. 423–429, 2019.
- [47] C. Su, T. Horseman, H. Cao, K. Christie, Y. Li, and S. Lin, "Robust Superhydrophobic Membrane for Membrane Distillation with Excellent Scaling Resistance," *Environ. Sci. Technol.*, vol. 53, pp. 11801–11809, Oct. 2019.
- [48] M. Gryta, "Fouling in direct contact membrane distillation process," *J. Memb. Sci.*, vol. 325, pp. 383–394, 2008.
- [49] Z. Xiao et al., "Scaling mitigation in membrane distillation: From superhydrophobic to slippery," *Desalination*, vol. 466, pp. 36–43, 2019, doi: 10.1016/j.desal.2019.05.006.
- [50] T. Horseman, Y. Yin, K. S. Christie, Z. Wang, T. Tong, and S. Lin, "Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies," *ACS ES&T Eng.*, vol. 1, pp. 117–140, 2021.
- [51] A. Ali et al., "A review of membrane crystallization, forward osmosis and membrane capacitive deionization for liquid mining," *Conserv. Recycl.*, vol. 168, p. 105273, 2021, doi: 10.1016/j.resconrec.2020.105273.
- [52] Z. Xiao et al., "Slippery for scaling resistance in membrane distillation: A novel porous micropillared superhydrophobic surface," *Water Res.*, vol. 155, pp. 152–161, 2019.
- [53] M. Frappa, F. Macedonio, A. Gugliuzza, W. Jin, E. Drioli, and B. S. Hsiao, "membranes Performance of PVDF Based Membranes with 2D Materials

- for Membrane Assisted-Crystallization Process Academic Editors: Marek Gryta and,” 2021, doi: 10.3390/membranes11050302.
- [54] S. Richardson, “On the no-slip boundary condition,” *J. Fluid Mech.*, vol. 59, pp. 707–719, Aug. 1973.
 - [55] D. M. Warsinger, E. W. Tow, J. Swaminathan, and J. H. Lienhard V, “Theoretical framework for predicting inorganic fouling in membrane distillation and experimental validation with calcium sulfate,” *J. Memb. Sci.*, vol. 528, pp. 381–390, 2017.
 - [56] X. Jiang, Y. Shao, L. Sheng, P. Li, and G. He, “Membrane Crystallization for Process Intensification and Control: A Review,” *Engineering*, vol. 7, pp. 50–62, 2021.
 - [57] C. M. Tun et al., “Membrane distillation crystallization of concentrated salts - Flux and crystal formation,” *J. Memb. Sci.*, vol. 257, pp. 144–155, 2005.
 - [58] F. Edwie and T. S. Chung, “Development of simultaneous membrane distillation-crystallization (SMDC) technology for treatment of saturated brine,” *Chem. Eng. Sci.*, vol. 98, pp. 160–172, 2013.
 - [59] D. M. Warsinger et al., “Effect of filtration and particulate fouling in membrane distillation,” *Int. Desalin. Assoc.*, pp. 0–14, 2015.
 - [60] J. Kim, H. W. Kim, L. D. Tijning, H. K. Shon, and S. Hong, “Elucidation of physicochemical scaling mechanisms in membrane distillation (MD): Implication to the control of inorganic fouling,” *Desalination*, vol. 527, p. 115573, 2022.
 - [61] M. Gryta, “Effectiveness of water desalination by membrane distillation process,” *Membranes (Basel)*, vol. 2, pp. 415–429, 2012.
 - [62] M. R. Elmarghany, A. H. El-Shazly, M. S. Salem, M. N. Sabry, and N. Nady, “Thermal analysis evaluation of direct contact membrane distillation system,” *Case Stud. Therm. Eng.*, vol. 13, p. 100377, 2019.
 - [63] X. Dou et al., “Collision dependent silver nucleation regulated by chemical diffusion and reaction,” *Chem. Eng. Sci.*, vol. 262, p. 117965, 2022.

2. A unifying kinetic framework for controlling scaling and crystal growth in membrane distillation crystallisation

A unifying kinetic framework for controlling scaling and crystal growth in membrane distillation crystallisation

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Abstract

While the metastable zone width (MSZW) is a critical control parameter in conventional crystallisation processes, it has yet to be applied for crystallisation and scaling control in membrane distillation crystallisation (MDC). Existing operating strategies have therefore relied on empirical recommendations of suitable operating conditions that are often contradictory due to lack of insight into the governing crystallisation mechanisms and kinetics. In this study, an inline turbidity probe and direct observation of the membrane surface using a digital microscope enabled the development of a MSZW-based framework for crystallisation and scaling control in MDC. In contrast to previous assumptions, scaling was revealed to occur via a homogeneous nucleation mechanism due to high interfacial supersaturation levels (S_{int}). Bulk nucleation occurred at lower S_{int} , likely facilitated by enhanced diffusion in the boundary layer with reduced supersaturation. An operating window in which scaling does not occur could therefore be defined by mapping the effect of interfacial supersaturation rate (R') on (i) the ratio of bulk to interfacial MSZWs (S_{bulk}/S_{int}) and (ii) the extent of scaling at bulk nucleation. Lower S_{bulk}/S_{int} ratios at induction were indicative of interfacial supersaturation levels which favoured scaling relative to bulk nucleation, thereby increasing scaling propensity. While R' was varied using temperature and temperature difference (ΔT) in this study, the significance of a mechanistic framework is that it can be applied to predict the likelihood of scaling for a wide range of MD variables which impact interfacial supersaturation conditions. Improved boundary-layer hydrodynamics are likely to increase the operating range of R' for scale-free crystallisation, thereby expanding the capability of MDC to achieve product specifications.

Keywords: *metastable zone width (MSZW), supersaturation, boundary layer, crystallisation kinetics, crystal nucleation*

2.1 Introduction

Crystallisation is an important unit operation for the production of solids in numerous sectors (e.g., pharmaceutical, environment and manufacturing) [1]. For crystallisation to occur, the concentration of the solution must exceed the solubility limit to generate a supersaturated solution [2]. While crystallisation has been used at an industrial scale to produce and separate valuable solid (crystalline) products from aqueous solutions for many decades [1, 3, 4], reactor geometries often comprise poorly-defined interfacial areas, which propagates into poor mixing conditions. Consequently, precise control of heat and mass transfer is difficult to achieve. This results in inconsistent regulation of supersaturation conditions within the reactor, which cause wide crystal size distributions (CSDs) with irreproducible product morphology and purity [3]. As these properties are important for the final use of the crystalline end product, strict control over supersaturation should ideally be achieved [2, 5].

Membrane distillation crystallisation (MDC) facilitates water vapour transport by establishing a vapour-pressure gradient across a hydrophobic microporous membrane to concentrate the feed solution [2]. The well-defined membrane area facilitates uniform heat and mass transfer, enabling the rate of vapour transfer across the membrane to be precisely controlled. This advances the regulation of supersaturation, therefore improving control over the kinetics of nucleation and crystal growth [2, 3, 6]. The laminar conditions in the feed channel also promote localised temperature and concentration polarisation phenomena to foster a highly-supersaturated boundary layer [4]. Consequently, it is proposed that nucleation and crystal growth may be independently controlled by the development of two distinct regions; an interfacial boundary layer, where nucleation is most likely to occur, and the bulk solution, where crystal growth is controlled [7, 8]. However, the individual roles of interfacial and bulk supersaturation conditions on crystal nucleation and growth kinetics have yet to be demonstrated.

The metastable zone width (MSZW) describes the maximum supersaturation achieved by a system. Although crystallisation can proceed at various locations across the metastable zone (MSZ), the level of supersaturation at induction

(MSZW) governs the kinetics of crystal nucleation and growth [5]. This will also affect the size, purity and habit of the crystal which are critical factors determining product quality. Consequently, nucleation should be regulated within specific regions of the MSZ, dependent upon the product specifications required, which can be facilitated by controlling the rate of supersaturation and the saturation temperature [5, 6]. To fully characterise the crystallisation mechanism within membrane processes, accurate determination of induction time and the supersaturation at induction is therefore required [8] to establish a relationship between membrane boundary operating conditions and crystallisation kinetics. However, to date the onset of crystallisation has generally been determined by the inflection point at which the permeate flux drastically declines [6, 9, 10]. This does not differentiate between membrane scaling and bulk crystallisation, and as the induction time for flux decline is thought to be independent of the induction time for scale formation, such detection methods cannot provide phenomenological descriptions of the primary nucleation mechanism(s) within MDC [11, 12]. This has led to very limited kinetic descriptions reported in the MD literature to date [8, 11].

The onset of both scaling and crystallisation can be described through classical nucleation theory (CNT). According to CNT, nucleation occurs on condition that the change in Gibbs free energy of the system (ΔG) exceeds the critical energy barrier for homogeneous nucleation ($\Delta G > \Delta G_{hom}^*$) or that the energy barrier is sufficiently reduced such that ΔG can overcome the activation energy barrier for heterogeneous nucleation ($\Delta G > \Delta G_{het}^*$) [2, 13, 14]. In MDC, the introduction of the membrane surface is said to initiate heterogeneous (surface) nucleation by reducing the interfacial energy which lowers the critical energy barrier [2, 8]. This reduction in energy barrier has also been linked to the promotion of scale formation at the membrane, leading to a cessation of flux, membrane wetting and salt breakthrough [15–17]. Hence, scaling and bulk nucleation have been reported to form via the same surface nucleation mechanism, only distinguished by adhesion (scaling) or release and transport of crystals from the interface to the bulk solution [8]. While MD studies of primary scalants such as CaSO_4 have described deleterious surface crystallisation

(scaling) phenomena [17, 18], Warsinger et al. [19] demonstrated negligible surface nucleation by CaSO_4 , instead evidencing nucleation to occur primarily in the bulk. According to Warsinger et al. [10], the hydrophobicity of the membrane used in MD should limit the probability for scaling. Such unintended contradictions can occur due to the present difficulty in discriminating between surface nucleation (classical 'heterogeneous' scaling) and the deposition of crystals on the membrane following formation in the bulk solution, since both effects will subsequently reduce membrane flux [20].

The lack of insight into crystallisation kinetics and mechanisms in MDC has resulted in conflicting empirical recommendations for the prevention of scaling caused by heterogeneous (surface) nucleation. For example, an increase in scaling propensity has been shown with higher bulk temperature differences (ΔT), which also raised interfacial supersaturation levels [9, 16]. Since supersaturation is the driving force for crystallisation, homogeneous rather than surface crystallisation should be favoured at the higher permeate fluxes initiated by higher ΔT , provided $\Delta G \geq \Delta G_{hom}^*$ [12]. Various MD studies have also found that increased temperatures enhanced scaling by widening the MSZW (raising) the maximum saturation level at which scaling occurred) [9, 10, 16]. Theoretically however, higher temperatures narrow the MSZW by enhancing the energy of solute molecules, thereby promoting molecular collisions. This reduces the critical energy required which increases the likelihood of nucleation [6, 13]. Jiang et al. [6] evidenced this by showing that increased temperatures promoted MD scaling by reducing the maximum supersaturation level at which it occurred. These seemingly opposing MSZW observations highlight the complex effects of variables, such as temperature and ΔT , on both crystallisation kinetics and the consequent scaling and bulk crystallisation mechanisms.

In this study, we therefore seek to undertake a systematic investigation of interfacial and bulk supersaturation conditions (MSZWs) to establish their role in determining nucleation and crystal growth phenomena within membrane distillation crystallisation (MDC). Jiang et al. [6] have provided the most definitive investigation of MSZWs in MD to date. This work complements and builds upon their research through the inclusion of in-situ techniques for the real-time

detection of induction to provide definitive description of the nucleation kinetics, and to discriminate between surface (scaling) and bulk crystallisation mechanisms. This will be completed with characterisation of the crystal product to describe how transitions in supersaturation conditions can inform on crystal size and morphology. We therefore propose to present the first complete characterisation of the thermodynamically and kinetically controlled MSZW as a unifying framework to permit the decoupling of scaling and bulk crystallisation mechanisms, which to date have often been viewed as interdependent [8, 11, 20]. The specific objectives are to:

- (i) improve accuracy of bulk induction time measurements to establish how MD operating conditions influence bulk nucleation kinetics;
- (ii) evaluate interfacial and bulk MSZW measurements and apply CNT to determine the supersaturation region(s) governing bulk nucleation and growth kinetics;
- (iii) independently discriminate the induction times of scaling and bulk nucleation to distinguish individual nucleation mechanisms;
- (iv) apply scanning electron microscopy (SEM) to analyse how crystal growth environments (location and operating conditions) inform resultant crystal morphologies;
- (v) provide a MSZW-based framework which can improve the independent control of scaling and bulk crystallisation by relating the effects of operating conditions on parameters governing crystallisation kinetics.

2.2 Materials and Methods

2.2.1 Membrane distillation crystallisation experimental setup and operation

A direct-contact membrane distillation (DCMD) setup was used (Figure 2.1). Sodium chloride was selected as the solute as it one of the most widely-researched scalants in DCMD systems [1, 2, 6, 8, 9, 16]. This will enable the kinetic mechanisms elucidated in this work to be directly compared and applied to explain the seemingly contrasting observations of existing MDC studies. As such, the experimental results of this work can be combined with a range of other MD scaling studies for a broader understanding of how to exploit crystallisation

kinetics for scaling control, During the experiments, a 0.95M sodium chloride (NaCl, 99.5%, ACROS Organics™, Fisher Chemicals, Loughborough, UK) feed solution and deionised water ($\approx 15.0 \text{ M}\Omega \text{ cm}$) permeate stream were recirculated counter-currently with peristaltic pumps (Watson-Marlow 530S, WMFTG, Falmouth, UK) through the vertically mounted membrane module. The feed Reynolds number (Re) was fixed at 1750. The volume of both the feed and permeate solutions was 500 mL. The permeate flow rate was set at 65% of the feed flow rate. Flat-sheet ePTFE membranes with a $0.1 \mu\text{m}$ pore size were used, comprising a surface area of 0.004 m^2 (Cobetter Filtration, Hangzhou, China). The feed solution was heated prior to entering the membrane module using an inline heat exchanger (LT ecocool 150, Grant Instruments (Cambridge) Ltd., Shepreth, UK). Fluid temperatures were monitored and recorded (two readings per second) using thermocouples ($\pm 0.22^\circ\text{C}$, EI-1034, Electronic Innovations Corporation, Colorado, USA) connected to a data logger (LabJack T7 Pro, LabJack Corporation, Colorado, USA). The feed solution was mixed (300 rpm) with an overhead stirrer (Hei-TORQUE Ultimate 400, Heidolph Instruments, Schwabach, Germany). The permeate stream was cooled in the permeate vessel by passing cold water from the chiller (LT ecocool 150, Grant Instruments (Cambridge) Ltd., Shepreth, UK) through the vessel jacket. A precision balance (Cole Parmer Symmetry PT-4202E, Antylia Scientific, Illinois, USA) was used to measure the mass of permeate every minute. Continual permeate conductivity measurements (every minute) (Seven2Go™ Pro S7, Mettler-Toledo Ltd, Leicester, UK) were taken to ensure that no salt breakthrough occurred. An inline turbidity probe (InPro 8200/S/Epoxy/120 turbidity sensor, Mettler-Toledo Ltd, Leicester, UK) was inserted in the feed solution and data were recorded every second. The dual optic fibre sensor uses backscatter technique to provide high resolution detection of induction time, providing reproducible particle detection which has been used extensively for nucleation kinetics characterisation [21, 22]. A digital microscope (AmScope UHM350-11 20-100x HDMI digital microscope, AmScope, UK) was used to provide non-invasive high-resolution imaging of the membrane surface in real time ($1280 \times 720 \text{ p}$). Working distances ranged 30-145mm. This was in excess of the polished Perspex wall thickness and channel

depth (combined 22 mm), and therefore enabled a field of view across the full membrane surface. Videos were recorded at 30 frames per second (fps) with observation of crystal growth at single pixel definition ($2.2 \mu\text{m pixel}^{-1}$). While this is beyond the scale of the critical nucleation event (nm scale event), this resolution is sufficient to provide detailed characterisation of membrane scaling kinetics. An example time series of digital microscope images is shown in Appendix A.

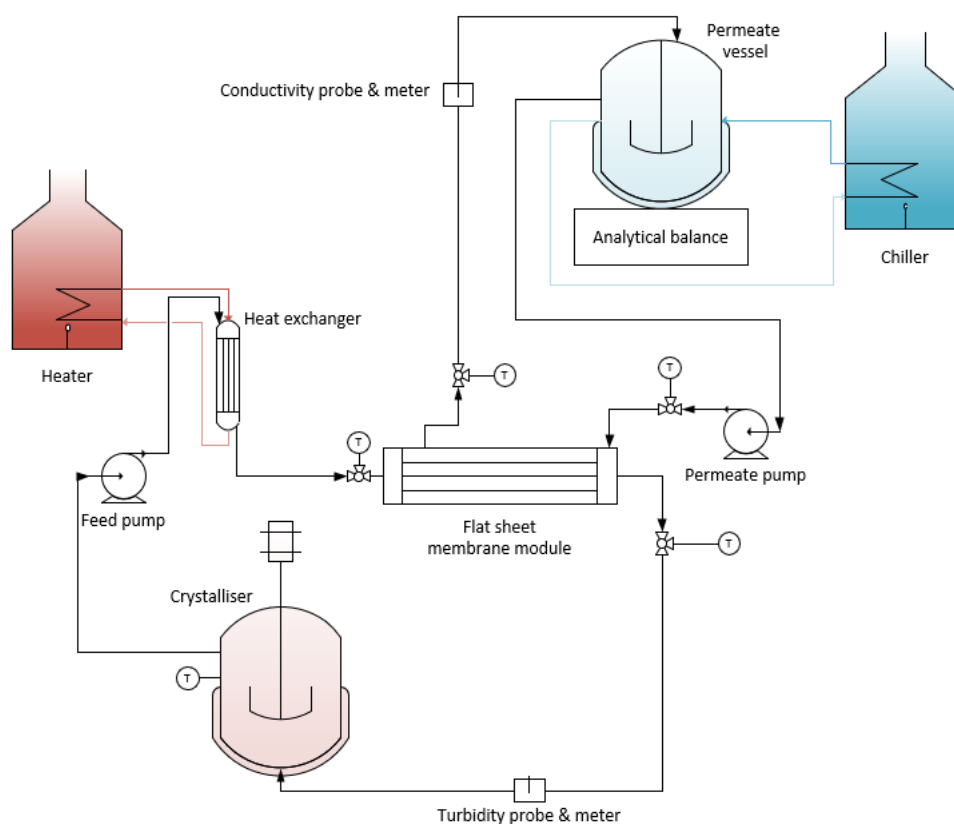


Figure 2.1. Schematic of MDC experimental setup showing a membrane module consisting of a flat-sheet, hydrophobic, ePTFE membrane across which water vapour is transferred from the hot feed side (red) to the colder permeate side (blue).

2.2.2 Experimental analysis

To obtain crystal size distributions (CSDs), the crystalliser suspension was vacuum filtered using a $0.45 \mu\text{m}$ pore nitrocellulose membrane filter (Whatman® NC45, Cytiva, Maidstone, UK) 10 minutes after the onset of bulk nucleation. The

filtered crystals were then allowed to dry in open air at room temperature for at least 48 hours before analysis using an optical microscope (Leica CTR 5500 B, Leica Microsystems Ltd, Milton Keynes, UK) in conjunction with a digital camera (Olympus SC50 5MP, Olympus, Southend-on-Sea, UK). A sample of at least 1000 crystals was analysed using Olympus Stream Image Analysis Software (Olympus, Southend-on-Sea, UK) to obtain the CSDs. The crystals deposited on the membrane surface were also filtered at the end of each experiment, i.e., 10 minutes after bulk nucleation. Crystal samples, along with membranes during experiments, were submitted for scanning electron microscopy (SEM) (Tescan VEGA 4, Tescan Orsay Holding, Czech Republic; acceleration voltage: 20 keV; beam current: 300 pA; working distance: 10 mm; 10 nm gold physical vapour deposition sample coating). SEM analyses were used to characterise the crystal nucleation and growth mechanisms of the product crystals.

2.2.3 Data analysis

For each experiment, the permeate flux was calculated based on the permeate mass accumulated over time:

$$J_p = \frac{\Delta m}{A_m \Delta t} \quad (2-1)$$

where J_p ($\text{kg m}^{-2} \text{h}^{-1}$) is the permeate flux, A_m (m^2) is the membrane surface area, and Δm (kg) and Δt (h) are the changes in permeate mass and time, respectively. A five-minute average of the permeate flux was used in calculations to account for experimental error. It was assumed that only water vapour passed through the membrane module. This assumption was validated by the permeate conductivity measurements which showed no evidence of salt breakthrough. Hence, the change in feed concentration could be directly calculated based on the mass of permeate vapour recovered.

The metastable zone width (MSZW) can be described using either the concentration (ΔC_{max} , kg m^{-3}) or supersaturation (S_{max}) at induction as follows:

$$\Delta C_{max} = C_{max} - C_{sat} \quad (2-2)$$

$$S_{max} = \frac{C_{max}}{C_{sat}} \quad (2-3)$$

where C_{max} (kg m⁻³) and C_{sat} (kg m⁻³) are the actual (maximum) and saturation concentrations at induction, respectively. The bulk induction time was determined based on the inflection point of the turbidity-time trends and the scaling induction time was obtained by analysis of online digital microscope videos. The temperature and concentration polarisation coefficients (TPC and CPC respectively) were calculated and applied to obtain the MSZWs at the membrane interface [23]:

$$\Delta C_{int} = C_{int} - C_{sat}(T_{int}) \quad (2-4)$$

$$S_{int} = \frac{C_{int}}{C_{sat}(T_{int})} \quad (2-5)$$

where the subscript *int* refers to the interface and $C_{sat}(T_{int})$ is the saturation concentration at the interfacial temperature (T_{int} , K). The interfacial concentration (C_{int} , kg m⁻³) is determined from the bulk concentration (C_b , kg m⁻³) as follows:

$$C_{int} = C_b(CPC) = C_b \exp\left(\frac{J_p}{\rho K}\right) \quad (2-6)$$

where ρ (kg m⁻³) is the solution density and K (m s⁻¹) is the mass transfer coefficient based on the L  v  que equation for laminar flow:

$$K = \frac{1.62D}{d_h} \left(\frac{V d_h^2}{DL} \right)^{\frac{1}{3}} \quad (2-7)$$

D (m² s⁻¹) is the molecular diffusivity or diffusion coefficient, d_h (m) is the hydraulic diameter, V (m s⁻¹) is the feed solution velocity, and L (m) is the length of the membrane surface. The TPC is the ratio between the interfacial and bulk temperature differences [24]:

$$TPC = \frac{\Delta T_{int}}{\Delta T_b} = \frac{T_{int} - T_{int,p}}{T_{b,f} - T_{b,p}} \quad (2-8)$$

where subscripts *b*, *f* and *p* refer to the bulk, feed and permeate, respectively. A steady-state energy balance of the heat transfer from the bulk feed to the bulk permeate solution yields the following equation for the interfacial feed temperature which must be solved iteratively using the subsequent equations:

$$T_{int} = \frac{\frac{k_m}{\delta_m} \left(T_p + \left(\frac{h_f}{h_p} \right) T_f + h_f T_f - J_p \Delta H_v \right)}{\frac{k_m}{\delta_m} + h_f + \frac{k_m}{\delta_m} \cdot \frac{h_f}{h_p}} \quad (2-9)$$

$$T_{int,p} = \frac{\frac{k_m}{\delta_m} \left(T_f + \left(\frac{h_p}{h_f} \right) T_p + h_p T_p + J_p \Delta H_v \right)}{\frac{k_m}{\delta_m} + h_p + \frac{k_m}{\delta_m} \cdot \frac{h_p}{h_f}} \quad (2-10)$$

where δ_m (m) is the thickness of the membrane. ΔH_v (J kg⁻¹) is the latent heat of vaporisation and k_m (W m⁻¹ K⁻¹) is the thermal conductivity of the membrane which is calculated using the isostress model [25]:

$$k_m = \left(\frac{\varepsilon}{k_{gas}} + \frac{1 - \varepsilon}{k_{solid}} \right)^{-1} \quad (2-11)$$

where ε is the membrane porosity. The thermal conductivities of the water vapour/air gas mixture (k_{gas} , W m⁻¹ K⁻¹) and solid polymer (k_{solid} , W m⁻¹ K⁻¹) were calculated using the following correlations [25]:

$$k_{gas} = 1.5 \times 10^{-3} \sqrt{T} \quad (2-12)$$

$$k_{solid} = 4.86 \times 10^{-4} T + 0.253 \quad (2-13)$$

h_f (W m⁻² K⁻¹) and h_p (W m⁻² K⁻¹) are the feed and permeate heat transfer coefficients, respectively:

$$h_f = \frac{Nu k_f}{d_h} \quad (2-14)$$

$$h_p = \frac{Nu k_p}{d_h} \quad (2-15)$$

where k_f (W m⁻¹ K⁻¹) and k_p (W m⁻¹ K⁻¹) are the feed and permeate conductivities, respectively. The Nusselt number, Nu , is described by the L  v  que equation which includes the Reynolds number (Re) and Prandtl (Pr) number [24]:

$$Nu = 0.023 Re^{0.8} Pr^{\frac{1}{3}} \quad (2-16)$$

$$Re = \frac{\rho V d_h}{\mu} \quad (2-17)$$

$$Pr = \frac{c_p \mu}{k} \quad (2-18)$$

where μ (Pa s) is the dynamic viscosity, c_p (J kg⁻¹ K⁻¹) is the specific heat capacity, and k (W m⁻¹ K⁻¹) is the thermal conductivity of the respective solutions. The solution properties were determined using Aspen Plus software and applying the

Elec-NRTL thermodynamic model which is an appropriate model for highly-concentrated electrolyte solutions [14].

According to Nyvlt [26], the operating window of a crystallisation process can be defined by applying MSZW measurements to characterise the nucleation kinetics. Nyvlt [26]'s method was based on classical nucleation theory (CNT) which assumes an empirical power law relationship between the nucleation rate and the MSZW:

$$B_m = k_m \Delta C_{max}^m \quad (2-19)$$

where B_m ($\text{kg m}^{-3} \text{s}^{-1}$) is the nucleation rate (mass basis), and k_m ($\text{kg m}^{-3} \text{s}^{-1}$) and m are the nucleation rate constant and apparent nucleation order, respectively. It is assumed that at the point of induction (onset of nucleation or vicinity of metastability), the rate of supersaturation is equal to the nucleation rate [26]. Therefore,

$$R' = k_m \Delta C_{max}^m \quad (2-20)$$

where R' ($\text{kg m}^{-3} \text{s}^{-1}$) is the supersaturation rate in the vicinity of metastability. The validity of this assumption is based on assuming that the surface area of the initial crystals is still very small, and the nucleation rate is therefore significantly higher than the growth rate. To account for experimental fluctuations, the supersaturation rate was taken as the average rate from the start of the experiment to the point of induction:

$$R' = \frac{\Delta C_{max} - \Delta C_0}{\Delta t_{nucl}} \quad (2-21)$$

where ΔC_0 is the starting saturation level and Δt_{nucl} is the time required for nucleation to take place from the start of the experiment. Linearisation of Eq. 2-21 yields:

$$\ln(R') = \ln(k_m) + m[\ln(\Delta C_{max})] \quad (2-22)$$

Linear regression of the plot of $\ln(\Delta C_{max})$ versus $\ln R'$ will then return the m as its gradient of the best-fit line. k_m can be obtained by calculating the exponential function of the y-intercept.

The crystal growth rate, G , was calculated based on the growth rate equation for mixed suspension mixed product removal (MSMPR) crystallisers [27]:

$$G = \frac{6L_{50}^4 \alpha B_n}{\varphi} \quad (2-23)$$

where L_{50} (m) and α are the median size and shape factor, respectively. B_n ($\text{m}^{-3} \text{s}^{-1}$) is the nucleation rate (number basis, assumed based on R') and φ is the volumetric holdup of crystals in suspension:

$$\varphi = \frac{V_c}{V_{susp}} = \frac{V_c}{V_c + V_{sol}} \quad (2-24)$$

where, V_c (m^3), V_{susp} (m^3) and V_{sol} (m^3) are the crystal, suspension and solution volumes, respectively.

The primary nucleation mechanism is dependent on the presence of a foreign surface to reduce the effective interfacial energy, thereby reducing the activation energy required for nucleation. Hence, the lower the interfacial energy, the greater the likelihood of heterogeneous nucleation over homogeneous nucleation [2, 28, 29]. By assuming an inversely proportional relationship between nucleation rate and induction time, CNT predicts the following relationship between induction time (t_{ind} , s) and the supersaturation level (S) at the onset of nucleation [29]:

$$\ln(t_{ind}) = K + \frac{16\pi\gamma^3 v^2}{3(k_B T)^2 \ln^2 S} \quad (2-25)$$

where K is a constant, γ (J m^{-2}) is the interfacial energy, v (m^3) is the volume of the solute molecule, k_B is the Boltzmann constant, and T (K) is the nucleation temperature. A plot of $\ln(t_{ind})$ against $\ln^{-2} S$ at constant temperature would therefore yield a linear trend with gradient (B):

$$B = \frac{16\pi\gamma^3 v^2}{3(k_B T)^2} \quad (2-26)$$

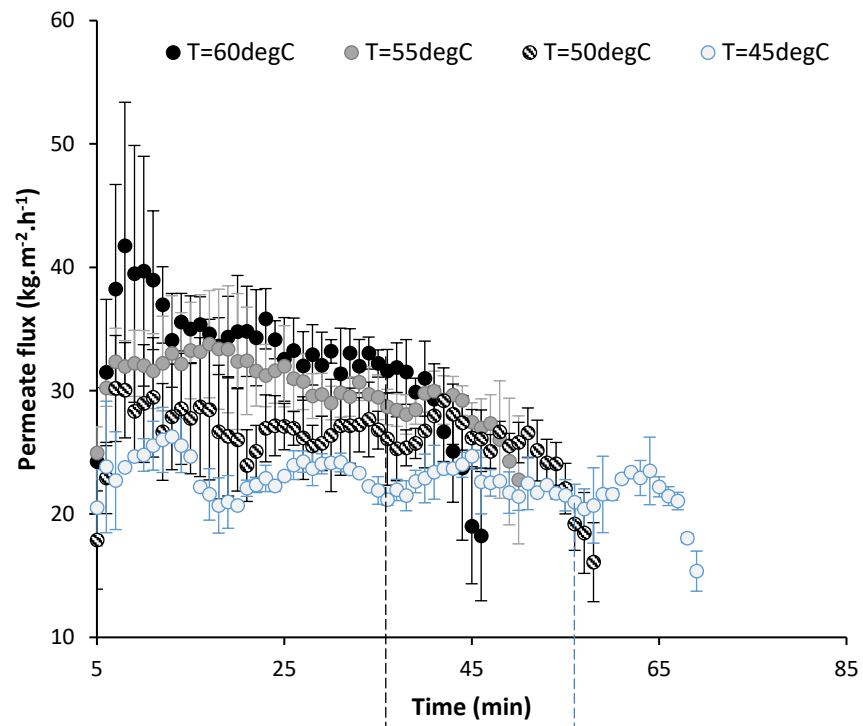
Hence, higher gradients indicate higher interfacial energies and a tendency towards homogeneous nucleation. Conversely, a lower gradient shows a reduction in effective interfacial energy and enhanced probability of heterogeneous nucleation [28, 29].

2.3 Results and discussion

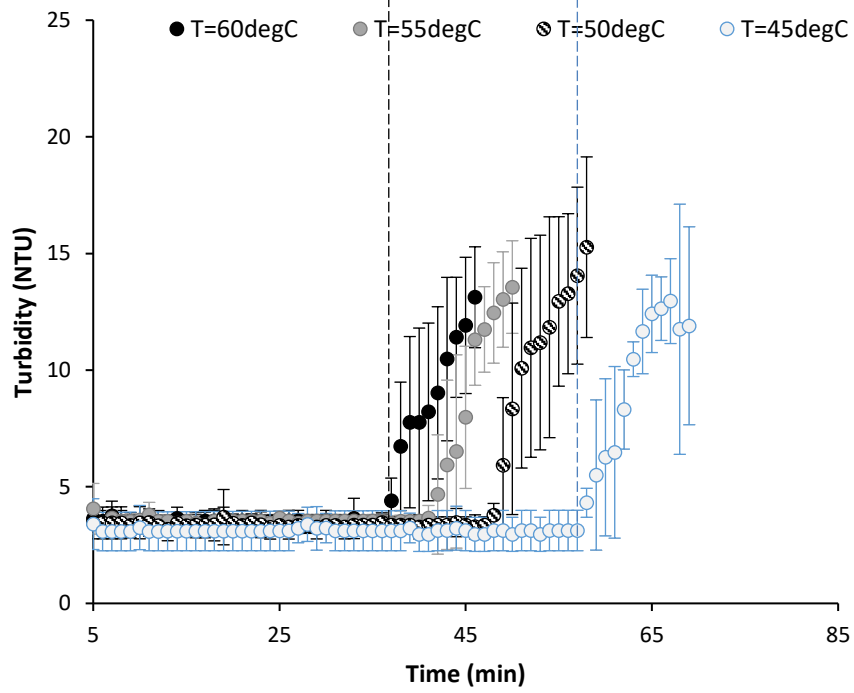
2.3.1 Permeate flux influences bulk crystallisation driving force

The permeate flux characterises the influence of operating conditions, such as feed temperature (T) and temperature difference (ΔT), on the membrane distillation (MD) process [9, 16]. T was varied from 45 to 60°C, while the permeate temperatures ranged from 20 to 45°C to achieve ΔT s of 15 to 30°C. At a fixed ΔT 25°C, increasing T from 45 to 60°C enhanced the permeate flux at bulk nucleation from 20.7 to 30.7 kg m⁻² h⁻¹ (Figure 2.2a & b). Mass transfer in MD is facilitated by the vapour-pressure difference across the membrane [30]. The promotion of permeate flux with T was therefore due to the exponential dependence of vapour-pressure difference on temperature in accordance with the Antoine equation [9, 16, 30]. For all T s considered (45 to 60°C), increases in ΔT from 15 up to 30°C resulted in higher permeate fluxes at induction (Figure 2.2c). Larger ΔT s between the feed and permeate solutions enhanced the difference in vapour pressure between them, thereby accelerating the driving force for mass transfer and increasing permeate flux [30].

(a)



(b)



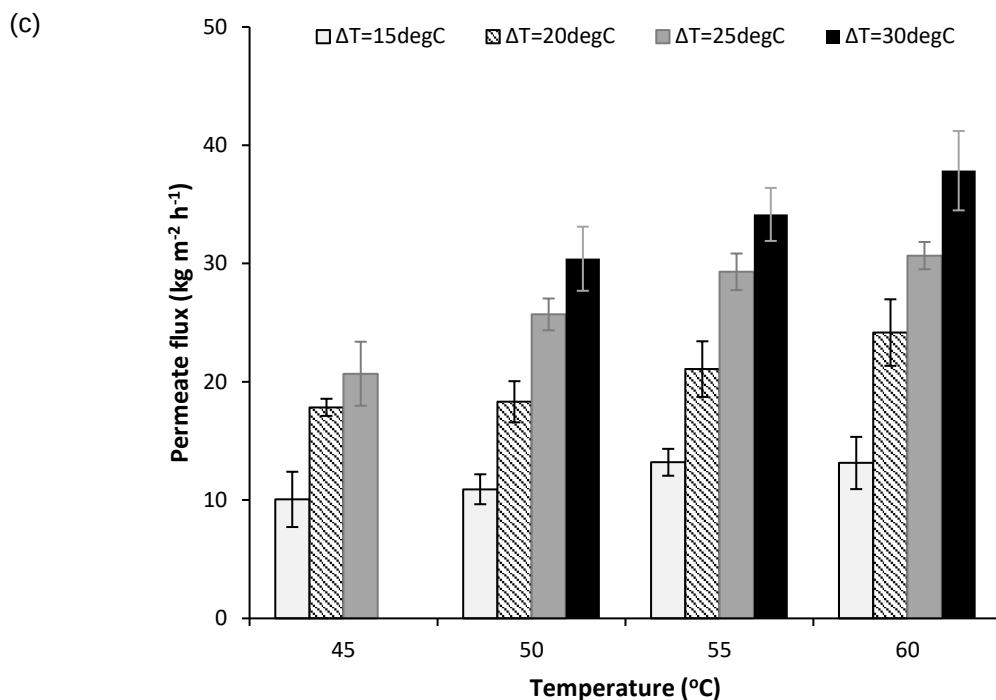


Figure 2.2. Analysis of permeate flux (five-minute running average) and turbidity responses with changes in temperature (T) and temperature difference (ΔT). (a) Permeate flux and (b) turbidity time series for T 45-60°C and ΔT 25°C. Black and blue dashed lines indicate onsets of bulk nucleation based on turbidity inflection points for T 60°C and T 45°C, respectively. (c) Permeate flux at the onset of bulk nucleation based on turbidity response for all experimental conditions, i.e., T 45-60°C and ΔT 15-30°C. Error bars indicate standard deviation of at least three replicates.

Since MD mediates the crystallisation process, the operating conditions controlling permeate flux are likely to influence crystallisation kinetics. As such, conditions which improved permeate flux also resulted in faster crystallisation kinetics. This was evidenced by shortened induction times with increases in T and ΔT (Figure 2.3a). To illustrate, the induction time at the lowest T and ΔT (45 and 15°C respectively) was 113 minutes, whereas an induction time of 32 minutes was observed at the maximum T and ΔT (60 and 30°C, respectively). Induction time therefore provides a link between MD operation and bulk crystallisation kinetics. Hence, its accurate quantification is essential for diagnostics of crystallisation in MDC.

