



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

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ABSTRACT

While mixing is considered critical in membrane distillation 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 crystal growth in membrane distillation crystallisation. Interfacial boundary layer mixing was investigated by changing Reynolds number (Re , 1300–2050), where an increase in Re also increased flux. This increased supersaturation within the boundary layer, shortened induction time, and was correlated to a higher nucleation rate. The high nucleation rates introduced smaller crystal sizes, which is an effect that can be correlated to classical nucleation theory. Mixing within the crystalliser did not modify the interfacial supersaturation at nucleation (Re_N 1562–18741). However, a decrease in induction time was observed when transitioning from lower to higher mixing, which may arise from the improved distribution of the supersaturated feed within the crystalliser. The effect of crystalliser mixing was also evident on crystal growth, where larger crystals were produced at higher crystalliser stirrer speeds due to improved diffusion-controlled growth. This study therefore demonstrates that bulk and interfacial mixing can be collectively used to control crystallisation by decoupling conditions that determine nucleation and crystal growth. Morphological assessment was subsequently undertaken that evidenced how dendritic breeding and wider secondary nucleation mechanisms that dominate crystal growth at high levels of supersaturation can be mitigated through mixing. Membrane crystallisation offers a scalable geometry in which we demonstrate mixing to facilitate good control over crystal growth which is more difficult to realise in existing evaporative crystalliser design.

1. Introduction

Crystallisation is an essential separation and purification process, used for the production of chemicals in numerous sectors (e.g. pharmaceutical, microelectronics), and is of increasing importance to the development of zero liquid discharge concepts in the water sector [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) integrates both membrane distillation (MD) and crystallisation into a single process, and

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 water vapour transport across the membrane concentrates the feed solution, resulting in crystal formation once the solubility limit of solution has been exceeded. The hydrophobic membrane and the highly-concentrated boundary layer that forms at the interface between membrane and feed solution, are also proposed to contribute to the control of nucleation through modifying the overall Gibbs free energy requirement for nucleation [2,3,5,6]. As such, MDC has been shown to reduce the induction time for various crystallisation systems. For example, Di Profio et al. [7] showed that the introduction of a microporous membrane 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-

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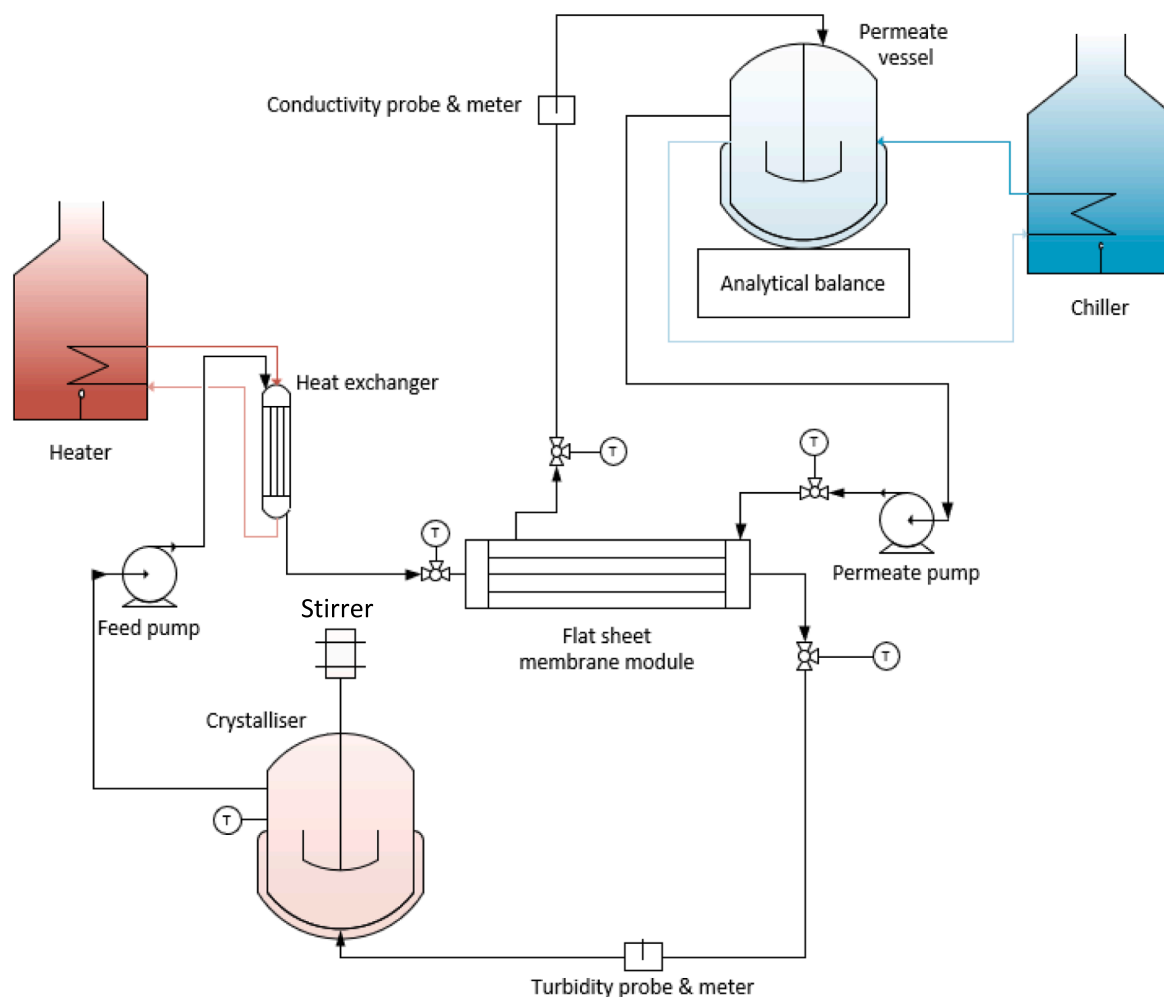


Fig. 1. Schematic of MDC experimental setup.

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 or crystal growth. 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]. It has been proposed that in addition to the decrease in concentration polarisation, increasing the feed flow rate lowers the residence time of the fluid in the membrane module relative to the scaling induction time, therefore reducing the likelihood of fouling [10]. 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 (Re) has also been shown to increase the permeate flux [12,13]. Jikazana et al. [41] introduced the supersaturation rate as a single term that collectively describes how flux, solute concentration and temperature, inclusive of the effects of temperature and concentration polarisation, modify the supersaturation driving force for nucleation within the

boundary layer. The authors demonstrated how an increase in Re , increased mass and heat transfer (resulting in an increase in flux), which broadened the metastable zone width (MSZW) within the boundary layer at induction. The MSZW is a measure of the metastability of solution ($c-c^*$), that characterises the extent of the supersaturation that has been developed at the onset of nucleation. This is of critical importance since supersaturation is the driving force for both nucleation and crystal growth [4,5]. Consequently, the hydrodynamics (Re) set within the feed play a crucial role in determining the crystal product characteristics in MDC systems. Analogous effects may be inferred from the work of Di Profio et al. [15] where glycine crystallisation was presumed to transition from thermodynamically-controlled to kinetically-controlled polymorphs following an increase in permeate flux. However, the role of mixing within the boundary layer has yet to be explicitly linked to the control of crystal size or morphology, which is critical for downstream separation and application.

