Sodium chloride precipitation reaction coefficient from crystallization experiment in a microfluidic device

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ABSTRACT

The crystal growth of sodium chloride from an aqueous solution is studied from evaporation experiments in microfluidic channels in conjunction with analytical and numerical computations. The crystal growth kinetics is recorded using a high speed camera in order to determine the intrinsic precipitation reaction coefficient. The study reveals that the crystal growth rates determined in previous studies are all affected by the ions transport phenomena in the solution and thus not representative of the precipitation reaction. It is suggested that accurate estimate of sodium chloride precipitation reaction coefficient presented here offers new opportunities for a better understanding of important issues involved in the damages of porous materials induced by the salt crystallization.

1. Introduction

The crystallization of sodium chloride from an aqueous solution is a key phenomenon in relation with evaporation from porous media [1], the generation of damages in buildings and monuments [2], or the injection of CO₂ in underground formations [3], to name only a few. The crystallization process is generally decomposed into two main steps: the nucleation step and the growth step. In this respect, it is important to distinguish the crystal growth kinetics [4] from the nucleation kinetics, which involves the induction time between the application of a supersaturation state and the appearance of the first crystals [5]. In the literature, they can both be found under the expression of "crystallization kinetics". In this paper, we focus on the crystal growth kinetics.

The crystal growth is studied within the framework of the diffusion reaction theory [6] (where other crystal growth theories: surface energy theory, adsorption layer theory and kinematic theory, are also presented). Crystal growth starts only once a stable nucleus, large enough to be stable, appears in the metastable solution. It relies on two coupled steps: an ion diffusion process from the solution to the crystal surface, followed by a reaction process where ions fit in the crystal lattice. These processes have been highlighted in Refs. [7,8].

As illustrated in Fig. 1, the two steps occur in series and three zones can be defined. The first zone corresponds to a stagnant film (or adsorption layer) at the crystal-liquid interface. Far from the crystal, there is the bulk solution with a constant concentration. The concentration increases following a diffusion law in the intermediate zone of size d between the crystal and the bulk.

The crystal growth rate, J (kg/m² s) in the adsorption zone and diffusion zone can be modelled as:

\[ J_D = \frac{1}{A} \frac{dM}{dt} = k_D (c_b - c_i), \] (1)

\[ J_R = \frac{1}{A} \frac{dM}{dt} = k_R (c_i - c_{eq})^n, \] (2)

where M (kg) is the mass of the crystal, A is the crystal total surface, c_b (kg/m³) is the bulk salt concentration of the solution, c_i is the salt concentration at the liquid crystal interface, and c_{eq} is the ion concentration at equilibrium; n is the order of the reaction and k_D and k_R (m/s) are the coefficients of mass transfer by diffusion and reaction, respectively. k_D can be seen as the ratio of the salt molecular diffusion coefficient D, to the diffusion length d.

Considering the diffusion zone and the adsorption layer as two mass transfer resistances in series (as sketched in Fig. 1) and for a first order reaction (n = 1, which is the case for sodium chloride), an equation combining these two steps can be obtained,

\[ J_G = \frac{1}{A} \frac{dM}{dt} = k_G (c_b - c_{eq}) \] (3)
with

\[ k_c = \frac{1}{k_e} = \frac{k_d k_g}{k_p + k_e}, \tag{4} \]

where \( k_c \) is referred to as the overall growth rate parameter. The equivalent of the mass transfer resistance is equal to the inverse of the growth rate parameter. In order to characterize the phenomenon driving the crystallization process, Garside [9] suggests to define the effectiveness factor for crystal growth \( \eta_g \) as the ratio between the overall growth rate and the growth rate obtained when the crystal surface is exposed to the bulk concentration:

\[ \eta_g = \frac{C}{C_0} = \frac{k_c}{k_e}. \tag{5} \]

In other words, it is the ratio between the overall growth rate and the growth rate obtained when the crystallization is limited only by reaction, with an infinitely fast diffusion; \( \eta_g \) can be expressed as:

\[ \eta_g = (1 - Da \eta_f), \tag{6} \]

where \( Da = \frac{D}{C} \) is the Damköhler number, which represents the ratio between the reaction flux and the mass transport flux. Thus

\[ \eta_f = \frac{1}{1 + Da}. \tag{7} \]

Therefore, the process is controlled by diffusion when \( Da \) is large and \( \eta_f \) is low. On the contrary, it is controlled by reaction (the controlling process is the slowest one) when \( Da \) is small and \( \eta_f \) is large.