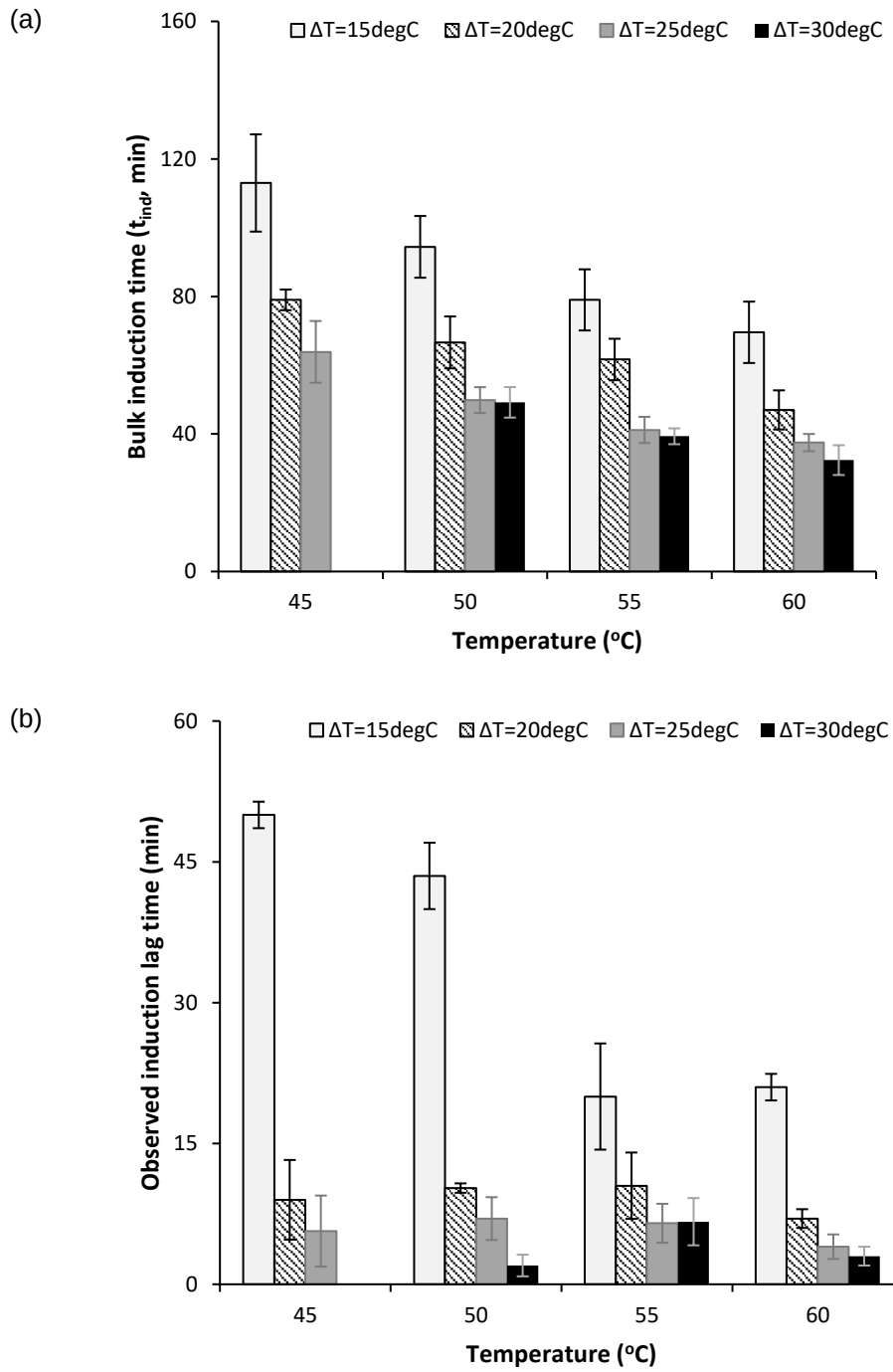


Figure 2.3. Induction time measurements for all experimental conditions of feed temperatures, T 45-60 $^{\circ}\text{C}$, and temperature differences, ΔT 15-30 $^{\circ}\text{C}$. (a) Bulk induction time based on turbidity-time trends and (b) observed lag time between initial turbidity and delayed flux response to bulk crystallisation. The precision and accuracy of conventional method of flux decline reduces with increases in T and ΔT , as evidenced by longer lag times. Error bars indicate standard deviation of at least three replicates.

A comparison between bulk induction times determined by turbidity and the conventional approach of rapid flux decline consistently showed that crystallisation was induced in the bulk solution prior to the flux decline (Figure 2.3b). The observed lag time increased with a reductions in T and ΔT , reaching a maximum of up to 50 minutes under conditions with the lowest driving force, i.e. a temperature of 45°C and ΔT of 15°C. Hence, the sensitivity of this method was further compromised at lower permeate fluxes. The rapid flux declines post bulk nucleation could be associated with loss of vapour permeation due to the deposition and further growth of crystals on the membrane surface. It is therefore likely that conditions which promote permeate flux also increase the rate of crystal deposition and growth on the membrane surface. This is affirmed by the enhanced rates of flux decline observed at higher T s, indicating a faster rates of deposition which led to earlier cessations in flux (and operation) after bulk nucleation (Figure 2.2). This work therefore corroborates the suggestions of several authors who have suggested that the deposition of bulk crystals is responsible for the rapid flux decline observed [11, 31]. This contrasts with the supposition that all crystals originate on the membrane surface (as scale) with subsequent release leading to bulk crystallisation [7, 8].

Permeate flux and induction time measurements at various T and ΔT have revealed a correlation between MD mass transfer and bulk crystallisation kinetics. The driving force for crystallisation is described by [13]:

$$\Delta\mu = \mu_{sol} - \mu_c = k_B T \ln S \quad (2-27)$$

where $\Delta\mu$ is the chemical potential difference, μ_{sol} and μ_c are the solute (NaCl) chemical potentials in the solution and solid crystal phases, respectively. Higher temperatures therefore enhanced the likelihood of nucleation by increasing the driving force. The nucleation is also promoted by enhanced supersaturation levels (Eq. 2-27) [13, 14]. Since permeate flux is the rate of solvent removal, it describes the rate of supersaturation while also governing the rate solute convection to the membrane interface [2]. These factors point to the influence of T and ΔT on the supersaturation conditions, via permeate flux, which ultimately govern bulk crystallisation kinetics. Confirmation of the mechanism of bulk

crystallisation therefore requires further analyses of the supersaturation conditions at the respective points of induction.

2.3.2 Bulk crystallisation kinetics are controlled by interfacial conditions

During MDC, concentration and temperature polarisation result in two distinct supersaturation regions in which bulk crystallisation can occur, namely, in the bulk solution and at the membrane interface [2]. The permeate-flux dependent concentration polarisation coefficient (CPC) was enhanced by higher T and ΔT , which raised the interfacial concentration level relative to the bulk solution (Figure 2.4a). Furthermore, increases in T and ΔT decreased the temperature polarisation coefficient (TPC), resulting in lower interfacial temperatures (Figure 2.4b). NaCl has an inverse solubility-temperature dependence. Hence, lower interfacial temperatures in conjunction with higher concentrations resulted in enhanced interfacial supersaturation levels (S_{int}) at bulk induction (Figure 2.5a). For example, at a constant T 60°C, S_{int} increased from 1.10 to 1.34 when ΔT rose from 15 to 30°C. Higher T and ΔT therefore increase the driving force for nucleation at the interface. This suggests an influence of interfacial conditions on bulk crystallisation kinetics, as indicated by the reduction in bulk induction time at higher S_{int} (Figure 2.3a and 2.5a). Compared to these drastic changes in S_{int} , minimal variations (within one standard deviation) were observed in the bulk supersaturation level (S_{bulk}) with increases in T and ΔT (Figure 2.5b). Instead, S_{bulk} remained centred around saturation, i.e., a supersaturation value of 1. For crystallisation to occur, $\Delta\mu > 1$, meaning that the chemical potential of NaCl in solution must exceed that of the crystal phase [13]. This requires a $S > 1$ (Eq. 2-27), at which point the system has sufficient energy to sustain a stable nucleus. The critical thermodynamic condition of $S_{\text{bulk}} > 1$ must therefore be met in order for bulk nucleation to occur. As such, the onset of bulk nucleation is thermodynamically controlled by S_{bulk} , despite S_{int} seemingly dictating the kinetic trajectory.

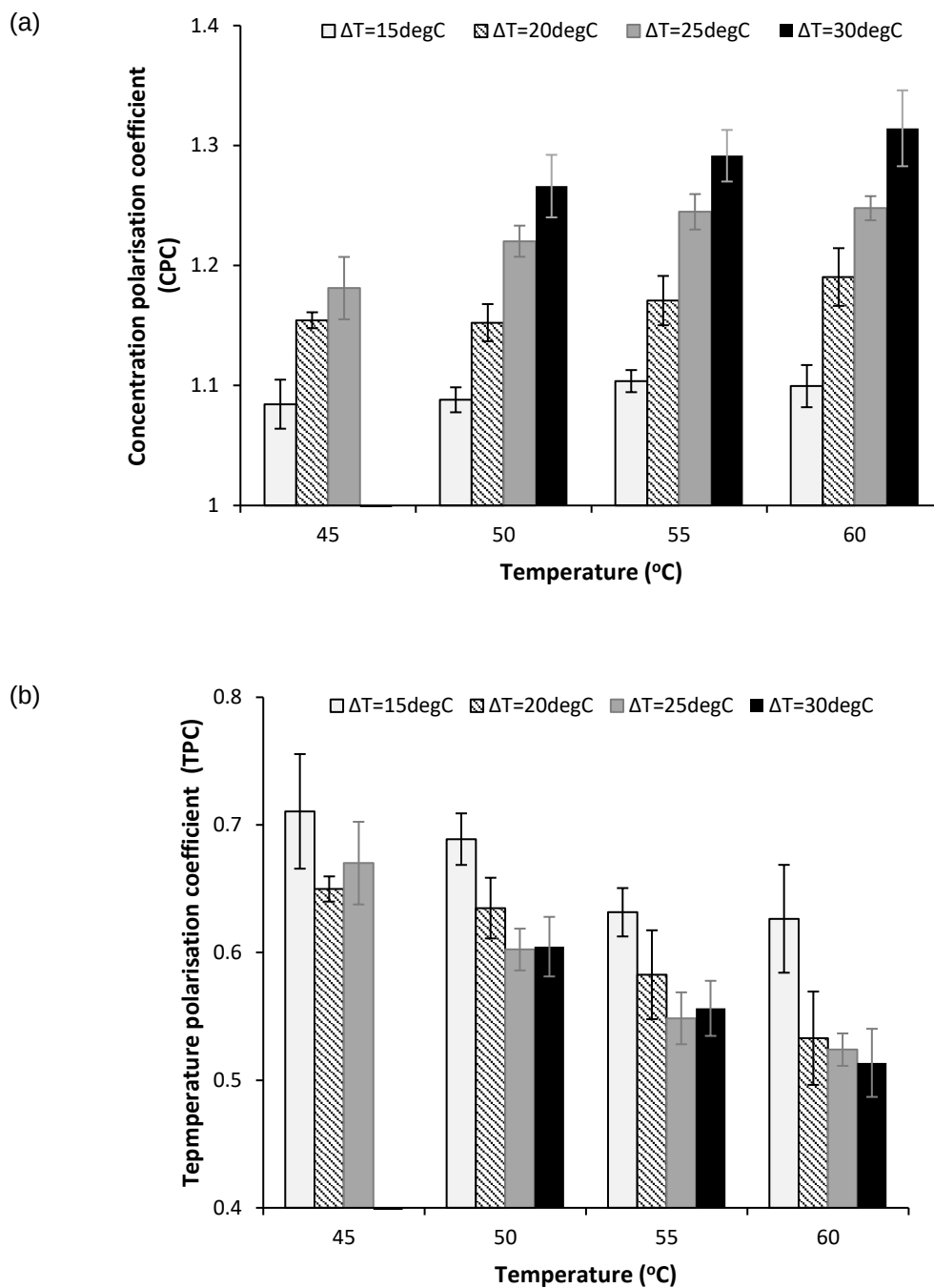


Figure 2.4. Characterisation of boundary layer polarisations which determine the interfacial saturation level at the onset of bulk nucleation: (a) concentration polarisation coefficient (CPC) and (b) temperature polarisation coefficient (TPC). Conditions: feed temperatures, T 45-60°C, and temperature differences, ΔT 15-30°C. Increases in CPC and lower TPC indicate that polarisation is exacerbated by operation at high T and ΔT . Error bars indicate standard deviation of at least three replicates.

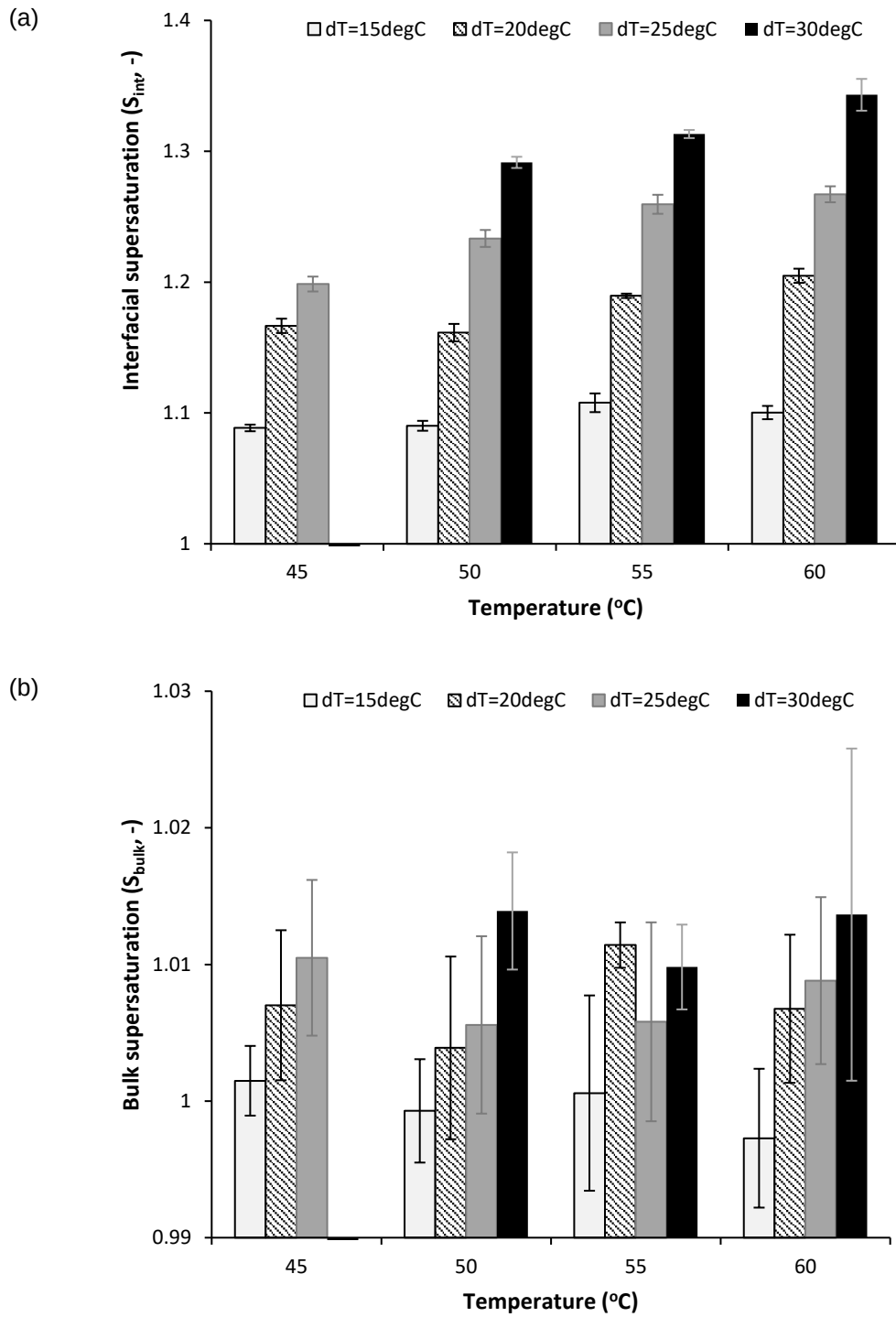


Figure 2.5. Comparison of supersaturation conditions at the onset of bulk nucleation as a result of concentration and temperature polarisation for feed temperatures, T 45-60°C and temperature differences, ΔT 15-30°C. (a) interfacial supersaturation level (S_{int}) and (b) bulk supersaturation level (S_{bulk}). Error bars indicate standard deviation of at least three replicates.

To further investigate this, the relationship between the nucleation rate (assumed to be the supersaturation rate at the onset of induction [26]) and the MSZW was investigated independently for the bulk and interfacial conditions (Figure 2.6). According to classical nucleation theory (CNT), the dependence of nucleation rate on the maximum supersaturation level is exponential [26]. Hence, by applying the method developed by Nyvlt [26], a linear relationship should be observed between the natural logarithms of the supersaturation rate and the MSZW. Similar to Jiang et al. [6], a linear relationship ($r^2=0.93$) was obtained for interfacial conditions at bulk induction. The observed increases in MSZW with T and ΔT due to higher permeate fluxes have also been noted by a number of authors [9, 10, 16]. In MDC, the supersaturation rate is related to the permeate flux [2]. Faster supersaturation rates at higher permeate fluxes mean that the system does not have sufficient time to adjust to each supersaturation level and its accompanying reduction in nucleation energy barrier. The perceived energy barrier is therefore higher than the actual energy barrier of the solution and the likelihood of nucleation is reduced. This lag between the perceived and actual states of solution results in a wider MSZW [32, 33]. In contrast, no relationship between supersaturation rate and MSZW was observed for bulk parameters at induction. This confirms that bulk nucleation kinetics are moderated at the membrane interface.

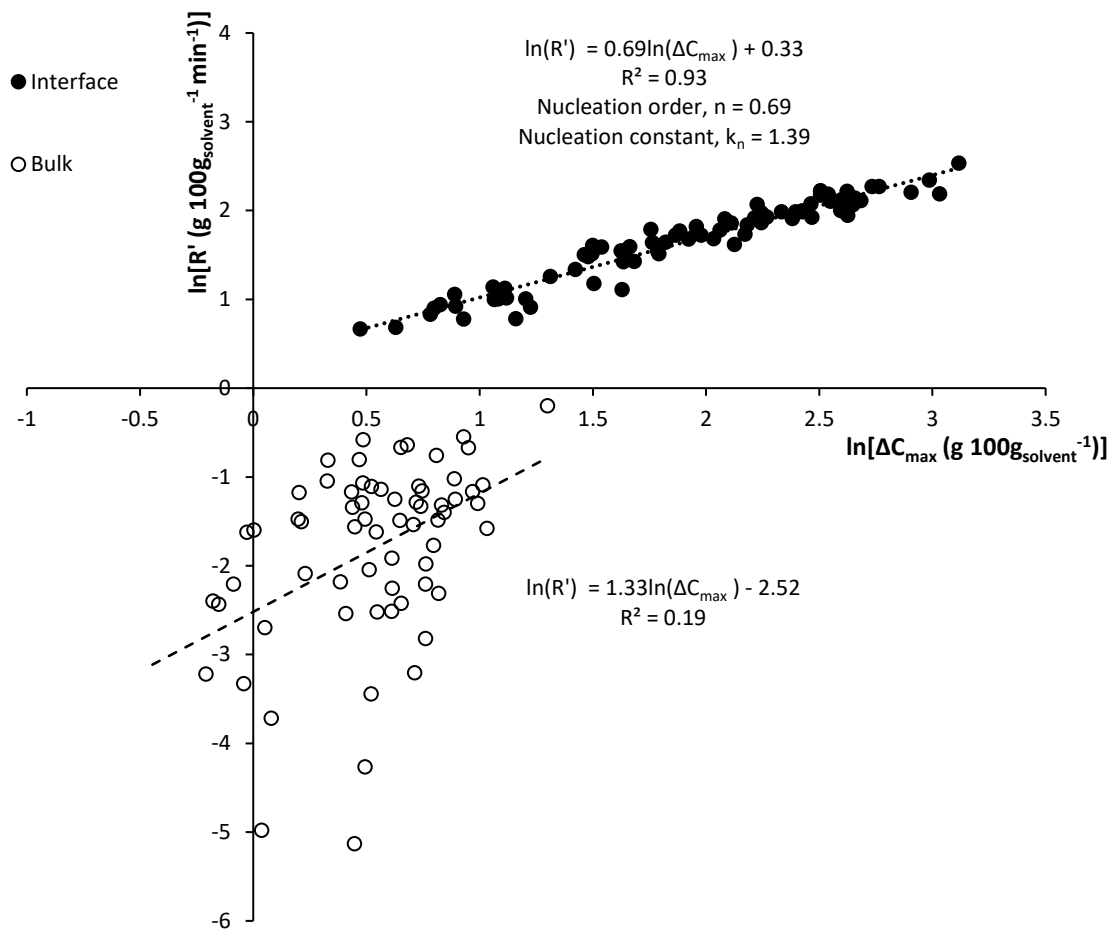
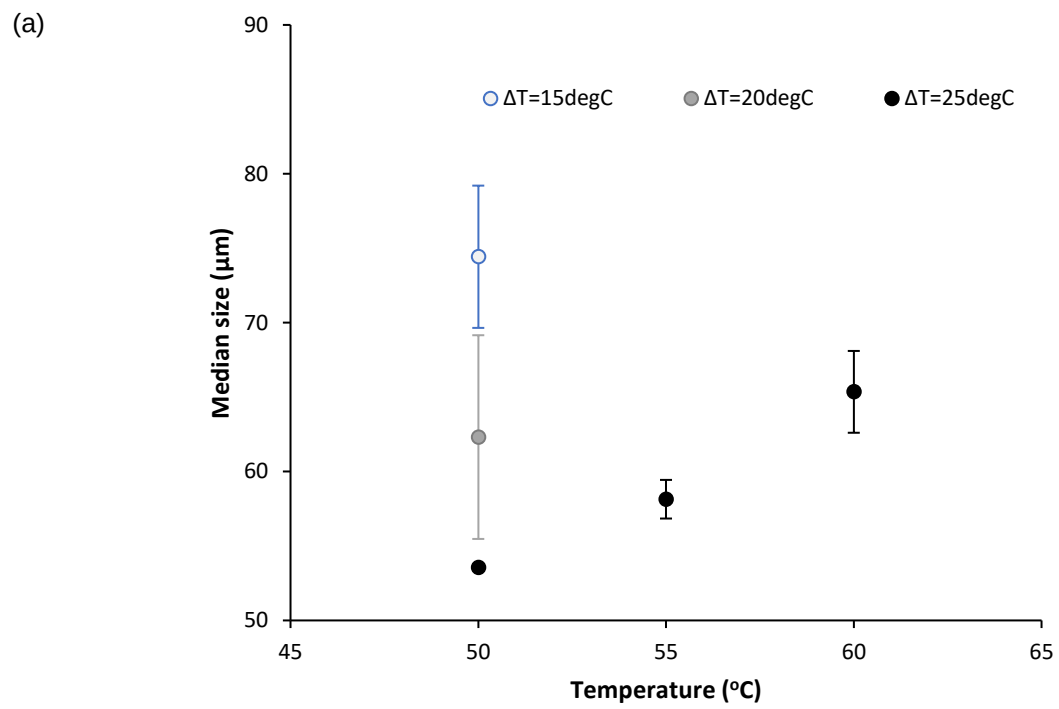
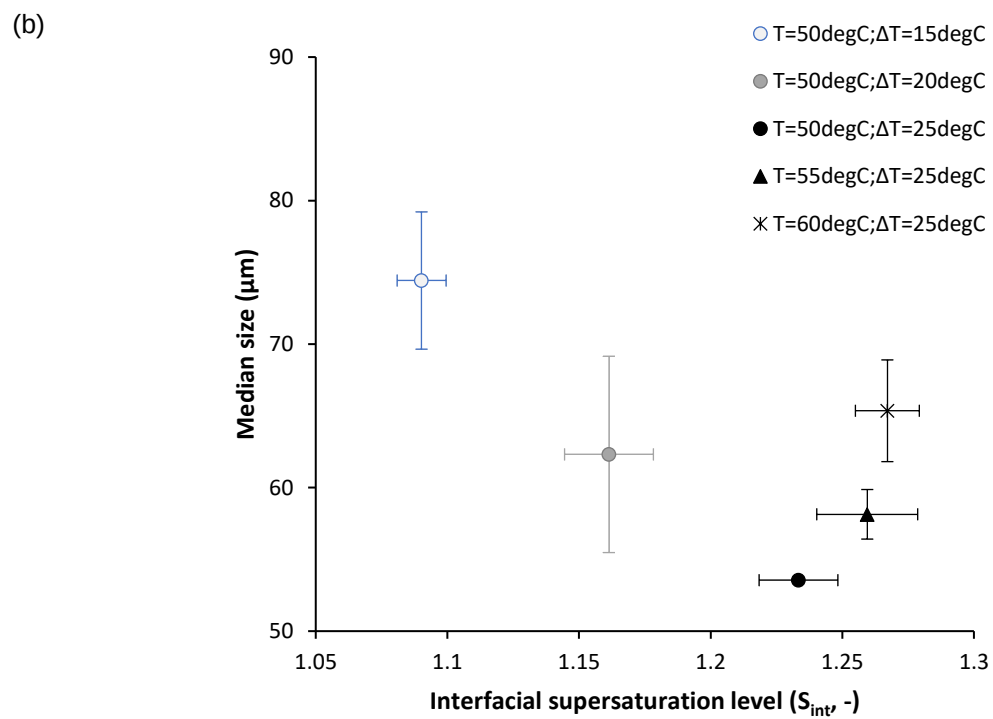


Figure 2.6. Comparing the relationship between metastable zone width (MSZW, $\Delta C_{\max}$) and supersaturation rate (R') at induction based on interfacial and bulk solution concentrations from the complete data set (feed temperatures, T 45-60°C; temperature differences, ΔT 15-30°C). Nyvlt [26]'s method (linear trend for each discrete dataset) provides a description of the nucleation kinetics. The stronger data fit to interfacial concentration suggests that crystals found in the bulk solution are primarily formed near the membrane interface.

Crystal growth is a kinetic process dependent on numerous factors one of which is the supersaturation, the driving force of the process [14]. Since supersaturation provides the driving force for both nucleation and growth, higher nucleation rates tend to inhibit the subsequent crystal growth, resulting in smaller crystals due to fewer ions available for growth [14]. As such, analysis of the crystal size distributions (CSDs) showed a decrease in median size from 70.4 to 53.6 μm as

the ΔT increased from 15 to 25°C at a fixed T 50°C (Figure 2.7a). While a nominal change in S_{bulk} was observed (Figure 2.5a), S_{int} at bulk nucleation increased with increasing ΔT (Figure 2.7b), resulting in a higher nucleation rate. More supersaturation was therefore consumed by nucleation at the higher ΔT , leaving growth to occur at a lower supersaturation and reducing the growth rate (Figure 2.7c) [34]. Similar observations were made in conventional crystallisation studies [29, 34]. At a constant ΔT 25°C, the median size rose from 53.6 to 65.4 μm with an increase in T from 50 to 60°C (Figure 2.7a). Although the S_{int} increased with T (Figure 2.7b), it was accompanied by a substantial rise in growth rate from 4.99×10^{-16} to $19.1 \times 10^{-16} \text{ m s}^{-1}$ (T 50 to 60°C, ΔT 25°C) (Figure 2.7c). It is therefore likely that similarly to Jiang et al. [35], an increase in T enhanced the diffusion-controlled growth rate which resulted in a larger median crystal size. For the conventional crystallisation of 1,1-diamino-2,2-dinitroethylene (FOX-7) in DMSO/water, Fan et al. [29] also noted that even though temperature increases the nucleation rate, it has a greater influence on the crystal growth rate. As a result, their study also observed an increase in crystal size at higher temperatures. In contrast, MD studies by Kim et al. [36] and Edwie and Chung [16] showed a decrease in crystal size with increase feed temperature. However, the permeate temperature was maintained constant as the feed temperature was increased, thereby also increasing the ΔT across the module. Hence, a combined effect of ΔT and T was observed, rather than the independent effect of temperature.



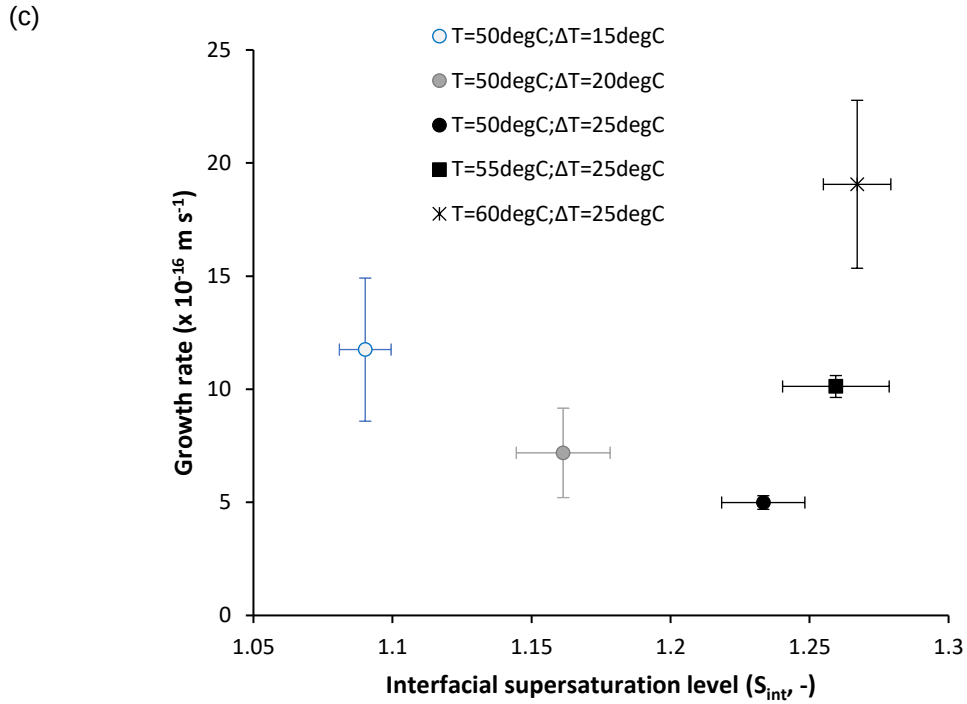
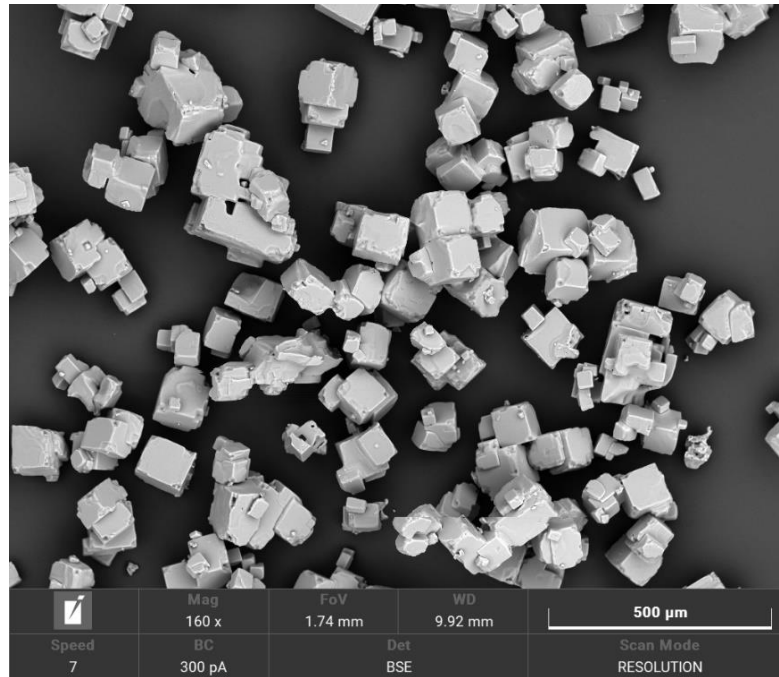


Figure 2.7. Effect of interfacial conditions on crystal growth (feed temperatures, T 50-60°C; temperature differences, ΔT 15-30°C). (a) primary median size data; (b) median size related to interfacial solution concentration; and, (c) crystal growth rate. Error bars indicate standard deviation of at least two replicates.

It has therefore been shown that similarly to scaling, bulk nucleation and crystal growth kinetics are controlled by conditions at the membrane interface. However, a comparison of scanning electron micrographs (SEMs) revealed distinctions in the morphologies of crystals extracted from the bulk solution (Figure 2.8a) and those previously adhered to the membrane surface (scale) (Figure 2.8b). Bulk crystals were cubic in shape, indicating that the growth process maintained the equilibrium or thermodynamic shape of the crystal, which minimises the total surface energy [37].

(a)



(b)

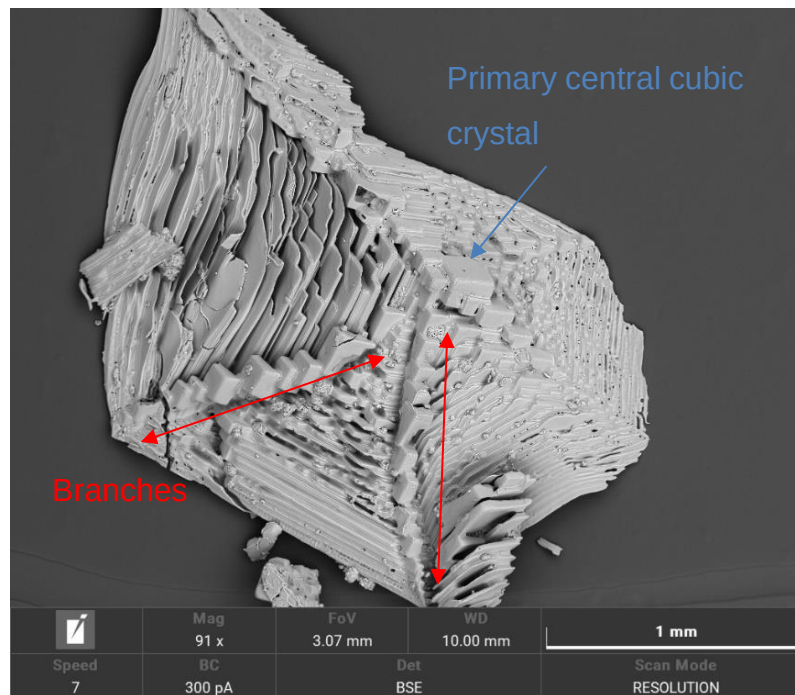
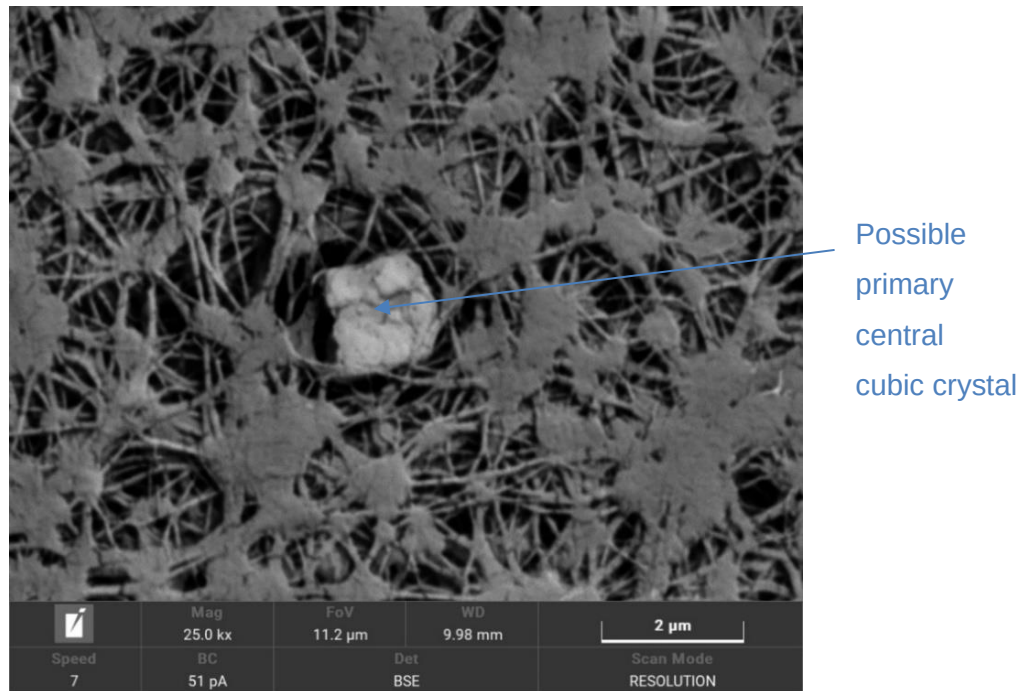


Figure 2.8. SEM images of crystals obtained after the same experimental conditions (T 55°C, ΔT 25°C) but different growth conditions/locations: (a) bulk solution where crystals exhibited cubic crystal morphology (b) membrane surface (scaling) where adhesive growth of dendritic hopper crystals was observed.

In contrast, membrane scale was characterised by a dendritic growth mechanism prevalent at high supersaturation levels when the crystal interface is highly unstable [38]. Desarnaud et al. [39] describe this dendritic form of the NaCl as a type of hopper growth which occurs at a rate up to 10 times that of polyhedral crystals. In small volumes, such as the pore regions of the membrane surface (Figure 2.9a), the likelihood of numerous primary nuclei is low [39]. Hence, the supersaturation available for growth remains high but the surface area of the primary nucleus is too small to incorporate the ions required to reduce supersaturation. As a result, the corners act as secondary nucleation sites and well-aligned “branches” or “chain-like” cubic sectors grow outwards from the primary central cubic crystal [38, 39]. Furthermore, the flat surface on the underside of the dendritic crystals reveals anisotropic supersaturation conditions where growth resulted in a pyramidal shape with the base adhered to the membrane surface (Figure 2.9b). In contrast, the cubic morphology of bulk crystals (Figure 2.8a) implies that the boundary layer surrounding the growing crystals tended toward isotropy, resulting in uniform growth conditions [40]. This suggests that bulk crystal growth initially occurs within the boundary layer solution adjacent to the membrane rather than on the membrane surface. This observation is corroborated by the combined kinetic and thermodynamic influences of S_{int} and S_{bulk} on bulk nucleation, respectively. Since bulk nucleation is induced in a region influenced by the membrane interface and the bulk solution, the interfacial solution, or boundary layer, is the most likely region where bulk nucleation is initiated. Hence, while both scaling and bulk crystallisation are governed by interfacial conditions, SEMs indicate distinctions in the respective crystal growth mechanisms which are likely governed by the interfacial supersaturation levels from which crystallisation propagates.

(a)



(b)

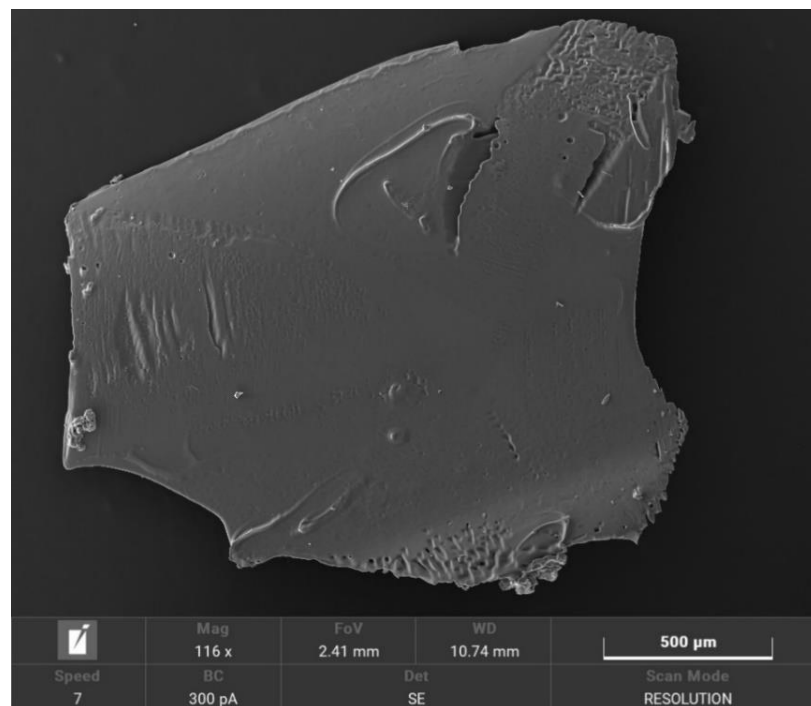


Figure 2.9. SEM images for evaluation of scaling mechanism: (a) porous ePTFE membrane surface showing crystal ($\leq 2 \mu\text{m}$ in size) entrapped in membrane pore ($T 60^\circ\text{C}$, $\Delta T 20^\circ\text{C}$). (b) Underside of dendritic hopper crystal evidencing adhesive growth on membrane surface ($T 45^\circ\text{C}$, $\Delta T 25^\circ\text{C}$).