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 a narrower MSZW [16–19]. Therefore, while it has been previously posited that primary nucleation is primarily controlled by the membrane module [11], it is important to confirm whether the crystalliser (bulk)

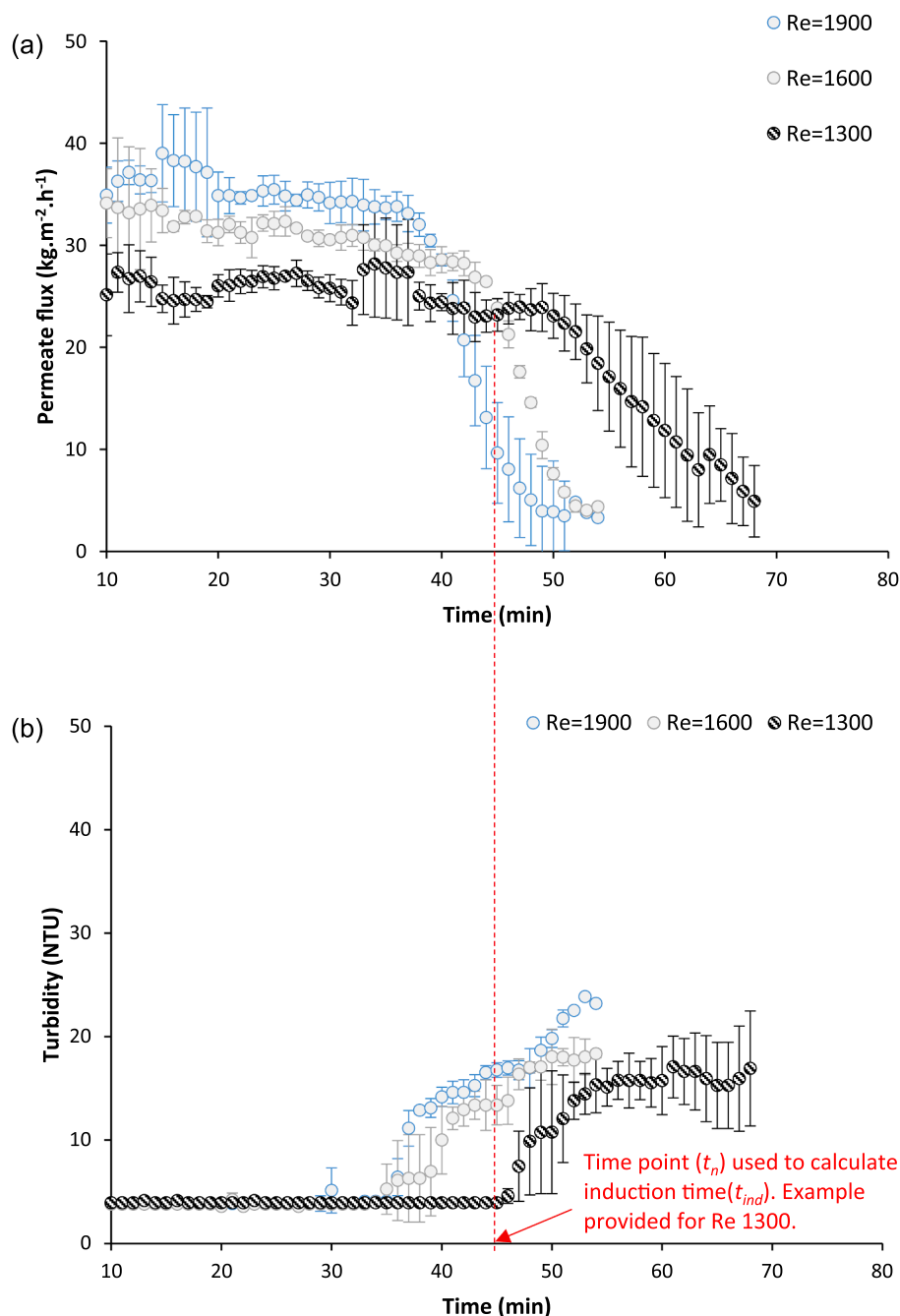


Fig. 2. Example time series to demonstrate primary data collection for flux and turbidity: (a) permeate flux; (b) turbidity. Conditions: Reynold's number (Re) 1300, 1600 and 1900; Crystalliser stirrer speed (N) 300 rpm. Red dotted line illustrates alignment between permeate flux and the onset of bulk nucleation as identified by turbidimetry (Re 1300; N 300 rpm). Data represents the average and standard deviation of at least three experimental replicates undertaken in the same conditions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mixing conditions may also contribute toward the regulation of nucleation which has yet to be investigated. Increased bulk mixing also promotes mass transfer around the crystalline solid phase and therefore improves the diffusion-controlled crystal growth rate [20,21].

There is currently a paucity of knowledge for how the hydrodynamics set within the membrane and crystalliser may independently influence crystal growth in MDC. High agitation rates are also associated with secondary nucleation mechanisms (SNMs) such as attrition which is detrimental to product quality [20,22–24]. The involvement of SNMs and agglomeration phenomenon are dependent on both the level of supersaturation and turbulence in the system [23,25]. The extent to which such effects will be observed, is therefore expected to be

determined by the hydrodynamics imposed in both the membrane and crystalliser. This study therefore aims to provide 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 dual optical fibre 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 through induction time and metastable zone width measurements, 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.

2. Materials and methods

2.1. Membrane distillation crystallisation experimental setup

The experimental setup consists of a direct contact membrane distillation (DCMD) flow cell which housed a 40×100 mm flat sheet 50 ± 20 μm thick ePTFE membrane with a 0.1 μm pore size (Cobetter Filtration, Hangzhou, China) (Fig. 1). The membrane-water contact angle was $142.3 \pm 0.9^\circ$. The feed side (NaCl solution) was connected to a crystalliser vessel (Reactor-Ready™, Radleys, Essex, UK) sited downstream of the membrane module which had a height (H) and inner diameter of 150 and 65.6 mm, respectively. The torispherical base and height to width ratio of the vessel contribute to effective mixing, mimicking the dimensionality of full-scale reactors, that can be used as a basis for scale-up through a factorial approach. A four-bladed PTFE turbine stirrer (Radleys, Essex, UK) with a 45° pitch and 35 mm outer diameter was inserted into the crystalliser. The pitched blade is important for heated mixtures as it creates an effective axial stirring pattern to ensure a consistent temperature profile. 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 $1/3H$. This is the standard depth recommended industrially to ensure effective downward mixing, and to avoid settling of particulate suspensions. The Reynolds number within the crystalliser was varied by varying the stirrer speed (N) which corresponds to the range used within industry, whereas the Reynolds number within the membrane boundary layer was varied by varying the feed velocity (V) in the membrane module, and is characteristic of the range studied in literature. The impeller and feed solution Reynolds numbers are specified in Appendix A. The NaCl feed solution was recirculated from the crystalliser to the membrane module through 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 crystals through light backscatter (InPro 8200/S/Epoxy/120 turbidity sensor, Mettler-Toledo Ltd, Leicester, UK). The dual optical-fibre sensor technology provides reproducible turbidity measurement with high resolution over a wide measuring range (<5 to 4000 FTU). Turbidity employs a light backscatter technique where the scattering and absorption of light are used to detect the presence of particles; the increase in turbidity in crystallisation systems indicates the time at which a crystal phase has formed and is the basis for the majority of nucleation detection systems used in industry. Similar to Di Profio et al. [7], this industrially-applied method is used for the non-invasive detection of the start of crystal nucleation and hence permits 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).