Moreover, because NaCl crystal has a cubic shape, the mass precipitation rate can be related to the mean linear velocity of its faces \( w_c \) (m/s) by (see Appendix A):

\[ w_c = \frac{dr}{dt} \frac{J_c}{\rho_c} = \frac{k_c}{\rho_c} (C_0 - C_0) \tag{8} \]

where \( r \) is the half length of the side of a cubic crystal (m) and \( \rho_c \) is the crystal density (kg/m³). In case of a spherical crystal or a growth in 1 dimension on both sides, Eq. (8) remains valid with \( r \) as the sphere radius or the crystal half length.

The above considerations clearly show that the crystal growth kinetics depends on both the local concentration \( C_1 \) at the interface and coefficients \( k_d \) and \( k_e \). The experiments typically allow determining \( w_c \) (references are given below in the section on the results). Since both \( C_1 \) and \( k_e \) are unknowns, it is clearly difficult to determine \( k_e \) from the experimental data. Also, as stated in [9], \( k_p \) is difficult to measure because it is hard to separate the reaction step from the diffusion one. In this context, the main objective of the paper is precisely to provide an accurate estimate of \( k_e \).

It should be mentioned that correct values of \( k_e \) are of the uttermost importance for correctly evaluating the crystallization pressure, which is the key concept in relation with the damages caused by the salt crystallization in porous materials [10]. As explained in [11], what matters for evaluating the crystallization pressure is the salt concentration at the crystal surface when it becomes confined between the pore walls. This concentration is highly dependent on \( k_e \) (see [11] for more details).

2. Materials and methods

2.1. Experiments

Experiments are performed in microfluidic chips such as the one sketched in Fig. 2. It is composed of a large channel used for supplying the fluids: salt solution or gaseous nitrogen. Holes are drilled at both extremities to connect the chip to the external part of the experimental set-up. Channels of smaller cross section surface areas, referred to as pore channels, are designed perpendicularly to the supply channel. Two pore channel cross sections are used in order to study its influence on crystal shape: 5 × 5 μm² and 20 × 20 μm². For each cross section, three lengths are tested so as to consider different initial amounts of dissolved salt: 100 μm, 200 μm, 300 μm and 200 μm, 400 μm, 800 μm respectively.

The chips are made of polydimethylsiloxane (PDMS) and glass. First, a mold is fabricated in a clean room by standard photolithography using, however, a DF-1000 series dry film instead of a liquid photoresist as SU-8. Then, PDMS Sylgard 184 with a ratio of curing agent 1:10 is degassed under vacuum during 45 min, poured on the mold and cured at 80 °C during 2 h. It is unmolded after at least 20 min of cooling at ambient temperature. After unmolding, holes are made with bio punch and the chips are cut with a scalpel. Then a cover glass is bonded on the channel side thanks to smooth air plasma during 1 min and 30 s. Finally, a second baking at 70 °C during 30 min is done to ensure a good adhesion between glass and PDMS.
For this reason, the problem is actually equivalent to the growth of a sufficient amount of water for the ion concentration marking the onset of crystallization to be reached. Two video cameras are used: an Andor Zyla SCMos to record the kinetics of evaporation, with a low frame rate (between 1 and 2 s per image) and a large field, and a Photron Fastcam SA3 camera to record the kinetics of crystal growth at 500 or 1000 frames per second.

In order to perform the experiments with different amounts of dissolved salt in excess at nucleation, sodium chloride solution is prepared with two different molalities: 1.89 and 4.25 mol/kg, the saturation being 6.15 mol/kg (corresponding to mass fractions of 10%, 20% and 26.4% respectively). Salt is provided by Sigma Aldrich, with a purity ensured to be higher than 99.5%. It is dissolved in deionized water.