2.3.3 Direct observation enables discrimination of nucleation mechanisms

Digital microscope imaging enabled the onset and extent of scaling at bulk nucleation to be analysed and related to interfacial supersaturation conditions. The most extensive scaling, characterised by a surface area coverage at bulk nucleation of $47 \times 10^{-4} \text{ m}^2$, was observed at the highest T and ΔT of 60 and 30°C, respectively (Figure 2.10). At this condition, the S_{int} at scaling induction was at a maximum of 1.37, in contrast to S_{int} 1.21 at a lower ΔT of 20°C (T 60°C) where $0.33 \times 10^{-4} \text{ m}^2$ of surface coverage was observed. Scaling was therefore promoted by the increases in S_{int} introduced by higher permeate vapour transport and solute convection at the interface [6, 16, 31]. A decrease in T also lowered S_{int} at scaling induction, along with the subsequent surface area covered at bulk nucleation. Edwie and Chung [16] also noted that increased temperatures led to enhanced membrane scaling. However, according to CNT, higher solution temperatures are expected to decrease the MSZW or maximum supersaturation level. This is due to the enhanced likelihood of molecular attachments and resultant reduction in the activation energy for nucleation [6, 13]. For MD experiments, Jiang et al. [6] observed that higher temperatures were accompanied by narrower MSZWs, as predicted by CNT. This was because a constant supersaturation rate was maintained at each temperature by adjusting permeate flux. In this study however, higher temperatures increased permeate flux, which yielded an increase in supersaturation rate and the resultant MSZW. Hence, based on Eq. 2-27, elevations in T and S_{int} (via both T and ΔT), promoted the driving force for crystallisation at scaling induction, thereby increasing scaling propensity. Nevertheless, while enhanced T 's were shown to exacerbate scaling, the lower scaling observed at T 60°C, ΔT 20°C compared to T 50°C, ΔT 25°C highlights that individual variables such as T can not be used as sole indicators of scaling propensity in MDC systems.

(a)

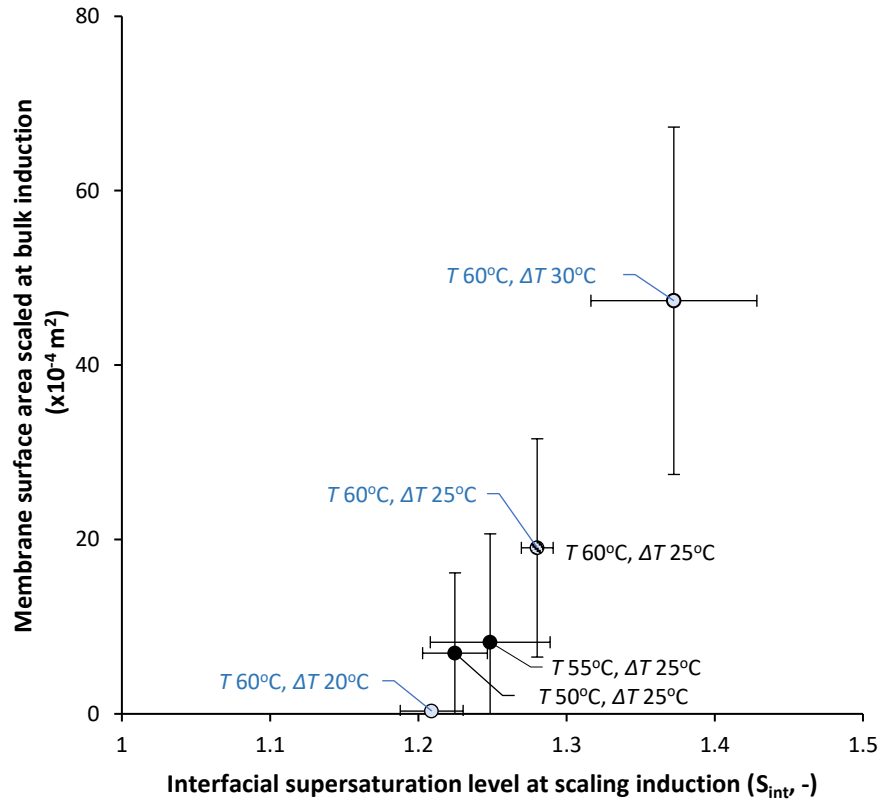


Figure 2.10. Effect of interfacial supersaturation level (S_{int}) on the extent of scaling at the onset of bulk nucleation. Example dataset provided (T 50-60°C, ΔT 15-25°C) highlights that scaling propensity is mediated by S_{int} rather than the individual operating conditions of T and ΔT . Error bars indicate standard deviation of at least two replicates.

For further insight into the scaling nucleation kinetics, the method developed by Nyvlt [26] was applied to the interfacial conditions at scaling induction (Figure 2.11). Similarly to bulk kinetics, the effects of T and ΔT on scaling nucleation kinetics were in line with CNT, where reduced linearity is likely due to the lower precision of the observational scaling detection compared to the turbidimetry used in the bulk. Although simplifications used in the derivation of Nyvlt [26]’s method mean that no physical meaning can be attributed to the nucleation order (m) and constant (k_m), it remains a useful method to analyse and compare the changes in nucleation kinetics of crystallisation systems [26, 41]. The change in m from 0.69 at bulk induction to 2.58 at scaling induction points to a change in nucleation mechanism [26]. The high R' values at scaling induction indicate

enhanced supersaturation rates which yielded wider MSZWs and nucleation rates compared to bulk induction [6]. For simplicity, the impact of scaling on the MSZW at bulk nucleation was assumed to be negligible. Despite this reduced accuracy, bulk nucleation occurred irrespective of scaling prior to induction. It is therefore highly unlikely that bulk crystallisation forms via a two-step scaling and release mechanism as widely assumed in MD literature [8].

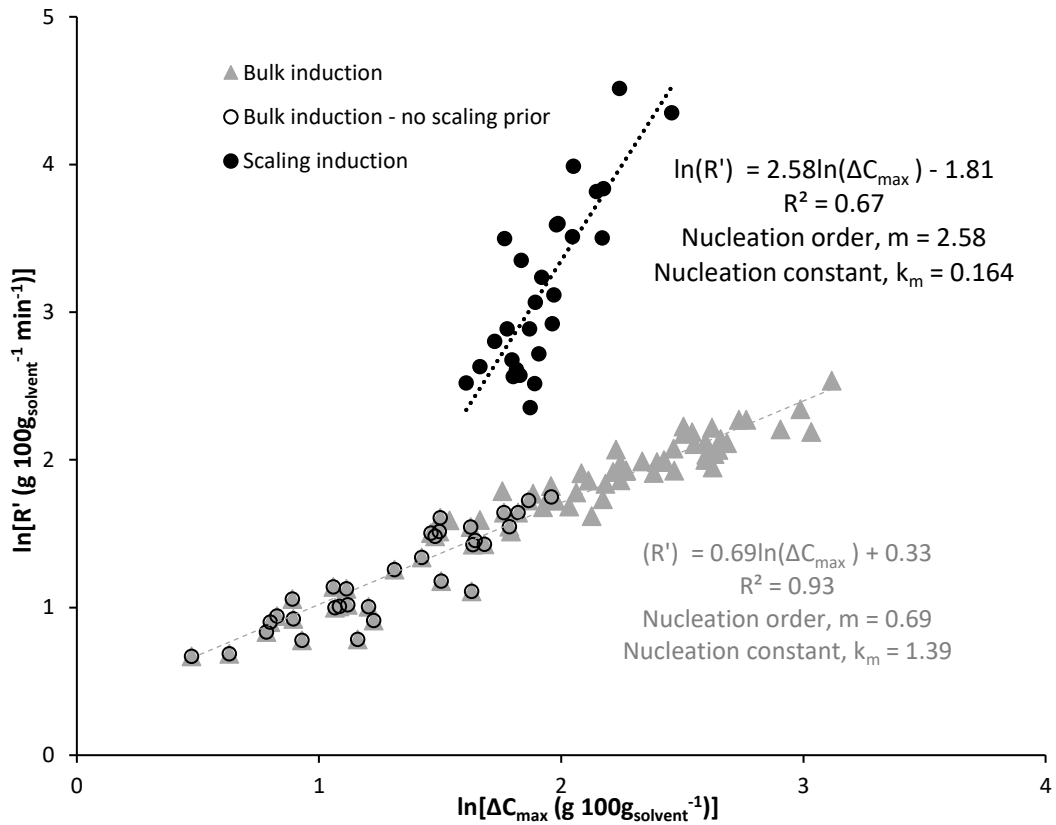


Figure 2.11. Comparing the relationship between metastable zone width (MSZW, ΔC_{max}) and supersaturation rate (R') at induction based on interfacial concentrations at (i) bulk induction (with and without scaling prior), (ii) bulk induction (without scaling prior), and (iii) scaling induction. Complete dataset (T 45-60°C, ΔT 15-30°C) is shown for bulk nucleation which occurred irrespective of scaling. In cases where scaling occurred prior to bulk nucleation, the effect of scale on the interfacial concentration at bulk nucleation was assumed negligible.

The mechanism of scaling can be elucidated and compared to that of bulk nucleation by relating the respective MSZWs to the induction times (Eq. 2-25)

(Figure 2.12). Compared to bulk induction (no scaling prior), scaling occurred at higher S_{int} and shorter induction times, resulting in a higher gradient (B) of 0.046 (dimensionless) compared to 0.002 for no scaling. This would indicate that scaling occurred via a homogeneous nucleation mechanism. Since high supersaturation levels result in high driving forces, the system had sufficient energy to overcome the activation energy barrier for homogeneous nucleation [28, 29]. The high S_{int} values also explain the fast crystallisation kinetics associated with the dendritic hopper growth observed for scaling (Figure 2.8b).

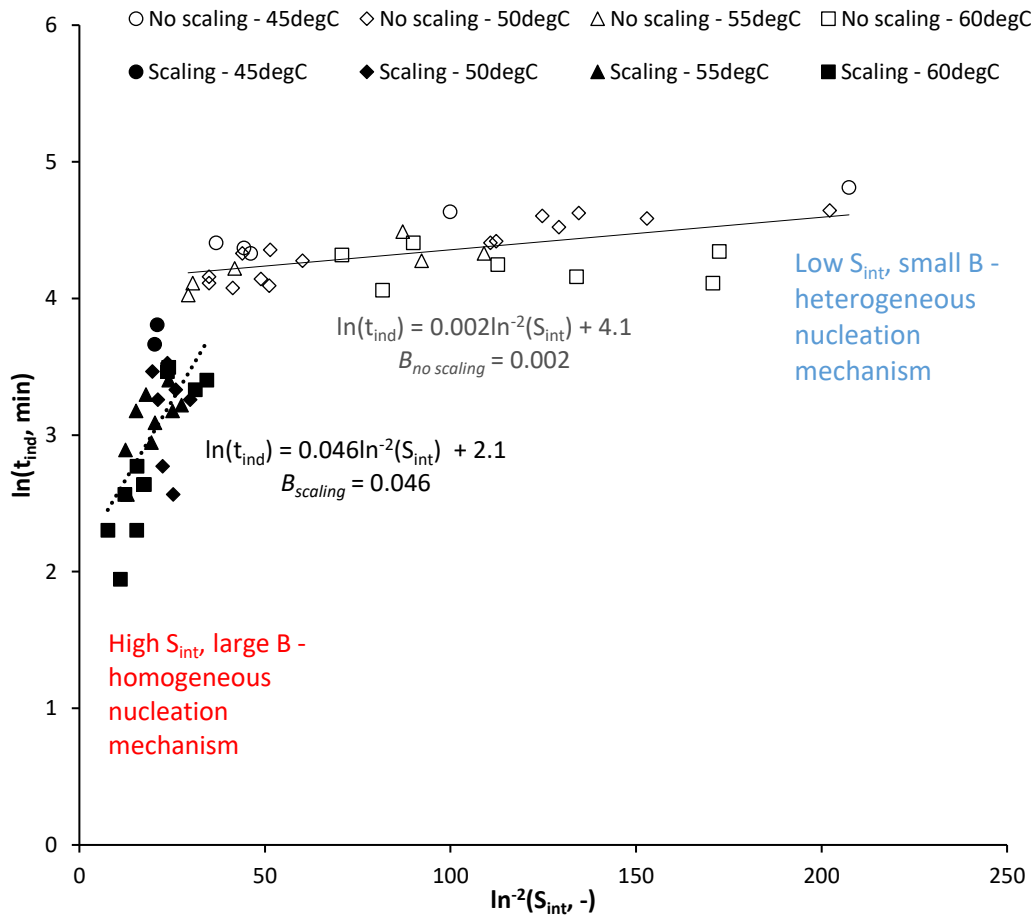


Figure 2.12. Relating respective induction times to the interfacial supersaturation levels at scaling and bulk inductions to distinguish governing nucleation mechanism (T 45-60°C, ΔT 15-30°C). Based on classical nucleation theory (CNT), a steeper gradient, B , indicates that scaling tends towards a homogeneous nucleation mechanism whereas the lower B value for bulk nucleation (no scaling) points to a heterogeneous mechanism [28, 29].

Bulk nucleation occurred at lower S_{int} , pointing to a heterogeneous nucleation mechanism [28, 29] as a result of the membrane surface reducing the activation energy by lowering the interfacial energy [2]. However, this would be in contradiction to SEM observations (Figure 2.8a) and the dual influences of S_{int} and S_{bulk} . Dou et al. [42] showed that similarly to supersaturation, enhanced diffusion reduced the critical size of stable nuclei, which diminished activation energy barrier for calcium carbonate nucleation. This was attributed to the increased likelihood of molecular collisions with both diffusion and supersaturation [42, 43]. As such, Dou et al. [43] concluded that the probability of nucleation can be more holistically predicted by solute collision frequency. They therefore proposed an additional diffusion-dependent collision mechanism for nucleation, which is analogous to the supersaturation-dependent CNT mechanism [43]. Since the diffusion coefficient of NaCl declines drastically with increased supersaturation [44], it is likely that the reduction in activation energy associated with heterogeneous nucleation was due to enhanced diffusion in the boundary layer at lower S_{int} . This is in addition to increases in fluid velocity (and therewith diffusion) across the boundary layer [2]. Hence, bulk nucleation could be induced in the boundary layer rather than on the membrane surface. The distinctions in crystallisation mechanisms observed in the SEMs have therefore been characterised and corroborated by CNT and the postulations of Dou et al. [43].

Since both bulk crystallisation and scaling kinetics in MDC are regulated by the interfacial MSZW (S_{int}), a framework is required to predict the likelihood and extent of scaling at various operating conditions. For crystallisation to propagate in the bulk solution, the bulk solution must be supersaturated ($S_{bulk} > 1$) to yield a positive crystallisation driving force (Eq. 2-27). It is therefore likely that lower S_{bulk} values at scaling induction result in greater surface area coverage prior to bulk induction at $S_{bulk} > 1$. Furthermore, scaling has been shown to increase with higher S_{int} . This would therefore indicate that scaling is promoted by lower bulk to interfacial MSZW ratios (i.e., S_{bulk}/S_{int}) at induction. Linear relationships were established between MSZW and R' for scaling and bulk nucleation (Figure 2.11).

Hence, a plot of $S_{\text{bulk}}/S_{\text{int}}$ against R' at the onset of bulk and scaling inductions revealed R' as the governing parameter by which scaling propensity can be predicted and controlled (Figure 2.13).

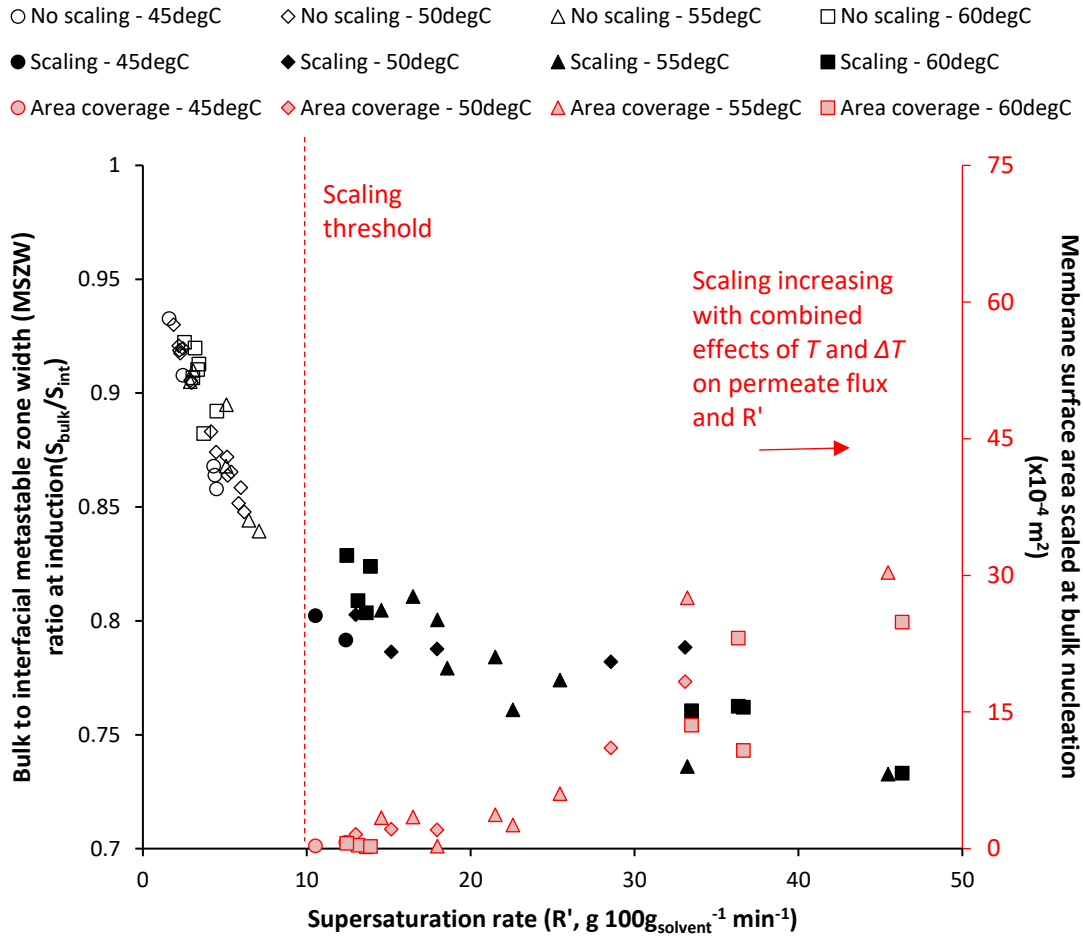


Figure 2.13. Framework for scaling control in MDC. Interfacial supersaturation rate, R' , is related to (i) the ratio of interfacial and bulk metastable zone with widths (MSZWs), $S_{\text{bulk}}/S_{\text{int}}$, at bulk (no scaling) and scaling inductions; and (ii) the extent of scaling at bulk induction. A scaling threshold is established at $R' \approx 10 \text{ g } 100\text{g}_{\text{solvent}}^{-1} \text{ min}^{-1}$, above which scaling occurs.

With an increase in R' , $S_{\text{bulk}}/S_{\text{int}}$ decreased. As expected, this decline was accompanied by a greater membrane surface area coverage at the onset of bulk nucleation. Based on this framework, scale-free crystallisation can be achieved when $R' \leq 10 \text{ g } 100\text{g}_{\text{solvent}}^{-1} \text{ min}^{-1}$, irrespective of the absolute values of T and ΔT .

It can therefore be deduced that conditions that minimise the difference between S_{bulk} and S_{int} (and increase $S_{\text{bulk}}/S_{\text{int}}$) at induction, promote the propagation of crystallisation in the bulk rather than on the membrane surface. This was shown to be achievable by reducing the permeate flux and therefore R' . Lower permeate fluxes also reduced CPC and TPC (Figure 2.4) which diminished the difference between S_{bulk} and S_{int} . While changes in permeate flux and polarisation were mediated by T and ΔT in this study, this diagnostic framework is applicable to any membrane crystallisation system and operating variables which influence R' and $S_{\text{bulk}}/S_{\text{int}}$. Hence, it is likely that by adjusting hydrodynamic boundary conditions to minimise polarisation and promote diffusion, operation at higher permeate fluxes (or R') can be achieved without membrane scaling prior to bulk nucleation, thereby increasing the flexibility of the crystallisation process and expanding the range of achievable product specifications.

2.4 Conclusions

By applying conventional crystallisation theory (CNT) to independent measurements of bulk and surface induction, this study has successfully distinguished the nucleation mechanisms of bulk crystallisation and scaling in MDC. The respective induction times were recorded using turbidimetry and an online digital microscope. Shifts in induction time with permeate flux revealed that operating conditions, T and ΔT , influenced bulk crystallisation kinetics by increasing the driving force for crystallisation. Bulk nucleation and growth kinetics were shown to be controlled by the interfacial MSZW or supersaturation level at induction (S_{int}), while the bulk supersaturation level at induction (S_{bulk}) governed the thermodynamic threshold for crystallisation to propagate in the bulk solution ($S_{\text{bulk}} \geq 1$). Bulk nucleation was observed at all conditions, regardless of scaling on the membrane surface, which contradicted the proposed two-step process of scaling leading to bulk nucleation. Compared to scaling, bulk nucleation was induced at a lower S_{int} via a heterogeneous nucleation mechanism which was likely facilitated by enhanced diffusion in the boundary layer. This led to the growth of cubic crystals in the bulk solution. At constant T , increasing ΔT resulted in higher S_{int} and enhanced nucleation rates. This reduced the supersaturation

level available for growth which ultimately decreased crystal size. Although increasing T also escalated S_{int} , T accelerated the diffusive growth rate which increased the crystal size. Surprisingly, scaling occurred via a homogeneous nucleation mechanism and was exacerbated by increased S_{int} . High supersaturation levels in the small volumes of the membrane pores likely resulted in the adhesive growth of dendritic hopper crystals observed in SEM images. Based on these findings, a MSZW-based framework was developed for crystallisation control in MDC. The framework enabled the prediction of scaling propensity by overlaying the extent of scaling on a plot of interfacial supersaturation (R') against the ratio of bulk to interfacial MSZWs ($S_{\text{bulk}}/S_{\text{int}}$). By applying CNT, R' was revealed as the control parameter for scaling. $S_{\text{bulk}}/S_{\text{int}}$ was defined to account for the thermodynamic and kinetic conditions governing bulk nucleation and represented the relative likelihood of bulk to interfacial nucleation. Based on this framework, scaling could be mitigated by reducing R' which increased $S_{\text{bulk}}/S_{\text{int}}$. The effects T and ΔT on the crystallisation mechanism was linked to their effect on permeate flux which mediated the R' as well as $S_{\text{bulk}}/S_{\text{int}}$ via CPC and TPC. This study has highlighted the importance of accurate induction time measurements to distinguish the mechanisms of scaling and bulk nucleation in MDC. The ability to control bulk nucleation and crystal growth kinetics at the interface, which is a well-defined hydrodynamic region, suggests that the improved control and scalability offered by MDC is not limited to nucleation as often assumed. The mechanistic rather than empirical nature of the framework developed extends its applicability to a wide range of membrane crystallisation systems and operating conditions. As such, it is postulated that the operating region for scale-free crystallisation can be expanded by hydrodynamically reducing the polarisation at the interface, thereby increasing $S_{\text{bulk}}/S_{\text{int}}$. Enhanced mixing in the boundary layer would also induce diffusion-controlled bulk nucleation. These hydrodynamic effects could potentially widen the scope of product qualities that can be achieved using MDC.

References

- [1] E. Chabanon, D. Mangin, and C. Charcosset, "Membranes and crystallization processes: State of the art and prospects," *J. Memb. Sci.*, vol. 509, pp. 57–67, 2016.
- [2] G. Di Profio, E. Curcio, and E. Drioli, "Supersaturation control and heterogeneous nucleation in membrane crystallizers: Facts and perspectives," *Ind. Eng. Chem. Res.*, vol. 49, pp. 11878–11889, 2010.
- [3] C. Charcosset, R. Kieffer, D. Mangin, and F. Puel, "Coupling between membrane processes and crystallization operations," *Ind. Eng. Chem. Res.*, vol. 49, pp. 5489–5495, 2010.
- [4] I. Ruiz Salmón and P. Luis, "Membrane crystallization via membrane distillation," *Chem. Eng. Process. Process Intensif.*, vol. 123, pp. 258–271, 2018.
- [5] J. Ulrich and C. Strege, "Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers," *J. Cryst. Growth*, vol. 237–239, pp. 2130–2135, 2002.
- [6] X. Jiang, X. Ruan, W. Xiao, D. Lu, and G. He, "A novel membrane distillation response technology for nucleation detection, metastable zone width measurement and analysis," *Chem. Eng. Sci.*, vol. 134, pp. 671–680, 2015.
- [7] X. Jiang, Y. Shao, L. Sheng, P. Li, and G. He, "Membrane Crystallization for Process Intensification and Control: A Review," *Engineering*, vol. 7, pp. 50–62, 2021.
- [8] M. C. Sparenberg, S. Chergaoui, V. Sang Sefidi, and P. Luis, "Crystallization control via membrane distillation-crystallization: A review," *Desalination*, vol. 519, p. 115315, 2022.
- [9] C. M. Tun et al., "Membrane distillation crystallization of concentrated salts - Flux and crystal formation," *J. Memb. Sci.*, vol. 257, pp. 144–155, 2005.
- [10] D. M. Warsinger, E. W. Tow, J. Swaminathan, and J. H. Lienhard V, "Theoretical framework for predicting inorganic fouling in membrane distillation and experimental validation with calcium sulfate," *J. Memb. Sci.*, vol. 528, pp. 381–390, 2017.

- [11] T. Horseman, Y. Yin, K. S. Christie, Z. Wang, T. Tong, and S. Lin, "Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies," *ACS ES&T Eng.*, vol. 1, pp. 117–140, 2021.
- [12] F. He, J. Gilron, H. Lee, L. Song, and K. K. Sirkar, "Potential for scaling by sparingly soluble salts in crossflow DCMD," *J. Memb. Sci.*, vol. 311, pp. 68–80, 2008.
- [13] D. Kashchiev and G. M. Van Rosmalen, "Review: Nucleation in solutions revisited," *Cryst. Res. Technol.*, vol. 38, pp. 555–574, 2003.
- [14] A. Lewis, M. M. Seckler, H. Kramer, and G. van Rosmalen, *Industrial Crystallization*. Cambridge: Cambridge University Press, 2015.
- [15] A. Alkhatib, M. A. Ayari, and A. H. Hawari, "Fouling mitigation strategies for different foulants in membrane distillation," *Chem. Eng. Process. - Process Intensif.*, vol. 167, p. 108517, 2021.
- [16] F. Edwie and T. S. Chung, "Development of simultaneous membrane distillation-crystallization (SMDC) technology for treatment of saturated brine," *Chem. Eng. Sci.*, vol. 98, pp. 160–172, 2013.
- [17] M. Gryta, "Calcium sulphate scaling in membrane distillation process," *Chem. Pap.*, vol. 63, pp. 146–151, 2009.
- [18] L. D. Tijjing, Y. C. Woo, J. S. Choi, S. Lee, S. H. Kim, and H. K. Shon, "Fouling and its control in membrane distillation-A review," *J. Memb. Sci.*, vol. 475, pp. 215–244, 2015.
- [19] D. M. Warsinger et al., "Effect of filtration and particulate fouling in membrane distillation," *Int. Desalin. Assoc.*, pp. 0–14, 2015.
- [20] S. Xie et al., "Gypsum scaling mechanisms on hydrophobic membranes and its mitigation strategies in membrane distillation," *J. Memb. Sci.*, vol. 648, p. 120297, 2022.
- [21] R. S. Harner, R. J. Ressler, R. L. Briggs, J. E. Hitt, P. A. Larsen, and T. C. Frank, "Use of a fiber-optic turbidity probe to monitor and control commercial-scale unseeded batch crystallizations," *Org. Process Res. Dev.*, vol. 13, pp. 114–124, 2009.

- [22] A. Triger, J. S. Pic, and C. Cabassud, "Determination of struvite crystallization mechanisms in urine using turbidity measurement," *Water Res.*, vol. 46, no. 18, pp. 6084–6094, 2012.
- [23] X. Jiang, D. Lu, W. Xiao, X. Ruan, J. Fang, and G. He, "Membrane assisted cooling crystallization: Process model, nucleation, metastable zone, and crystal size distribution," *AIChE J.*, vol. 62, pp. 829–841, 2016.
- [24] Ó. Andriessdóttir et al., "An experimentally optimized model for heat and mass transfer in direct contact membrane distillation," *Int. J. Heat Mass Transf.*, vol. 66, pp. 855–867, 2013.
- [25] A. Alkhudhiri, N. Darwish, and N. Hilal, "Membrane distillation: A comprehensive review," *Desalination*, vol. 287, pp. 2–18, 2012.
- [26] J. Nyvlt, "Kinetics of nucleation in solutions," *J. Cryst. Growth*, vol. 3, pp. 377–383, 1968.
- [27] A. Mersmann and K. Bartosch, "How to predict the metastable zone width," *J. Cryst. Growth*, vol. 183, pp. 240–250, 1998.
- [28] G. Zeng, H. Li, S. Huang, X. Wang, and J. Chen, "Determination of metastable zone width and the primary nucleation kinetics of sodium sulfate," *Theor. Found. Chem. Eng.*, vol. 49, pp. 869–876, 2015.
- [29] S. Fan, X. Gu, X. Zhou, X. Duan, and H. Li, "Determination of nucleation kinetics from the induction time of 1,1-diamino-2,2-dinitroethylene (FOX-7) in DMSO/Water," *Energ. Mater. Front.*, vol. 2, no. 1, pp. 62–68, 2021.
- [30] M. Gryta, "Effectiveness of water desalination by membrane distillation process," *Membranes (Basel)*, vol. 2, pp. 415–429, 2012.
- [31] Y. Choi, G. Naidu, L. D. Nghiem, S. Lee, and S. Vigneswaran, "Membrane distillation crystallization for brine mining and zero liquid discharge: Opportunities, challenges, and recent progress," *Environ. Sci. Water Res. Technol.*, vol. 5, pp. 1202–1221, 2019.
- [32] C. Bian, H. Chen, X. Song, and J. Yu, "Metastable zone width and the primary nucleation kinetics for cooling crystallization of NaNO₃ from NaCl-NaNO₃-H₂O system," *J. Cryst. Growth*, vol. 518, pp. 5–13, 2019.

- [33] S. A. Kulkarni, S. S. Kadam, H. Meekes, A. I. Stankiewicz, and J. H. Ter Horst, "Crystal nucleation kinetics from induction times and metastable zone widths," *Cryst. Growth Des.*, vol. 13, pp. 2435–2440, 2013.
- [34] A. Mersmann, "Crystallization and precipitation," *KONA Powder Part. J.*, vol. 16, pp. 60–67, 1998.
- [35] X. Jiang et al., "Hybrid Control Mechanism of Crystal Morphology Modification for Ternary Solution Treatment via Membrane Assisted Crystallization," *Cryst. Growth Des.*, vol. 18, pp. 934–943, 2017.
- [36] J. Kim, J. Kim, and S. Hong, "Recovery of water and minerals from shale gas produced water by membrane distillation crystallization," *Water Res.*, vol. 129, pp. 447–459, 2018.
- [37] J. A. Dirksen and T. A. Ring, "Crystallization review," *Chemical Engineering Science*, vol. 46, no. 10, pp. 2389–2427, 1991.
- [38] S. Sarig and F. Tartakovsky, "Crystal habit modifiers," *J. Cryst. Growth*, vol. 28, pp. 300–305, 1975.
- [39] J. Desarnaud, H. Derluyn, J. Carmeliet, D. Bonn, and N. Shahidzadeh, "Metastability limit for the nucleation of NaCl crystals in confinement," *J. Phys. Chem. Lett.*, vol. 5, pp. 890–895, 2014.
- [40] R. F. Sekerka, "Role of instabilities in determination of the shapes of growing crystals," *J. Cryst. Growth*, vol. 128, no. 1–4, pp. 1–12, 1993.
- [41] K. Liang, G. White, D. Wilkinson, L. J. Ford, K. J. Roberts, and W. M. L. Wood, "Examination of the Process Scale Dependence of L-Glutamic Acid Batch Crystallized from Supersaturated Aqueous Solutions in Relation to Reactor Hydrodynamics," *Ind. Eng. Chem. Res.*, vol. 43, pp. 1227–1234, 2004.
- [42] X. Dou, H. Huang, and Y. Han, "The role of diffusion in the nucleation of calcium carbonate," *Chinese J. Chem. Eng.*, vol. 43, pp. 275–281, 2022.
- [43] X. Dou et al., "Collision dependent silver nucleation regulated by chemical diffusion and reaction," *Chem. Eng. Sci.*, vol. 262, p. 117965, 2022.
- [44] N. E. R. Zimmermann, B. Vorselaars, D. Quigley, and B. Peters, "Nucleation of NaCl from Aqueous Solution: Critical Sizes, Ion-Attachment

Kinetics, and Rates,” J. Am. Chem. Soc., vol. 137, pp. 13352–13361, 2015.

Appendix A. Digital microscope image analysis

Scaling on the membrane surface was analysed based on experimental video footage taken using a digital microscope. An example of this analysis is shown in Figure A1 for an experiment at T 60°C, ΔT 25°C. At the onset of nucleation (t_{36}), the image was converted to a coverage through image analysis to obtain a surface area coverage of $10.8 \times 10^{-4} \text{ m}^2$ which equated to 2.7% of the membrane surface area. Evidence of deposition and growth of crystal deposits are observed after bulk nucleation for images taken at 41 and 46 minutes from the start of the experiment. This technique was used to determine scaling induction and the extent of scaling at bulk nucleation for all conditions investigated (T 45-60°C, ΔT 15-30°C), and when complemented with turbidimetry, enabled the discrimination between scaling and bulk crystallisation.

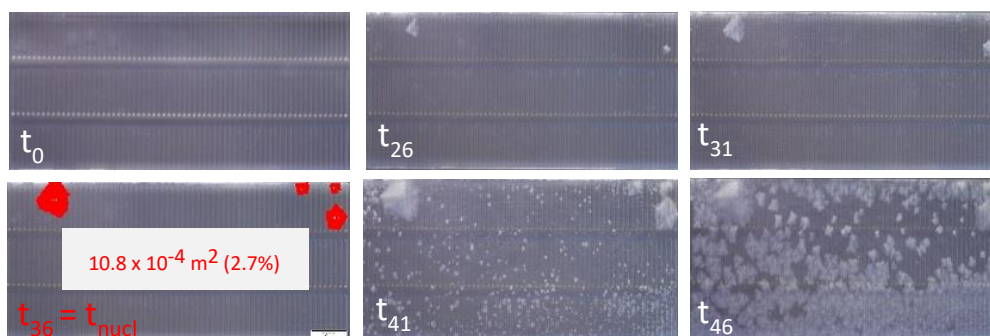


Figure A1. Digital microscope images depicting a times series of crystallisation on the membrane surface at a temperature (T) and temperature difference (ΔT) of 60 and 25°C, respectively. “ t ” denotes experimental time with the subscript displaying minutes. Bulk nucleation occurred at 36 minutes ($t_{36} = t_{nucl}$).

- 3. Reynolds number establishes boundary-layer characteristics that determine nucleation and crystal growth kinetics (including scaling) in membrane distillation crystallisation**

Reynolds number establishes boundary-layer characteristics that determine crystal nucleation and growth kinetics (including *scaling*) in membrane distillation crystallisation

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Abstract

High Reynolds numbers (Re) are often recommended for scaling mitigation strategies in membrane distillation, but the exact role of hydrodynamics in regulating crystallisation is not yet clear. This study therefore introduces non-invasive techniques for the determination of induction time at the membrane and within the bulk solution, to relate the kinetics of nucleation and crystal growth to system hydrodynamics. Increase of Re reduced boundary-layer thickness and enhanced mass and heat transfer which raises permeate flux. This was demonstrated to increase supersaturation rate, which elevated supersaturation and shortened induction time to *bulk* crystal nucleation. The interfacial conditions set by Re were therefore shown to determine nucleation, which was confirmed through analysis using classical nucleation theory. For temperature differences (ΔT) below 20°C, scaling was not observed before *bulk* crystallisation, which does not conform with the two-step mechanism formerly proposed of adhesive growth at the membrane followed by crystal backtransport to the bulk solution under applied shear stress. At ΔT 25°C, scaling was observed and was not suppressed with an increase in Re as higher fluxes raised local solute concentration. Scaling did not conform to the kinetic analysis provided by classical nucleation theory. This was explained by complex transport phenomena within the interfacial region and could be related to a modified concentration polarisation coefficient which identified a critical interfacial saturation threshold below which scaling did not occur. Interfacial characterisation also demonstrated Re to provide distinct regions that favour diffusion limited or surface-integration limited growth. This study therefore provides direct evidence for how Re can be used to underpin scaling mitigation strategies and foster the regulation of nucleation kinetics to ensure strict control over crystal product quality in membrane crystallisation applications.

Keywords: *scaling, boundary layer, mixing, heterogeneous nucleation*

3.1 Introduction

Membrane distillation crystallisation (MDC) has emerged as a promising technology for zero-liquid discharge (ZLD), the production of high value chemicals, and for resource recovery in the circular economy [1, 2]. In MDC, the vapour-pressure gradient established across the hydrophobic microporous membrane fosters the selective transport of water vapour. This concentrates the feed solution to develop a supersaturated state, after which crystallisation can proceed [1, 3]. The fixed interfacial area enables the precise control of solvent transfer which advances the regulation of supersaturation, thereby improving control over the kinetics of nucleation and crystal growth when compared to conventional crystalliser designs [4]. Temperature and concentration polarisation are also introduced by the confined laminar flow conditions to create a discrete region of elevated supersaturation within the boundary layer that forms at the membrane-solution interface [2]. Consequently, it has been postulated that nucleation and crystal growth can be independently controlled within MDC through two discrete domains: a highly supersaturated interfacial boundary layer, where nucleation is dominant, and a saturated bulk solution that primarily mediates growth [5, 6]. The fully developed hydrodynamic characteristics of this supersaturated environment may therefore improve the control of crystallisation kinetics during scale-up; an acknowledged barrier for most existing crystallisation process environments [7].

However, the probability for inorganic fouling (scaling) increases through concentration and temperature polarisation that are set by heat and mass transfer processes local to the membrane [2]. This leads to the adhesive growth of crystals on the membrane surface and/or inside the pores (scaling), that is commonly described to proceed through a heterogeneous primary nucleation mechanism [2, 8]. Scaling contributes to process failure by increasing resistance to heat and mass transfer, in addition to blocking micropores which collectively hinder water vapour permeability [9]. Shin and Sohn [10] described how scaling occurred at low flow rates due to concentration polarisation. However, enhanced scaling was observed at higher flow rates, which the authors attributed to the deposition of crystals formed within the bulk rather than through adhesive growth

on the membrane surface. Warsinger et al. [11] also indicated that nucleation occurred preferentially in the bulk solution (generally characterised as homogeneous primary nucleation). The authors proposed this to be the most plausible mechanism in MDC as the hydrophobicity of the membrane provides only a nominal reduction in the activation energy required for nucleation. This contradiction as to which primary nucleation mechanism is dominant in MDC is largely due to the present use of permeate flux decline to indirectly infer the onset of scaling, which is insufficient in resolution to differentiate between heterogeneous or homogeneous mechanisms, risking misinterpretation of the relevance of concentration polarisation to the primary nucleation pathway [2].