2.2. Crystal sampling and analysis

To obtain crystal samples for analysis, the experiments were stopped 10 min after induction time was reached in the bulk solution. Induction time was calculated using the point in time at which the turbidity of the feed solution increased (Fig. 2). 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 h. Crystal size distributions (CSDs) were obtained with an optical microscope (Leica CTR 5500B, 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 vapour deposition and images collected at an acceleration voltage of 20 keV, a beam current of 300 pA and a working distance of 10 mm. Each Re number and N speed were undertaken as independent experiments. Experiments for each Re number and N speed were undertaken in triplicate as a minimum. Each of the data points is represented as the mean and error of those replicated experiments. The same quality assurance strategy was employed for the primary data used (e.g. temperature, flux, solute concentration, concentration and temperature polarisation). The secondary analysis (including the nucleation kinetic analysis) is therefore based on the data replication described.

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]:

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

where J is the nucleation rate ($\text{kg m}^{-3} \text{s}^{-1}$), A is the pre-exponential factor, B is a constant and S is the supersaturation level. Sangwal (2009) assumed an empirical power law relationship between the nucleation rate and supersaturation level achieved at induction:

$$J = k(\ln S)^m \quad (2)$$

where k and m are the nucleation constant ($\text{kg m}^{-3} \text{s}^{-1}$) and order, respectively. With this approach, the rate of supersaturation (R' , $\text{kg m}^{-3} \text{s}^{-1}$) at the onset of bulk induction is assumed to be analogous to the nucleation rate. Hence for the membrane interface (within the boundary layer) at the onset of bulk nucleation, Eq. (2) can be re-written as:

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

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

$$R' = \frac{d(\Delta C)}{dt} = \frac{[\Delta C_{ind} - \Delta C_0]_{int}}{T_{ind} - T_0} = \frac{[(C_{ind} - C_{ind}^*) - (C_0 - C_0^*)]_{int}}{T_{ind} - T_0} \quad (4)$$

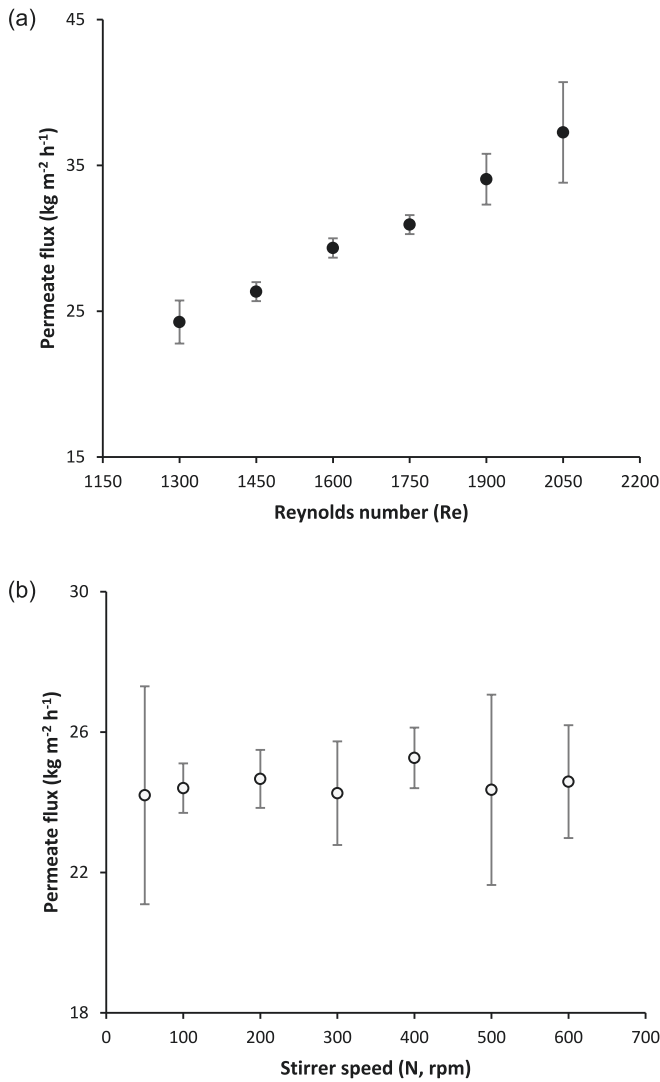


Fig. 3. Understanding the influence of mixing on the permeate flux (five-minute moving average) at the onset of bulk nucleation when: (a) Interfacial Reynold's number (Re) is increased from 1300 to 2050 at a fixed agitation of 300 rpm and (b) Crystalliser mixing (N) is varied from 50 to 600 rpm, with Re constant at 1300. Data represents the average and standard deviation of at least three experimental replicates undertaken in the same conditions.

C is the concentration (kg m⁻³), T is time (s), the superscript $*$ indicates saturation, and subscripts ind , 0 and int represent the induction point, the starting point and the interface, respectively. Through this characterisation method, the supersaturation rate represents the role of flux, solute concentration, solubility, TPC and CPC within a single term, which can be directly related to the nucleation kinetics. Following from Eq. (3), S_{int} is the interfacial supersaturation level at induction. It is given by:

$$S_{int} = \left(\frac{C_{ind}}{C^*} \right)_{int} \quad (5)$$

The methodology adopted to calculate the interfacial concentration (C_{int}) is provided in [Appendix B](#). The change in permeate mass was used to determine the bulk concentration of the feed solution at each point in time and hence the bulk supersaturation level (S_{bulk}) at induction is calculated using the following Eq. (6):

$$S_{bulk} = \left(\frac{C_{ind}}{C^*} \right)_{bulk} \quad (6)$$

By linearising Eq. (3), a plot of $\ln(R')$ versus $\ln(\ln S_{int})$ results in a linear relationship from which the nucleation order (m) and constant (k) can be derived based on classical nucleation theory (CNT):

$$\ln(R') = m \ln(\ln S_{int}) + \ln k \quad (7)$$

Since induction time (t_{ind}) is considered inversely proportional to the nucleation rate [30], t_{ind} can be substituted into Eq. (1) and linearised such that:

$$\ln(t_{ind}) = \ln A + \frac{B}{\ln^2 S_{int}} \quad (8)$$

Based on CNT, a plot of $\ln(t_{ind})$ versus $\ln^2 S_{int}$ therefore yields a linear trend. The induction time is related to the nucleation rate as it is a measure of the metastability of solution, or the time over which the solution exists in a supersaturated state before nucleation occurs. The gradient (B) therefore represents the nucleation work:

$$B = \frac{16\pi\gamma^3 v^2}{3(k_B T)^2} \quad (9)$$

Hence, higher gradients indicate higher interfacial energies and a tendency towards homogeneous nucleation. Conversely, a lower gradient evidences a lower interfacial energy and enhanced probability of heterogeneous nucleation [28,29]. The induction time (t_{ind}) is therefore defined as the difference between the time at which nucleation is observed through turbidimetry (t_n) and the time at which the solubility limit for solution was reached ($t_{c/c^*=1}$):