Salt crystals form within the pore channels after evaporation of a sufficient amount of water for the ion concentration marking the onset of crystallization to be reached. Two video cameras are used: an Andor Zyla SCMos to record the kinetics of evaporation, with a low frame rate (between 1 and 2 s per image) and a large field, and a Photron Fastcam SA3 camera to record the kinetics of crystal growth at 500 or 1000 frames per second.

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Movies are exploiting thanks to the ImageJ® and Matlab® softwares to track the crystal liquid interface so as to determine the kinetics of crystal growth.

More details on the experimental setup are given in Appendix C.

### 2.2. Numerical simulations

A numerical model is developed and solved using the commercial software Comsol multiphysics 5.2® in order to analyze the experimental results. We focus on the beginning of the crystallization process over a very short period during which evaporation is negligible. Thus, this model is used to simulate the crystal growth of an initial nucleus in a solution when the crystal size is small compared to the size of the computational domain (see Fig. 3). For this reason, the problem is actually equivalent to the growth in an “infinite” domain. This means that the numerical domain is sufficiently large for the diffusive front of the dissolved salt concentration not to reach the domain boundary.

At initial time, the solution is supersaturated and a small nucleus is in the solution. Initial supersaturation $S_0$ (see below for a definition) is set to the mean experimental value ($S = 1.72$, see below). We checked that the specified initial size of nucleus has not influence on final result. The transport of dissolved salt by diffusion and convection is taken into account as well as the crystal growth due to the precipitation reaction. The coefficient of mass transfer by reaction $k_R$ is varied between $10^{-2}$ and $10^{-4}$ m/s so as to study its influence. The ion molecular diffusion coefficient $D_i$ is taken equal to $1.3 \times 10^{-9}$ m$^2$/s.

Technical details and equations are presented in Appendix D.

### 3. Results

#### 3.1. Supersaturation at nucleation

The supersaturation of the solution is defined as

$$S = \frac{m}{m_0}$$

where $m$ (mol/kg) is the molality and subscript $0$ refers to the reference state where the crystal is in equilibrium with the solution. As recalled in Appendix E, the molality can be determined from the solution concentration. A simple method to determine the salt concentration is to track the position of the receding meniscus in the pore channel at the onset of crystallization and to perform a simple mass balance. Knowing the initial volume $V_0$ of the salt solution of concentration $c_0$, the average concentration when the first crystal is detected on the images (nucleation), $c_n$, is given by:

$$c_n = c_0 \frac{V_n}{V_0}$$

where $V_n$ is the volume of solution in the channel when the first crystal is detected on the images since the total amount of salt remains constant (only pure water evaporates).

An implicit hypothesis when using Eq. (10) is that the concentration is about the same everywhere in the solution. To validate this assumption, it is possible to define a Peclet number by the
leads to does not and also with \[12–13\] where the crystal grows in the middle of a solution. 

The latter can be referred to as a Hopper crystal. These cases are discarded to determine the kinetics of crystal growth because we assume that it is influenced by the transport of ions in the wedge formed by the liquid-air interface. In other terms, we consider that the geometrical confinement. In other terms, we consider that the shape of the crystal depends on the channel size and on the location of the nucleation. When the crystal appears far from the liquid air interface, a “cubic” crystal is observed in the 5 × 5 \(\mu\)m\(^2\) channel (Fig. 5a, “Crystal growth 1”) whereas a “star” crystal is observed in the 20 × 20 \(\mu\)m\(^2\) channel (Fig. 5a, “Crystal growth 2”). The latter can be referred to as a Hopper crystal. When the crystal appears on the liquid gas interface, it is directly confined by the channel wall and the liquid-gas interface (Fig. 5a, “Crystal growth 2”). These cases are discarded to determine the kinetics of growth because we assume that it is influenced by the geometrical confinement. In other terms, we consider that the transport of ions in the wedge formed by the liquid-air interface and the channel wall is different from the situation considered in the theoretical and numerical approaches (see Sections 2.2 and 4) where the crystal grows in the middle of a solution.

\[
Pe = \frac{\rho v H}{D_s}, \tag{11}
\]

\(z_m\) represents the position of the meniscus (distance to the channel entrance) and \(H\) is the length of the liquid part (see Fig. 2). The assumption of uniform concentration is valid only if the Pe number is much lower than 1 (low evaporation rate in comparison with the diffusion velocity), which is always the case in our experiment. Using Eq. (11) leads to \(Pe = 0.08 \pm 0.07\) taking into account all the experiments, indicating that assuming the concentration as uniform is reasonable.