Hydrodynamics within the feed solution are also used as a critical control parameter in membrane distillation scaling mitigation strategies [2, 9]. High shear stress has been proposed as a method for limiting scaling. This assumes a two-stage mechanism that involves scaling firstly, with sufficient force applied by crossflow to overcome the intermolecular and frictional forces of adhesion subsequently detaching adhered crystals from the membrane [3, 5, 8]. Shin and Sohn [10] instead attributed the inhibition of scaling at increased flow rates to a reduction in concentration polarisation. In principle, the induction of turbulence through the adoption of high Reynolds numbers improves mixing within the boundary layer to mitigate concentration polarisation [12]. However, since Reynolds number (Re) determines the interfacial rate of heat and mass transfer, it collectively governs the permeate flux, interfacial solute concentration, and solubility constant, which ultimately inform on the supersaturation rate and solubility curve of the crystallising solution [3, 4]. It is the supersaturation rate that determines the difference between the solubility curve and the metastable limit curve at which induction proceeds, and therefore establishes the kinetic trajectory for nucleation [3, 13]. This is empirically observed by Kim et al. [14] noting surface scaling at low velocities, and the deposition of bulk crystals at high velocities, suggesting that quite distinct kinetic trajectories are initiated by adjusting Re , which to date has been relatively underexplored.

Modelling from Warsinger et al. [15] substantiates the assertion that solute concentration is not solely responsible for scaling. The authors proposed that

scaling can be prevented in a highly saturated solution, provided the residence time of a fluid volume at the membrane interface is shorter than the induction time required for a stable nucleus to form. This establishes a relationship between boundary-layer characteristics and classical nucleation theory (CNT), thus recognising that higher feed flow rates also reduce the probability for scaling by limiting the residence time of the fluid. The model was based on an empirically derived induction time, which does not take into consideration how Re will adjust the supersaturation rate and fluid physics within the boundary layer; these properties will determine the induction time and set the conditions for solute back transport which dictate the likelihood for scaling. The interfacial solute concentration, boundary-layer thickness, and concentration-dependent interfacial diffusion coefficient also represent the driving force for crystal growth [16] and are defined by the Re adopted. Consequently, it may be inferred that boundary-layer hydrodynamics have the potential to mediate both nucleation and crystal growth.

This study therefore aims to provide a complete description of how Re governs the kinetics of nucleation and crystal growth to permit rationalisation for the selection of hydrodynamic conditions that can minimise scale and foster controlled crystal growth in the bulk solution to improve product quality, and process sustainability. To achieve this, boundary layer characteristics are related to CNT through determining solution metastability with the use of non-invasive techniques for the experimental derivation of induction time at the membrane and in the bulk solution. Specific objectives are to:

- (i) Characterise the interfacial region to describe the transition in metastable zone width when Reynolds number alters the interfacial supersaturation rate to relate hydrodynamics to nucleation rate;
- (ii) Determine the induction time for scaling, correlating with interfacial conditions to confirm how hydrodynamic conditions increase the probability for scaling;
- (iii) Describe the mechanism for crystal growth via adhesive and bulk mechanisms to identify how the boundary layer properties can control crystal size and product quality;

- (iv) Relate interfacial conditions to solute transport to provide a mechanistic basis for the description of nucleation and growth of scale in MDC that can subsequently be used to underpin scaling mitigation strategies.

3.2 Materials and Methods

3.2.1 Membrane distillation crystallisation experimental setup and operation

A Perspex membrane module was used to incorporate a 100x40 mm ePTFE flat-sheet microporous membrane comprising 0.1 μm pores (Cobetter Filtration, Hangzhou, China). The membrane was configured for direct contact, with a 0.95 mol L⁻¹ sodium chloride (NaCl, 99.5%, ACROS Organics™, Fisher Chemicals, Loughborough, UK) feed solution passed counter-current to a permeate stream of deionised water (resistivity $\approx 15.0 \text{ M}\Omega \text{ cm}$). The feed solution Reynolds number (Re) was varied between 1300 and 2050 using a peristaltic pump (Watson-Marlow 530S, WMFTG, Falmouth, UK). The permeate flow rate was fixed to 65% of the feed solution. An overhead stirrer within the crystalliser vessel was set to 300 rpm (Hei-TORQUE Ultimate 400, Heidolph Instruments, Schwabach, Germany). The feed temperature at the entrance of the membrane module was maintained at 60°C by an inline heat exchanger connected to a heater (LT ecocool 150, Grant Instruments (Cambridge) Ltd., Shepreth, UK). Inside the heat exchanger, hot water from the heater flowed counter-current to the feed solution. The permeate temperature was regulated by recirculating chiller water around the jacketed permeate vessel (LT ecocool 150, Grant Instruments (Cambridge) Ltd., Shepreth, UK). Permeate temperatures at the inlet of the membrane were varied between 35 and 45°C to achieve temperature differences (ΔT) of 15 to 25°C. Four thermocouples (EI-1034, Electronic Innovations Corporation, Colorado, USA) were inserted inline to measure entrance and exit temperatures. Conductivity of the permeate stream was monitored for salt breakthrough using an inline conductivity probe and meter (Seven2Go™ Pro S7, Mettler-Toledo Ltd, Leicester, UK). A precision balance beneath the permeate vessel recorded permeate mass over time to calculate water vapour flux (Cole Parmer Symmetry PT-4202E, Antylia Scientific, Illinois, USA).

3.2.2 Crystal detection and measurement

To detect bulk nucleation, an inline turbidity probe (InPro 8200/S/Epoxy/120 turbidity sensor, Mettler-Toledo Ltd, Leicester, UK) was installed in the feed solution downstream of the membrane module and data recorded every second. The dual fibre optical sensor is an industrially proven method using backscatter technique for detecting the onset of bulk nucleation [21]. Non-invasive images of the membrane were acquired using an online digital microscope (AmScope UHM350-11 HDMI digital microscope, AmScope, UK). The digital microscope was focused on the feed side of the membrane through the Perspex cell wall and set within the maximum working distance of 145 mm. The wide-angle lens, long working distance and broad magnification range (x20-100) permitted the full area of the membrane to be examined in real time with resolution provided by a scale equivalent to 2µm per pixel. Consequently, while the exact moment at which the first nucleus was formed could not be precisely determined by surface imaging (a nanoscale event), the imaging technique was able to capture the early onset and growth of scaling. Captured images were analysed using Olympus Stream Image Analysis Software (Olympus, Southend-on-Sea, UK) and transformed into surface area coverage. For SEM analysis, crystal samples were taken from the bulk crystalliser and membrane surface 10 minutes after the onset of bulk nucleation. After vacuum filtration through a 0.45 µm pore nitrocellulose membrane filters (Whatman® NC45, Cytiva, Maidstone, UK), crystals were left to dry at room temperature for at least 48 hours before submission for scanning electron microscopy (SEM). Crystal samples were coated by physical vapor deposition with 10 nm gold prior to analysis at an acceleration voltage, beam current and working distance of 20 keV, 300 pA and 10 mm, respectively (Tescan VEGA 4, Tescan Orsay Holding, Czech Republic).

3.2.3 Introduction of revised concentration polarisation coefficient

The concentration polarisation coefficient (CPC) is conventionally defined as [18]:

$$CPC = \frac{C_{int}}{C_b} = \exp\left(\frac{J_p}{\rho K}\right) \quad (3-1)$$

where C is concentration; subscripts int and b represent the interface and bulk respectively; and ρ is the solution density. J_p is the permeate flux:

$$J_p = \frac{\Delta m}{A_m \Delta t} \quad (3-2)$$

where A_m is the membrane surface area. Δm and Δt are the changes in permeate mass and time, respectively. To calculate J_p , experimental data was smoothed with a five-minute average. K is the mass transfer coefficient and was resolved using the L  v  que solution [18]:

$$K = \frac{1.62D}{d_h} \left(\frac{V d_h^2}{DL} \right)^{\frac{1}{3}} \quad (3-3)$$

where D is the molecular diffusivity, V is the solution velocity, d_h is the hydraulic diameter and L is the membrane surface length. However, Lokare and Vidic [19] noted that the conventional analytical method employed can underpredict the CPC. Hence, a more accurate determination of CPC is required to better understand the effect of Re on boundary-layer phenomena and the subsequent extent of scaling. Chang and Myerson [20] evidenced the concentration dependency of the diffusion coefficient within a supersaturated NaCl solution. In the conventional CPC analysis method, the diffusion coefficient is determined based on the bulk concentration, which is usually lower than the interfacial concentration due to polarisation effects. Since the diffusion coefficient of NaCl decreases drastically as supersaturation increases [20–22], this likely contributes to the underestimation of CPC previously observed [19]. To improve the precision of the CPC, a revised CPC value, based on the interfacial diffusion coefficient, D_{int} , was introduced. This involved initially calculating the interfacial concentration (C_{int}) using the conventional CPC (Eq. 3-1). C_{int} was then applied to empirical data to determine D_{int} (Appendix B) which was subsequently substituted into Eq. 3-1 to obtain the revised CPC. This revised CPC provides a basis on which to improve the characterisation of solute mass transport, allowing for better scaling control within MDC.

3.2.4 Crystallisation kinetics

Through characterising the metastable zone width (MSZW) or maximum supersaturation level, the primary nucleation kinetics of a system can be determined [18]. According to classical three-dimensional (3D) nucleation theory [22, 23]:

$$J = A \exp\left(-\frac{B}{\ln^2 S}\right) \quad (3-4)$$

where A is the pre-exponential factor and B is a parameter defined by:

$$B = \frac{16\pi}{3} \left(\frac{\gamma v^{\frac{2}{3}}}{k_B T} \right)^3 \quad (3-5)$$

γ is the interfacial energy, v is the volume of the solute molecule, k_B is the Boltzmann constant, and T is the nucleation temperature. S is the supersaturation level. Crystallisation kinetics were analysed based on the interfacial supersaturation level (S_{int}) given by:

$$S_{int} = \frac{C_{int}}{C_{int}^*} \quad (3-6)$$

where C_{int}^* is the interfacial saturation concentration at the interfacial temperature. The interfacial temperature was determined iteratively based on the temperature polarisation coefficient (TPC) [18]:

$$TPC = \frac{T_{int,f} - T_{int,p}}{T_{b,f} - T_{b,p}} \quad (3-7)$$

where T is temperature and subscripts f and p represent the feed and permeate solutions, respectively.

$$T_{int,f} = T_{b,f} - (T_{b,f} - T_{b,p}) \left(\frac{\frac{1}{h_f}}{\frac{1}{h_f} + \frac{1}{h_p} + \frac{1}{h_c + h_v}} \right) \quad (3-8)$$

$$T_{int,p} = T_{b,p} + (T_{b,f} - T_{b,p}) \left(\frac{\frac{1}{h_p}}{\frac{1}{h_f} + \frac{1}{h_p} + \frac{1}{h_c + h_v}} \right) \quad (3-9)$$

h is the overall heat transfer coefficient for each solution, i :

$$h_i = \frac{Nuk_i}{d_h}, i = f, p \quad (3-10)$$

where Nu is the Nusselt number based on the L  v  que solution:

$$Nu = 0.023Re^{0.8}Pr^{\frac{1}{3}} \quad (3-11)$$

$$Re = \frac{\rho V d_h}{\mu} \quad (3-12)$$

$$Pr = \frac{c_p \mu}{k} \quad (3-13)$$

where μ is the dynamic viscosity, c_p is the specific heat capacity, and k is the thermal conductivity of the respective solutions. h_c is the conduction heat transfer coefficient:

$$h_c = \frac{k_m}{\delta_m} \quad (3-14)$$

δ_m is the thickness of the membrane and k_m is the membrane thermal conductivity [25]:

$$k_m = \left(\frac{\varepsilon}{k_{gas}} + \frac{1 - \varepsilon}{k_{solid}} \right)^{-1} \quad (3-15)$$

where ε is the membrane porosity; k_{gas} and k_{solid} are the thermal conductivities of the water vapour/air gas mixture and solid polymer, respectively [25]:

$$k_{gas} = 1.5 \times 10^{-3} \sqrt{T} \quad (3-16)$$

$$k_{solid} = 4.86 \times 10^{-4} T + 0.253 \quad (3-17)$$

h_v is the vapour heat transfer coefficient:

$$h_v = \frac{J_p \Delta H_v}{T_{int,f} - T_{int,p}} \quad (3-18)$$

where ΔH_v is the latent heat of vaporisation. All solution properties were obtained from Aspen Plus software using the Elec-NRTL thermodynamic model which is suitable highly-concentrated electrolyte solutions [26].

By assuming an empirical power law relationship between the nucleation rate and supersaturation at induction, Sangwal [23] characterised the nucleation rate, B_n , using the nucleation constant, k , and nucleation order, m , as follows:

$$B_n = k(\ln S)^m \quad (3-19)$$

It can be assumed that the nucleation rate is equal to the supersaturation rate (R') at the metastable limit (the onset of nucleation) [13, 23]:

$$R' = \frac{d(\Delta C_{int})}{dt}, \quad \Delta C = C_{int} - C_{int}^* \quad (3-20)$$

where R' is defined as the change in interfacial supersaturation (ΔC_{int}) over time (t). In a study by Jiang et al. [13], R' was equated to the concentrating rate ($\frac{dC}{dt}$). In MDC however, the interfacial supersaturation rate differs from the concentrating rate due to temperature polarisation which can change C_{int}^* over time. As such, a supersaturation rate was applied in this work in accordance with CNT [23]. Substitution of R' into Eq. 3-20 and linearising yields:

$$\ln(R') = m[\ln(\ln S_{int})] + \ln(k) \quad (3-21)$$

Hence, a plot of $\ln(R')$ versus $\ln(\ln S_{int})$ provides a linear trend, from which the nucleation constants k and m can be derived.

The primary nucleation mechanism is dependent on whether a reduction in the activation energy barrier required for nucleation in the system can be achieved. For a homogeneous nucleation mechanism, the critical Gibbs free energy required for nucleation (ΔG^*) is [3, 27]:

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma^3 v^2}{(k_B T)^2 \ln^2 S} \quad (3-22)$$

At a constant temperature, this energy barrier is reduced by increasing the supersaturation level of the system. The energy barrier can also be reduced by the introduction of a foreign substrate (such as the membrane surface) which would decrease the effective interfacial energy such that heterogeneous nucleation takes place at a lower activation energy [3]:

$$\Delta G^*(\gamma_{eff}) < \Delta G^*(\gamma) = \Delta G_{het}^* < \Delta G_{hom}^* \quad (3-23)$$

where γ_{eff} is the effective interfacial energy and ΔG_{het}^* and ΔG_{hom}^* are the critical energy barriers for heterogeneous and homogeneous nucleation, respectively. By considering that the induction time is inversely proportional to the nucleation rate, the primary nucleation mechanism can be determined from induction time measurements. Hence, by substituting into Eq. 3-4 and linearising:

$$\ln(t_{ind}) = -\ln A + \frac{B}{\ln^2 S_{int}} \quad (3-24)$$

A plot of $\ln(t_{ind})$ against $\ln^{-2} S_{int}$ therefore yields a straight line with a gradient of B . From Eq. 3-5 it can be deduced that at constant temperature, lower gradients, i.e., B values, show a tendency towards heterogeneous nucleation by reducing γ [3, 27, 28].

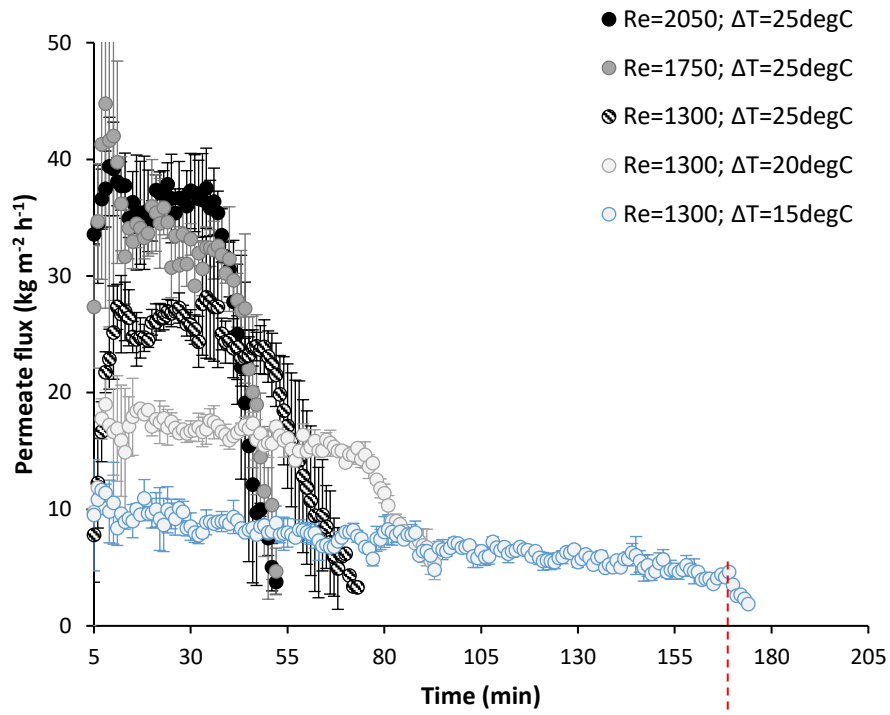
3.3 Results and Discussion

3.3.1 Reynolds number determines flux and the onset of nucleation

Solute convection toward the membrane surface in direct contact MDC is a balance between the vapour pressure gradient fixed by the transmembrane temperature difference (ΔT), and the boundary layer characteristics prescribed by the hydrodynamic conditions [29, 30]. Since permeate flux is an indication of the rate of solute convection [19], the effects of ΔT and Re on permeate flux were independently examined (Figure 3.1a). Permeate flux increased from 7.0 to 23.4 $\text{kg m}^{-2} \text{h}^{-1}$ as ΔT was raised from 15 to 25°C (Re 1300). Similarly, an increase in Re from 1300 to 2050 at a fixed ΔT (25°C shown here to illustrate), yielded an enhancement in permeate flux from 23.4 to 37.3 $\text{kg m}^{-2} \text{h}^{-1}$. While increasing ΔT enhances the vapour-pressure driving force [30], higher Re promotes boundary-layer mixing thereby improving heat and mass transfer conditions [29]. Hence, both variables increase the rate of solute transport to the membrane interface.

For each condition, bulk nucleation was demonstrated by an increase in turbidity (Figure 3.1b). Bulk nucleation was observed to occur more quickly at higher ΔT . The onset of the turbidity peak was noted at 98, 65 and 45 minutes for 15, 20 and 25°C respectively. An increase in Re at a fixed ΔT of 25°C also decreased the time at which bulk nucleation was observed, recording 45, 37 and 31 minutes for Re 's of 1300, 1750 and 2050 respectively. The onset of a rapid flux decline, which authors previously used to indirectly infer nucleation, showed a lag time of 72 minutes relative to the turbidity peak (red dashed line: Re 1300; ΔT 15°C) [15]. This emphasises how earlier methodologies do not allow for the direct detection of induction time as suggested by Horseman et al. [2] and therefore cannot be used to determine nucleation kinetics within MDC.

(a)



(b)

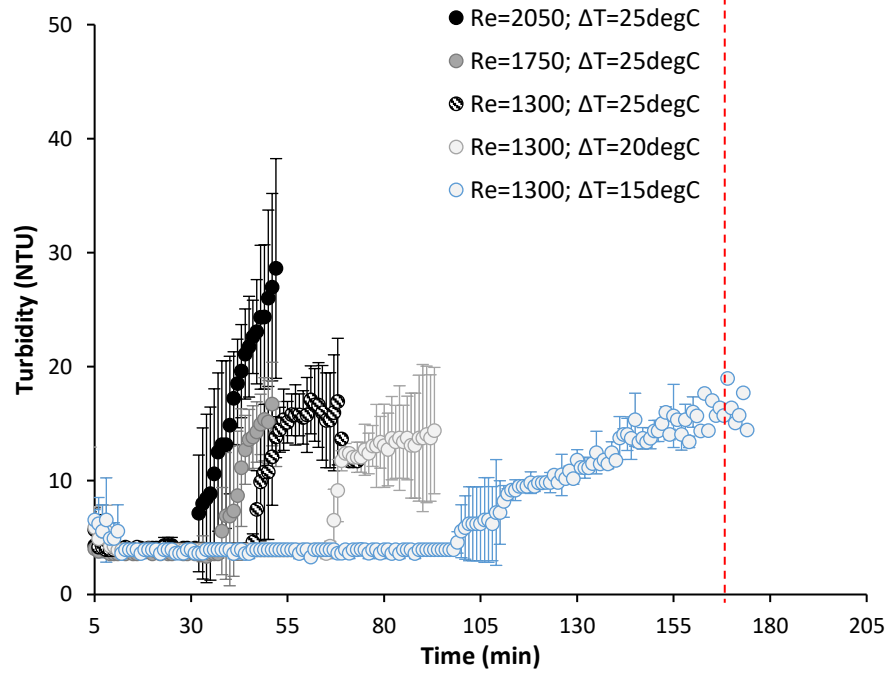


Figure 3.1. Illustration of how temperature difference (ΔT 15–25°C) and Reynolds number (Re 1300–2050) alter the water vapour flux (a), and the onset of bulk nucleation, which is identified with turbidimetry (b). Dotted line indicates onset of bulk nucleation based on the conventional approach of using the flux inflection point to infer induction. Error bars indicate standard deviation of at least three replicates.

3.3.2 Reynolds number determines the kinetics of nucleation and growth

The interfacial supersaturation rate (R') provides an analogy to the nucleation rate [23], while the interfacial supersaturation level gives a measure of the metastable zone width (MSZW) at induction [13] (Figure 3.2). A power-law dependency between R' and MSZW (S_{int}) was determined for each ΔT when Re was increased. This was characterised by a linear relationship whose gradient describes the nucleation order (Eq. 3-21). Since R' is governed by the rate of solvent removal, higher Re values facilitated the improvements in R' by increasing the permeate flux (Figure 3.1a) [3, 4]. At a ΔT of 15°C, a low nucleation order (<5 [31]) was observed ($m = 1.17 < 5$ (dimensionless)) indicating strong diffusive interactions between the solute (NaCl) and solvent (water) which promoted the aggregation and growth of nuclei near the membrane interface. These interactions were facilitated by the high interfacial NaCl concentration, which reduced the distance between the solute molecules and is expected to favour cluster formation [23, 31]. While a similar response was identified for ΔT of 20 and 25°C, higher nucleation orders of 1.89 and 2.03 were observed respectively [23, 31].

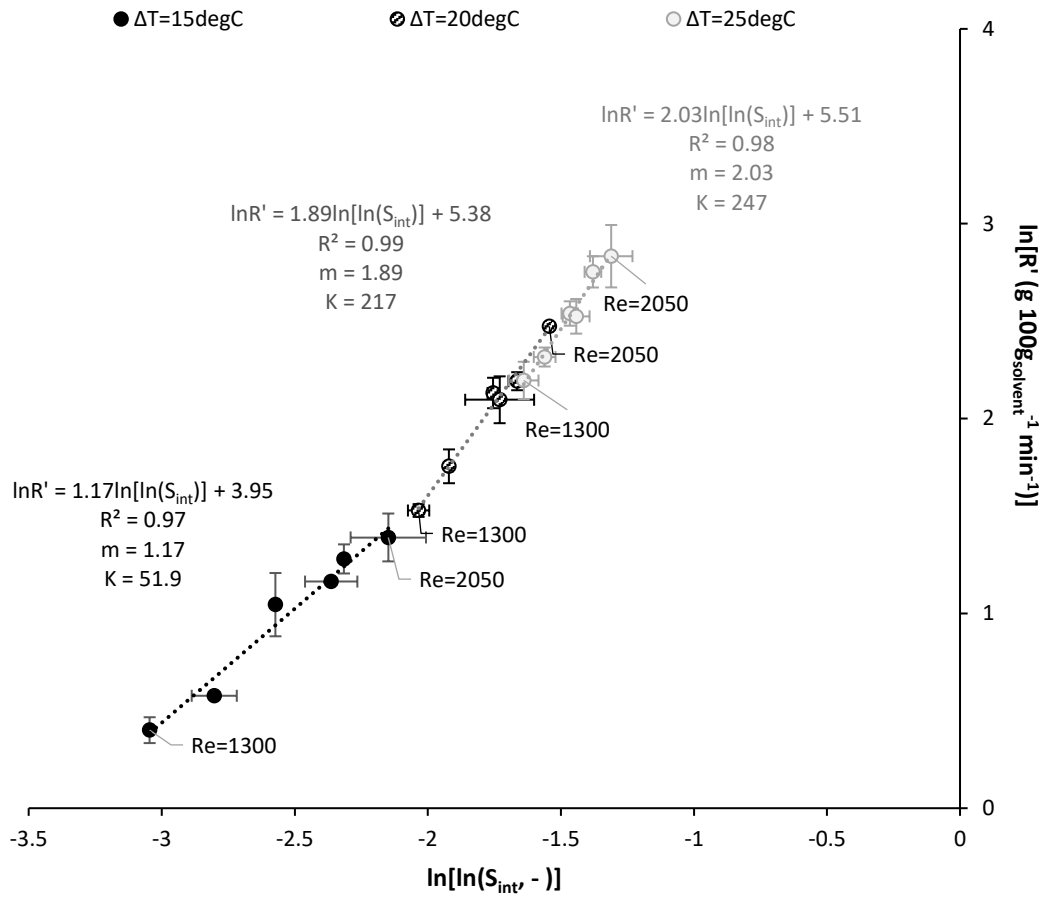


Figure 3.2. Characterisation of nucleation kinetics based on bulk nucleation using the CNT-based power-law relationship proposed by Sangwal [23]. The relationship between interfacial supersaturation rate (R') and metastable zone width (MSZW, $\ln(S_{int})$) enables determination of the apparent nucleation order (m) and nucleation constant (K) for the system. Experimental conditions: ΔT 15–25°C, Re 1300–2050, feed temperature 60°C. Error bars indicate standard deviation of at least three replicates.

Induction time is the time interval between reaching saturation and the time at which nucleation occurs, indicating the metastability of a solution [32]. As Re was increased, a higher S_{int} was achieved at a shorter induction time (Figure 3.3). This inverse relationship between induction time and supersaturation conforms to nucleation theory since higher supersaturation levels increase the likelihood of nucleation [28, 32]. As such, Re reduces the induction time by increasing the rate of solute transport to the interface, thereby increasing the S_{int} . The gradient of the slope represents the relative interfacial energy which is the main contributor to

the nucleation barrier [27]. Gradients of 0.08, 0.34 and 0.50 (dimensionless, Eq. 3-23) were recorded for ΔT of 15, 20 and 25°C, respectively. Crystallisation systems are typically characterised by the transition between two discrete regions of metastability within the metastable zone; an initial region of low supersaturation for which primary nucleation is expected to proceed via a heterogeneous mechanism, and a second highly supersaturated region where primary homogeneous nucleation is dominant [3, 15, 27, 28, 33]. In this study, the shallow gradient for ΔT 15°C corresponds to the lower S_{int} region which indicates that lower activation energies were required for primary heterogeneous nucleation to occur, whereas for ΔT 20 and 25°C, enhanced S_{int} increased the likelihood of primary nucleation proceeding via a homogeneous pathway [28].

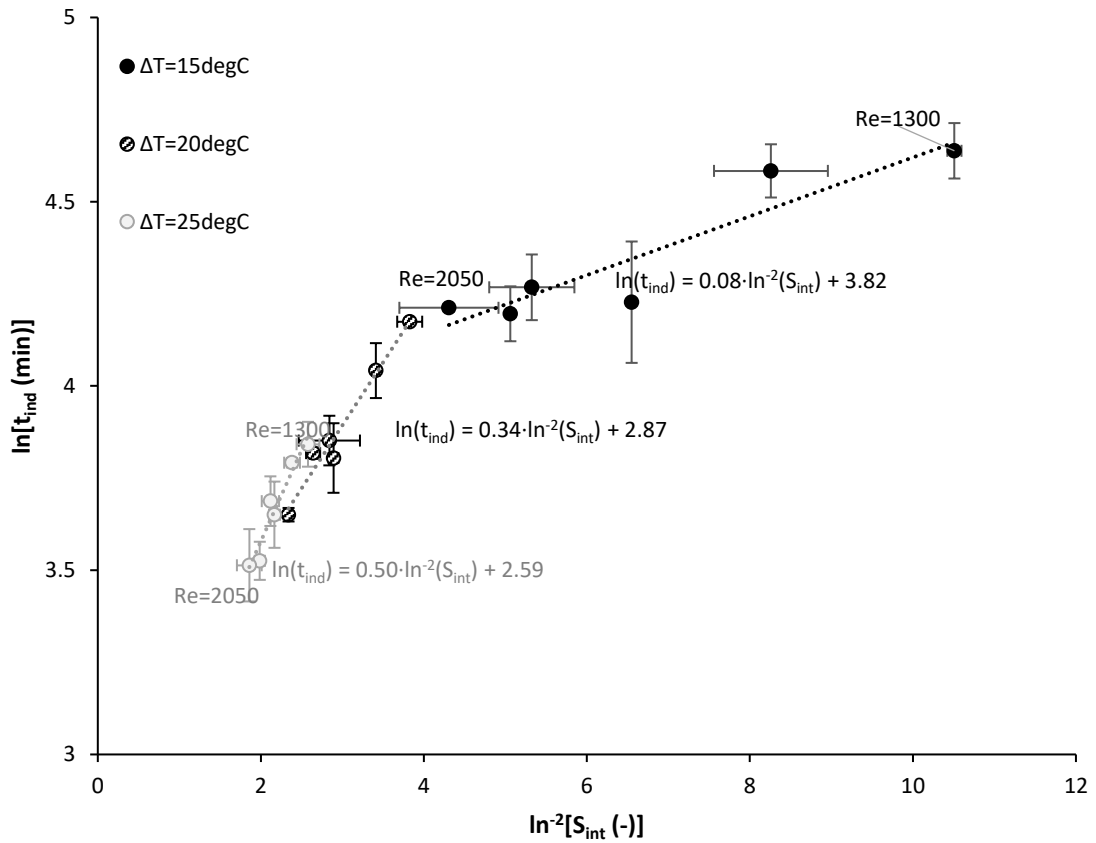


Figure 3.3. Evaluation of primary nucleation mechanism(s) for bulk crystallisation. The relationship between induction time and metastable zone width (MSZW, $\ln(S_{int})$) enables estimation of the activation energy required for nucleation. The steeper gradient established for at ΔT 20 and 25°C typically indicates homogeneous primary nucleation,

whereas the curve established at ΔT 15°C indicates a heterogeneous primary nucleation mechanism similarly to conventional crystallisation literature [3, 15, 27, 28, 33]. Experimental conditions: ΔT 15-25°C, Re 1300-2050, feed temperature 60°C. Error bars indicate standard deviation of at least three replicates.

Distinctions in crystal morphology were observed when exposed to different hydrodynamic conditions, alluding to distinct crystal growth mechanisms (Figure 3.4). Crystals formed at Re 1300 (ΔT 25°C) comprised of cubic crystals, many of which contained a hollow within which a stepped surface structure was observed (Figure 3.4a). This form is referred to as a hollow or skeletal, cubic hopper crystal [34, 35]. The hopper cube morphology occurs in conditions of relatively low supersaturation, which can propagate a heterogeneous distribution of supersaturation at the crystal faces [35, 36]. Consequently, higher supersaturation levels occur at the edges and corners compared to the crystal faces due to the '*Berg effect*' [34]. Hence crystal growth proliferates preferentially at the edges and corners, resulting in the formation of hollows [34, 35]. Aquilano et al. [37] observed that an increase in supersaturation rate transitioned crystal morphology from cubic crystals to the co-existence of octahedral and cubic forms. The onset of the octahedral form was observed in this study for Re 2050 (ΔT 25°C) by the loss of faces around the edges and corners of the crystal, which can be accounted for by the kinetic competition between cubic and octahedral forms (Figure 3.4b). Development of the hollow hopper structure was also constrained at Re 2050. This can be explained by the increased mixing which promotes solute diffusion by forced convection sufficient to overcome diffusion-controlled growth [38]. Increasing supersaturation rate through Re is therefore shown to transition both the morphology and quality of the crystal product, which can be of critical importance for downstream application.

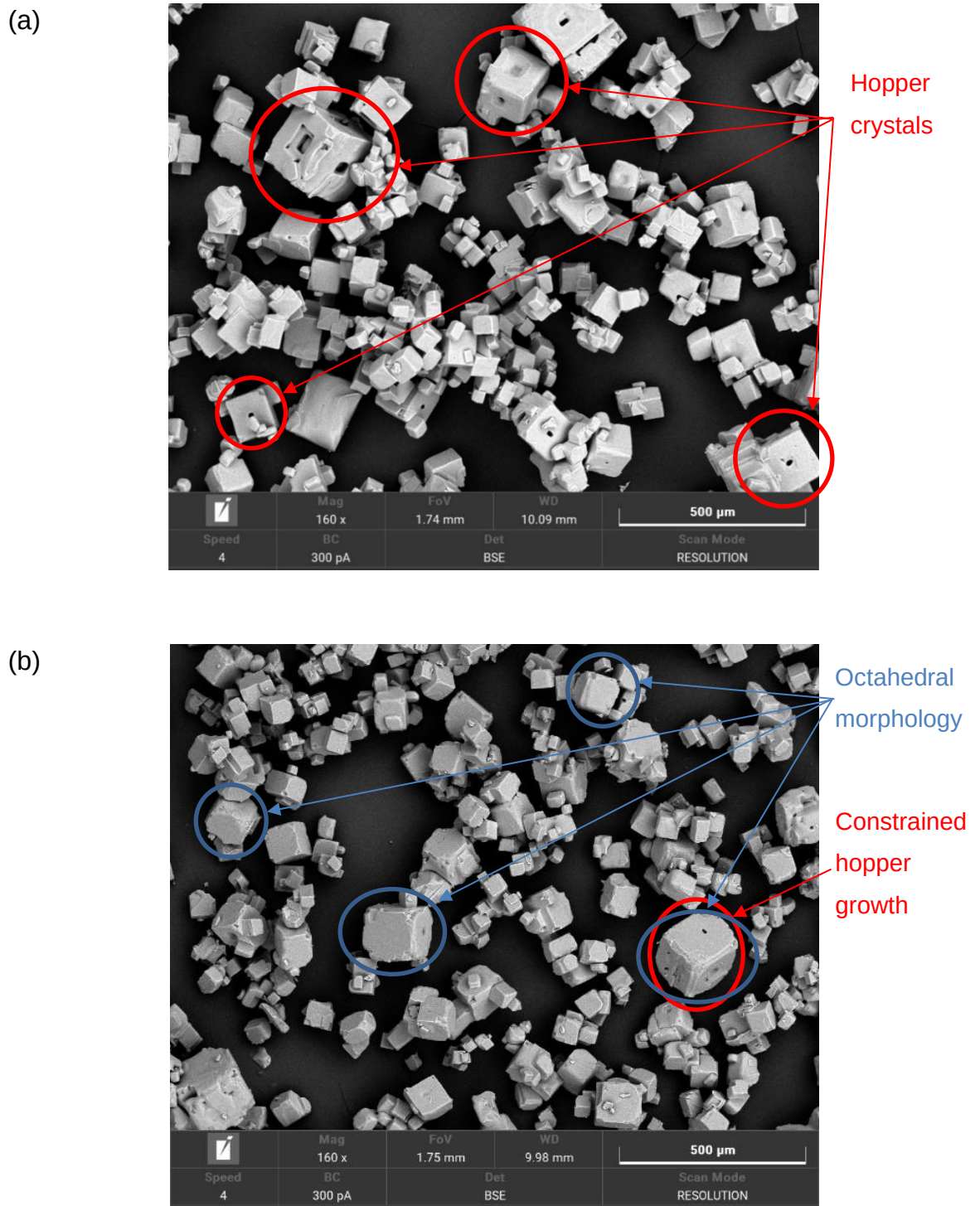


Figure 3.4. High-resolution scanning electron microscopy (SEM) images of crystals collected 10 minutes after onset of bulk nucleation: (a) Re 1300; and (b) Re 2050. Experimental conditions: ΔT 25°C, feed temperature 60°C.

3.3.3 Comparison of surface and bulk crystallisation kinetics

Membrane scaling (per unit surface area) was characterised at the time of bulk nucleation from across a broad range of Re 's for each ΔT studied (Figure 3.5 and Appendix C). At ΔT 15°C, negligible scaling was observed at the onset of bulk induction, despite the heterogeneous nucleation mechanism (Figure 3.3). Heterogeneous nucleation implies that the membrane behaved as a foreign substrate to lower the activation energy requirement for nucleation [3]. However, this would not provide sufficient explanation as to why crystallisation propagated in the bulk solution rather than on the membrane surface. For calcium carbonate crystallisation, Dou et al. [39] observed that enhanced diffusion rates lowered the critical size of stable nuclei and caused an exponential increase in the nucleation rate. While these effects are usually associated with supersaturation, parallels can be drawn based on both diffusion and supersaturation stimulating molecular collisions [39,40]. We therefore propose that bulk nucleation is primarily mediated from within the interfacial boundary layer, which has a greater fluid velocity (and increased diffusion) compared to the interfacial velocity of zero, as per the no-slip boundary condition [2, 41]. In addition, since the diffusion coefficient increases with reduced supersaturation [22], the lower supersaturation levels associated with ΔT 15°C (Figure 3.2) resulted in enhanced boundary-layer diffusion rates compared to ΔT 20°C and 25°C. This suggestion of boundary-layer mediated bulk nucleation is further supported by the strong correlation between bulk induction time and the interfacial MSZW, which is fixed by the physical characteristics within the boundary layer (Figure 3.3). Hence, the reduced activation energy commonly associated with heterogeneous nucleation can be attributed to pronounced solute diffusion decreasing the supersaturation level required for nucleation.