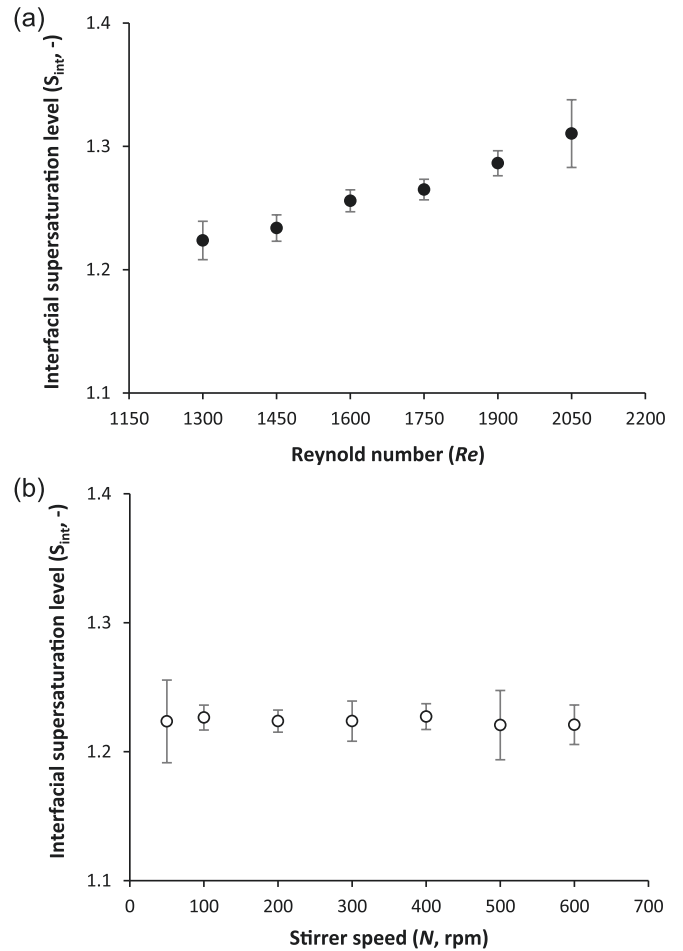


Fig. 4. The effects of (a) Reynolds number (Re) and (b) crystalliser stirrer speed on interfacial supersaturation (defined as the supersaturation achieved at induction); For (a) crystalliser mixing fixed at 300 rpm, and (b) Reynolds number in the membrane fixed to Re 1300.

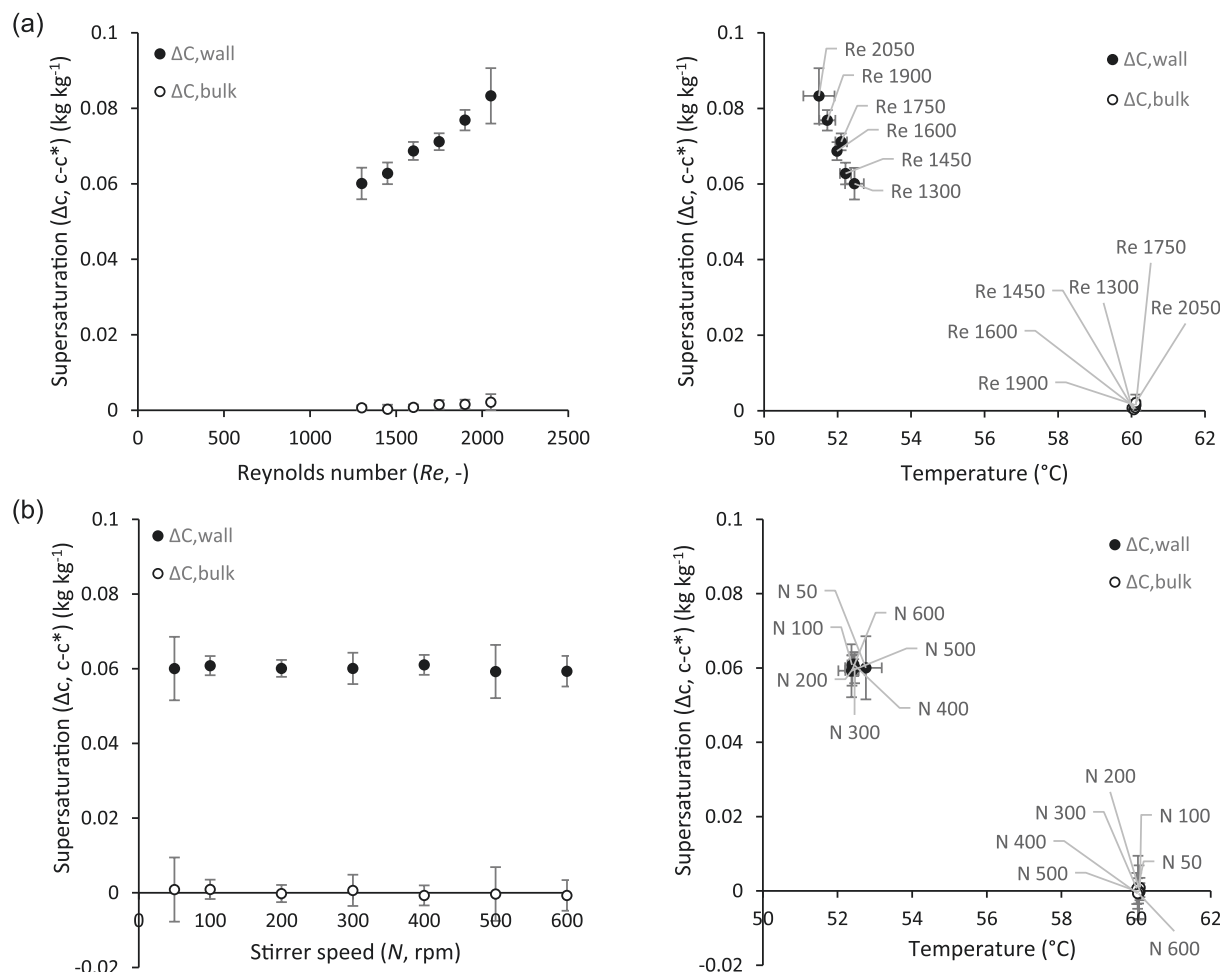


Fig. 5. Characterisation of the supersaturation achieved at nucleation for each mixing condition when: (a) modifying Re (N fixed to 300 rpm); and (b) modifying stirrer speed (Re fixed to 1300). The temperatures refer to those in the bulk and boundary layer (wall) at nucleation.

$$t_{ind} = t_n - t_{c/c^*=1} \quad (10)$$

3. Results and discussion

3.1. Differentiating the role of bulk and interfacial mixing on primary nucleation

In MDC, the permeate flux is one of the primary contributing factors determining the rate of supersaturation [39]. Permeate flux was characterised at the onset of nucleation for each mixing condition, by determining the flux corresponding to the detection of nucleation (Fig. 2). The onset of nucleation was determined based on the point of inflection in the turbidity-time trend, which signifies the time at which crystal phase is first formed. The Re within the membrane module was varied between 1300 and 2050 which covered the laminar to transitional regime, while the crystalliser stirring rate (N) was fixed to 300 rpm. Raising the Re from 1300 to 2050 increased the permeate flux recorded at the onset of nucleation from 24.3 to $37.3\ kg\ m^{-2}\ h^{-1}$ (Fig. 3a). This was due to the reduction in boundary layer thickness which promoted heat and mass transfer across the membrane [9,13]. This flux value together with the solute concentration and solubility (corrected for the effects of temperature and concentration polarisation) corresponding to the onset of nucleation are used to calculate the supersaturation rate (Eq. (4)). The impeller 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]. Crystalliser stirrer speeds of 50 to 600 rpm were examined, which corresponded to Re_N in

the range 1562 to 18741. During crystalliser mixing studies, Re within the membrane was fixed to 1300. An increase in N from 50 to 600 rpm did not modify the permeate flux (Fig. 3b). This confirms that solution conditions within the boundary layer contribute strongly to mass transport (specifically water vapour flux) [13], whereas mixing within the crystalliser does not.