The value of supersaturation is measured in 99 experiments (Fig. 4). The mean value is found to be equal to \(S = 1.72\), which is consistent with previous studies [12–13]. No dependence with pore channel length, depth or initial concentration is noticed.

3.2. Crystallization kinetics

The crystallization kinetics is recorded over very short periods (between 0.1 and 2 s) at 1000 frames per second. Pictures from three experiments of crystal growth are shown in Fig. 5a. The kinetics of crystal growth is extracted by tracking the liquid crystal interface in the main growth direction (black line in Fig. 5a). Note that the crystallization kinetics is studied from the images obtained using the high speed camera. The latter has a much smaller field of view compared to the low frame rate camera. As result, this is not 99 experiments as for the supersaturation study but only 10 which have been considered for studying the kinetics.

As illustrated in Fig. 5b, two steps in the crystal growth can be distinguished: a very fast one over a period of about 10–100 ms, with a quasi-constant kinetics (the crystal surface moves linearly), and a second one characterized by a decreasing kinetics (the liquid-crystal interface slows down).

The shape of the crystal depends on the channel size and on the location of the nucleation. When the crystal appears far from the liquid air interface, a “cubic” crystal is observed in the 5 × 5 \(\mu\)m\(^2\) channel (Fig. 5a, “Crystal growth 1”) whereas a “star” crystal is observed in the 20 × 20 \(\mu\)m\(^2\) channel (Fig. 5a, “Crystal growth 2”). The latter can be referred to as a Hopper crystal. When the crystal appears on the liquid gas interface, it is directly confined by the channel wall and the liquid-gas interface (Fig. 5a, “Crystal growth 2”). These cases are discarded to determine the kinetics of growth because we assume that it is influenced by the geometrical confinement. In other terms, we consider that the transport of ions in the wedge formed by the liquid-air interface and the channel wall is different from the situation considered in the theoretical and numerical approaches (see Sections 2.2 and 4) where the crystal grows in the middle of a solution.

It appears that the crystal growth is very fast at the onset of crystallization, much faster than the fastest kinetics reported in previous studies. For example, a liquid-crystal interface velocity \(dr/dt\) of around 10 \(\mu\)m/s is reported in [16]. However, the low camera rate acquisition (0.5 frames per second) used in [16] does not allow to measure the beginning of the growth. Here, thanks to the high speed camera, we can focus on the first milliseconds when the kinetics of crystal growth is constant. The crystal growth velocity \(dr/dt\) is estimated after 10 ms for all the experiments, when the crystal has still a compact shape. This leads to a mean value equal to \(dr/dt = 271 \pm 62\) \(\mu\)m/s (the mean value and its standard deviation are calculated considering the 10 experiments and the growth on each side of crystal). It is convenient to express the growth kinetics in term of the overall growth parameter \(k_G\), in order to compare our data with values from previous experiments. \(k_G\) is computed using Eq. (8) with \(c_0\) corresponding to the concentration at the onset of crystallization. This gives \(k_G = 2.33 \times 10^3 \pm 0.1 \times 10^3\) \(\mu\)m/s.

4. Discussion

As mentioned before, the crystal growth kinetics observed in our experiments is much faster than in previous experiments. In order to compare with our values, we have extracted the kinetics of sodium chloride crystal growth from different previous papers.
The kinetics is expressed in term of \( k_G \), thanks to Eq. (8). Values are presented in Table 1 (the determination of \( k_G \) for each reference is presented in Appendix F).