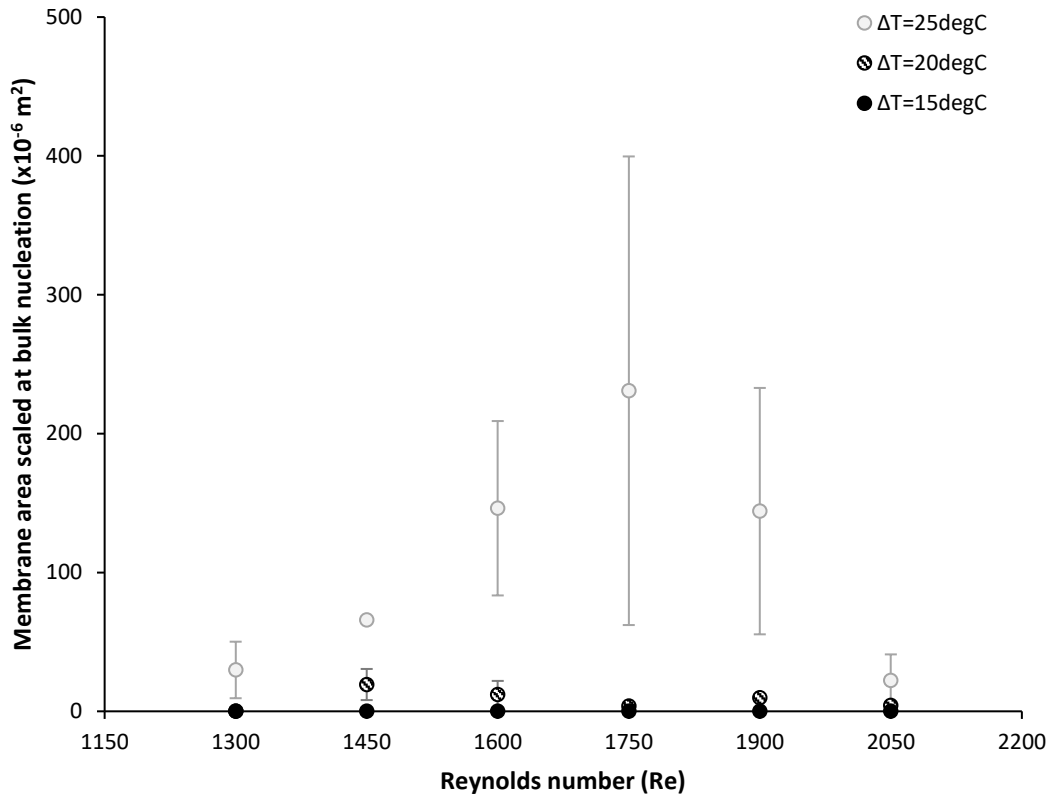


Figure 3.5. Extent of scaling at the onset of bulk nucleation as determined by non-invasive digital microscopy. Experimental conditions: ΔT 15-25°C, Re 1300-2050, feed temperature 60°C. Error bars indicate standard deviation of at least two replicates.

While minor scaling was observed at ΔT 20°C within the Re range 1450-1900, comparatively greater scaling was observed at each Re for ΔT 25°C. This may be explained by an increase in the supersaturation rate following an increase in ΔT , where the increased flux improves supersaturation at induction (Figures 3.1 and 3.2). The increased heat and mass transfer imposed by higher fluxes, and the lower permeate temperature used to fix ΔT to 25°C, also reduced the solubility constant due to an increase in temperature polarisation, which can raise the probability for localised nucleation of scale despite the relatively flat solubility-temperature dependency of NaCl [30]. At the time of bulk induction, the scaled membrane area was $30 \times 10^{-6} \text{ m}^2$ at Re 1300, rising at a maximum of $231 \times 10^{-6} \text{ m}^2$ at Re 1750. A further increase in Re to 2050, considerably reduced membrane scaling at induction to $22 \times 10^{-6} \text{ m}^2$. This convex response to scale formation

following an increase in Re contrasts with the predictions of Warsinger et al. [15], who postulated that an increase in Re may reduce the likelihood of scaling by lowering the solute residence time at the membrane, and highlights that the boundary-layer characteristics controlled by Re are complex due to simultaneous heat and mass transfer processes occurring in the dynamic interfacial boundary region.

The nucleation and growth of scale is presumed to follow classical nucleation theory (CNT) [13, 15]. Accordingly, the nucleation kinetics of scaling were characterised at different Re and compared to those of bulk nucleation at an equivalent ΔT of 25°C (Figure 3.6). A weak linear correlation between supersaturation rate and supersaturation was evidenced when analysing scaling kinetics based on the power-law relationship proposed by Sangwal [23]. However, the nucleation rate (an analogy to $\ln R'$ at the onset of scaling) is considerably higher for scaling. This is supported by the reduced nucleation order, which implies greater solute-solvent interactions at the onset of scaling which can increase nucleation rate [23, 31]. Whereas nucleation rate ($\ln R'$) increased proportionally for bulk nucleation with an increase in Re , the same proportional relationship between nucleation rate and Re did not extend to scaling.

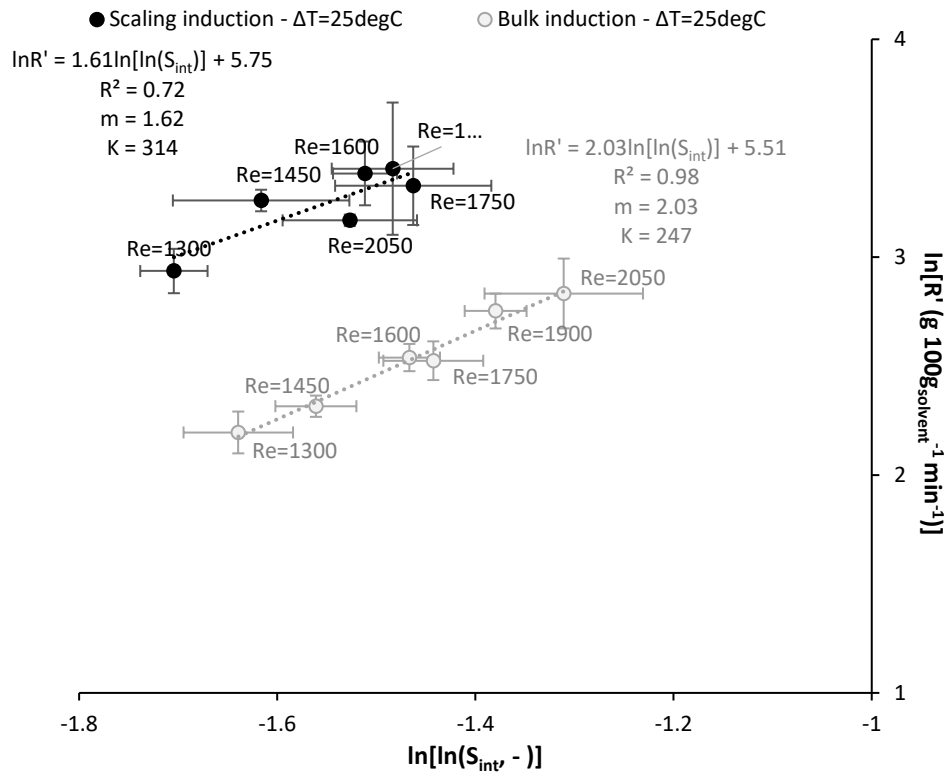


Figure 3.6. Characterisation of nucleation kinetics based on scaling using the CNT-based power-law relationship proposed by Sangwal [23]. The relationship between interfacial supersaturation rate (R') and metastable zone width (MSZW, $\ln(S_{int})$) enables determination of the apparent nucleation order (m) and nucleation constant (K) for the system. Bulk nucleation data is provided for comparison. Experimental conditions: ΔT 25°C , Re 1300-2050, feed temperature 60°C . Error bars indicate standard deviation of at least two replicates.

This is supported by characterisation of the metastable zone width (Figure 3.7). For bulk nucleation, the maximum Re trialled (Re 2050) achieved the highest supersaturation at the shortest induction time in accordance with CNT [28]. In contrast, while scaling was greatest within the most supersaturated conditions (Re 1750), the extent of supersaturation did not inform the time to induction. Consequently, whereas the kinetics of bulk nucleation can be well described by CNT, the mechanism of scale formation is seemingly more complex. This suggests that the mechanism for scale formation is distinct from that of bulk nucleation when the interfacial conditions that determine supersaturation are established by regulating Re .

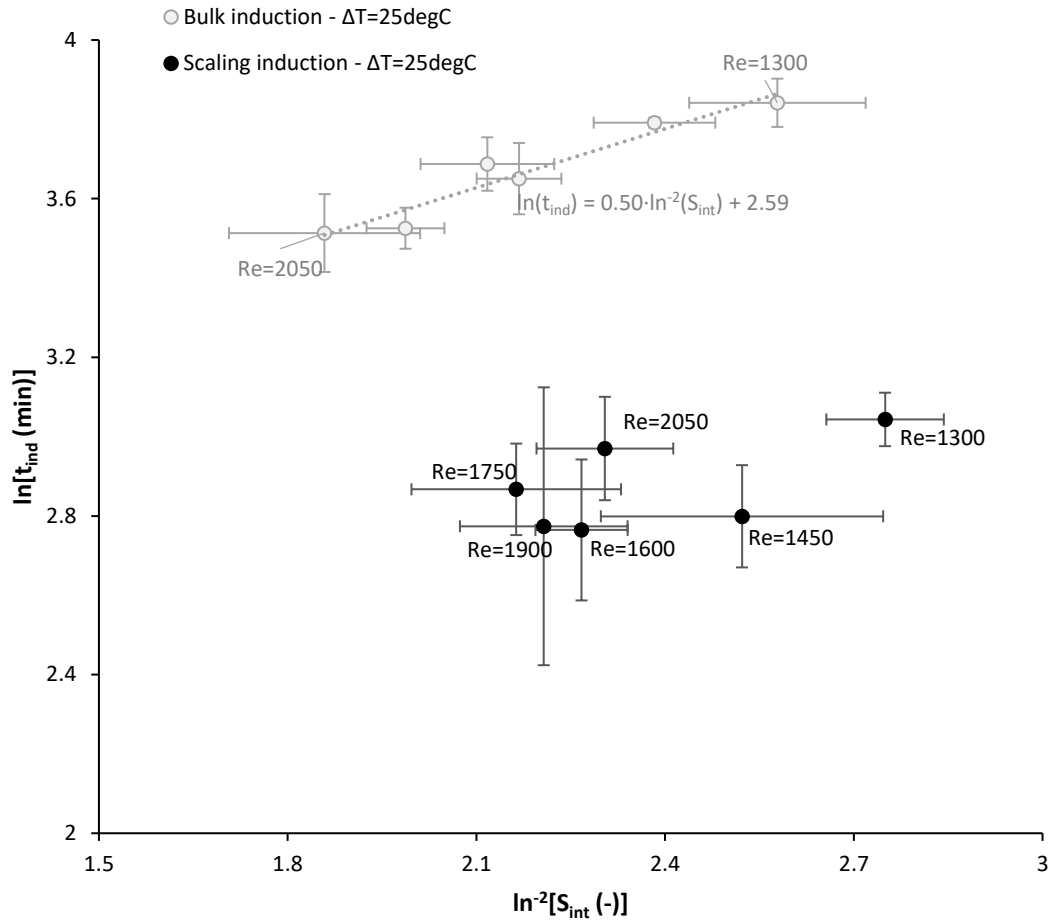


Figure 3.7. Evaluation of primary nucleation mechanism(s) for scaling. The relationship between induction time and metastable zone width (MSZW, $\ln(S_{\text{int}})$) is more difficult to discern for scaling. Bulk nucleation data is provided for comparison. Experimental conditions: ΔT 25°C, Re 1300-2050, feed temperature 60°C. Error bars indicate standard deviation of at least two replicates.

Microscopic examination of membrane scaling emphasised distinction in the crystal growth mechanism for adhesive growth (scaling) (Figure 3.8). The dendritic (branched) scaling morphology is distinct from the growth of singular cubic hopper crystals observed in the bulk (Figure 3.4). This dendritic interconnected hopper growth profile is characteristic of crystal growth within highly-supersaturated and confined homogeneous solutions, similar to the stagnant interfacial region established in MDC [42]. Highly supersaturated regions shift crystal growth from diffusion limited to surface-integration limited,

which encourages creation of surface area as interconnected cubes formed by secondary nucleation from the central nucleus [42]. The polyhedral growth evidenced at *Re* 1300 is consistent with the findings of Desarnaud et al. [42] and Sarig and Tartakovsky [36] who noted an inversely proportional relationship between the size of the cubes in the branches and the initial supersaturation at which they are formed. Consequently, the interconnected cubes comprising the branches were much smaller in size for *Re* 2050, resulting in a more layered, vicinal surface and enhanced branching (more twigs) which is characteristic of higher supersaturation levels coincident with these conditions [36]. Several authors have proposed a two-step shear dependent mechanism in which membrane surface nucleation dominates and is followed by the dislocation of crystals from the membrane into the bulk solution once the shear stress imposed by crossflow is sufficient to disrupt the intermolecular and frictional forces of adhesion [3, 5, 8]. In this study, direct evidence for discrete regions of growth is provided by contrasting crystal morphologies that infer the growth mechanisms for scaling and bulk crystallisation to be seemingly distinct.

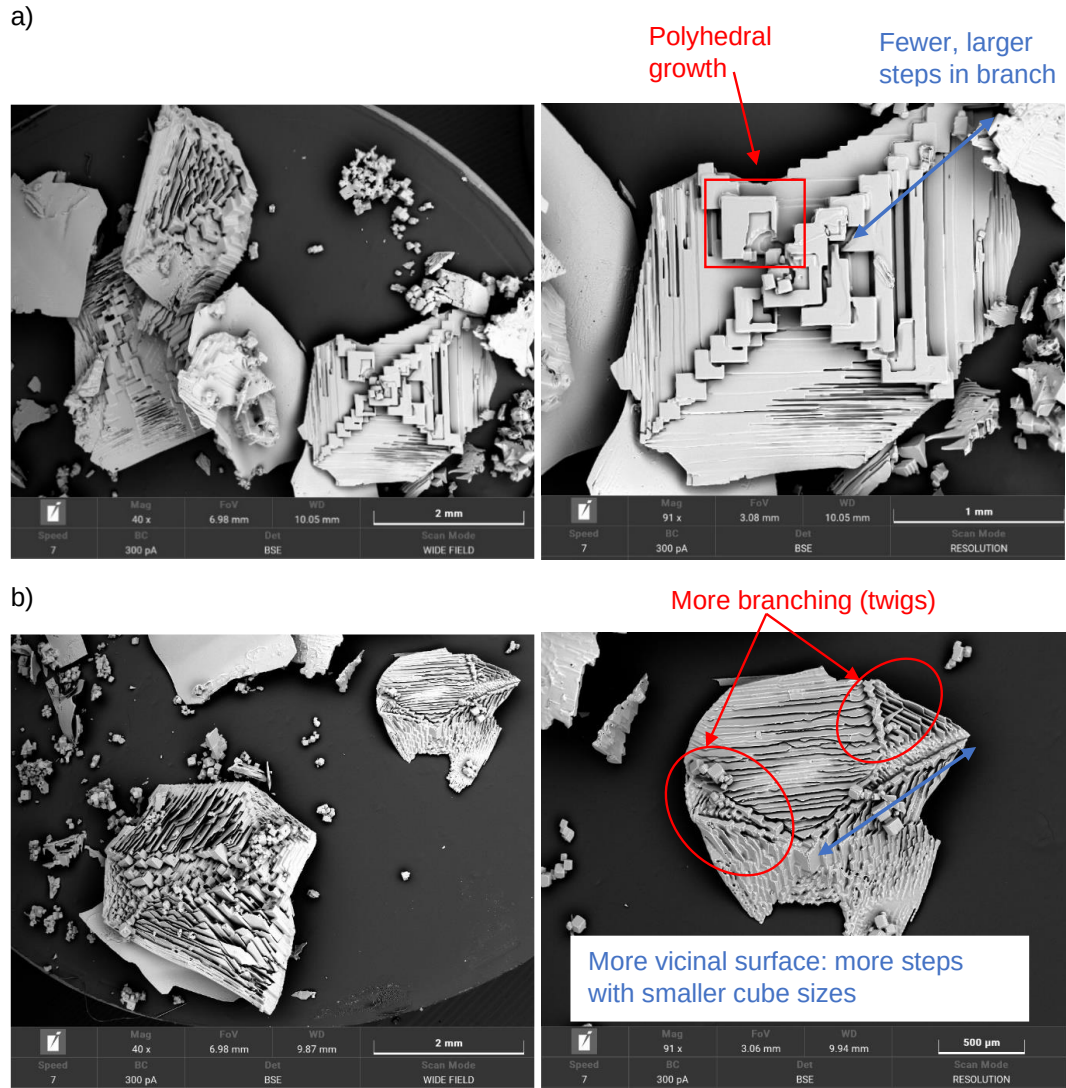


Figure 3.8. High-resolution scanning electron microscopy (SEM) images of scaling formed at the membrane: (a) Re 1300; and (b) Re 2050. Experimental conditions: ΔT 25°C, feed temperature 60°C.

3.3.4 Relating scaling to boundary-layer phenomena using solute mass transport

To determine how boundary layer properties may initiate scale formation, an accurate characterisation of the interfacial solute concentration is required, in addition to defining the solute concentration dependent parameters such as the interfacial diffusion coefficient (D_{int}) [19]. The concentration polarisation coefficient (CPC) is a measure of the rate of solute convection to the interface relative to the diffusive solute back flux from the interface to the bulk solution [43].

The CPC therefore represents the solute balance facilitated within the boundary layer, for which properties (boundary-layer thickness, concentration and interfacial diffusion coefficient, D_{int}) will change as Re is adjusted. At lower Re , a thicker boundary layer is formed that is characterised by a relatively dilute solute concentration (Figure 3.9).

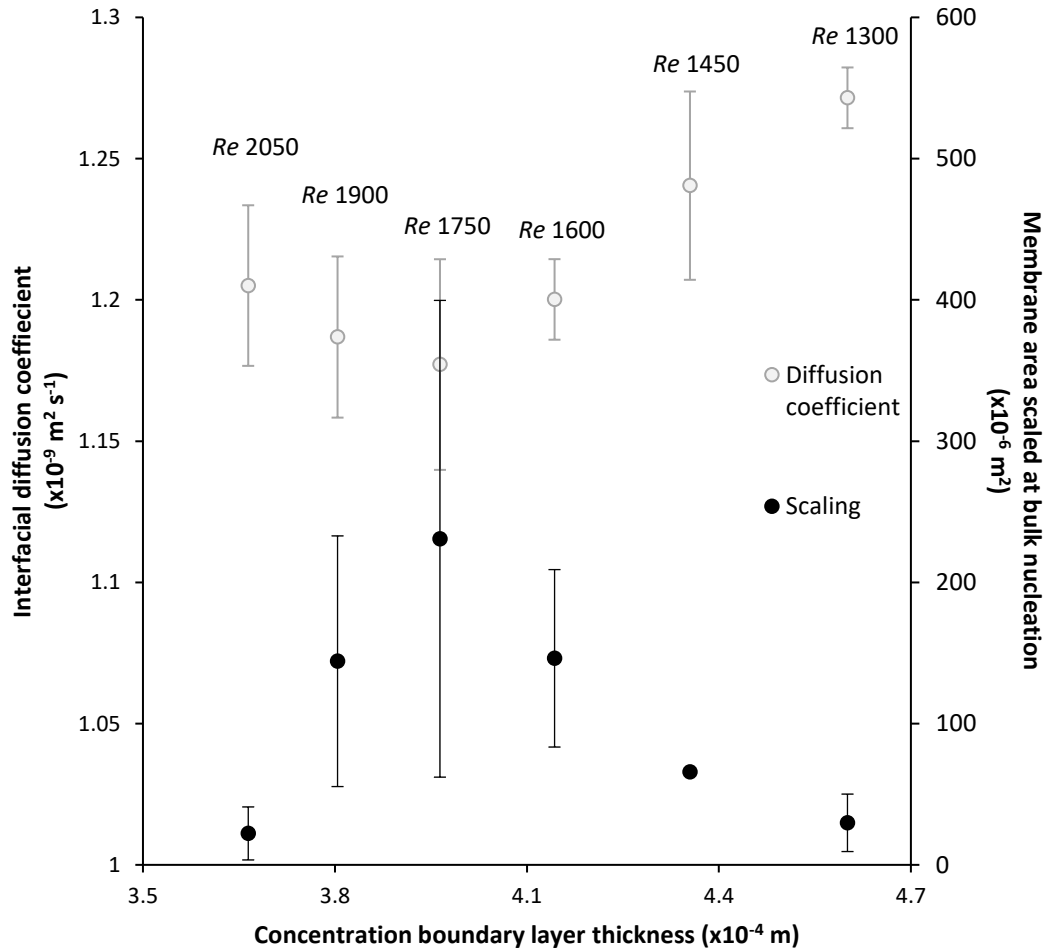


Figure 3.9. Illustration of how the interfacial diffusion coefficient is affected by mass and heat transfer phenomena, which has a key role in defining solute back transport within the boundary layer. Scaling rate data is included for comparison, and to illustrate an analogous criticality for scaling rate when the interfacial diffusion coefficient approaches a minimum. Experimental conditions: ΔT 25°C, feed temperature 60°C, Re 1300-2050. Error bars indicate standard deviation of at least two replicates.

However, as Re increases, a thinner boundary layer is established which enhances the interfacial solute concentration through improved mass and heat transfer, subsequently increasing concentration polarisation (Figure 3.10a). The increased local solute concentration reduced D_{int} to a minimum at Re 1750, corresponding to the region where scaling was most prevalent. At higher Re 's (>1750), the thinner boundary corresponded to a reduction in scaling. As the velocity within the boundary layer tends toward zero, mass transport becomes dominated by natural diffusion, and as such, D_{int} primarily regulates the back flux of material to the bulk solution (Figure 3.9). This reduction in scaling can therefore be explained by Fick's First Law of mass transport:

$$J_{solute} = -D \frac{dC}{dx} \quad (3-25)$$

where J_{solute} is the diffusional flux of solute from the interface to the bulk solution and $\frac{dC}{dx}$ is the concentration gradient which increases as the boundary-layer thickness, dx , decreases. The thinner boundary layer improved the diffusion of solute away from the membrane surface by enhancing the concentration gradient. A reduction in the interfacial concentration also contributes to a higher D_{int} [19, 20]. Hence, higher $\frac{dC}{dx}$ and D raise J_{solute} sufficiently to overcome the solute convection instigated by the higher permeate flux, providing an overall reduction in CPC.

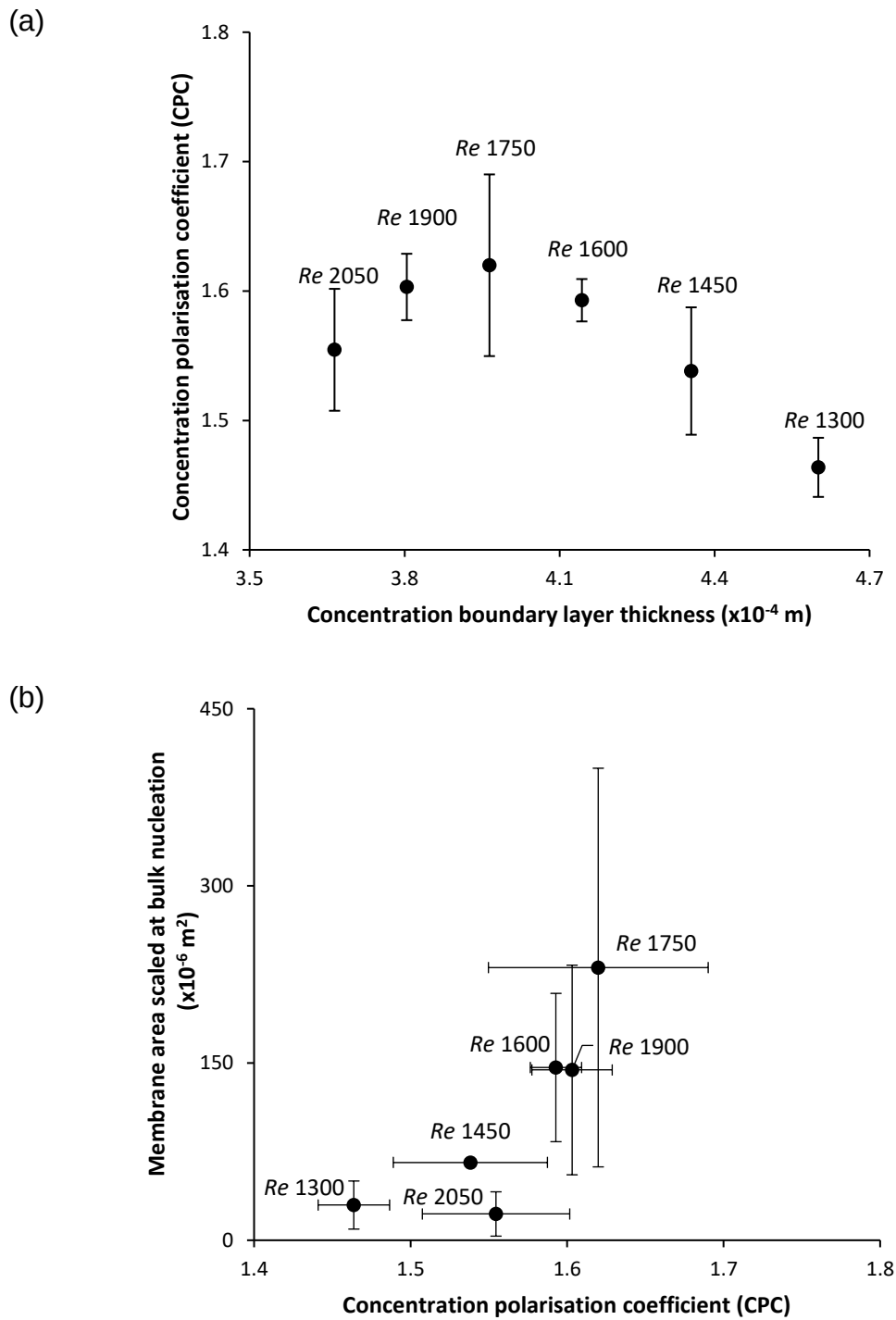


Figure 3.10. Demonstration of how: (a) the thinner concentration boundary layer thickness does not necessarily lead to reduction in the concentration polarisation coefficient (CPC) due to complex mass and heat transfer phenomena; (b) an increase in CPC is likely to increase scaling rate. Experimental conditions: ΔT 25°C, feed temperature 60°C, Re 1300-2050. Error bars indicate standard deviation of at least two replicates.

At the maximum CPC, substantial local supersaturation reduces the activation energy required for nucleation to a minimum, which is synonymous with conditions that classically favour homogeneous primary nucleation (or bulk nucleation) [31]. This was corroborated by kinetic analyses of the MSZW (Figures 3.3 and 3.7) which implies that crystallisation does not require the membrane to initiate nucleation, and yet corresponds to where maximum scaling was observed (Figure 3.10b). The strong corollary observed between the modified CPC and scaling emphasises the importance of adjusting the local fluid physics to provide a more accurate description of local mass transport phenomena. Modification of the supersaturation rate using Re , adjusts the supersaturation level at induction, while also altering related boundary layer characteristics that can change the free energy barrier for nucleation. This explains why scaling does not clearly conform to classical nucleation theory, as the effect on the stagnant region of the boundary layer where scaling predominates is particularly pronounced. Mixing within this region is constrained to natural diffusion, and the diffusion coefficient exhibits a concentration dependency within supersaturated conditions which collectively determine the solute collision frequency (a factor that determines the likelihood for nucleation) [26, 32]. The reduced rate of backtransport at the higher supersaturation level is likely to extend solute residence time, a factor that is thought to be exacerbated by the entrapment of solute within pores or surface crevices (roughness) [3]. Warsinger et al. [15] advised that to minimise scaling, shorter residence times at the interface must be imposed relative to the induction time. Their study considered fluid advection as the primary mechanism for solute transport from the interface to the bulk solution, rather than the axial description in this study which introduces the interrelationship between supersaturation and supersaturation rate that are imposed by Re .

Distinctions in crystal morphology imply that the nucleation of scale and bulk crystals proceed within different positions of the interfacial region. While this hypothesis requires further detailed examination to validate, conditions are identified in which bulk crystals, characterised by classical cubic habit, can be produced without scale formation. Previous literature suggests that the dendritic

hopper growth of NaCl can only occur when $S \geq 1.45$ [42]. This supersaturation level was only achieved at ΔT 25°C and is coincident to where scaling was observed (Figure 3.11). A critical saturation threshold is therefore introduced, below which adhesive dendritic growth is difficult to sustain, that can be used to inform scaling mitigation strategies in favour of the crystal production in the bulk. It is worth noting that a maximum S_{int} of only 1.26 (Re 1750, ΔT 25°C) was obtained using the conventional CPC method, well below the suggested threshold for NaCl dendritic growth [42]. This highlights the importance of the revised-CPC approach for more precise analysis of solute transport and subsequent scaling prediction in MDC. Importantly, two hydrodynamic regions are also exposed which can achieve comparable CPCs but produce distinct crystal habits, emphasising that it is not solely the extent of CPC but rather the boundary-layer conditions that promote CPC which can also inform the mechanism of growth.

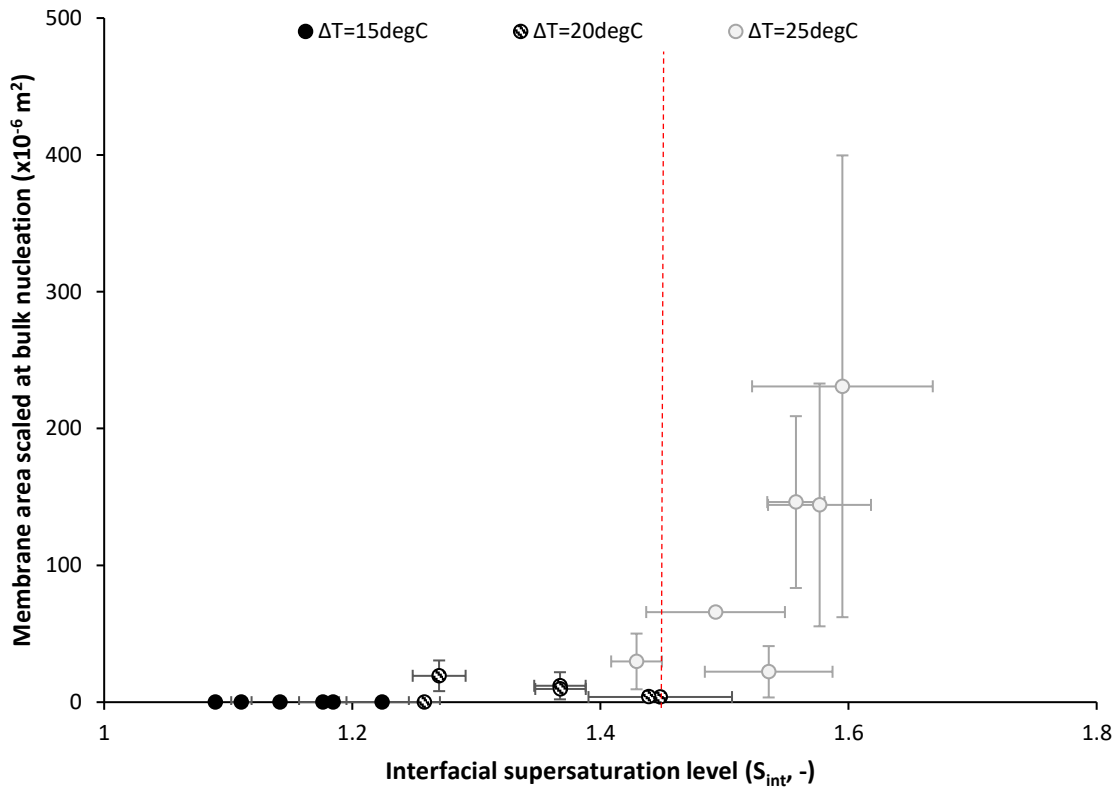


Figure 3.11. A critical supersaturation threshold is indicated beyond which the scaling rate becomes significant (S 1.45, red dashed line). This threshold represents the

transition from the formation of singular cubic NaCl crystals to the growth of hopper crystals characterised by series of interconnected cubes [39]. Error bars indicate standard deviation of at least two replicates.

3.4 Conclusions

In this study, Reynolds number (Re) is demonstrated to directly inform the kinetics of nucleation and crystal growth. This constitutes a considerable advancement to existing literature, which has previously assumed that the primary role of Re is to provide shear-induced backtransport of crystals adhered to the membrane into the bulk solution. Re controlled interfacial supersaturation, which is the driving force for nucleation. The simultaneous increase in mass and heat transfer at higher Re raised the supersaturation rate and shortened induction time. The interfacial conditions correlated favourably to classical nucleation theory to describe bulk crystallisation, which evidences that it is the boundary layer which controls primary nucleation. However, contrary to previous hypotheses, it was shown that conditions in which the lower energy barrier favours heterogeneous primary nucleation, no scaling was observed, leading to the preferential growth of crystals in the bulk solution. The reduction in energy barrier was attributed to enhanced diffusion in the boundary layer rather than the membrane surface decreasing the interfacial energy. It is in conditions that theoretically favour primary homogeneous nucleation where scaling was observed, which does not conform to classical nucleation theory. Characterisation of the concentration polarisation coefficient demonstrated complex interfacial backtransport phenomena to rationalise the onset of scaling above a critical supersaturation threshold. This insight suggests that Re is distinct from other methods used to modify supersaturation rate (e.g. ΔT). Boundary-layer characteristics are identified that can limit scaling and create discrete conditions for growth of crystals with distinctive morphologies, for example through adaptation to diffusion or integration-controlled growth. This was confirmed through microscopic examination of crystal habit, which supports our broader proposition that the mechanisms which underpin the nucleation and growth of scale and bulk crystals are distinct. Significantly, this study provides a quantitative framework to describe how the boundary-layer characteristics set by Re can be exploited to inform

scaling mitigation strategies, and for the controlled nucleation and growth of high value crystalline products, where exploitation of this dimensionless quantity can ensure replication across systems of various configuration and scale, provided fully developed laminar flow is established.

References

- [1] Y. Choi, G. Naidu, L. D. Nghiem, S. Lee, and S. Vigneswaran, "Membrane distillation crystallization for brine mining and zero liquid discharge: Opportunities, challenges, and recent progress," *Environ. Sci. Water Res. Technol.*, vol. 5, pp. 1202–1221, 2019.
- [2] T. Horseman, Y. Yin, K. S. Christie, Z. Wang, T. Tong, and S. Lin, "Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies," *ACS ES&T Eng.*, vol. 1, pp. 117–140, 2021.
- [3] G. Di Profio, E. Curcio, and E. Drioli, "Supersaturation control and heterogeneous nucleation in membrane crystallizers: Facts and perspectives," *Ind. Eng. Chem. Res.*, vol. 49, pp. 11878–11889, 2010.
- [4] C. Charcosset, R. Kieffer, D. Mangin, and F. Puel, "Coupling between membrane processes and crystallization operations," *Ind. Eng. Chem. Res.*, vol. 49, pp. 5489–5495, 2010.
- [5] M. C. Sparenberg, S. Chergaoui, V. Sang Sefidi, and P. Luis, "Crystallization control via membrane distillation-crystallization: A review," *Desalination*, vol. 519, p. 115315, 2022.
- [6] Y. N. Nariyoshi, C. E. Pantoja, M. M. Seckler, Y. N. Nariyoshi, C. E. Pantoja, and M. M. Seckler, "Evaluation of sodium chloride crystallization in membrane distillation crystallization applied to water desalination," *Brazilian J. Chem. Eng.*, vol. 33, pp. 675–690, 2016.
- [7] E. Chabanon, D. Mangin, and C. Charcosset, "Membranes and crystallization processes: State of the art and prospects," *J. Memb. Sci.*, vol. 509, pp. 57–67, 2016.

- [8] X. Jiang et al., "Interface-based crystal particle autoselection via membrane crystallization: From scaling to process control," *AIChE J.*, vol. 65, pp. 723–733, 2019.
- [9] A. Alkhatib, M. A. Ayari, and A. H. Hawari, "Fouling mitigation strategies for different foulants in membrane distillation," *Chem. Eng. Process. - Process Intensif.*, vol. 167, p. 108517, 2021.
- [10] Y. Shin and J. Sohn, "Mechanisms for scale formation in simultaneous membrane distillation crystallization: Effect of flow rate," *J. Ind. Eng. Chem.*, vol. 35, pp. 318–324, 2016.
- [11] D. M. Warsinger et al., "Effect of filtration and particulate fouling in membrane distillation," *Int. Desalin. Assoc.*, pp. 0–14, 2015.
- [12] F. Edwie and T. S. Chung, "Development of simultaneous membrane distillation-crystallization (SMDC) technology for treatment of saturated brine," *Chem. Eng. Sci.*, vol. 98, pp. 160–172, 2013.
- [13] X. Jiang, X. Ruan, W. Xiao, D. Lu, and G. He, "A novel membrane distillation response technology for nucleation detection, metastable zone width measurement and analysis," *Chem. Eng. Sci.*, vol. 134, pp. 671–680, 2015.
- [14] J. Kim, J. Kim, and S. Hong, "Recovery of water and minerals from shale gas produced water by membrane distillation crystallization," *Water Res.*, vol. 129, pp. 447–459, 2018.
- [15] D. M. Warsinger, E. W. Tow, J. Swaminathan, and J. H. Lienhard V, "Theoretical framework for predicting inorganic fouling in membrane distillation and experimental validation with calcium sulfate," *J. Memb. Sci.*, vol. 528, pp. 381–390, 2017.
- [16] A. Borissova, "Driving Force of Crystallization Based on Diffusion in the Boundary and the Integration Layers," *Chem. Eng. Technol.*, vol. 42, pp. 661–668, 2019.
- [17] R. S. Harner, R. J. Ressler, R. L. Briggs, J. E. Hitt, P. A. Larsen, and T. C. Frank, "Use of a fiber-optic turbidity probe to monitor and control commercial-scale unseeded batch crystallizations," *Org. Process Res. Dev.*, vol. 13, pp. 114–124, 2009.

- [18] X. Jiang, D. Lu, W. Xiao, X. Ruan, J. Fang, and G. He, "Membrane assisted cooling crystallization: Process model, nucleation, metastable zone, and crystal size distribution," *AIChE J.*, vol. 62, pp. 829–841, 2016.
- [19] O. R. Lokare and R. D. Vidic, "Impact of Operating Conditions on Measured and Predicted Concentration Polarization in Membrane Distillation," *Environ. Sci. Technol.*, vol. 53, pp. 11869–11876, 2019.
- [20] Y. C. Chang and A. S. Myerson, "The diffusivity of potassium chloride and sodium chloride in concentrated, saturated, and supersaturated aqueous solutions," *AIChE J.*, vol. 31, pp. 890–894, 1985.
- [21] J. A. Rard and D. G. Miller, "The Mutual Diffusion Coefficients of NaCl-H₂O and CaCl₂-H₂O at 25°C from Rayleigh Interferometry," *J. Solution Chem.*, vol. 8, 1979.
- [22] N. E. R. Zimmermann, B. Vorselaars, D. Quigley, and B. Peters, "Nucleation of NaCl from Aqueous Solution: Critical Sizes, Ion-Attachment Kinetics, and Rates," *J. Am. Chem. Soc.*, vol. 137, pp. 13352–13361, 2015.
- [23] K. Sangwal, "A novel self-consistent Nývlt-like equation for metastable zone width determined by the polythermal method," *Cryst. Res. Technol.*, vol. 44, pp. 231–247, 2009.
- [24] S. Wang, M. Feng, H. Du, J. J. Weigand, Y. Zhang, and X. Wang, "Determination of metastable zone width, induction time and primary nucleation kinetics for cooling crystallization of sodium orthovanadate from NaOH solution," *J. Cryst. Growth*, vol. 545, p. 125721, 2020.
- [25] A. Alkhubiri, N. Darwish, and N. Hilal, "Membrane distillation: A comprehensive review," *Desalination*, vol. 287, pp. 2–18, 2012.
- [26] A. Lewis, M. M. Seckler, H. Kramer, and G. van Rosmalen, *Industrial Crystallization*. Cambridge: Cambridge University Press, 2015.
- [27] G. Zeng, H. Li, S. Huang, X. Wang, and J. Chen, "Determination of metastable zone width and the primary nucleation kinetics of sodium sulfate," *Theor. Found. Chem. Eng.*, vol. 49, pp. 869–876, 2015.
- [28] Z. Guo, L. Li, W. Han, J. Li, B. Wang, and Y. Xiao, "Interpretation of the microwave effect on induction time during CaSO₄ primary nucleation by a cluster coagulation model," *J. Cryst. Growth*, vol. 475, pp. 220–231, 2017.