The increase in water vapour flux following a modification of Re from 1300 to 2050, increased the interfacial boundary layer supersaturation (S_{int}) from 1.22 to 1.31 (Fig. 4a). In the current MDC literature, an increase in Re is generally presumed to lower S_{int} due to a reduction in temperature (TPC) and concentration polarisation (CPC) [9,13]. While Re can contribute to a reduction in CPC, the reduction in boundary layer thickness increases permeate flux, which subsequently enhances the convective flux of solute to the interface. Therefore, CPC can increase in response to raising Re [33]. Higher water vapour fluxes imposed by Re also increase the supersaturation rate, due to the increase in the rate at which solute is concentrated in the feed solution and is exacerbated within the boundary layer by the CPC. Consequently, a wider MSZW is established at the onset of nucleation (Fig. 5). The MSZW describes the supersaturation achieved at nucleation, which is the difference between the solute concentration and the solubility limit at the specified temperature ($\Delta C = C - C^*$). Through modification of the MSZW, more advanced control over the nucleation process can be achieved which is helpful to obtain desired crystal size, shape, and purity. The temperatures refer to the temperatures in bulk solution and interfacial boundary layer (wall) at the point of nucleation. The supersaturation measured within the bulk solution and the boundary layer (wall) at the point of

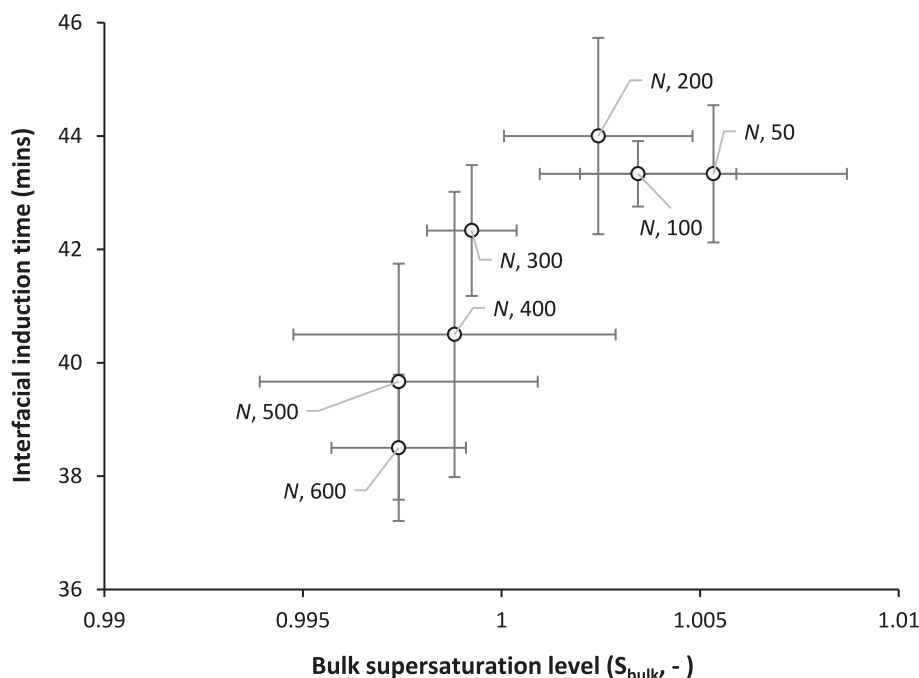


Fig. 6. Relating transition in bulk supersaturation (S_{bulk}) to the reduction in induction time (t_{ind}) due to crystalliser mixing. Stirrer speed (N) 50 to 600 rpm (Re 1300). Higher N shortens induction time and narrows the bulk MSZW, which is characteristic of classical stirred crystallisers. Data represents the average and standard deviation of at least three experimental replicates undertaken in the same conditions.

nucleation are reported for each Re (Fig. 5a) and crystalliser stirring speed (Fig. 5b) investigated.

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]. This was evidenced in this study at higher Re , where broader MSZW ($\Delta C = C - C^*$) were achieved within the boundary layer at the onset of nucleation. This can be attributed to two effects: (i) the reduction in boundary layer temperature (wall) at higher Re due to temperature polarisation lowers the solubility limit (C^*); and (ii), the interfacial concentration (C) is increased by the CPC and water vapour flux. These two effects increase the supersaturation achieved by the boundary layer at induction. The solubility-temperature dependency of NaCl is relatively flat, and so the solute concentration within the interfacial boundary layer primarily determines the supersaturation. Whereas the temperature in the boundary layer (wall) reduced with an increase in Re , the temperature in the bulk solution was consistently $\sim 60^\circ\text{C}$, and as such modifications to the boundary layer did not change the solubility limit in the bulk solution (C^*). Comparison of supersaturation measurements between the bulk and boundary layer evidenced that while an increase in Re , increased the interfacial boundary supersaturation (wall) at induction, supersaturation within the bulk solution at the onset of nucleation was consistently close to zero. A MSZW of zero (or supersaturation of zero) indicates that the solute concentration in the bulk solution at nucleation is equivalent to the solubility limit of solution, i.e. the solution has achieved saturation but is not supersaturated ($c/c^* = 1$). Therefore, a MSZW equal to zero (equal to the solubility limit, $c/c^* = 1$) was established in the bulk solution, which represents the lower limit of the metastable zone. As the bulk solution does not achieve supersaturation before nucleation, there is insufficient supersaturation to serve as the driving force to initiate primary nucleation. This is amongst the first direct evidence that confirms it is the boundary layer (wall) which controls the onset of primary nucleation, rather than the bulk conditions. However, the consistency with which the bulk solute concentration tends toward saturation (i.e. the solubility limit) at induction, may

also indicate a role for the bulk solution in instigating nucleation, since a thermodynamically stable crystal phase is unlikely to be achieved unless saturation is reached in solution due to the prospect for dissolution of crystals at a saturation threshold below the solubility limit.

Following modifications to crystalliser stirrer speed, N (Re , fixed to 1300 rpm), the interfacial concentration was consistently higher than in the bulk solution. A comparable interfacial MSZW was sustained for each mixing condition (ΔC , $\sim 0.06\text{ kg kg}^{-1}$), which can be attributed to the consistent mass and heat transfer processes occurring across the membrane for each crystalliser stirrer speed studied (Fig. 3). The bulk solution ΔC was $\sim 0\text{ kg kg}^{-1}$, which indicates that the solute concentration was equal to the solubility limit at nucleation (the minimum limit of the MSZW). The difference in supersaturation between the interfacial boundary layer and bulk solution confirm that it is the boundary layer characteristics of the membrane that predominantly set the supersaturation driving force for primary nucleation. While the range of ΔC within the bulk solution is quite narrow, a statistically significant decrease in bulk supersaturation from 1.005 to 0.997 was observed with an increase in crystalliser stirrer speed (N) (Re fixed to 1300) and was coincident with a reduction in the interfacial induction time (Fig. 6). This is consistent with the response to mixing within classical crystallisers where an increase in N leads to a decrease in MSZW [16]. Nývlt et al. [40] proposed that increasing mixing intensity with agitation in the vicinity of nuclei, displaced solution that has transferred its supersaturation, which is then replaced with fresh saturated liquor. The probability for the survival of nuclei can then be expected to increase. Whereas in classical crystallisers, the MSZW is explicitly set within the vessel where nucleation occurs, in MDC, we demonstrate that the supersaturation driving force for nucleation (i.e. MSZW) is set within the boundary layer of the membrane but the hydrodynamic analysis for both membrane and bulk crystalliser imply that there is also a critical dependency on the bulk solution to reach or exceed the solubility limit at nucleation for a thermodynamically stable crystal phase to be established. The mixing intensity in the crystalliser vessel appears to reduce the critical solubility limit at which the crystal phase can be formed. This evidence for the complex and subtle interplay between reactor hydrodynamics and the nucleation process, emphasises a unique proposition