The time of measurement corresponds to the time \( t_m \) used to calculate the velocity experimentally, i.e. from Eq. (8)

\[
 w_c r = \frac{dr}{dt} = \frac{r(t_m) - r(0)}{t_m} = \frac{k_c}{\rho_c} (c_b - c_{eq})
\]  

(12)

As can be seen from Table 1, the value of \( k_c = 2.33 \text{ mm/s} \) after 10 ms from our experiments is 20–500 times higher than the values extracted from the literature. Table 1 makes clear that the overall growth rate parameter depends on the duration of the experiment. In particular, the lower the time of velocity integration, the higher the growth rate parameter. We can explain this result with the variation of the coefficient of mass transfer by diffusion, \( k_D \), with time. According to the diffusion reaction theory, the coefficient of mass...

Fig. 5. (a) Pictures of crystal growth in pore channels. The black lines show the direction along which the kinetics of crystal growth is measured. Red scale bar represents 10 \( \mu \text{m} \); Time is in millisecond; (b) and (c) represent the kinetics of crystal growth corresponding to 1 and 3 of (a) respectively. The position of liquid crystal interface as a function of time is shown in blue in the right direction and in red in the left direction. The insert in (b) focuses on the first 100 ms. In (c), the kinetics of growth is not extracted after 100 ms because the crystal rotates in the channel. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
transfer by reaction, \( k_R \), is an intrinsic property of the crystal whereas \( k_T \) depends on a diffusive length property which evolves in time. This can be illustrated from a simple model of the crystal growth in one dimension controlled only by diffusion, i.e., assuming a very large \( k_T \). The corresponding problem with boundary condition 1 is sketched in Fig. 6.

In this model, the convection induced by the crystal liquid interface motion is not taken into account. The solution for a semi-infinite domain is used because of its simplicity in comparison to the case of a finite domain. This approximation is correct if the diffusive front which starts from the crystal has not the time to reach the other boundary (end of pore channels in our experiments). In other words, the two solutions are equivalent for times much lower than the diffusive time, \( t_0 = L^2/D_c \), where \( L \) is the length of the considered finite domain (for instance, if \( L = 1 \) mm, \( t_0 = 769 \) s). The solution to this problem is given in [19]:

\[
\frac{c(z,t) - c_{eq}}{c_{eq} - c_T} = \text{erf} \left( \frac{z}{2\sqrt{D_c t}} \right)
\]

where \( c_{eq} = c_T = c_0 \) is the ion concentration at the onset of crystallization (thus corresponding to the supersaturation). From Eq. (13) we can express the velocity of crystal growth controlled only by diffusion as:

\[
W_{cr,D} = \frac{dr}{dt} \left[ \frac{\partial c}{\partial z} \right]_{z=0} = \frac{(c_{eq} - c_T)}{\rho_{cr}} \sqrt{\frac{D_c}{\pi t}}
\]

The mean velocity of crystal growth between nucleation \((t=0)\) and a time \( t_m \) is then obtained integrating Eq. (14) over the duration \( t_m \):

\[
W_{cr,D,mean} = \frac{r(t_m)}{t_m} = \frac{2(c_{eq} - c_T)}{\rho_{cr}} \sqrt{\frac{D_c}{\pi t_m}}
\]

Combining Eqs. (15) and (8) leads to the following theoretical evolution of \( k_c \) as a function of measurement time \( t_m \):

\[
k_c = k_D = 2\sqrt{D_c/\pi t_m}
\]

This law is plotted in blue dotted line for different values of \( k_D \) in Fig. 7. As can be seen, the kinetics of crystal growth follows the diffusive law for a measurement time of 10 ms only if the coefficient of mass transfer by reaction is bigger than \( 10^{-3} \) m/s.

Since Eq. (20) gives the solution in 1D using a linear Cartesian coordinate and for a fixed crystal – solution interface, numerical simulations are performed to extract the kinetics of growth for different values of \( k_R = 10^{-4}, 10^{-3} \) and \( 10^{-2} \) m/s for conditions closer to the experimental situation (moving crystal – solution interface in a 3D domain). The numerical results for \( k_R \) are compared with the experimental and theoretical ones in Fig. 7. As can be seen, Fig. 7 shows a very good agreement between the experimental and the numerical results. The difference with the theoretical values from the 1D solution is about of a factor 4, which can be explained by the fact that the numerical simulations (and the experiments) correspond to a growth in a 3D domain whereas the theoretical solution is developed only in 1 dimension. In addition, the theoretical solution does not take into account the motion of the crystal solution interface.