- [29] M. Gryta, "Effectiveness of water desalination by membrane distillation process," *Membranes (Basel)*, vol. 2, pp. 415–429, 2012.
- [30] C. M. Tun et al., "Membrane distillation crystallization of concentrated salts - Flux and crystal formation," *J. Memb. Sci.*, vol. 257, pp. 144–155, 2005.
- [31] C. Devos, T. Van Gerven, and S. Kuhn, "A Review of Experimental Methods for Nucleation Rate Determination in Large-Volume Batch and Microfluidic Crystallization," *Cryst. Growth Des.*, vol. 21, pp. 2541–2565, 2021.
- [32] D. Kashchiev and G. M. Van Rosmalen, "Review: Nucleation in solutions revisited," *Cryst. Res. Technol.*, vol. 38, pp. 555–574, 2003.
- [33] H. Takiyama, "Morphology of NaCl crystals in drowning-out precipitation operation," *Chem. Eng. Res. Des.*, vol. 76, pp. 809–814, 1998.
- [34] I. Sunagawa, "Growth and Morphology of Crystals," *Forma*, vol. 14, pp. 147–166, Jun. 1999.
- [35] D. Pettit and P. Fontana, "Comparison of sodium chloride hopper cubes grown under microgravity and terrestrial conditions," *npj Microgravity*, vol. 5, pp. 1–7, 2019.
- [36] S. Sarig and F. Tartakovsky, "Crystal habit modifiers," *J. Cryst. Growth*, vol. 28, pp. 300–305, 1975.
- [37] D. Aquilano, L. Pastero, M. Bruno, and M. Rubbo, " $\{1\ 0\ 0\}$ and $\{1\ 1\ 1\}$ forms of the NaCl crystals coexisting in growth from pure aqueous solution," *J. Cryst. Growth*, vol. 311, pp. 399–403, 2009.
- [38] W. R. Wilcox, "Transport phenomena in crystal growth from solution," *Prog. Cryst. Growth Charact. Mater.*, vol. 26, pp. 153–194, 1993.
- [39] X. Dou et al., "Collision dependent silver nucleation regulated by chemical diffusion and reaction," *Chem. Eng. Sci.*, vol. 262, p. 117965, 2022.
- [40] X. Dou, H. Huang, and Y. Han, "The role of diffusion in the nucleation of calcium carbonate," *Chinese J. Chem. Eng.*, vol. 43, pp. 275–281, 2022.
- [41] J. Amigo, R. Urtubia, and F. Suárez, "Exploring the interactions between hydrodynamics and fouling in membrane distillation systems – A multiscale approach using CFD," *Desalination*, vol. 444, pp. 63–74, 2018,

- [42] J. Desarnaud, H. Derluyn, J. Carmeliet, D. Bonn, and N. Shahidzadeh, "Hopper Growth of Salt Crystals," *J. Phys. Chem. Lett.*, vol. 9, pp. 2961–2966, 2018.
- [43] Y. Yun, R. Ma, W. Zhang, A. G. Fane, and J. Li, "Direct contact membrane distillation mechanism for high concentration NaCl solutions," *Desalination*, vol. 188, pp. 251–262, 2006.

Appendix B. Determination of interfacial diffusion coefficient

In membrane distillation crystallisation (MDC), the solute back transport through the stagnant boundary layer is diffusive [40]. The rate of this diffusive solute flow is dependent on the diffusion coefficient, which is an important parameter in the calculation of the concentration polarisation coefficient (CPC). To improve the precision of this parameter in the revised-CPC approach, the diffusion coefficient as a function of (temperature independent) molality was derived based on literature data from Chang and Myerson [20] as well as that of Rard and Miller [21] (Figure B1). According to Zimmerman et al. [22], after the observed maximum, the diffusion coefficient is expected to decrease monotonically with further increases in molality. Based on this assumption, a linear trendline was fitted using the four available literature data points of highest molality. The resultant equation was then applied to determine the interfacial diffusion coefficient at experimental molalities above $6 \text{ mol kg}_{\text{water}}^{-1}$.

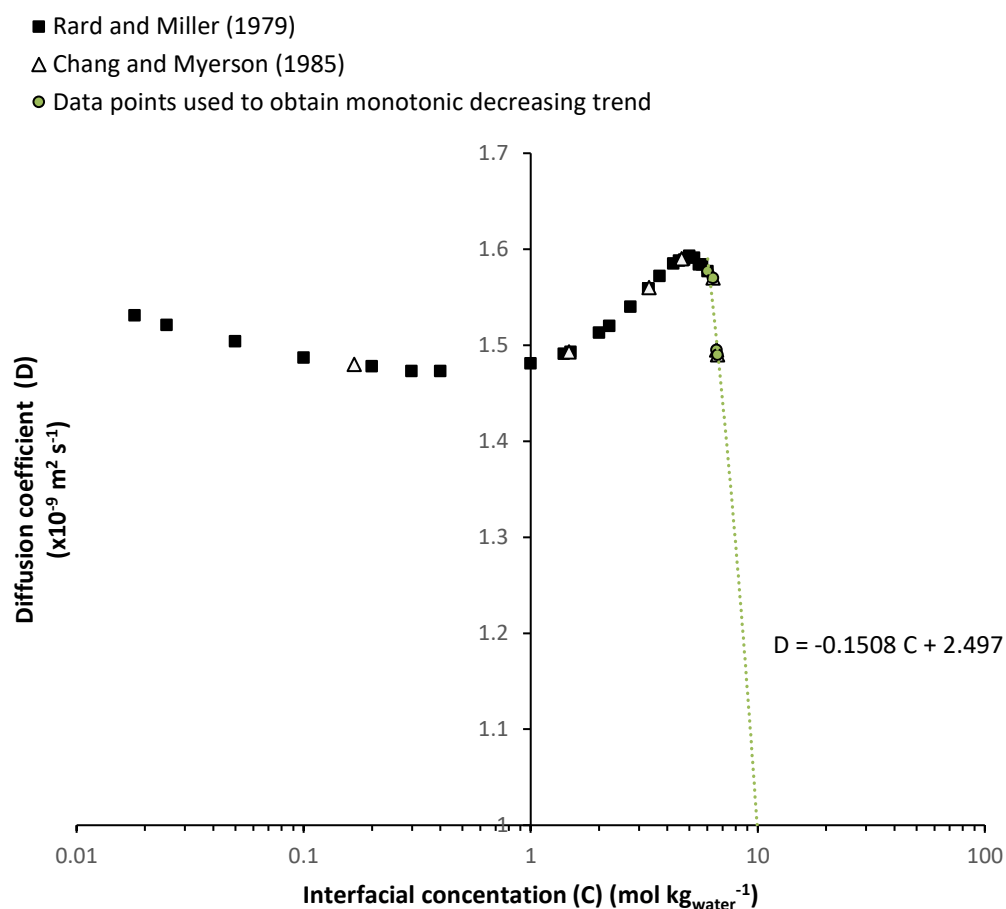
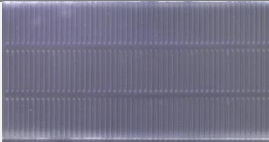
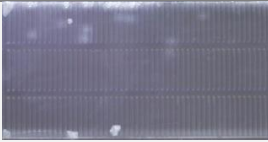
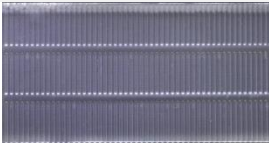
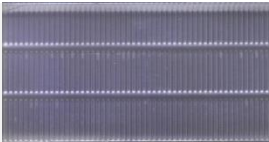
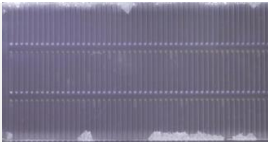
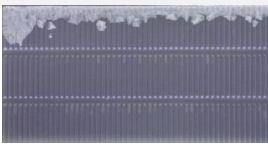


Figure B1. Determination of diffusion coefficient based on interfacial concentration (molality). Figure shows literature data used to derive diffusion coefficients with extrapolation based on assumption of monotonic decrease in molality within supersaturated conditions [22].

Appendix C. Digital microscope images of scaling at bulk induction

To determine the extent of scaling at bulk induction, the membrane surface area covered by crystals was determined by analysing digital microscope images at the onset of bulk nucleation. Examples of the images analysed at each experimental condition (ΔT 15-25°C, Re 1300-2050, feed temperature 60°C) are shown in Table C1, where the greatest surface coverage can be observed at Re 1750 and ΔT 15°C.

Table C1. Examples of digital microscope images taken at the onset of bulk nucleation. Experimental conditions: ΔT 15-25°C, Re 1300-2050 and feed temperature 60°C.

Re	$\Delta T = 15^{\circ}\text{C}$	$\Delta T = 20^{\circ}\text{C}$	$\Delta T = 25^{\circ}\text{C}$
1300			
1450			
1600			
1750			
1900			
2050			

4. The role of mixing on the kinetics of nucleation and crystal growth in membrane crystallisation

The role of mixing on the kinetics of nucleation and crystal growth in membrane crystallisation

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Abstract

While mixing is considered critical in membrane crystallisation, an explicit link between mixing and crystallisation mechanisms has yet to be made. This study therefore used in-line nucleation detection to determine induction time and metastable zone width, as a method to characterise the independent roles of interfacial boundary layer mixing and bulk crystalliser mixing on the kinetics of nucleation and growth in membrane distillation crystallisation. Interfacial boundary layer mixing was investigated by changing Reynolds number (Re 1300-2050) which was shown to shift the primary nucleation rate, principally due to the change in permeate flux, which also set the interfacial supersaturation level (S_{int}) at the onset of bulk nucleation. Consequently, high Re introduced smaller crystal sizes due to higher nucleation rates. At high Re , crystal morphology also showed evidence of dendritic breeding, which suggests that boundary layer mixing can set conditions for secondary nucleation; an effect that dominates crystal growth at high levels of supersaturation. Bulk mixing within the crystalliser did not markedly change bulk or interfacial supersaturation at nucleation (Re_N 1562-18741). However, bulk mixing did reduce induction time by increasing molecular collisions. This is supported by the crystal growth mechanisms observed, where larger crystals were produced at higher crystalliser stirrer speeds due to improved diffusion-controlled growth. This study demonstrates that bulk and interfacial mixing can be collectively used to control crystallisation, by decoupling conditions that determine nucleation and crystal growth. A broader set of kinetic trajectories are therefore achievable than with classical crystallisation approaches, thus evidencing membrane crystallisation to be a powerful platform technology for developing well-controlled crystal growth.

Keywords: *crystal nucleation, crystal growth, secondary nucleation, agglomeration, supersaturation, induction time, metastable zone width (MSZW)*

4.1 Introduction

Crystallisation is an essential separation and purification process, used in the production of chemicals in industries such as pharmaceuticals and microelectronics [1,2]. Sustaining consistent crystal product quality is challenging in existing industrial crystallisation systems [1, 3], as the mixing conditions are often poorly defined, making it difficult to regulate supersaturation. It is the extent (and rate) of supersaturation at induction which determines the kinetics of nucleation and crystal growth. This defines the purity, size and shape of the final crystal product which can be critical for specific applications [4].

Membrane distillation crystallisation (MDC) provides an opportunity for enhanced supersaturation control due to its ability to strictly regulate the rate of vapour transport across a defined membrane surface area [2, 5]. The hydrophobic membrane and highly-concentrated boundary layer that forms adjacent to the membrane surface also contribute to promoting nucleation [2, 3, 5, 6]. As such, MDC has been shown to reduce the induction times of various crystallisation systems. For example, Di Profio et al. [7] showed that the introduction of a microporous membrane significantly reduced the induction time of lysozyme crystallisation compared to conventional crystallisers. Tsai et al. [6] also observed shorter induction times for NaCl membrane crystallisation compared to crystallisation in the bulk solution. These nucleation-promoting benefits of MDC have been attributed to the interactions between the membrane surface and molecules of the solvent and solute which are dependent not only on the membrane properties [3, 6], but also the fluid dynamics of the solution adjacent to the membrane surface [3].

The study of hydrodynamics in membrane distillation (MD) systems has largely focused on scaling inhibition rather than nucleation control. Turbulent conditions at the boundary layer are recommended for the disruption of concentration and temperature polarisation, thereby reducing the likelihood of scaling due to oversaturation at the interface [8, 9]. Warsinger et al. [10] noted that in addition to decreased concentration polarisation, increasing the feed flow rate lowers the residence time of the fluid in the membrane module relative to the scaling induction time, in so doing, reducing the likelihood of scaling. High wall

shear stress, instigated by elevated crossflow velocities, has also been considered beneficial for the detachment of crystals from the membrane surface [11]. However, the improved heat and mass transfer associated with higher feed Reynolds numbers has also been shown to increase the permeate flux [12, 13]. As permeate flux controls the rate of supersaturation in MDC, this is likely to broaden the metastable zone width (MSZW) [14]. The metastable zone defines the operating region for crystallisation because its width at the onset of nucleation determines the rates of nucleation and crystal growth [4, 5]. Hence, the feed Reynolds number (Re) likely plays a crucial role in determining the crystal product characteristics in MDC systems. This was illustrated in the work of Di Profio et al. [15] where glycine crystallisation was inferred to transition from thermodynamically-controlled to kinetically-controlled polymorphs following an increase in permeate flux.

In conventional crystallisers, hydrodynamics are also critical for determining the crystallisation kinetics and crystal product quality [16]. High impeller stirring rates promote nucleation by increasing the likelihood of molecular collisions. This results in a reduced induction time and narrower MSZW [16-19]. Increased bulk mixing also promotes mass transfer around growing crystals and therefore improves the diffusion-controlled crystal growth rate [20, 21]. On the other hand, high agitation rates are also associated with secondary nucleation by attrition which is detrimental to product quality [20, 22-24]. While it has been previously inferred that primary nucleation mainly occurs within the membrane module, with crystal growth controlled in the downstream crystalliser [11], the impact of crystalliser mixing conditions on the crystallisation kinetics have yet to be investigated. Furthermore, crystallisation phenomena such as secondary nucleation mechanisms and agglomeration are dependent on both the level of supersaturation and turbulence in the system [23, 25]. Hence, it is essential to understand how Re within the membrane and agitation within the crystalliser may independently govern such phenomena in MDC.

This study therefore aims to provide a systematic investigation into the effect of mixing in MDC to establish a framework that describes how membrane boundary layer hydrodynamics and downstream crystalliser mixing

independently and collectively inform on the kinetics of nucleation and crystal growth. To date, the challenge in relating hydrodynamic conditions to classical nucleation theory (CNT) has been in the accurate determination of induction time [8]. We have therefore incorporated twin-axial, fibre-optic turbidimetry, as an industrially-accepted technique for the determination of nucleation, which can be used as a basis to provide detailed characterisation of crystallisation kinetics. Specific objectives are to:

- (i) Relate interfacial boundary layer hydrodynamics and crystalliser mixing to induction time and metastable zone width, to complete characterisation of nucleation kinetics;
- (ii) Determine how interfacial boundary layer hydrodynamics and crystalliser mixing impact on crystal size and crystal size distribution (CSD); and
- (iii) Characterise crystal morphology to inform how interfacial boundary layer hydrodynamics and crystalliser mixing will contribute to secondary nucleation and agglomeration phenomena, which can ultimately affect crystal product quality.

4.2 Materials and methods

4.2.1 Membrane distillation crystallisation experimental setup

Membrane distillation crystallisation (MDC) was conducted using a 40×100 mm flat-sheet ePTFE membrane with a 0.1 µm pore size (Cobetter Filtration, Hangzhou, China) (Appendix D). On the feed side (NaCl solution), the membrane module was connected to a crystalliser vessel (Reactor-Ready™, Radleys, Essex, UK) which had a height (H) and inner diameter of 150 and 65.6 mm, respectively. A four-bladed PTFE turbine stirrer (Radleys, Essex, UK) with a 45° pitch and 35 mm outer diameter was inserted into the crystalliser. The shaft was connected to an overhead stirrer (Hei-TORQUE Ultimate 400, Heidolph Instruments, Schwabach, Germany) with the stirrer blades sited at an off-bottom clearance of 1/3H. The impeller and feed solution Reynolds numbers are specified in Appendix E. The NaCl feed solution was recirculated from the crystalliser to the membrane module by a peristaltic pump (Watson-Marlow 530S, WMFTG, Falmouth, UK). Prior to entering the membrane module, the feed

solution was heated with an inline heat exchanger in which hot water from the heater (LT ecocool 150, Grant Instruments (Cambridge) Ltd., Shepreth, UK) was passed counter-currently to ensure a feed temperature of 60°C at the module inlet. A turbidity probe was inserted downstream of the membrane module to measure the presence of particles through light backscatter (InPro 8200/S/Epoxy/120 turbidity sensor, Mettler-Toledo Ltd, Leicester, UK). The twin-axial, fibre-optic sensor technology provides reproducible turbidity measurement with high resolution over a wide measuring range (<5 to 4000 FTU). Similarly to Di Profio et al. [7], this industrially-applied method therefore provided the non-invasive detection of crystal nucleation and hence the direct measurement of induction time. Turbidity data was recorded every second. Deionised water (permeate) flowed counter-currently to the feed solution in the membrane module. The permeate side consisted of a jacketed permeate vessel around which cold water from the chiller (LT ecocool 150, Grant Instruments (Cambridge) Ltd., Shepreth, UK) was continually circulated to maintain a module inlet temperature of 35°C. To determine membrane flux, permeate mass was measured over time and recorded using a precision balance (Cole Parmer Symmetry PT-4202E, Antylia Scientific, Illinois, USA). To monitor salt breakthrough, the conductivity of the permeate was recorded each minute by an inline probe and meter (Seven2Go™ Pro S7, Mettler-Toledo Ltd, Leicester, UK). The feed and permeate inlet and outlet temperatures from the membrane along with the crystalliser temperature were measured with thermocouples (EI-1034, Electronic Innovations Corporation, Colorado, USA). For each experiment, the feed solution consisted of a 500 ml 0.95 M sodium chloride solution (NaCl, 99.5%, ACROS Organics™, Fisher Chemicals, Loughborough, UK).

4.2.2 Crystal sampling and analysis

To obtain crystal samples for analysis, the experiments were stopped 10 minutes after bulk induction. Induction was determined based on the point in time at which the turbidity of the feed solution increased. The crystalliser solution was then vacuum filtered through a 0.45 µm nitrocellulose filter (Whatman® NC45, Cytiva, Maidstone, UK) before air-drying at room temperature for at least 48 hours.

Crystal size distributions (CSDs) were obtained with an optical microscope (Leica CTR 5500 B, Leica Microsystems Ltd, Milton Keynes, UK) connected to digital camera (Olympus SC50 5MP, Olympus, Southend-on-Sea, UK). Olympus Stream Image Analysis Software (Olympus, Southend-on-Sea, UK) was used for the CSD analyses in which 1000 crystals were analysed for each sample, to minimise the standard error of the distribution. Crystal samples were also subject to scanning electron microscopy (SEM) (Tescan VEGA 4, Tescan Orsay Holding, a.s., Czech Republic). Samples were coated with 10 nm gold by using physical vapor deposition and images collected at an acceleration voltage of 20 keV, a beam current of 300 pA and a working distance of 10 mm.

4.2.3 Crystallisation kinetic measurements and analysis

In MDC, primary nucleation is assumed to be controlled by interfacial conditions [14]. The method developed by Sangwal [26] was used to determine whether the primary nucleation kinetics at the interface were in accordance with the relationship predicted by classical three-dimensional nucleation theory which states [26, 27]:

$$B_n = A \exp\left(-\frac{B}{\ln^2 S}\right) \quad (4-1)$$

where B_n is the nucleation rate, A is the pre-exponential factor, B is a constant and S is the supersaturation level. Sangwal [26] assumed an empirical power law relationship between the nucleation rate and supersaturation at induction:

$$B_n = k(\ln S)^m \quad (4-2)$$

where k and m are the nucleation constant and order, respectively. The nucleation rate was assumed to be the rate of supersaturation (R') at the onset of bulk induction [26]. Hence, for the membrane interface at the onset of bulk nucleation, Eq. 4-2 can be re-written as:

$$R' = k(\ln S_{int})^m \quad (4-3)$$

where R' can also be defined as [19]:

$$R' = \frac{d(\Delta C)}{dt} = \frac{[\Delta C_{ind} - \Delta C_0]_{int}}{t_{ind} - t_0} = \frac{[(C_{ind} - C_{ind}^*) - (C_0 - C_0^*)]_{int}}{t_{ind} - t_0} \quad (4-4)$$

C is the concentration, t is the experimental time, the superscript $*$ indicates saturation, and subscripts ind , 0 and int represent the induction point, the starting point, and the interface, respectively. The interfacial concentration was calculated by applying the concentration polarisation coefficient (CPC) to the bulk concentration (C_b) [5]:

$$C_{int} = CPC \cdot C_b \quad (4-5)$$

$$C_{int} = \exp\left(\frac{J_p}{\rho K}\right) \cdot C_b \quad (4-6)$$

where J_p is the permeate flux, ρ is the solution density and K is the mass transfer coefficient given by the L  v  que equation as follows [5]:

$$K = \frac{1.62D}{d_h} \left(\frac{V d_h^2}{DL} \right)^{\frac{1}{3}} \quad (4-7)$$

where D and V are the solution diffusion coefficient and velocity, respectively; d_h and L are the hydraulic diameter and length of the feed-solution channel in the membrane module. The temperature polarisation coefficient (TPC) was applied to determine the saturation concentration at the interfacial temperature (T_{int}):

$$TPC = \frac{T_{int,f} - T_{int,p}}{T_{b,f} - T_{b,p}} \quad (4-8)$$

where subscripts f and p represent the feed and permeate solutions, respectively, and the subscript b indicates bulk (rather than interfacial) conditions. T_{int} is calculated by iteratively solving Eq. 4-8 in conjunction with the following equations:

$$T_{int,f} = T_{b,f} - (T_{b,f} - T_{b,p}) \left(\frac{\frac{1}{h_f}}{\frac{1}{h_f} + \frac{1}{h_p} + \frac{1}{h_c + h_v}} \right) \quad (4-9)$$

$$T_{int,p} = T_{b,p} + (T_{b,f} - T_{b,p}) \left(\frac{\frac{1}{h_p}}{\frac{1}{h_f} + \frac{1}{h_p} + \frac{1}{h_v + h_c}} \right) \quad (4-10)$$

where h is the overall heat transfer coefficient for each solution, i :

$$h_i = \frac{Nuk_i}{d_h}, \quad i = f, p \quad (4-11)$$

Nu is the Nusselt number:

$$Nu = 0.023Re^{0.8}Pr^{\frac{1}{3}} \quad (4-12)$$

$$Re = \frac{\rho V d_h}{\mu} \quad (4-13)$$

$$Pr = \frac{c_p \mu}{k} \quad (4-14)$$

where μ , c_p and k are the dynamic viscosity, specific heat capacity and thermal conductivity of the respective solutions. h_v is the vapour heat transfer coefficient:

$$h_v = \frac{J_p \Delta H_v}{T_{int,f} - T_{int,p}} \quad (4-15)$$

where ΔH_v is the latent heat of vaporisation. h_c is the heat transfer coefficient of conduction:

$$h_c = \frac{k_m}{\delta_m} \quad (4-16)$$

where δ_m and k_m are the thickness and thermal conductivity of the membrane, respectively. k_m was determined as follows [28]:

$$k_m = \left(\frac{\varepsilon}{k_{gas}} + \frac{1 - \varepsilon}{k_{solid}} \right)^{-1} \quad (4-17)$$

$$k_{gas} = 1.5 \times 10^{-3} \sqrt{T} \quad (4-18)$$

$$k_{solid} = 4.86 \times 10^{-4} T + 0.253 \quad (4-19)$$

where ε is the membrane porosity. k_{gas} and k_{solid} are the thermal conductivities of the water vapour/air gas mixture and solid polymer, respectively. The Elec-NRTL thermodynamic model, which is appropriate for highly-concentrated electrolyte solutions [30], was applied to determine solution properties using Aspen Plus software.

Following from Eq. 4-3, S_{int} is the interfacial supersaturation level at induction, i.e., the metastable zone width (MSZW). It is given by:

$$S_{int} = \left(\frac{C_{ind}}{C^*} \right)_{int} \quad (4-20)$$

The change in permeate mass was used to determine the bulk concentration at each point in time. Linearising Eq. 4-3 yields:

$$\ln(R') = m \ln(\ln S_{int}) + \ln k \quad (4-21)$$

Such that plotting $\ln(R')$ versus $\ln(\ln S_{int})$ results in a linear relationship if the classical nucleation theory (CNT) relationship holds. Since induction time (t_{ind}) is considered inversely proportional to the nucleation rate [30], t_{ind} can be substituted into Eq. 4-1 and linearised such that:

$$\ln(t_{ind}) = \ln A + \frac{B}{\ln^2 S_{int}} \quad (4-22)$$

As a result, plotting $\ln(t_{ind})$ versus $\ln^{-2} S_{int}$ yields a linear trend, provided interfacial nucleation kinetics conform to CNT.

4.3 Results and discussion

4.3.1 Differentiating the role of bulk and interfacial mixing on primary nucleation

In MDC, the permeate flux controls the rate of supersaturation [14]. The permeate flux at the onset of bulk nucleation was determined based on the point of inflection in the turbidity-time trend (Appendix F). Since no increases in permeate conductivity were observed during the experiments, it was concluded that no salt breakthrough or membrane wetting had occurred and accurate permeate flux readings were obtained. The Re within the membrane was varied between 1300 and 2050 which covered the laminar to transitional regime [31]. An increase in Re from 1300 to 2050, at a fixed stirring rate (N) of 300 rpm, enhanced the permeate flux at bulk induction from 24.3 to 37.3 kg m⁻² h⁻¹ (Figure 4.1a). This was due to improved mixing at the interfacial boundary layer which promoted heat and mass transfer across the membrane [9, 13]. The agitator Reynolds number (Re_N) was maintained below the fully turbulent threshold of 2×10^4 , which is within the mixing range that is of industrial relevance [32]. For stirrer speeds of 50 to 600 rpm, Re_N ranged from 1562 to 18741. At a fixed Re of 1300, increasing N from 50 to 600 rpm had no significant effect on the permeate flux (Figure 4.1b). As such, the rate at which supersaturation was achieved remained constant. This confirms that solution conditions within the boundary layer contribute strongly to mass transport (specifically water vapour flux) [13], whereas stirring within the crystalliser does not.

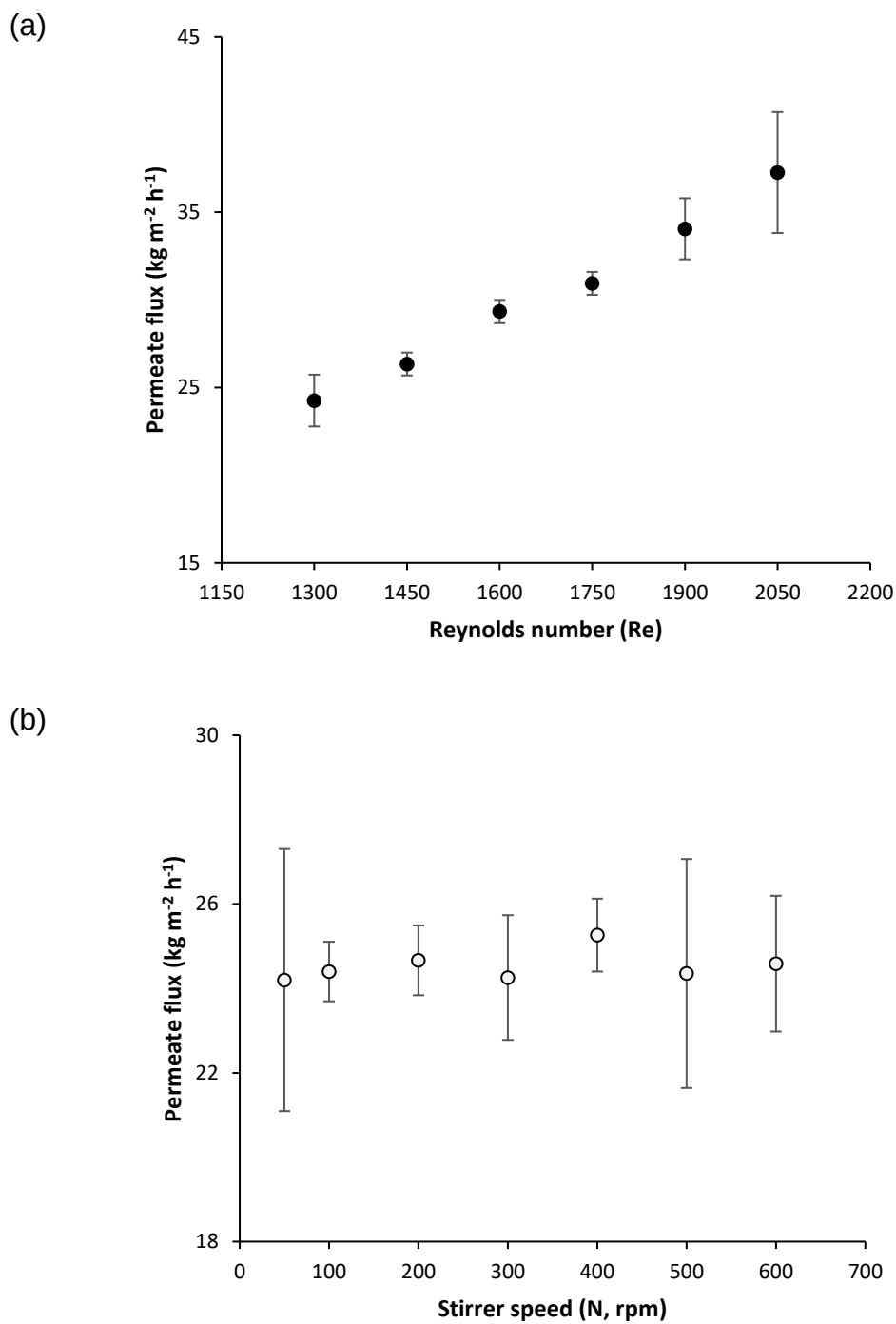


Figure 4.1. Understanding the influence of mixing on the permeate flux (five-minute moving average) at the onset of bulk nucleation when: (a) Interfacial Reynolds number (Re) is increased from 1300 to 2050 at a fixed agitation of 300 rpm and (b) Crystalliser mixing (N) is varied from 50 to 600 rpm, with Re constant at 1300. Error bars represent standard deviation of at least three replicates.

The effect of mixing on the metastable zone width was characterised by evaluating the supersaturation that was achieved in the bulk and interfacial regions at nucleation. Increasing Re (N , 300 rpm) widened the MSZW which contradicts the response in classical crystallisers, where higher agitation rates are expected to narrow the MSZW [17-19] (Figure 4.2a). Interfacial boundary layer supersaturation (S_{int}) increased from 1.22 to 1.31 when Re was increased from 1300 to 2050. In MDC, higher Re is also thought to lower S_{int} due to a reduction in temperature and concentration polarisation [9, 13]. However, Lokare and Vidic [33] noted that although increasing Re contributed to reducing CPC by thinning the boundary layer, the accompanying increase in permeate flux must be taken into account as this increases the convective flux of solute to the interface, thereby increasing CPC. Increasing Re therefore widened the MSZW by increasing permeate flux which enhanced the supersaturation rate. At high supersaturation rates, the reduction in critical cluster size and activation energy required for nucleation is faster than the response time of the system [17]. Hence, there is a lag time which allows much higher supersaturation levels to be achieved before the system recognises that it has sufficient energy for nucleation [17, 34]. An increase in solution supersaturation, shortened induction time (Figure 4.2b). To illustrate, interfacial induction time decreased from 44 minutes at Re 1300 to 33.7 minutes at Re 2050. While the difference in S_{int} between Re 1300 and Re 1600 was statistically significant (larger than one standard deviation), the same could not be said for the difference between Re 1300 and Re 1450 (Figure 4.2a). This similarity in S_{int} values likely explains the slight, statistically insignificant increase in induction time from Re 1300 and Re 1450.

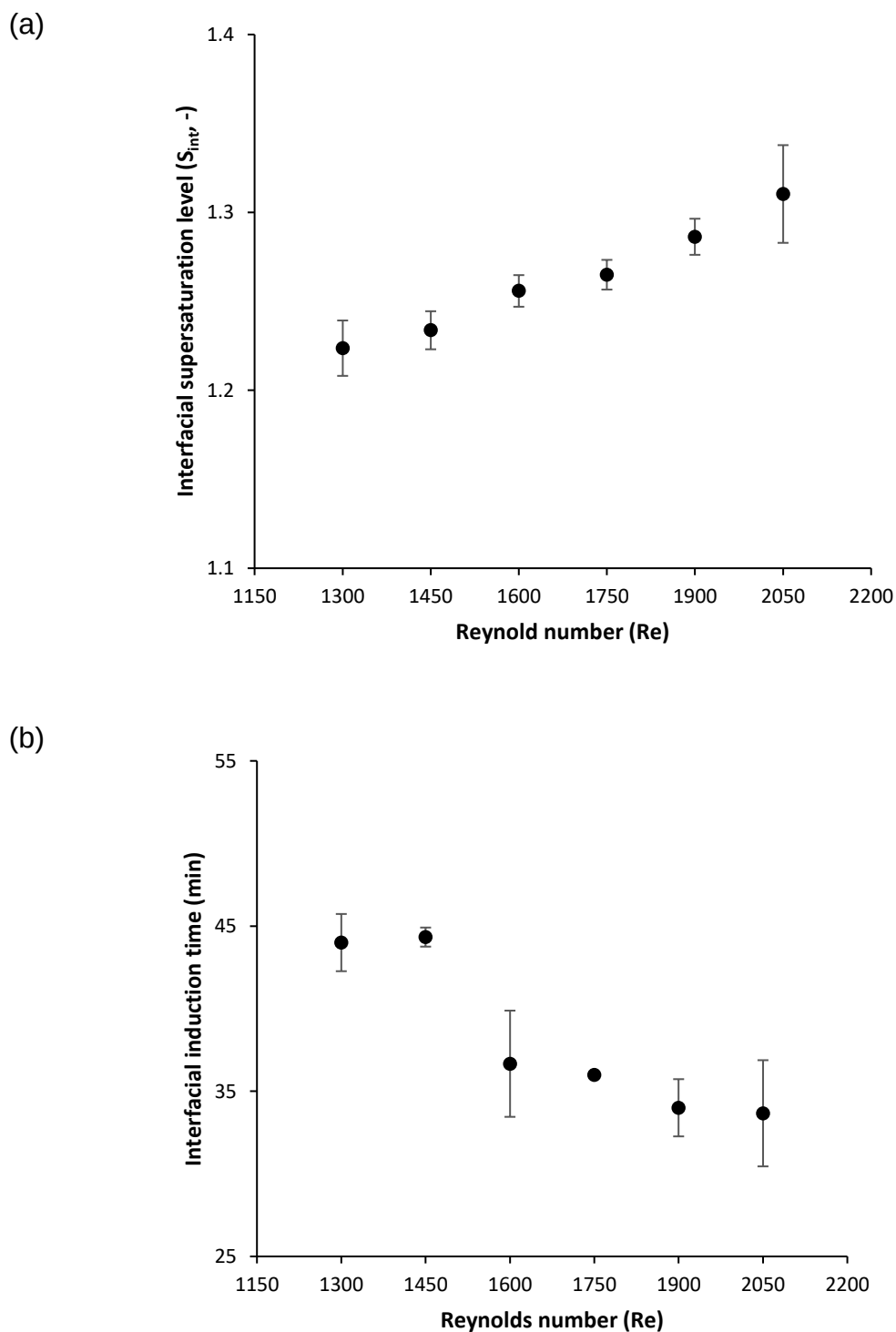


Figure 4.2. The effects of Reynolds number (Re) (1300 to 2050; constant crystalliser mixing, 300 rpm) on (a) interfacial supersaturation (defined as the maximum supersaturation achieved at induction (bulk nucleation)); and (b) the interfacial induction time. Error bars represent standard deviation of at least three replicates.

Bulk supersaturation (S_{bulk}) approached a value of 1 at induction (Figure 4.3). A crystal can only begin to grow once the nucleus forms a critical size that is thermodynamically stable [35]. Therefore, while a supersaturated interfacial boundary layer was established at each Re tested, the crystal phase was not observed until the bulk solution approached saturation (i.e., $S_{\text{bulk}} \approx 1$). A small increase (within one standard deviation) in S_{bulk} was observed with an increase in Re from 1300 to 2050 (N 300 rpm) (Figure 4.3a). However, S_{bulk} decreased from 1.005 to 0.997 with an increase in N from 50 to 600 rpm (Re 1300), respectively (Figure 4.3b). While the quantitative distinction between S_{bulk} values determined across the mixing range studied appear small, the difference is statistically significant (value at N 600 rpm is more than one standard deviation smaller than those at N 50 and 100 rpm). This is likely to be due to the higher agitation rate narrowing the MSZW by promoting diffusion, thereby increasing the likelihood of collisions and formation of nuclei [17-19].

The interfacial induction time also decreased from 43.3 to 38.5 minutes with an increase in N from 50 to 600 rpm (Figure 4.4a; Re , 1300). Induction time describes the ability of a solution to maintain a supersaturated state [35]. Hence, shorter induction times indicate an increased probability for nucleation. A constant S_{int} of 1.22 was observed as N was increased from 50 to 600 rpm (Figure 4.4b). Therefore, while mixing within the crystalliser can shorten induction time, the rate at which supersaturation is achieved, and the interfacial supersaturation level at which nucleation occurs are independent of N .