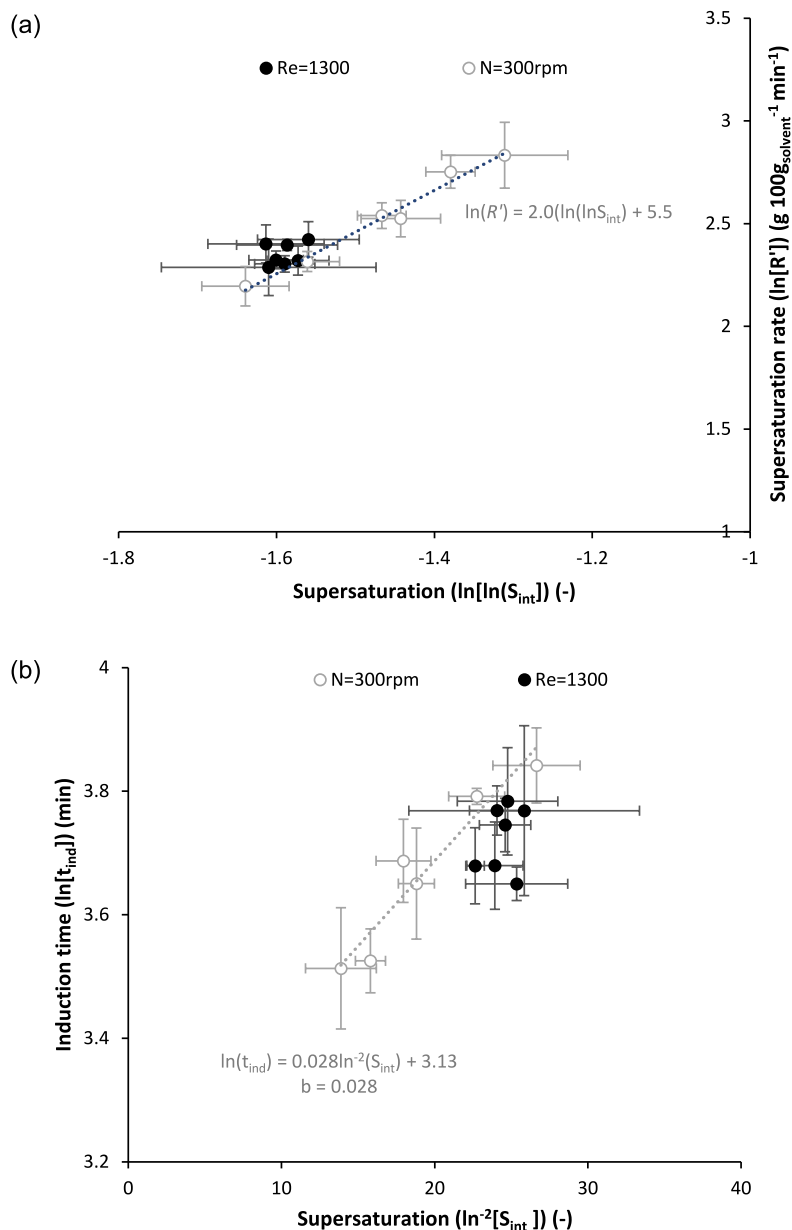


Fig. 7. Using classical nucleation theory to explain how mixing controls the onset of nucleation and nucleation rate: (a) Sangwal's power-law relationship between supersaturation rate and supersaturation level at induction describing the kinetics; and (b) relating induction time to supersaturation level 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). Data represents the average and standard deviation of at least three experimental replicates undertaken in the same conditions.

for MDC where induction time may be controlled independent of supersaturation.

3.2. Characterising nucleation kinetics based on interfacial supersaturation

To characterise the primary nucleation kinetics, the interfacial boundary layer conditions were used [14]. The method developed by Sangwal [26] (Eq. (2)) was adapted to establish how mixing modifies nucleation rate. Classical nucleation theory (CNT) can be described by a power-law relationship between nucleation rate and the MSZW (defined by the extent of supersaturation at induction, S) [26,27]. Through this approach, the nucleation rate can be considered an analogy to the supersaturation rate (R') at the onset of nucleation. Supersaturation rate incorporates the effects of modifications in flux, concentration and temperature polarisation independently introduced through

adjustments of Re or N . A linear trend was observed between the supersaturation rate (R') and interfacial supersaturation (S_{int}) when Re (N , fixed to 300 rpm) was increased (Fig. 7, Eq. (7)). An increase in Re therefore increases nucleation rate. The nucleation order ($m = 2.03$) indicates strong diffusive interactions between the solute (NaCl) and solvent (water) that promote the aggregation and growth of nuclei [26]. In CNT, induction time is inversely proportional to nucleation rate [39]. The use of CNT to effectively characterise nucleation for MDC, was evidenced in this study by the linear response observed between induction time and interfacial supersaturation (Fig. 7b, Eq. (8)). Induction time decreased from 44 min to 33 min with an increase in Re . This illustrates that the increase in supersaturation rate facilitated by Re reduces the time required to transition across the metastable zone, but enables a higher degree of supersaturation at induction which imposes a greater nucleation rate. The slope of the curve (B , 0.028) describes the energy barrier for nucleation within the system [35] (Eq. (9)). When