Therefore, the conclusion is that the crystal growth is only controlled by diffusion in all of the mentioned papers. Thus \( k_c = k_T \), in those experiments and the data are not sufficient to extract \( k_R \). Consequently, \( D_a \) is large and \( \eta_s \) is low in all these experiments.

Concerning the dependence of \( k_c \) on \( k_T \), the numerical simulation confirms that the crystal growth is limited by diffusion after 10 ms only if the parameter of crystal growth by reaction \( k_R \) is larger than \( 10^{-3} \) m/s. This result allows us to propose as a lower bound \( k_R = 2.3 \times 10^{-3} \) m/s, which is the kinetics we measure as reported in Section 4.

5. Summary and conclusions

In this study, we present a microfluidic device allowing the accurate observation of sodium chloride crystal growth from a supersaturated solution. A frequency of acquisition as high as 1000 Hz is employed. This gives the possibility of studying the crystal growth in the regime controlled by the reaction. To the best of our knowledge, it is the first time that the kinetics of crystal growth is measured in the early stage of the growth where the growth is not controlled only by the ion transport phenomena toward the crystal but also by the precipitation reaction. This enables us to propose a new order of magnitude for the coefficient of mass transfer by reaction: \( k_R > 2.3 \times 10^{-3} \) m/s, ten to hundred times higher than the values used in literature. The comparison with analytical and numerical simulation results highlight that the difference comes from the averaging time of measurement. When it is too long, the crystal growth is controlled by diffusion and not by reaction and the value of the reaction coefficient \( k_R \) cannot be deduced from the experimental data.

Similar experiments could be performed with other salts so to make a new data bank of the coefficient of mass transfer by reaction. To mention only one application, correct values of \( k_R \)
are crucial for determining the crystallization pressure responsible of the generation of damages due to crystallization in porous materials. Accordingly, the variability of $k_B$ with the salt nature could contribute to explain why some salts cause more damages than others.

Finally, the study illustrates one more time the effectiveness of microfluidic devices for characterizing chemical or physical properties.

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Appendix A. Relation between the overall crystal growth rate $J_C$ and the mean linear velocity of its faces $w_C$ (m/s)

Considering a sodium chloride cubic crystal and taking $r$, the half length of its side as the reference length, the mass variation of the crystal can be expressed as:

$$
\frac{dM}{dt} = \rho \frac{dV}{dt} = \rho \frac{d(2r)^3}{dt} = \rho(2r^2) \frac{dr}{dt} = \rho_A \frac{dr}{dr}.
$$

where $A_r$ is the surface of the crystal. Combined with Eq. (3), we obtain the relationship (Eq. [8] in the text):

$$
w_C = \frac{dr}{dt} \frac{J_C}{\rho_C} = \frac{k_C}{\rho_C} (c_0 - c_{eq}),
$$

Appendix B. Relation between volume ratio and concentration

The salt mass conservation during evaporation implies:

$$
\frac{c_0 V_n}{V_0} = \frac{V_n}{V_0} c_{eq}.
$$

Index $n$ refers to the time of nucleation and $c_0$ the initial time. It gives:

$$
x_{na}\rho_{i,n} = \frac{V_n}{V_0} x_{i,n}\rho_{i,0}.
$$

Using the relation between salt mass fraction and salt solution density given in [15]:

$$
x_{na} \rho_{n} = \frac{V_n}{V_0} x_{i,n}\rho_{i,0} \frac{1 - 0.7x_{i,n}}{1 - 0.7x_{i,0}}.
$$

As a result, it is obtained that:

$$
x_{na} = \frac{x_{i,0}}{x_{i,0} + 0.7x_{i,0} \left(1 - \frac{V_n}{V_0}\right)}.
$$

Appendix C. Fabrication of experimental devices

As sketched in Fig. 1, experiments are performed on a microfluidic chip made of glass and PDMS. A picture of a chip is presented in Fig. C1.

C.1. Mold fabrication

Molds are made for channel of $5 \times 5 \mu m^2$ cross section with DF-1005 and for channel of $20 \times 20 \mu m^2$ cross section with DF-1020 respectively. They are made in a clean room by standard photolithography, excepted that photoresist is a dry film DF-1000 series. The silicon wafer surface is first cleaned and activated in an O$_3$ plasma (Tepla 300) during 5 min with a power of 400 W and under a pressure equal to 1.5 mbar.