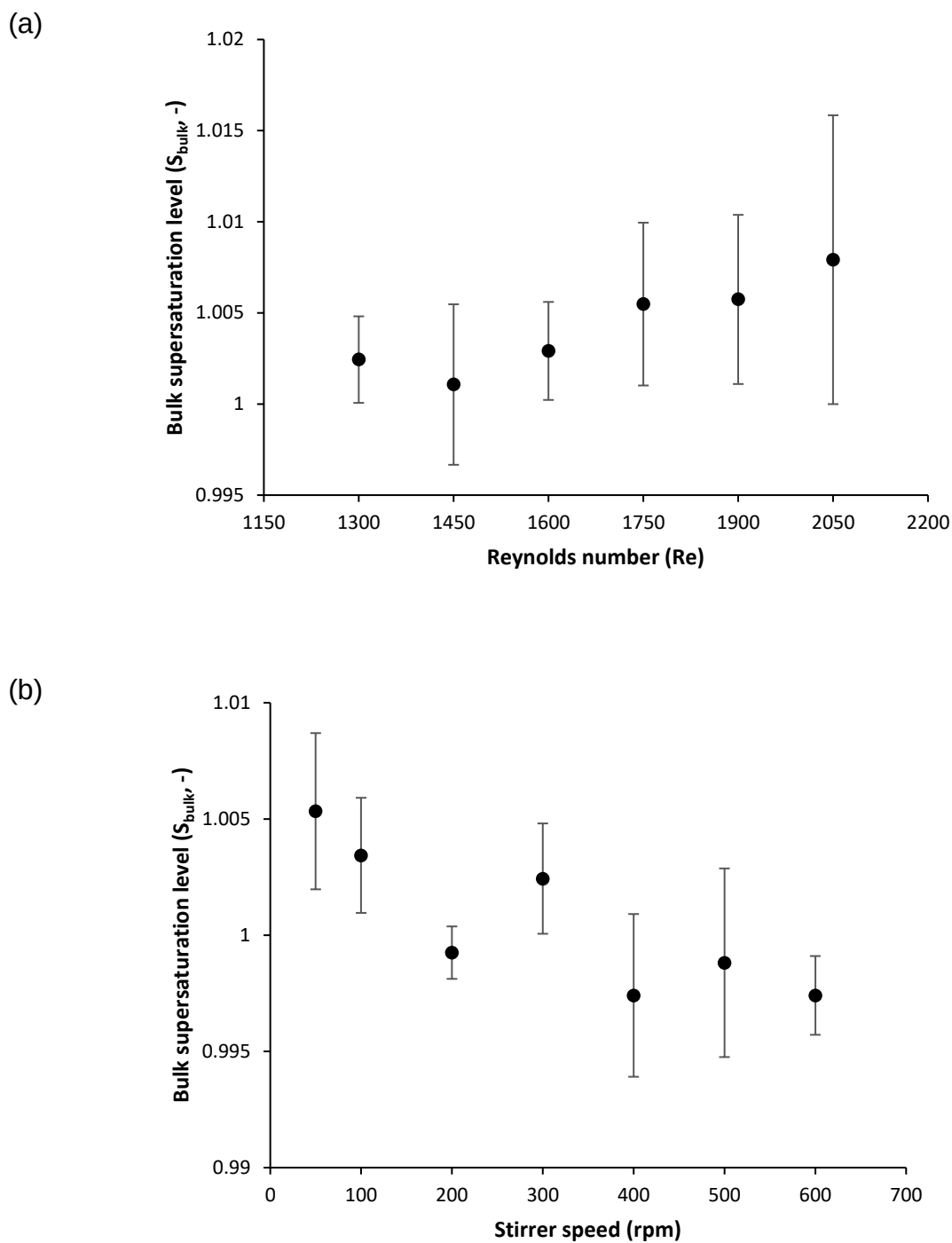


Figure 4.3. The effects of (a) Reynolds number (Re) (1300 to 2050; constant crystalliser mixing, 300 rpm); and (b) crystalliser agitation (N) (50 to 600 rpm; Re 1300) on supersaturation in the bulk solution. These are defined as the maximum supersaturation achieved at induction (bulk nucleation). Error bars represent standard deviation of at least three replicates.

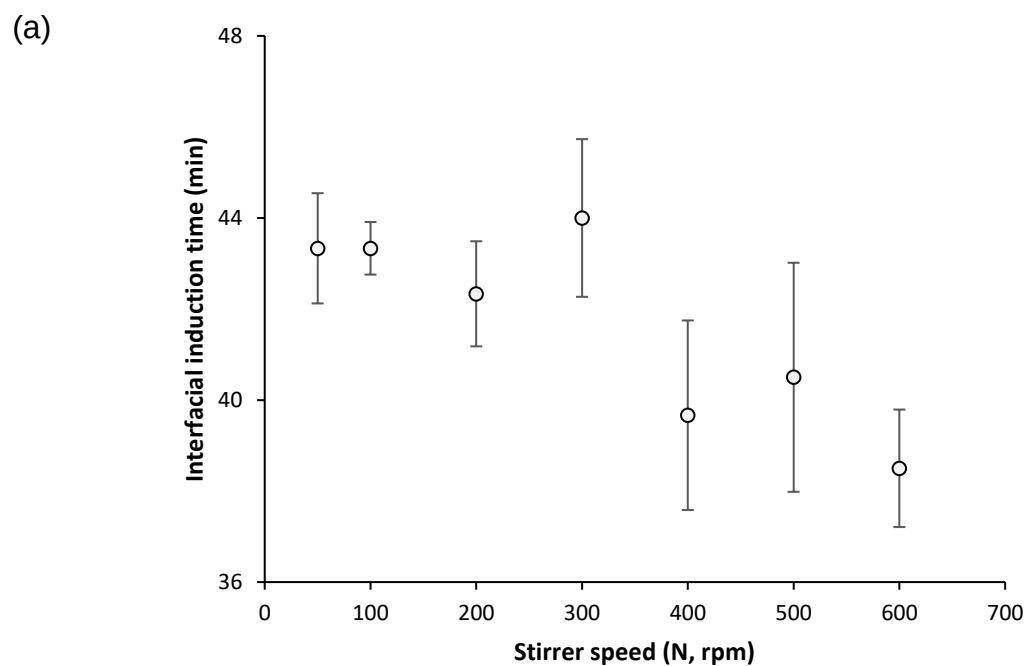
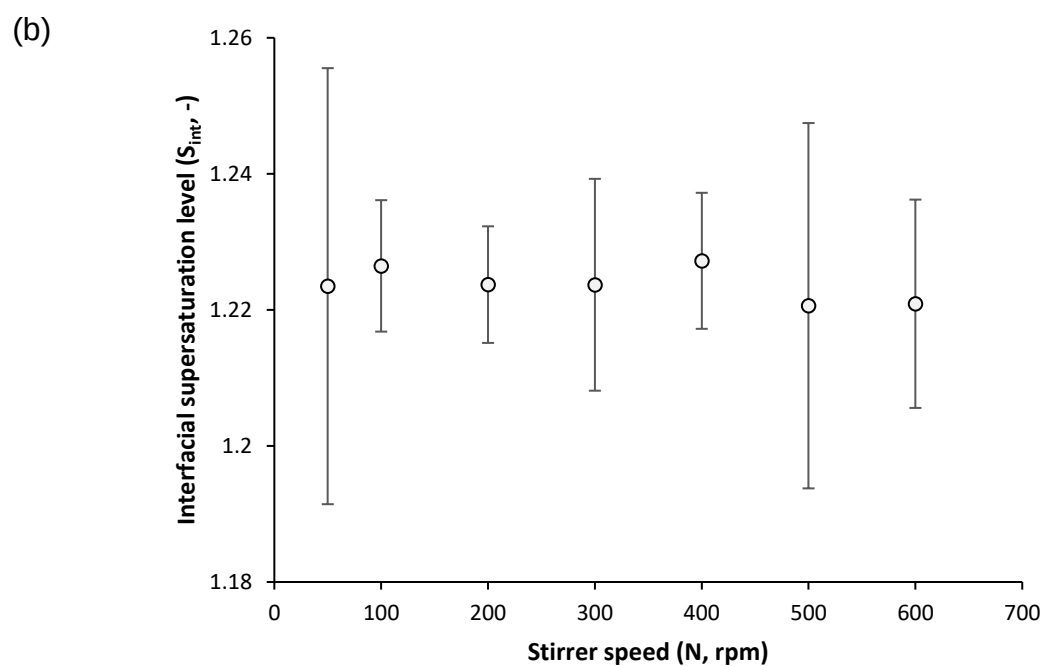


Figure 4.4. Determining how crystalliser mixing (N 100-600 rpm; Re 1300) informs: (a) interfacial induction time; and (b) interfacial supersaturation level achieved at induction (bulk nucleation). Error bars represent standard deviation of at least three replicates.

4.3.2 How bulk and interfacial mixing inform nucleation kinetics in membrane systems

Since supersaturation is highest at the interface, it is expected that the primary nucleation kinetics are controlled at the interfacial boundary layer rather than the bulk solution [14]. The method developed by Sangwal [26] (Eq. 4-2) was therefore applied to investigate the interfacial conditions at bulk nucleation (Figure 4.5a). Classical nucleation theory (CNT) presumes a power-law relationship between nucleation rate (assumed to be the supersaturation rate at metastability, R^*) and the MSZW (defined by the extent of supersaturation at induction, S) [26, 27]. The linear trend observed between the natural logarithms of supersaturation rate (R^*) and supersaturation when Re was increased, therefore confirms that the interfacial region adjacent to the membrane is likely to determine nucleation kinetics within MDC. This is supported by the linear response observed between induction time and interfacial supersaturation following an increase in Re where the slope of the curve ($B = 0.028$ - dimensionless) helps to describe the energy barrier for nucleation within the system [36] (Figure 4.5b). In contrast, mixing in the crystalliser did not yield a linear response between supersaturation rate and interfacial supersaturation, confirming that stirrer speed does not inform on the kinetics of nucleation.

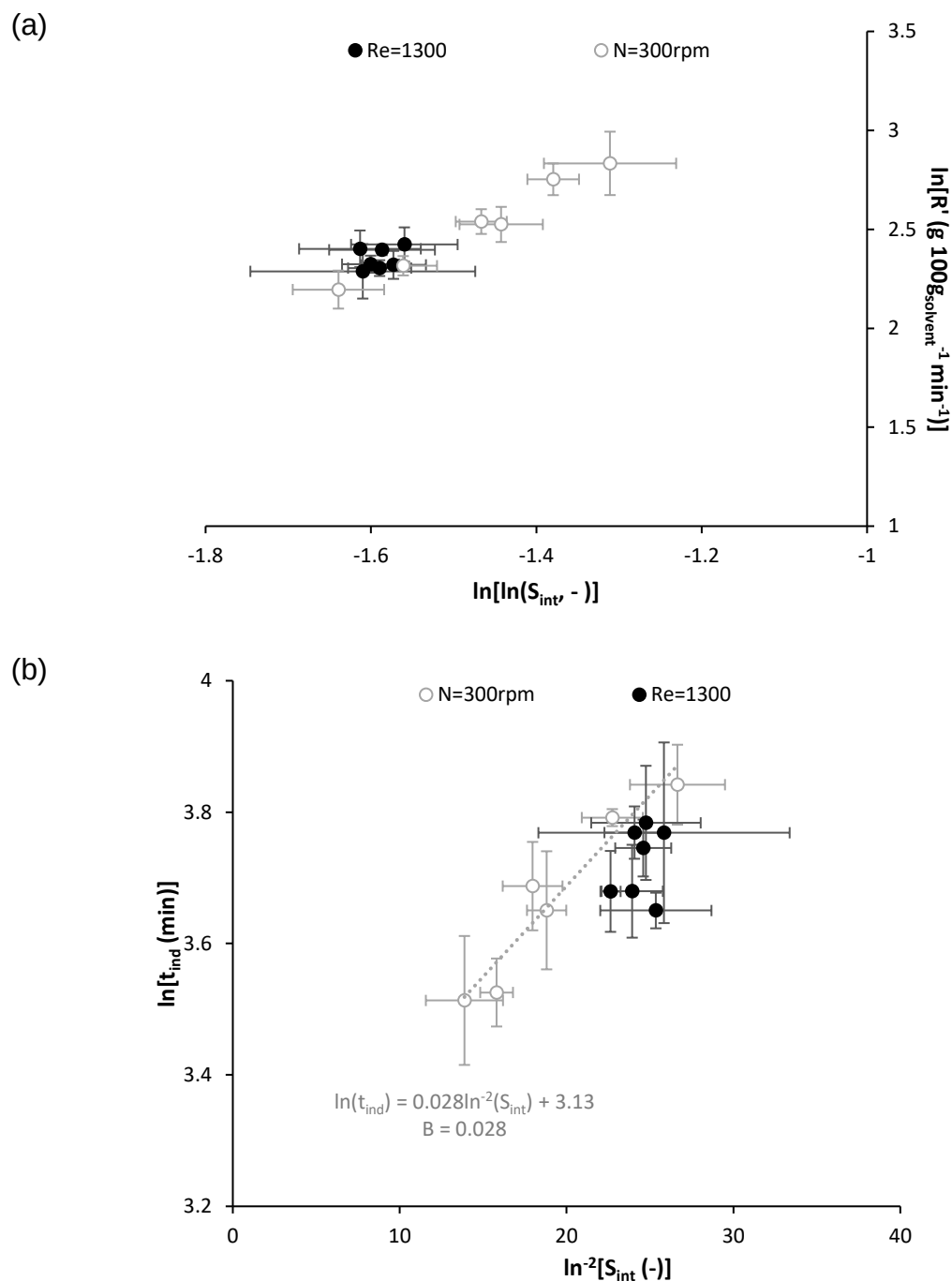


Figure 4.5. Using classical nucleation theory to explain how mixing controls the onset of nucleation and nucleation rate: (a) Sangwal [26]'s power-law relationship between supersaturation rate and supersaturation level at induction describing the kinetics; and (b) relating induction time to supersaturation level at induction to relate to the activation energy for nucleation. For interfacial mixing, Re 1300 to 2050 (N 300 rpm), and for crystalliser mixing, N 50 to 600 rpm (Re 1300). Error bars represent standard deviation of at least three replicates.

However, crystalliser mixing did reduce interfacial induction time independently of the MSZW (Figure 4.4) which does not conform to CNT. We propose that this is made possible by the transition in bulk conditions that are introduced through mixing where an increase in stirrer speed reduced the bulk MSZW while simultaneously reducing induction time (Figure 4.6). This observation deviates from CNT since higher supersaturation levels are expected to reduce the time required for nucleation [10, 17, 30]. Crystalliser mixing therefore reduced induction time by enhancing convective solute diffusion to increase collision frequency [18]. While this does not affect supersaturation within the interfacial boundary layer, a narrowing of the bulk MSZW is instigated, which shortens induction time. The metastability of the bulk solution therefore plays a decisive role in determining when crystals are detected in the bulk solution. Consequently, crystalliser mixing can be used to decouple induction time from interfacial supersaturation rate and set conditions that may inform on the kinetics of crystal growth in the bulk solution.

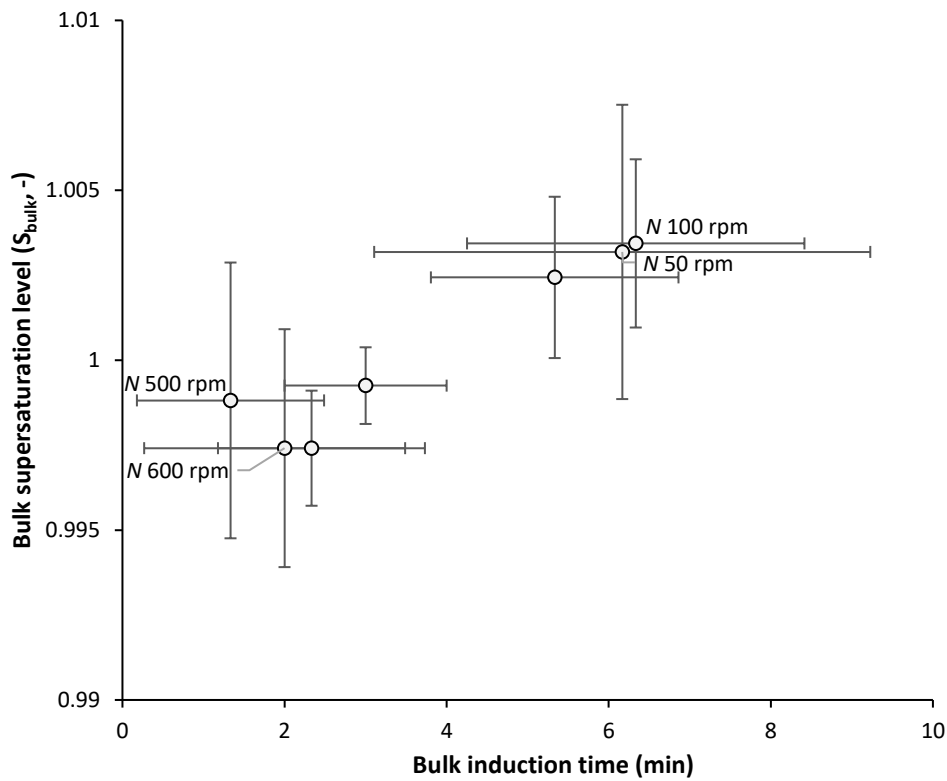
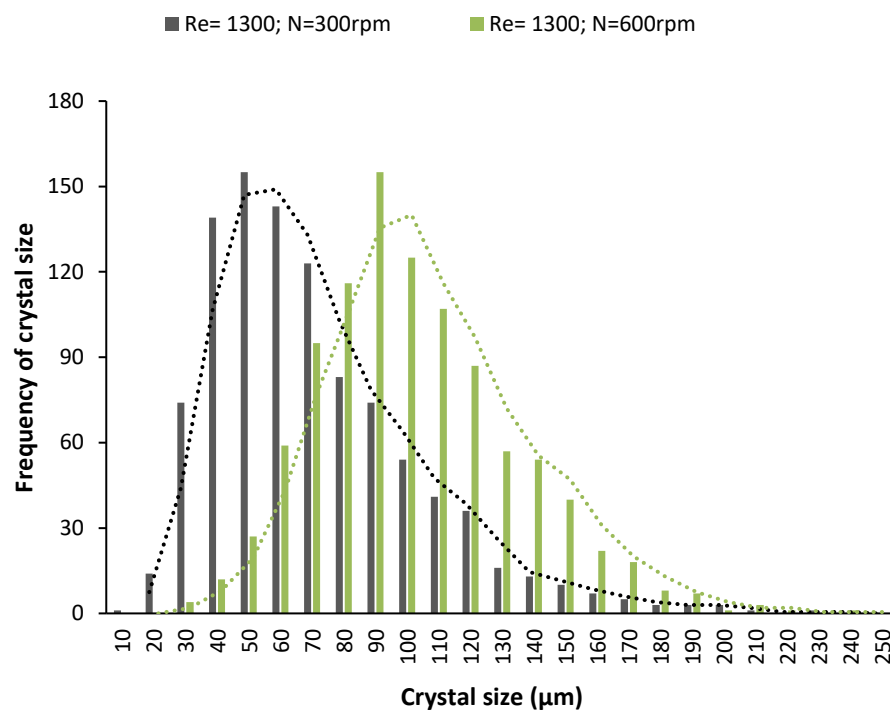


Figure 4.6. Influence of crystalliser mixing on bulk induction time and MSZW (S_{bulk}). Stirrer speed (N) 50 to 600 rpm (Re 1300). Higher N shortens induction time which narrows the MSZW. Error bars represent standard deviation of at least three replicates.

4.3.3 Bulk and interfacial mixing set the kinetic trajectory for crystal growth

An increase in median crystal size from 74.8 to 92.4 μm was observed for crystalliser mixing speeds of 300 and 600 rpm respectively (Figure 4.7a). The growth rate of NaCl is diffusion controlled [29]. The increase in crystal size was therefore provided by higher agitation rates which enhanced solute mass transfer [21, 24]. Higher agitation rates increase the risk of secondary nucleation mechanisms (SNM), including attrition breeding (macro-attrition/attrition) which causes fragmentation of the parent crystals due to collisions with other crystals, the impeller, and/or other process equipment [22, 37]. Secondary nucleation therefore broadens the size distribution by incorporating a higher frequency of smaller crystals [37], skewing the crystal size distribution (CSD) to the right. In this study, skewness of the CSD reduced from 1.35 to 0.789 when increasing N from 300 to 600 rpm (Re 1300). This indicates that crystalliser mixing can promote growth dominated conditions over SNMs.

(a)



(b)

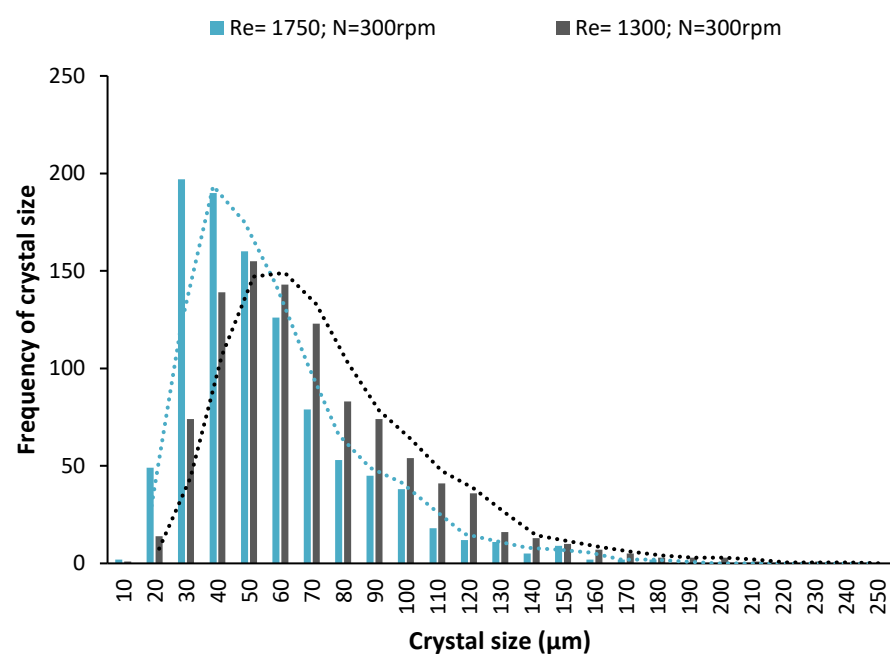


Figure 4.7. Determining how mixing informs crystal growth. Crystal size distributions (CSD) from: (a) Crystalliser mixing with stirrer speeds (N) of 300 and 600 rpm (Reynolds number, Re , 1300); (b) Interfacial mixing with Re of 1300 and 1750 (N , 300 rpm).

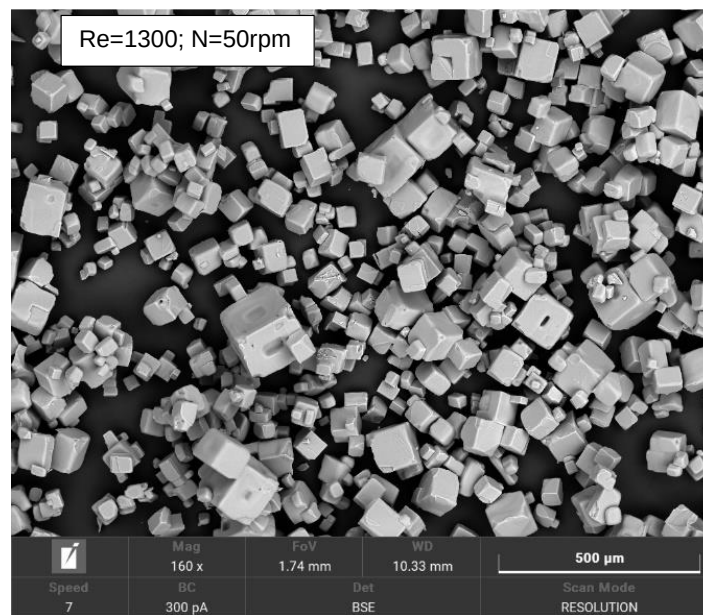
Median crystal size decreased from 74.8 to 56.2 μm when Re was increased from 1300 to 1750 (N 300 rpm) (Figure 4.7b). At higher Re , the boundary layer thins to improve heat and mass transfer across the membrane which increases the permeate flux [33]. This results in higher supersaturation rates which widens the MSZW [14, 17, 34]. According to CNT, nucleation rate increases exponentially with supersaturation [38]. The primary nucleation rate is therefore determined by the MSZW that is achieved at induction [4], where higher supersaturation values provide greater nucleation rates, which result in a greater number of smaller crystals [39]. Consequently, CNT can be used to describe how Re may set conditions for crystal growth by relating process conditions to the supersaturation rate. However, if water vapour transport across the membrane is sustained in MDC following nucleation, the feed solution can become more supersaturated. This supersaturated state can exceed the secondary nucleation threshold (SNT) where secondary nucleation mechanisms (SNMs) are expected to dominate and may broaden the CSD by increasing fines production through attrition, and reduce product purity through changes to crystal morphology [37, 40].

4.3.4 Morphology infers growth mechanisms initiated by bulk and interfacial mixing

To establish the role of mixing on crystal product quality, crystal morphology was compared in conditions where mixing was at the lower (Re 1300, N 50 rpm) and upper (Re 2050, N 600 rpm) thresholds tested (Figure 4.8). At a low mixing intensity, the cubic crystal habit, which is characteristic of NaCl, was clearly observed. However, some evidence of attrition was identified on larger crystals by the chipping of corners, which is consistent with literature that outlines crystals exceeding 100 μm to be most susceptible to attrition [39]. Greater evidence of attrition was found at the higher mixing intensity, as the increased shear rate enhances the likelihood of crystal breakage [24]. Attrition breeding (a SNM) may therefore have also contributed to the smaller median crystal size identified with an increase in Re (Figure 4.7b). Dendritic breeding, which is another SNM, was also observed at the higher mixing intensity but not at the lower mixing intensity.

Dendritic breeding is characterised by acicular outgrowth on the surface of the crystal that generally only occurs at supersaturation levels exceeding the SNT [22, 37]. As an equivalent S_{bulk} of approximately 1 was reached in both conditions, it is postulated that the interfacial supersaturation sets conditions for secondary nucleation and growth. Dendritic breeding should be avoided due to its disruption to crystal product uniformity, but also because the more fragile structure can initiate attrition breeding following breakage. The higher mixing intensity also increased the number and size of agglomerates (Figure 4.8b). Nariyoshi et al. [25] similarly correlated agglomeration to higher permeate fluxes as this increased interfacial supersaturation, resulting in higher primary nucleation rates. High primary nucleation rates produce a large number of small crystals which collide and aggregate before cementation into agglomerates which are detrimental to product quality by creating irregularly-shaped, non-uniform crystals [20, 23]. Crystal product quality is therefore supersaturation and shear dependent.

(a)



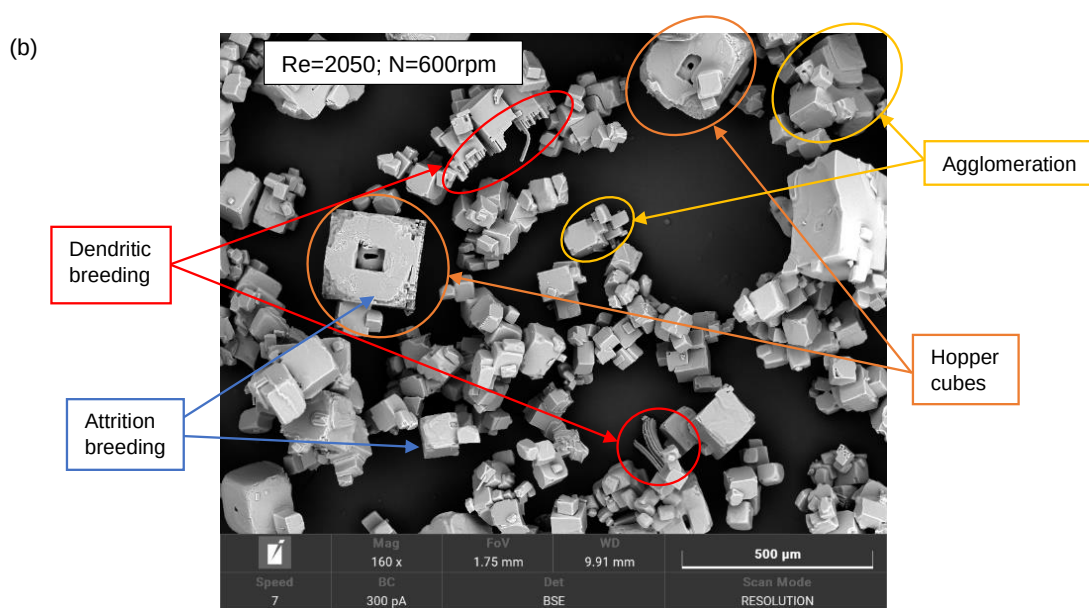


Figure 4.8. SEM micrographs depicting the morphological impacts of increasing mixing intensity: (a) Reynolds number (Re) 1300, stirrer speed (N) 50 rpm; and (b) Re 2050, N 600 rpm.

4.4 Conclusions

In this study, the independent contributions of bulk and interfacial mixing to the control of nucleation, crystal growth and product purity have been demonstrated. While previous studies have hypothesised how the interfacial boundary layer modulates nucleation, we provide direct evidence of its role, by combining the use of non-invasive nucleation detection with Sangwal's method for characterisation of the metastable zone width. It was shown how Reynolds number (Re) governs nucleation rate by adjusting boundary-layer conditions to set the interfacial supersaturation level and supersaturation rate. The power law relationship between supersaturation and induction time provides a framework founded on classical nucleation theory that relates regulation of nucleation rate by Re to the activation energy requirement for nucleation. Importantly, since Re is well defined in membrane systems characterised by fully developed flow, reproducible nucleation rates can be achieved following scale-up, which is a key challenge to existing industrial crystallisers.

While mixing in the crystalliser (N) did not directly control the nucleation rate, supersaturation in the bulk determined when a thermodynamically stable crystal phase can form. Increasing N therefore shortens induction time by improving solute collisions, thereby increasing the likelihood of nucleation. The practical significance is that mixing within the crystalliser can broaden the nucleation kinetic trajectory in MDC, which may hold greater significance for solutes characterised by wider metastable zones (e.g., proteins which typically exhibit longer induction times). Mixing also affected the rate of crystal growth. However, distinct mechanisms of growth were facilitated by the bulk and interfacial regions. Mixing in the crystalliser aids diffusion-controlled growth, whereas Re in the interfacial region primarily controlled growth by setting the metastable zone width. High interfacial supersaturation can result in small crystals of poor product quality. Consequently, it may be possible to employ mixing within the crystalliser in MDC to adjust the crystal growth process independently of the interfacial conditions, permitting preferential morphologies to be formed in a larger region of the metastable zone. This study has therefore provided new knowledge on the role of mixing, establishing a framework for how to control the kinetics of nucleation and crystal growth without having to change the driving force explicitly through temperature or temperature difference. Consequently, an entirely new mechanism for crystallisation control within MDC is provided, while evidencing membrane crystallisation as a scalable and highly controllable platform technology.

References

- [1] E. Chabanon, D. Mangin, and C. Charcosset, "Membranes and crystallization processes: State of the art and prospects," *J. Memb. Sci.*, vol. 509, pp. 57–67, 2016.
- [2] C. Charcosset, R. Kieffer, D. Mangin, and F. Puel, "Coupling between membrane processes and crystallization operations," *Ind. Eng. Chem. Res.*, vol. 49, pp. 5489–5495, 2010.

- [3] G. Di Profio, E. Curcio, and E. Drioli, "Supersaturation control and heterogeneous nucleation in membrane crystallizers: Facts and perspectives," *Ind. Eng. Chem. Res.*, vol. 49, pp. 11878–11889, 2010.
- [4] J. Ulrich and C. Strege, "Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers," 2002.
- [5] X. Jiang, D. Lu, W. Xiao, X. Ruan, J. Fang, and G. He, "Membrane assisted cooling crystallization: Process model, nucleation, metastable zone, and crystal size distribution," *AIChE J.*, vol. 62, pp. 829–841, 2016.
- [6] J.-H. H. Tsai et al., "Membrane-Assisted Crystallization: A Molecular View of NaCl Nucleation and Growth," *Appl. Sci.*, vol. 8, p. 2145, 2018.
- [7] G. Di Profio, E. Curcio, A. Cassetta, D. Lamba, and E. Drioli, "Membrane crystallization of lysozyme: Kinetic aspects," *J. Cryst. Growth*, vol. 257, pp. 359–369, 2003.
- [8] T. Horseman, Y. Yin, K. S. Christie, Z. Wang, T. Tong, and S. Lin, "Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies," *ACS ES&T Eng.*, vol. 1, pp. 117–140, 2021.
- [9] F. Edwie and T. S. Chung, "Development of simultaneous membrane distillation-crystallization (SMDC) technology for treatment of saturated brine," *Chem. Eng. Sci.*, vol. 98, pp. 160–172, 2013.
- [10] D. M. Warsinger, E. W. Tow, J. Swaminathan, and J. H. Lienhard V, "Theoretical framework for predicting inorganic fouling in membrane distillation and experimental validation with calcium sulfate," *J. Memb. Sci.*, vol. 528, pp. 381–390, 2017.
- [11] M. C. Sparenberg, S. Chergaoui, V. Sang Sefidi, and P. Luis, "Crystallization control via membrane distillation-crystallization: A review," *Desalination*, vol. 519, p. 115315, 2022.
- [12] M. R. Elmarghany, A. H. El-Shazly, M. S. Salem, M. N. Sabry, and N. Nady, "Thermal analysis evaluation of direct contact membrane distillation system," *Case Stud. Therm. Eng.*, vol. 13, p. 100377, 2019.
- [13] M. Gryta, "Effectiveness of water desalination by membrane distillation process," *Membranes (Basel)*, vol. 2, pp. 415–429, 2012.

- [14] X. Jiang, X. Ruan, W. Xiao, D. Lu, and G. He, "A novel membrane distillation response technology for nucleation detection, metastable zone width measurement and analysis," *Chem. Eng. Sci.*, vol. 134, pp. 671–680, 2015.
- [15] G. Di Profio, S. Tucci, E. Curcio, and E. Drioli, "Selective Glycine Polymorph Crystallization by Using Microporous Membranes," *Cryst. Growth Des.*, vol. 7, pp. 526–530
- [16] K. Liang, G. White, D. Wilkinson, L. J. Ford, K. J. Roberts, and W. M. L. Wood, "Examination of the Process Scale Dependence of L-Glutamic Acid Batch Crystallized from Supersaturated Aqueous Solutions in Relation to Reactor Hydrodynamics," *Ind. Eng. Chem. Res.*, vol. 43, pp. 1227–1234, 2004.
- [17] C. Bian, H. Chen, X. Song, and J. Yu, "Metastable zone width and the primary nucleation kinetics for cooling crystallization of NaNO₃ from NaCl-NaNO₃-H₂O system," *J. Cryst. Growth*, vol. 518, pp. 5–13, 2019.
- [18] L. Wang, H. Feng, J. Peng, N. Dong, W. Li, and Y. Dong, "Solubility, metastable zone width, and nucleation kinetics of sodium dichromate dihydrate," *J. Chem. Eng. Data*, vol. 60, pp. 185–191, 2015.
- [19] G. Zeng, H. Li, S. Huang, X. Wang, and J. Chen, "Determination of metastable zone width and the primary nucleation kinetics of sodium sulfate," *Theor. Found. Chem. Eng.*, vol. 49, pp. 869–876, 2015.
- [20] M. Akrap, N. Kuzmanić, and J. Prić-Kardum, "Effect of mixing on the crystal size distribution of borax decahydrate in a batch cooling crystallizer," *J. Cryst. Growth*, vol. 312, pp. 3603–3608, 2010.
- [21] W. R. Wilcox, "Transport phenomena in crystal growth from solution," *Prog. Cryst. Growth Charact. Mater.*, vol. 26, pp. 153–194, 1993.
- [22] A. S. Myerson, D. Erdemir, and A. Y. Lee, *Crystal nucleation*. 2019.
- [23] M. Brunsteiner, A. G. Jones, F. Pratola, S. L. Price, and S. J. R. Simons, "Toward a Molecular Understanding of Crystal Agglomeration," *Cryst. Growth Des.*, vol. 5, pp. 3–16, Jan. 2005.
- [24] Y. Bao, J. Zhang, Q. Yin, and J. Wang, "Determination of growth and breakage kinetics of l-threonine crystals," *J. Cryst. Growth*, vol. 289, pp. 317–323, 2006.

- [25] Y. N. Nariyoshi, C. E. Pantoja, M. M. Seckler, Y. N. Nariyoshi, C. E. Pantoja, and M. M. Seckler, "Evaluation of sodium chloride crystallization in membrane distillation crystallization applied to water desalination," *Brazilian J. Chem. Eng.*, vol. 33, pp. 675–690, 2016.
- [26] K. Sangwal, "A novel self-consistent Nývlt-like equation for metastable zone width determined by the polythermal method," *Cryst. Res. Technol.*, vol. 44, pp. 231–247, 2009.
- [27] S. Wang, M. Feng, H. Du, J. J. Weigand, Y. Zhang, and X. Wang, "Determination of metastable zone width, induction time and primary nucleation kinetics for cooling crystallization of sodium orthovanadate from NaOH solution," *J. Cryst. Growth*, vol. 545, p. 125721, 2020.
- [28] A. Alkhudhiri, N. Darwish, and N. Hilal, "Membrane distillation: A comprehensive review," *Desalination*, vol. 287, pp. 2–18, 2012.
- [29] A. Lewis, M. M. Seckler, H. Kramer, and G. van Rosmalen, *Industrial Crystallization*. Cambridge: Cambridge University Press, 2015.
- [30] Z. Guo, L. Li, W. Han, J. Li, B. Wang, and Y. Xiao, "Interpretation of the microwave effect on induction time during CaSO₄ primary nucleation by a cluster coagulation model," *J. Cryst. Growth*, vol. 475, pp. 220–231, 2017.
- [31] M. Gryta, M. Tomaszewska, and A. W. Morawski, "Membrane distillation with laminar flow," *Sep. Purif. Technol.*, vol. 11, pp. 93–101, 1997.
- [32] D. Chapple, S. M. Kresta, A. Wall, and A. Afacan, "The effect of impeller and tank geometry on power number for a pitched blade turbine," *Chem. Eng. Res. Des.*, vol. 80, pp. 364–372, 2002.
- [33] O. R. Lokare and R. D. Vidic, "Impact of Operating Conditions on Measured and Predicted Concentration Polarization in Membrane Distillation," *Environ. Sci. Technol.*, vol. 53, pp. 11869–11876, 2019.
- [34] S. A. Kulkarni, S. S. Kadam, H. Meekes, A. I. Stankiewicz, and J. H. Ter Horst, "Crystal nucleation kinetics from induction times and metastable zone widths," *Cryst. Growth Des.*, vol. 13, pp. 2435–2440, 2013.
- [35] D. Kashchiev and G. M. Van Rosmalen, "Review: Nucleation in solutions revisited," *Cryst. Res. Technol.*, vol. 38, pp. 555–574, 2003.

- [36] N. Kubota, "A new interpretation of metastable zone widths measured for unseeded solutions," *J. Cryst. Growth*, vol. 310, pp. 629–634, 2008.
- [37] S. G. Agrawal and A. H. J. Paterson, "Secondary Nucleation: Mechanisms and Models," *Chem. Eng. Commun.*, vol. 202, pp. 698–706, 2015.
- [38] J. Nyvlt, "Kinetics of nucleation in solutions," *J. Cryst. Growth*, vol. 3, pp. 377–383, 1968.
- [39] A. Mersmann, "Crystallization and precipitation," *KONA Powder Part. J.*, vol. 16, pp. 60–67, 1998.
- [40] T. L. Threlfall and S. J. Coles, "A perspective on the growth-only zone, the secondary nucleation threshold and crystal size distribution in solution crystallisation," *CrystEngComm*, vol. 18, pp. 369–378, 2016.

Appendix D. Experimental setup

A photograph of the setup used for the MDC experiments is shown in Figure D1. The highlighted crystalliser vessel and membrane module are the main regions in which the respective effects of bulk and boundary-layer hydrodynamics on crystallisation kinetics were investigated.