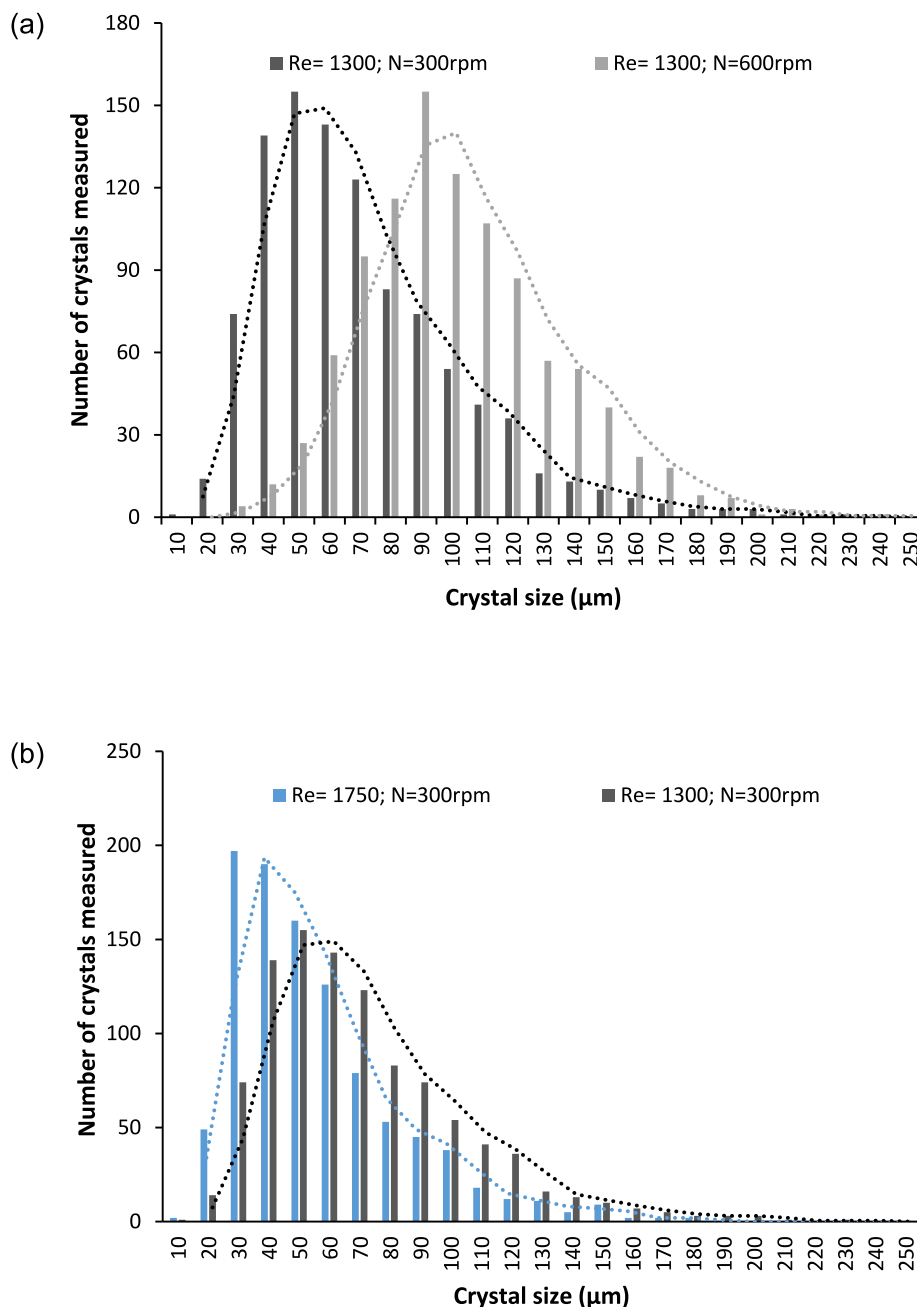


Fig. 8. Determining how mixing informs crystal growth. Crystal size distributions (CSD) from: (a) Crystalliser mixing with stirrer speeds (N) of 300 and 600 rpm (Reynolds number, Re , 1300); (b) Interfacial mixing with Re of 1300 and 1750 (N , 300 rpm).

increasing mixing in the crystalliser (Re , fixed to 1300), the supersaturation rate (R') and interfacial supersaturation were not modified, as the mass and heat transfer conditions remained constant across the membrane. While a modification in interfacial induction time was evident (Fig. 6), this was not linearly correlated to the interfacial supersaturation (Fig. 7). This illustrates that the interfacial boundary layer supersaturation is not responsible for the shift in induction time observed with an increase in crystalliser mixing speed, which further supports the proposition that the shift in induction time is due to the surface renewal of supersaturation in the bulk solution.

3.3. Relating bulk and interfacial mixing to crystal size distribution

Crystal size distributions were evaluated for crystalliser mixing using the maximum stirring speed (N , 600 rpm) and the mixing speed (N) of

300 rpm since this was adopted during the testing for both mixing conditions (Re and N). 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 (Fig. 8). The crystal growth rate for NaCl is diffusion controlled [29]. The increase in crystal size provided by higher agitation rates is therefore due to the enhanced solute mass transfer that can compensate for the diffusion-controlled growth [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 [22,36]. When SNM are observed, the crystal size distribution therefore typically broadens due to the higher frequency of smaller crystals, skewing the crystal size distribution (CSD) to the right. However, in this study, skewness of the CSD reduced from 1.35 to 0.789 when increasing N from 300 to 600 rpm

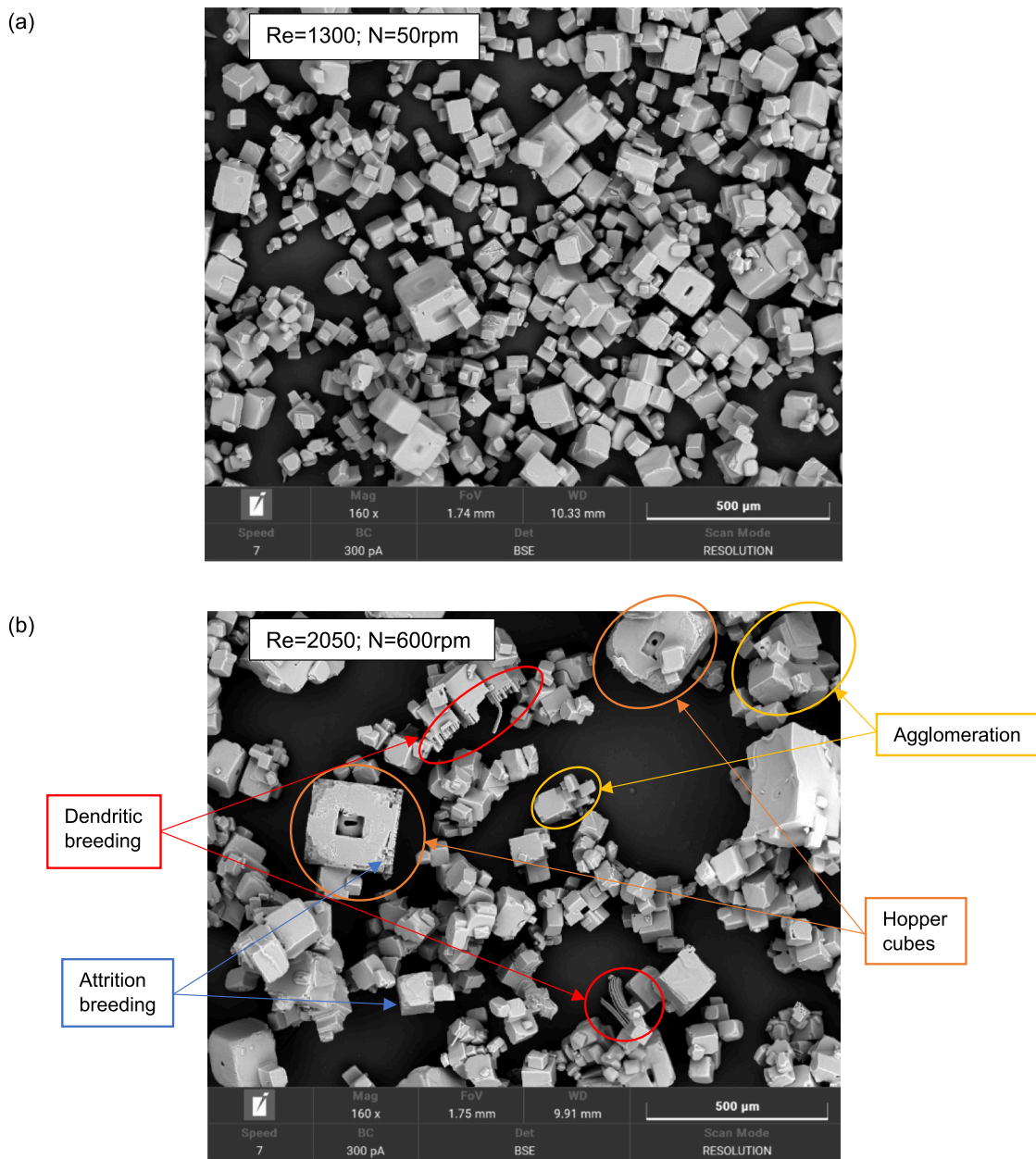


Fig. 9. SEM micrographs depicting the morphological differences imposed when increasing mixing intensity: (a) Reynold's number (Re) 1300, Stirrer Speed (N) 50 rpm; and (b) Re 2050, N 600 rpm).

(Re 1300). This indicates that the crystalliser mixing imposed does not promote SNMs and instead establishes conditions that preference growth over secondary nucleation.

When Re was increased from 1300 to 1750 (N , 300 rpm), median crystal size decreased from 74.8 to 56.2 μm (Fig. 8). At higher Re , the narrow boundary layer improves heat and mass transfer across the membrane which increases the permeate flux [33]. This results in higher supersaturation rates which widen the MSZW [14,17,34]. According to CNT, nucleation rate (R' in this study) increases exponentially with supersaturation [37], which was evidenced in this study for the interfacial conditions studied (Fig. 7a). 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 [38]. Consequently, CNT can be used to describe how Re may set conditions for crystal growth by relating process conditions to the supersaturation rate.

3.4. Relating mixing to secondary nucleation and growth mechanisms

Both mixing conditions were collectively combined to illustrate the role of mixing on crystal product morphology by comparing the upper (Re , 2050; N , 600 rpm) and lower (Re , 1300; N , 50 rpm) thresholds of the mixing range studied (Fig. 9). At a low mixing intensity, the cubic crystal habit, which is characteristic of sodium chloride, 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 [38]. Greater evidence of attrition breeding (or 'mechanical breeding') was found at the higher mixing intensity, as the increased shear rate enhances the likelihood for breakage from the crystal lattice [24]. Attrition breeding (a SNM) may therefore have also contributed to the smaller median crystal size identified with an increase in Re (Fig. 8b). 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 [22,36]. As an equivalent S_{bulk} of approximately 1 was reached in both conditions, it is postulated that the interfacial boundary layer 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 (Fig. 9b). 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, and both factors can be simultaneously controlled through mixing.

4. Conclusions

In this study, the independent contributions of bulk and interfacial mixing for the control of nucleation, crystal growth and crystal morphology have been demonstrated. While previous studies have hypothesised that it is the interfacial boundary layer that modulates nucleation, we provide the first direct evidence of its role and differentiate the underlying mechanisms that inform nucleation and crystal growth from those of the bulk solution. Reynolds number adjusts boundary layer conditions to set the interfacial supersaturation level at induction by modifying the supersaturation rate. The use of non-invasive nucleation detection enabled a power law relation between supersaturation and induction time to be established based on classical nucleation theory that illustrated how Re can be used to regulate nucleation rate. This is important since Re can be accurately estimated in membrane systems due to their well-defined geometry. Hence, we suggest reproducible nucleation kinetics may be achievable following scale-up which is a key challenge to existing industrial crystallisers, and is critical for the control of crystal size, crystal quality and morphology. Forced circulation evaporative crystallisers are also ordinarily limited to temperature as the primary control variable since mass and heat transfer processes are separated. Evidence for the role of mixing within the boundary layer presented in this study therefore illustrates that additive opportunities for the regulation of nucleation may exist in MDC versus the main incumbent technology.

For both regions of mixing studied, induction only occurred once the bulk solution approached the solubility limit which infers a critical dependency exists between bulk and boundary conditions. Crystalliser mixing of the bulk solution reduced the induction time by increasing contact between growing nuclei and the saturation available for growth to overcome mass transfer limitations, which is characteristic of classically stirred crystallisers. While a shorter induction time was

demonstrated, the interfacial supersaturation level at induction was not modified since this is controlled by the mass and heat transfer processes established across the membrane. This is distinct from classically stirred crystallisers in which shorter induction times are complemented with a narrowing of the MSZW. MDC is therefore unique in combining to forms of mixing which can modulate induction time, while setting supersaturation independently and within a more easily scalable geometry. The practical significance is that mixing within the crystalliser can broaden the nucleation kinetic trajectory in MDC, which may be particularly advantageous for solutes characterised by larger metastable zone widths or longer induction times (e.g. proteins). Crystalliser mixing promoted diffusion-controlled growth, whereas Re determined where in the metastable zone that growth proceeded. Crystal growth strategies that combine mixing phenomena may therefore be realised through adjusting interfacial conditions to establish crystal size, and crystalliser mixing to control growth, which is unique to MDC. Through longer term exposure to mixing, secondary nucleation effects may become more evident due to shear imposed from the impeller, membrane and pipe-work. Adoption of a retreat curve for crystalliser mixing could reduce direct mechanical breeding by lowering local shear, together with managing the residence time of the crystal phase through continuous separation, thus also reducing interparticle collisions to retain the preferred cubic morphology.

CRedit authorship contribution statement

A. Jikazana: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **K. Garg:** Writing – review & editing, Formal analysis, Data curation. **K. Le Corre Pidou:** Writing – review & editing. **P. Campo:** Writing – review & editing, Supervision, Methodology. **E.J. McAdam:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

We will provide a link to all data once review is complete

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Appendix A. 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. $Re_N < 2 \times 10^4$:

$$Re_N = \frac{\rho N D_N}{\mu} \quad (A1)$$

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 $D_N = 0.035m$.

Table A1
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	12,494
500	8.333	15,617
600	10	18,741

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

$$Re = \frac{\rho V d_h}{\mu} < 2100 \quad (A2)$$

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

$$d_h = \frac{4A}{P} \quad (A3)$$

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 (Appendix A).

Table A2
Interfacial Reynolds number specifications.

V (m/s)	$Re(-)$
0.224	1300
0.250	1450
0.276	1600
0.302	1750
0.328	1900
0.354	2050

Appendix B. Interfacial concentration calculations

The interfacial concentration was calculated by applying the concentration polarisation coefficient (CPC) to the bulk concentration (C_b):

$$C_{int} = CPC \bullet C_b \quad (A4)$$

$$C_{int} = \exp\left(\frac{J_p}{\rho K}\right) \bullet C_b \quad (A5)$$

where J_p is the permeate flux ($\text{kg m}^{-2} \text{s}^{-1}$), ρ is the solution density (kg m^{-3}) and K is the mass transfer coefficient (m/s) given by the L  v  que equation as follows:

$$K = \frac{1.62D}{d_h} \left(\frac{V d_h^2}{DL} \right)^{\frac{1}{3}} \quad (A6)$$

where D and V are the solution diffusion coefficient (m^2/s) and velocity (m/s), respectively; d_h and L are the hydraulic diameter (m) and length (m) 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} , $^\circ\text{C}$):

$$TPC = \frac{T_{int,f} - T_{int,p}}{T_{b,f} - T_{b,p}} \quad (A7)$$

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. (8) in conjunction with the following equations:

$$T_{int,f} = T_{b,f} - (T_{b,f} - T_{b,p}) \left(\frac{\frac{1}{h_f}}{\frac{1}{h_f} + \frac{1}{h_p} + \frac{1}{h_c + h_v}} \right) \quad (A8)$$

$$T_{int,p} = T_{b,p} + (T_{b,f} - T_{b,p}) \left(\frac{\frac{1}{h_p}}{\frac{1}{h_f} + \frac{1}{h_p} + \frac{1}{h_v + h_c}} \right) \quad (A9)$$

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

$$h_i = \frac{Nu k_i}{d_h}, \quad i = f, p \quad (A10)$$

Nu is the Nusselt number:

$$Nu = 0.023 Re^{0.8} Pr^{\frac{1}{3}} \quad (A11)$$

$$Re = \frac{\rho V d_h}{\mu} \quad (A12)$$

$$Pr = \frac{c_p \mu}{k} \quad (A13)$$

where μ (Pa/s), c_p (J kg⁻¹ K⁻¹) and k (W m⁻¹ K⁻¹) are the dynamic viscosity, specific heat capacity and thermal conductivity of the respective solutions. h_v is the vapour heat transfer coefficient:

$$h_v = \frac{J_p \Delta H_v}{T_{int,f} - T_{int,p}} \quad (A14)$$

where ΔH_v is the latent heat of vaporisation (J kg⁻¹), and h_c is the heat transfer coefficient of conduction:

$$h_c = \frac{k_m}{\delta_m} \quad (A15)$$

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

$$k_m = \left(\frac{\epsilon}{k_{gas}} + \frac{1 - \epsilon}{k_{solid}} \right)^{-1} \quad (A16)$$

$$k_{gas} = 1.5 \times 10^{-3} \sqrt{T} \quad (A17)$$

$$k_{solid} = 4.86 \times 10^{-4} T + 0.253 \quad (18)$$

where 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 [29], was applied to determine solution properties using Aspen Plus software.

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