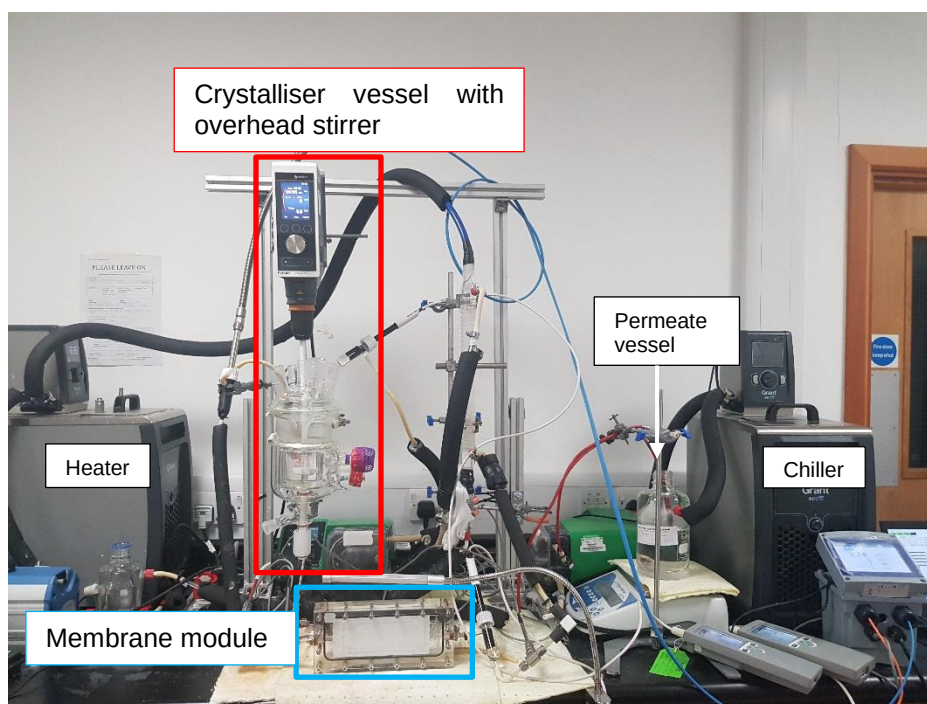


Figure D1: Photograph of experimental setup

Appendix E. Reynolds number calculations

In turbulent flow, the hydrodynamics in the crystalliser are considered independent of the mixer speed [32]. Hence, the impeller speeds were specified such that the impeller Reynolds number (Re_N) was below the turbulent criterion of 20000, i.e., $Re_N < 2 \times 10^4$:

$$Re_N = \frac{\rho N D_N}{\mu} \quad (\text{E-1})$$

where ρ and μ are the solution density and dynamic viscosity, respectively. N and D_N are the impeller speed and diameter, respectively. The N values and respective Re_N values are outlined in the table below based on the solution properties at 60°C and $D_N = 0.035 \text{ m}$.

Table E1. Impeller Reynolds number specifications

N (rpm)	N (rps)	Re_N (-)
50	0.834	1562
100	1.667	3123
200	3.333	6247
300	5	9370
400	6.667	12494
500	8.333	15617
600	10	18741

For consistency, the interfacial Reynolds number (Re) was also maintained below the turbulent regime, corresponding to an industrially-relevant mixing range [31].

$$Re = \frac{\rho V d_h}{\mu} < 2100 \quad (\text{E-2})$$

where, V is the velocity of the feed solution in the membrane module and d_h is the module hydraulic diameter determined by:

$$d_h = \frac{4A}{P} \quad (\text{E-3})$$

where A and P are the area and perimeter of the rectangular duct of the membrane module. The feed velocities and respective Re values can therefore be specified (Table E2).

Table E2. *Interfacial Reynolds number specifications*

$V \text{ (m s}^{-1}\text{)}$	$Re \text{ (-)}$
0.224	1300
0.250	1450
0.276	1600
0.302	1750
0.328	1900
0.354	2050

Appendix F. Permeate flux and turbidity time series analysis

During membrane distillation crystallisation (MDC) experiments, the trends of permeate flux and feed-solution turbidity over time characterise the distillation and crystallisation processes, respectively. The inflection point of the turbidity trend indicates the onset of crystallisation. Hence the induction time can be obtained from the turbidity-time trend and the flux (five-minute average) at this induction time can then be determined (Figure F1). The permeate flux at induction was used to compare the permeate fluxes at different hydrodynamic conditions. For example, the permeate flux at induction improves from 24.3 to 34.1 kg m⁻² h⁻¹ as Reynold number (Re) is increased from 1300 to 1900 at 300 rpm (Figure D1). The permeate flux at induction was also applied to determine the supersaturation rate (R') which provided the basis for crystallisation kinetics calculations.

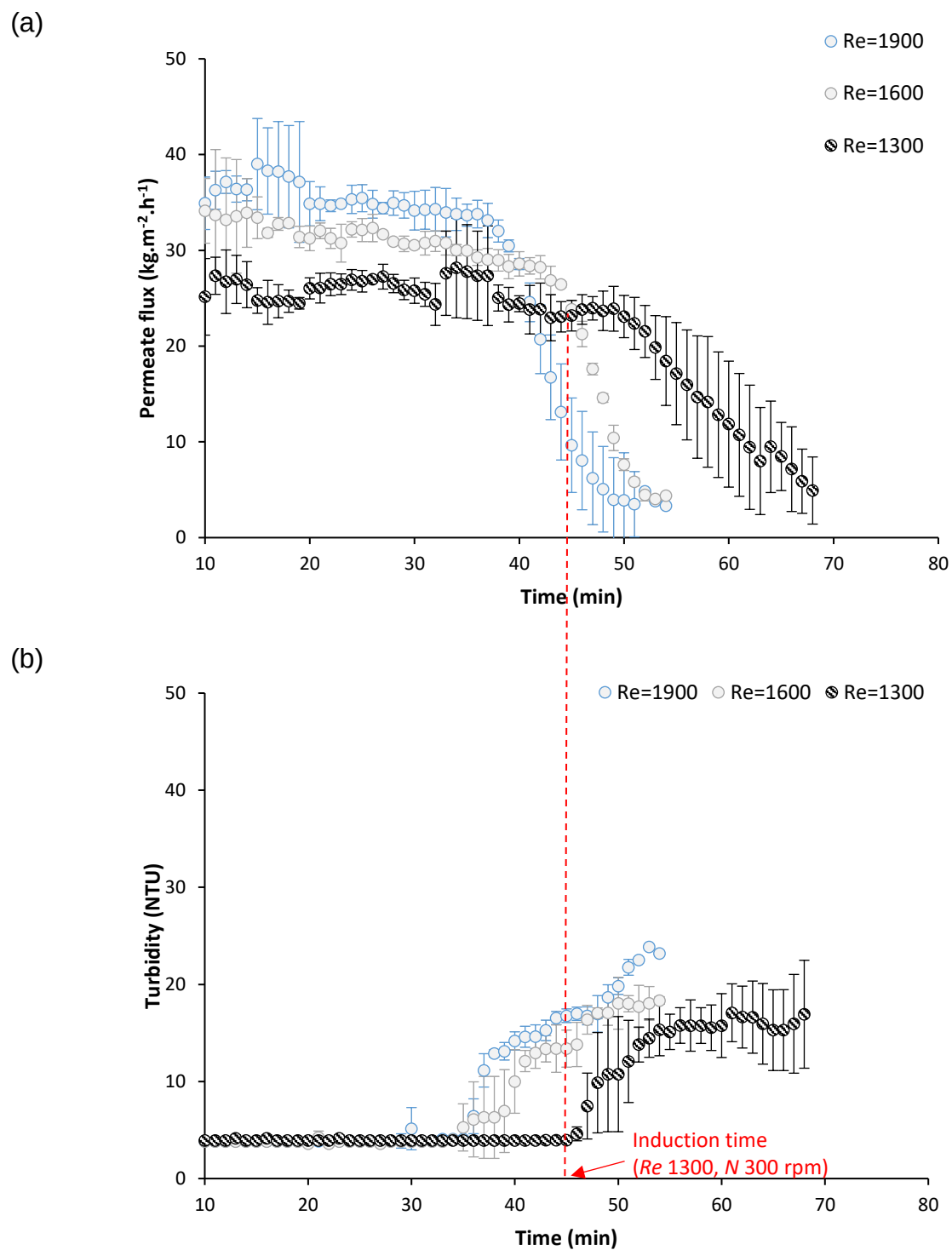


Figure F1: Example time series to demonstrate primary data collection for flux and turbidimetry: (a) permeate flux; (b) turbidity. Conditions: Reynolds numbers (Re) 1300, 1600 and 1900; Crystalliser stirrer speed (N) 300 rpm. Red dotted line illustrates alignment between permeate flux and the onset of bulk nucleation as identified by turbidimetry (Re 1300; N 300 rpm). Error bars represent standard deviation of at least three replicates.

5. Discussion

5.1 Is scaling in membrane distillation due to heterogeneous nucleation?

It is widely assumed that scaling in membrane distillation (MD) occurs via a heterogeneous nucleation mechanism assisted by the membrane surface [1–3]. However, Warsinger et al. [4] pointed to a bulk nucleation mechanism where scaling was caused by surface deposition, since the hydrophobicity of the membrane surface decreases the likelihood of heterogeneous (surface) nucleation by reducing the solute and surface interactions [5]. Shin and Sohn [6] pointed to a similar nucleation mechanism, further proposing the presence of two distinct scaling mechanisms, surface nucleation and surface deposition, based on experimental observations and deductions. However, these mechanistic conjectures were not validated by fundamental crystallisation theory. As such, the governing nucleation mechanism(s) for scaling in MD systems had yet to be confirmed.

In this study, a digital microscope was introduced to obtain a temporal view of crystallisation on the membrane surface in conjunction with an inline turbidity probe for the detection of bulk nucleation. This combined use of visual and fibre-optic telemetry enabled independent detection of bulk and surface nucleation events in MD for the first time. Significantly, both induction times were distinct from the point of drastic flux decline conventionally used for scaling detection [1, 5, 7, 8]. For example, turbidity trends showed that bulk nucleation occurred up to 50 minutes earlier than the onset of drastic flux decline (Chapter 2). Furthermore, flux decline lag times in excess of 18 minutes (up to 31 minutes) were obtained relative to the onset of scaling on the membrane surface (Figure 5.1).

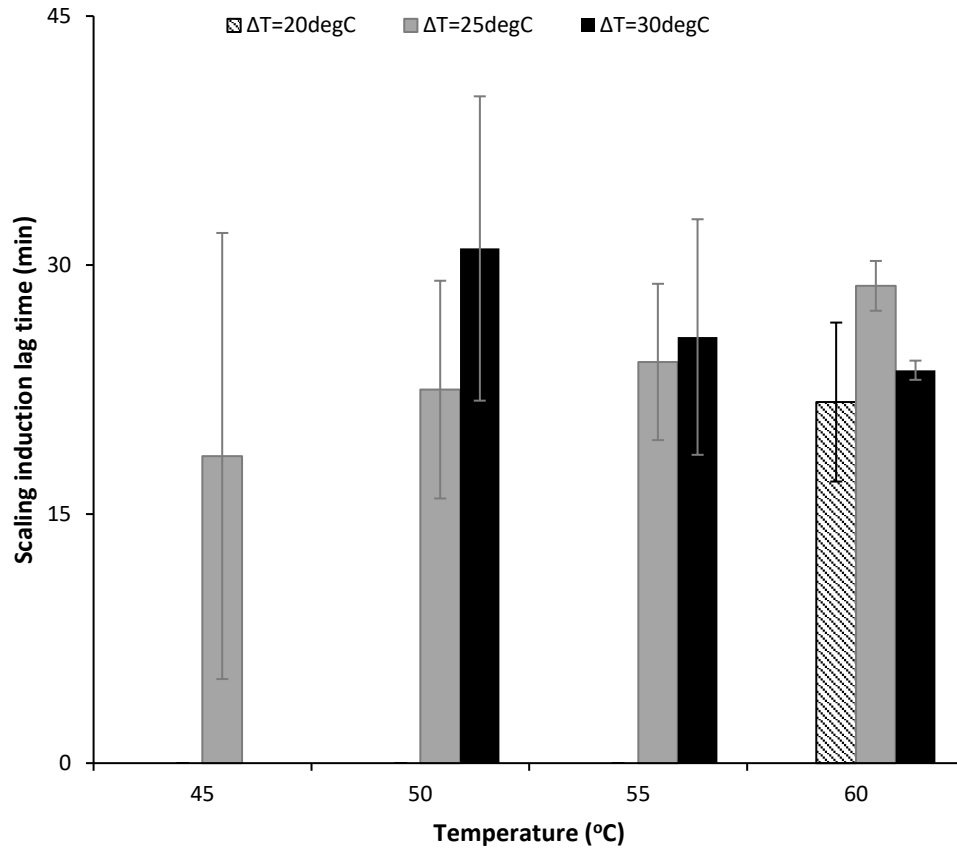


Figure 5.1. Lag time between scaling induction observed using online digital microscope and onset of permeate flux decline. Based on Chapter 2 experimental work at Reynolds number (Re) 1750 for temperatures (T) 45 to 60°C and temperature differences (ΔT) 20 to 30°C. Error bars represent standard deviation of at least two replicates.

This confirms literature reports that the conventional method is not only limited by the description of a single induction time, but also incorrectly describes both the scaling and bulk induction times [3, 9]. Instead, drastic flux decline could be attributed to surface coverage from deposition constraining heat and mass transfer at the interface (Chapter 2). Hence, the advancements in telemetry made in this study enabled improved the diagnosis of nucleation kinetics based on more representative induction time, and therewith metastable zone width (MSZW), measurement.

Contrary to previous assumptions, a homogeneous nucleation mechanism was found to be responsible for scaling (Chapter 2), indicating that sufficiently high interfacial supersaturation levels (S_{int}) were reached to overcome the energy barrier for homogeneous nucleation (ΔG_{hom}^*) [10]. The SEM image of a $\leq 2 \mu m$

crystal trapped in a membrane pore (Chapter 2) seemingly substantiates the solute entrapment mechanism proposed by Di Profio et al. [2], where surface roughness creates cavities which inhibit solute back transport at the interface. This then creates localised highly-supersaturated stagnant regions [2] which likely promotes homogeneous nucleation. This finding potentially validates one of the proposed mechanisms for the scaling inhibition observed for superhydrophobic membranes [9, 11, 12]. It is suggested that superhydrophobic membranes inhibit scaling by creating an air layer between the membrane surface and feed solution, thereby reducing the contact area between the solute and membrane [9]. The presence of an air layer would likely increase the relative smoothness of the surface in contact with the interfacial solution, resulting in a lower probability of entrapment and homogeneous nucleation. Hence, the mechanistic determination of the scaling mechanism facilitates more focused strategies towards scale-free operation.

5.2 Can scale-free desalination be achieved using membrane distillation?

Along with scaling prevention, the viability of MD as a desalination technology is dependent on its thermal process efficiency [9, 13, 14]. In desalination systems, thermal efficiency is described by the gained output ratio (GOR) which relates the latent heat of evaporation to the thermal energy input required to produce a unit mass of permeate [13]. Unfortunately, many existing MD scaling mitigation strategies are in direct contradiction with thermal energy saving operation. For example, the GOR is maximised by higher feed temperatures due to nominal conductive heat losses relative to the heat of vaporisation, thereby enhancing the mass of permeate produced per unit energy [13–15]. In contrast, Edwie and Chung [16] advised against high MD feed temperatures of 60 and 70°C due to enhanced scaling propensity. This was corroborated by Warsinger et al. [5] who proposed that higher temperatures increase the likelihood of scaling by reducing the solute induction time relative to the residence time in the membrane module. The GOR has also been shown to decline at higher feed flow rates which increase heating duties [13, 14]. However, operation at enhanced feed velocities and Reynolds numbers have been central to scaling inhibition in MD [17]. Turbulent

conditions are recommended for (i) reduced temperature and concentration polarisation [16]; (ii) the promotion of crystal detachment [18]; and (iii) the reduction of solute residence time in the membrane module [5]. Positively, through mechanistic rather than empirical scaling diagnostics, this work achieved scale-free operation at temperatures up to 60°C as well as a wide range of laminar Reynolds numbers (Re 1300 – 2050), thus negating the low-temperature and high-shear obligation for scaling prevention in MD (Chapters 2 and 3). Hence, this work has evidenced that scaling mitigation does not have to come at the cost of GOR, thereby improving the competitiveness of MD as a thermal desalination technology.

5.3 How can membrane distillation crystallisation be controlled?

Temperature is a critical control parameter in crystallisation systems as it influences the thermodynamics (solubility) and kinetics (crystallising rate) of a solute [10]. It can therefore dictate the viability, efficiency, and quality of a crystallisation process [10, 19, 20]. This is particularly true for multi-component systems where temperature modulates the solubilities of different solutes at various stages of a process [21–23]. Hence, the revelation of scale-free operation at a wide range of temperatures broadens the suitability of MDC for various crystallising systems. As such, based on the findings of this work, a scale-free MDC control strategy can be imagined for multi-component systems. Examples of such systems are shown in Figure 5.2. System A requires the initial removal of an impurity (A1) followed by the crystallisation of a high-value product (A2), which must meet specifications regarding size and purity (Figure 5.2a). Since losses of A2 must be avoided during the removal of A1, crystallisation of A1 occurs at temperature T_1 , where A1 is highly soluble relative to A2. Product losses are further prevented by operating at a narrow MSZW to prevent co-crystallisation, agglomeration and/or solute inclusions which occur at excessive nucleation rates [10], potentially reducing product recovery. Hence, MDC would occur at low ΔT and Re , where relatively low S_{int} and scale-free operation has been proven (Chapters 2 and 3). Thereafter, the inverse temperature-solubility relationship of A2 requires crystallisation at a high temperature T_2 . Lower ΔT can be

implemented to reduce S_{int} via the supersaturation rate which minimises the risk of scaling (Chapter 2). Although the system is now relatively pure, excessively wide MSZWs or high (S_{int}) should be avoided to prevent agglomeration and solute inclusions which reduce product purity [10]. However, wider MSZWs increase yield (and product recovery rate) by increasing the driving force for crystallisation [2]. Hence, Re can be used for a more moderate increase in S_{int} while accounting for possible scaling by considering the accompanying effect on the concentration polarisation coefficient (CPC) (Chapter 3). After induction, the specified crystal size can be achieved by mediating the growth rate using N and/or temperature (T), both of which stimulate diffusion and solute collisions [24–26] (Chapters 2 and 4).

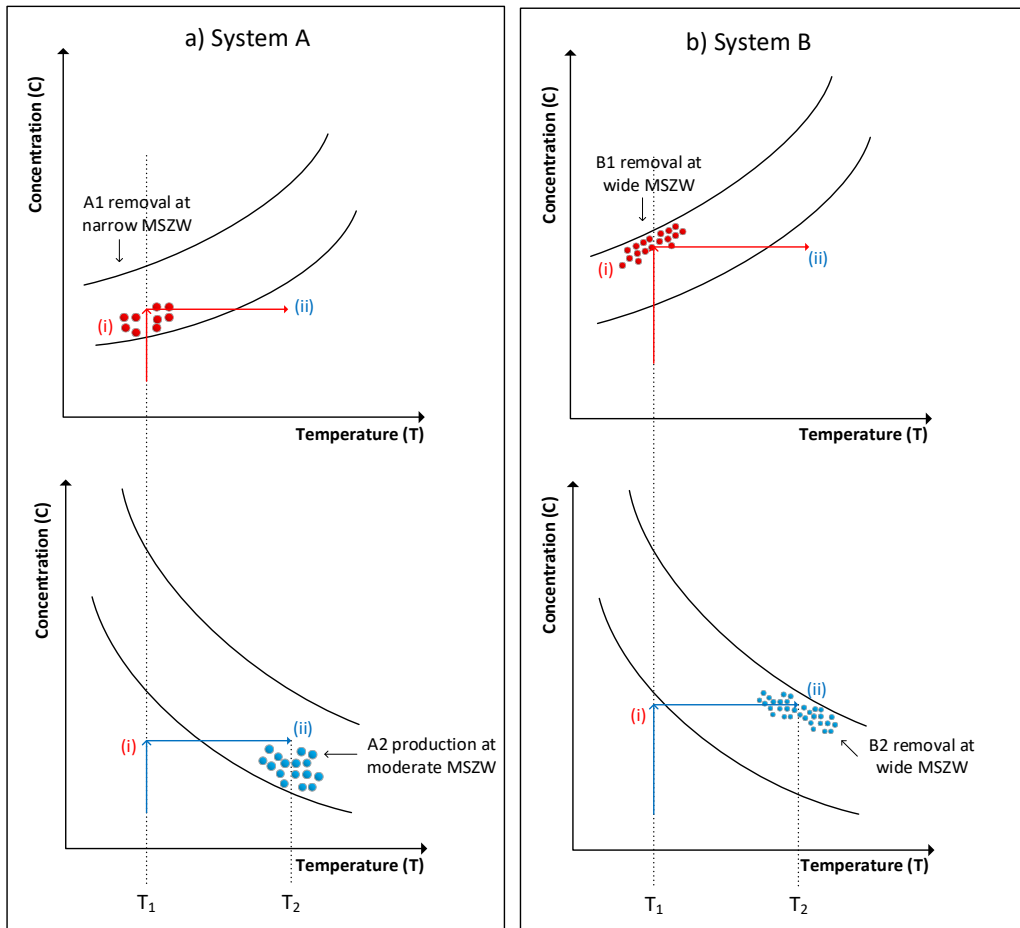


Figure 5.2. Examples of MDC control strategies for multi-component systems. System A (a) describes the removal of impurity, A1, and recovery of product, A2. System B (b) involves the removal of impurities B1 and B2 to maximise solvent recovery.

In System B (Figure 5.2b), solvent purity is of primary concern, which is often the case for water reuse and zero-liquid discharge applications [27]. As such, maximum removal/recovery is required for both solutes. The solubility of component B1 increases with temperature whereas B2 is inversely soluble with temperature. Hence, B1 is crystallised at a lower temperature, where the reduced temperature requires high ΔT and Re to maximise S_{int} . Minimal scaling at high S_{int} is enabled by enhanced Re which promotes the back-transport of solute to the bulk solution [28] (Chapter 3). Thereafter, B2 is removed at a higher temperature where ΔT is reduced to compensate for the increased supersaturation rate and scaling propensity with T (Chapter 2). In addition to scaling, the detrimental impact of high nucleation rates on downstream processes such as filtration must be considered [2, 29, 30]. However, these effects can potentially be offset by high N which was shown to increase the growth rate without impacting S_{int} (Chapter 4). More generally, crystallisation at high supersaturation levels or wide MSZWs may also be required for applications such as polymorph selection [31]. This further highlights the significance of a wide range of kinetic trajectories afforded by the flexible MDC scaling control strategy developed in this work.

5.4 How scalable is membrane crystallisation?

The scale-up of industrial crystallisers is notoriously difficult [32]. Due to the complex interactions between crystallisation kinetics and process hydrodynamics [34, 35], scalability requires controlled environments which facilitate predictable crystallisation kinetics [32]. Fortunately, membrane systems are inherently scalable [33]. They are modular and have high surface-to-volume ratios which increase productivity per unit area [34]. Defined module configurations and surface geometries also mean that hydrodynamics of bulk and boundary-layer solutions in the module can be characterised [35]. Hence, in MDC, the fluid physics in the membrane module, where crystallisation is initiated, are reproducible and therefore scalable [3]. Within this controlled hydrodynamic environment, the supersaturation rate (and therewith the nucleation rate [36]) can be strictly regulated by adjusting the operating variables governing the interfacial

conditions which dictate heat and mass transfer across the membrane [2, 23]. As such, the enhanced control of nucleation kinetics offered by MDC has been well documented [2, 33, 37] and further validated by this study through classical nucleation theory (CNT). The effects of temperature (T) (Chapter 2) transmembrane temperature difference (ΔT) (Chapters 2 and 3) and Re (Chapter 3) on the bulk nucleation rate were unified by their predictable and controllable effects on supersaturation rate. It can therefore be deduced that by moderating MDC supersaturation rate, the number of nuclei produced per unit surface area of membrane can be predicted at scale-up.

Studies have suggested that MDC further enhances crystallisation control by decoupling the regions of nucleation and growth, where nucleation is regulated in the membrane module and growth in the downstream crystalliser [3, 38]. To date however, the impact of the downstream crystalliser on scalability has yet to be considered [3]. This poses a potential vulnerability in the scale-up of MDC systems, since conventional crystallisers remain hampered by poorly-defined mixing conditions which result in unevenly distributed supersaturation conditions and irreproducible crystal product properties [2]. Fortunately, this study revealed that interfacial conditions in the membrane boundary layer play a dominant role in crystal growth kinetics. This is due to the intimate link between nucleation and growth rates [39], rendering the initial growth rate as controllable and predictable as the nucleation rate. However, this work also revealed that the growth rate is highly affected by bulk temperature (Chapter 2) and agitation rate (N) (Chapter 4). Hence, poor bulk hydrodynamic control may lead to inhomogeneous temperature and supersaturation conditions for further crystal growth, thereby compromising product quality [2]. Hence, while the scalability of the membrane module offers partial scalability of crystal growth, the critical understanding of how best to scale-up a complete MDC system (i.e., membrane module and downstream crystalliser) remains limited.

References

- [1] X. Jiang, X. Ruan, W. Xiao, D. Lu, and G. He, "A novel membrane distillation response technology for nucleation detection, metastable zone width measurement and analysis," *Chem. Eng. Sci.*, vol. 134, pp. 671–680, 2015.
- [2] G. Di Profio, E. Curcio, and E. Drioli, "Supersaturation control and heterogeneous nucleation in membrane crystallizers: Facts and perspectives," *Ind. Eng. Chem. Res.*, vol. 49, pp. 11878–11889, 2010.
- [3] M. C. Sparenberg, S. Chergaoui, V. Sang Sefidi, and P. Luis, "Crystallization control via membrane distillation-crystallization: A review," *Desalination*, vol. 519, p. 115315, 2022.
- [4] D. M. Warsinger et al., "Effect of filtration and particulate fouling in membrane distillation," *Int. Desalin. Assoc.*, pp. 0–14, 2015.
- [5] D. M. Warsinger, E. W. Tow, J. Swaminathan, and J. H. Lienhard V, "Theoretical framework for predicting inorganic fouling in membrane distillation and experimental validation with calcium sulfate," *J. Memb. Sci.*, vol. 528, pp. 381–390, 2017.
- [6] Y. Shin and J. Sohn, "Mechanisms for scale formation in simultaneous membrane distillation crystallization: Effect of flow rate," *J. Ind. Eng. Chem.*, vol. 35, pp. 318–324, 2016.
- [7] C. M. Tun et al., "Membrane distillation crystallization of concentrated salts - Flux and crystal formation," *J. Memb. Sci.*, vol. 257, pp. 144–155, 2005.
- [8] J. Kim, H. W. Kim, L. D. Tijing, H. K. Shon, and S. Hong, "Elucidation of physicochemical scaling mechanisms in membrane distillation (MD): Implication to the control of inorganic fouling," *Desalination*, vol. 527, p. 115573, 2022.
- [9] T. Horseman, Y. Yin, K. S. Christie, Z. Wang, T. Tong, and S. Lin, "Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies," *ACS ES&T Eng.*, vol. 1, pp. 117–140, 2021.
- [10] A. S. Myerson, D. Erdemir, and A. Y. Lee, *Crystal nucleation*. 2019.
- [11] C. Su, T. Horseman, H. Cao, K. Christie, Y. Li, and S. Lin, "Robust Superhydrophobic Membrane for Membrane Distillation with Excellent

- Scaling Resistance,” *Environ. Sci. Technol.*, vol. 53, pp. 11801–11809, 2019.
- [12] T. Horseman, C. Su, K. S. S. Christie, and S. Lin, “Highly effective scaling mitigation in membrane distillation using a superhydrophobic membrane with gas purging,” *Environ. Sci. Technol. Lett.*, vol. 6, pp. 423–429, 2019.
 - [13] E. K. Summers, H. A. Arafat, and J. H. Lienhard V, “Energy efficiency comparison of single-stage membrane distillation (MD) desalination cycles in different configurations,” *Desalination*, vol. 290, pp. 54–66, 2012.
 - [14] D. Winter et al., “Comparative analysis of full-scale membrane distillation contactors - methods and modules,” *J. Memb. Sci.*, vol. 524, pp. 758–771, 2017.
 - [15] M. R. Elmarghany, A. H. El-Shazly, M. S. Salem, M. N. Sabry, and N. Nady, “Thermal analysis evaluation of direct contact membrane distillation system,” *Case Stud. Therm. Eng.*, vol. 13, p. 100377, 2019.
 - [16] F. Edwie and T. S. Chung, “Development of simultaneous membrane distillation-crystallization (SMDC) technology for treatment of saturated brine,” *Chem. Eng. Sci.*, vol. 98, pp. 160–172, 2013.
 - [17] D. M. Warsinger, J. Swaminathan, E. Guillen-Burrieza, H. A. Arafat, and J. H. Lienhard V, “Scaling and fouling in membrane distillation for desalination applications: A review,” *Desalination*, vol. 356, pp. 294–313, 2015.
 - [18] X. Jiang et al., “Interface-based crystal particle autoselection via membrane crystallization: From scaling to process control,” *AIChE J.*, vol. 65, pp. 723–733, 2019.
 - [19] J. Ulrich and C. Strege, “Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers,” *J. Cryst. Growth*, vol. 237–239, pp. 2130–2135, 2002.
 - [20] D. Kashchiev and G. M. Van Rosmalen, “Review: Nucleation in solutions revisited,” *Cryst. Res. Technol.*, vol. 38, pp. 555–574, 2003.
 - [21] X. K. Wang, D. C. Yin, C. Y. Zhang, Q. Q. Lu, Y. Z. Guo, and W. H. Guo, “Effect of temperature programmes on protein crystallisation,” *Cryst. Res. Technol.*, vol. 45, pp. 479–489, 2010.

- [22] Y. S. Chang, B. S. Ooi, A. L. Ahmad, C. P. Leo, and S. C. Low, "Vacuum membrane distillation for desalination: Scaling phenomena of brackish water at elevated temperature," *Sep. Purif. Technol.*, vol. 254, p. 117572, 2021.
- [23] R. Sheikholeslami and M. Ng, "Calcium sulfate precipitation in the presence of nondominant calcium carbonate: Thermodynamics and kinetics," *Ind. Eng. Chem. Res.*, vol. 40, pp. 3570–3578, 2001.
- [24] S. Fan, X. Gu, X. Zhou, X. Duan, and H. Li, "Determination of nucleation kinetics from the induction time of 1,1-diamino-2,2-dinitroethylene (FOX-7) in DMSO/Water," *Energ. Mater. Front.*, vol. 2, no. 1, pp. 62–68, 2021.
- [25] M. Akrap, N. Kuzmanić, and J. Prić-Kardum, "Effect of mixing on the crystal size distribution of borax decahydrate in a batch cooling crystallizer," *J. Cryst. Growth*, vol. 312, pp. 3603–3608, 2010.
- [26] W. R. Wilcox, "Transport phenomena in crystal growth from solution," *Prog. Cryst. Growth Charact. Mater.*, vol. 26, pp. 153–194, 1993.
- [27] T. Tong and M. Elimelech, "The Global Rise of Zero Liquid Discharge for Wastewater Management: Drivers, Technologies, and Future Directions," *Environ. Sci. Technol.*, vol. 50, pp. 6846–6855, 2016.
- [28] O. R. Lokare and R. D. Vidic, "Impact of Operating Conditions on Measured and Predicted Concentration Polarization in Membrane Distillation," *Environ. Sci. Technol.*, vol. 53, pp. 11869–11876, 2019.
- [29] J. Ulrich and P. Froberg, "Problems, potentials and future of industrial crystallization," *Front. Chem. Sci. Eng.*, vol. 7, pp. 1–8, 2013.
- [30] S. K. Jha, S. Karthika, and T. K. Radhakrishnan, "Modelling and control of crystallization process," *Resour. Technol.*, vol. 3, pp. 94–100, 2017.
- [31] A. Lewis, M. M. Seckler, H. Kramer, and G. van Rosmalen, *Industrial Crystallization*. Cambridge: Cambridge University Press, 2015.
- [32] M. Trampuž, D. Teslić, and B. Likozar, "Crystal-size distribution-based dynamic process modelling, optimization, and scaling for seeded batch cooling crystallization of Active Pharmaceutical Ingredients (API)," *Chem. Eng. Res. Des.*, vol. 165, pp. 254–269, 2021.

- [33] C. Charcosset, R. Kieffer, D. Mangin, and F. Puel, "Coupling between membrane processes and crystallization operations," *Ind. Eng. Chem. Res.*, vol. 49, pp. 5489–5495, 2010.
- [34] E. Chabanon, D. Mangin, and C. Charcosset, "Membranes and crystallization processes: State of the art and prospects," *J. Memb. Sci.*, vol. 509, pp. 57–67, 2016.
- [35] I. Ruiz Salmón and P. Luis, "Membrane crystallization via membrane distillation," *Chem. Eng. Process. Process Intensif.*, vol. 123, pp. 258–271, 2018
- [36] J. Nyvlt, "Kinetics of nucleation in solutions," *J. Cryst. Growth*, vol. 3, pp. 377–383, 1968.
- [37] J.-H. H. Tsai et al., "Membrane-Assisted Crystallization: A Molecular View of NaCl Nucleation and Growth," *Appl. Sci.*, vol. 8, p. 2145, 2018.
- [38] X. Jiang, Y. Shao, L. Sheng, P. Li, and G. He, "Membrane Crystallization for Process Intensification and Control: A Review," *Engineering*, vol. 7, pp. 50–62, 2021.
- [39] A. Mersmann, "Crystallization and precipitation," *KONA Powder Part. J.*, vol. 16, pp. 60–67, 1998.

6. Conclusions and Further Work

6.1 Conclusions

This thesis has demonstrated that bulk crystallisation and scaling kinetics in membrane distillation crystallisation (MDC) can be independently controlled by regulating supersaturation and hydrodynamic conditions in the bulk solution and interfacial boundary layer.

- (i) Two distinct mechanisms for scaling and bulk nucleation have been demonstrated. Not only does this work highlight the shortcomings of previous empirical approaches, but it provides a mechanistic framework for more targeted and incisive control of scaling and bulk crystallisation (Objective 1).
- (ii) The revelation of a homogeneous nucleation mechanism has brought the validity of current scaling mitigation strategies in MDC, and potentially other membrane systems such as reverse osmosis/nanofiltration (RO/NF), into question. While the surface properties of RO/NF membranes may be different, this emphasises the need for adequate telemetry and kinetic analysis of crystallisation phenomena in membrane scaling studies (Objective 1).
- (iii) The dependence of bulk nucleation kinetics on interfacial supersaturation conditions was well described by classical nucleation theory (CNT). Hence, the bulk nucleation rate can be predicted and scaled up based on the influence of interfacial operating conditions on the supersaturation rate (Objective 1).
- (iv) Since crystal growth kinetics were shown to be highly influenced by interfacial conditions, it is likely that the MDC enhances the scalability of both crystal nucleation and growth (Objective 1). However, downstream hydrodynamics also play a decisive role in growth kinetics, which may hinder the overall scalability of the process (Objective 3).
- (v) While Reynolds number (Re) as a turbulence promoter is a critical parameter for scaling inhibition in a wide range of systems, this work has evidenced its complex effects on interfacial solute transport and

polarisation phenomena. Significantly, high Re did not guarantee scaling inhibition as increasing Re could potentially promote highly-supersaturated, diffusion-limited conditions, a finding which may have broad implications for other scaling systems such as heat exchangers, where polarisation effects are prevalent (Objective 2).

- (vi) Scale-free bulk crystallisation was facilitated at a high temperature (T 60°C) and relatively quiescent conditions (laminar Re), conditions previously associated with scaling. As such, the perceived range of kinetic trajectories and product specifications achievable with MDC has been broadened (Objective 2).
- (vii) Although scale-free operation was achieved at high S_{int} and high Re , this may not be in the best interest of product quality due to excessive primary nucleation rates which reduce crystal size and increase the likelihood of agglomeration. Increases in S_{int} also increase the likelihood of growth in the “crystal proliferation zone” where secondary nucleation mechanisms such as dendritic breeding are observed, thus further reducing product quality (Objective 3).
- (viii) Higher crystalliser agitation rates (N) promoted crystal growth without reducing the interfacial MSZW (S_{int}) and resultant nucleation rate. This demonstrates that high yields of larger crystals can be obtained by decoupling the regions of nucleation and growth (Objective 3).
- (ix) Bulk induction times declined with improvements in bulk hydrodynamics due to enhanced molecular collisions. Although the following effect was not considered in this work, enhancing N can potentially reduce scaling in MDC by reducing the time available for scaling prior to bulk nucleation (Objective 3).

6.2 Further work

The following areas are recommended for future research:

- (i) While factors such as membrane material and solute transport may vary, the mechanistic framework and experimental techniques outlined in this work should be applied to elucidate the nucleation mechanism(s)

governing scaling in other membrane systems such as RO/NF, where contact angles are generally below 90° , thereby favouring heterogeneous nucleation. Since kinetic analyses have been limited in these systems, validation of the governing mechanism would provide greater clarity and distinctions on how best to operate different membrane systems for minimal scaling.

- (ii) A single salt (NaCl) was used in this study. This was to avoid the occurrence phenomena such as co-crystallisation and the inhibition of nucleation and growth, which would distort the governing crystallisation kinetics and mechanisms. In real systems such as brine management for zero-liquid discharge however, numerous organic and inorganic solutes can be present in solution. It is therefore recommended that future studies build on the foundations of this work by investigating the effects of different solute interactions on crystallisation kinetics in MDC. This would also potentially inform the pre-treatment steps required prior to the recovery of a specified solute using MDC technology.
- (iii) In this work, process failure due to drastic flux decline was attributed to the deposition of crystals on the membrane surface. The rate of deposition is dependent on factors such as concentration, temperature and velocity gradients [1]. As such, future studies considering the effects of interfacial conditions and system configurations on deposition rate, with subsequent recommendations of how best to mitigate deposition, are essential steps toward continuous MDC operation.
- (iv) Solute transport in the boundary layer has been shown to play a critical role in mediating between scaling and bulk nucleation. To account for variations in operating conditions (e.g., supersaturation, temperature, and mixing) in addition to further complexities such as solute entrapment by surface roughness, CFD studies are recommended for better characterisation of boundary-layer solute transport. This will facilitate precise scaling prevention and crystallisation control, especially during scale-up.

- (v) While the analyses of this study were limited to the onset of bulk nucleation, the presence of solids after primary nucleation will alter the hydrodynamic and supersaturation conditions in the system, both of which dictate crystal growth kinetics. Hence, CFD studies which incorporate the transport and growth of crystals in a dynamic solution are recommended for the optimisation of product quality.
- (vi) The hydrodynamics of the bulk crystalliser have been identified as a possible vulnerability for the scale-up of MDC systems. In contrast, the boundary layer facilitated greater hydrodynamic control through a defined membrane geometry. As such, future studies into module configurations (e.g., longer membrane modules or modules in series) which would facilitate boundary-layer controlled growth without the need of a downstream crystalliser, could potentially guarantee complete scalability of MDC.
- (vii) The potential for bulk hydrodynamics to inhibit scaling by stimulating bulk nucleation requires further investigation. Since bulk crystallisation is dependent on the metastability of the bulk solution, future studies considering low-solubility salts or proteins, which have higher metastabilities, are recommended for a broader understanding of how bulk hydrodynamics can be exploited to govern nucleation kinetics at the interface.

References

- [1] A. Guha, "A unified Eulerian theory of turbulent deposition to smooth and rough surfaces," J. Aerosol Sci., vol. 28, pp. 1517–1537, 1997.