Then, the dry films are laminated with laminator Shipley 3024 at ambient temperature.

After exposure, the wafer is baked at 100 $^\circ$C during 3 or 5 min and developed in a solution of cyclohexanone during 3 or 4 min.

To avoid the PDMS adhesion on the mold during the casting and curing steps, the mold is rendered hydrophobic. It is immersed in a bath of 50 ml of xylene and 0.5 ml of OTS (using this solution under nitrogen inert atmosphere is better to avoid the OTS oxidation).

C.2. Fabrication of PDMS chip

PDMS Sylgard 184 with a ratio of curing agent 1:10 is degassed under vacuum during 45 min, poured on the mold and cured at 80 $^\circ$C during 2 h. It is unmolded after at least 20 min of cooling at ambient temperature.
and the species continuity (NaCl) equation are expressed as:

$$\frac{\partial \rho_i c_i}{\partial t} + \nabla \cdot (\rho_i c_i \mathbf{v}_i) = \nabla \cdot (\rho_i D_i \nabla c_i)$$  \hspace{1cm} (D3)

Eq. (D3) is written considering that the salt flux is composed of a convective contribution and a diffusive one:

$$\mathbf{J}_i = \mathbf{c}_i \mathbf{v}_i + \mathbf{j}_i = \mathbf{c}_i \mathbf{v}_i - \rho_i D_i \nabla c_i$$  \hspace{1cm} (D4)

The interface conditions at the crystal-liquid interface are expressed as follows. Two conditions can be derived. The first one expresses that water cannot cross this interface:

$$\mathbf{c}_w \cdot \mathbf{n}_{cr} = [\mathbf{c}_w (\mathbf{v}_w - \mathbf{W}_{cr})] \cdot \mathbf{n}_{cr} = 0.$$

Replacing $$x_w$$ with 1 $$-$$ $$c_i$$ and $$c_w$$ with $$\rho_l - c_i$$ gives:

$$[\mathbf{c}_w (\mathbf{v}_w - \mathbf{W}_{cr})] \cdot \mathbf{n}_{cr} = [\rho_l \mathbf{v}_l - (\rho_l - c_i) \mathbf{W}_{cr}] \cdot \mathbf{n}_{cr} = 0.$$  \hspace{1cm} (D6)

The condition of salt solution velocity is obtained by adding Eqs. (D6) and (D7). This yields:

$$\mathbf{v}_l \cdot \mathbf{n}_{cr} = \left(1 - \frac{\rho_l}{\rho_c}\right) \mathbf{W}_{cr} \cdot \mathbf{n}_{cr}.$$  \hspace{1cm} (D9)

Finally, $$\mathbf{w}_{cr}$$ is given by Eq. (8):

$$w_{cr} = \frac{k_c}{\rho_c} (c - c_{eq}).$$  \hspace{1cm} (D10)

The robustness of the model is done by checking the mass conservation of salt in the entire domain (solution + crystal). It can be noted that it is more difficult for the solver to converge for simulations performed for the highest value of $$k_b = 10^{-2} \text{ m/s}$$ because of the higher kinetics of fluid motion and mesh deformation.

### Appendix E. Relation between mass fraction, mass concentration, and molality

Study of crystal growth involves determining the amount of ions in solutions. The mixture composition can be expressed using various definitions such as mass fraction, mass concentration or molality. The variable choice differs from one paper to the other. The following defines each variable and recalls the link between them. These relations are used in the next section to express of the overall growth rate parameter found in different papers in the same units.

**Subscript** $$s$$ refers to the salt solution, which is a binary mixture composed of dissolved salt (subscript $$s$$) and water (subscript $$w$$).

#### E.1. Definition

- Mass concentration, $$c_i$$ (kg m$$^{-3}$$):
  \[ c_i = \frac{\text{mass of specie } i}{\text{volume of solution}} = \frac{M_i}{V_i}. \]

- Mass fraction, $$x_i$$ (\%):
  \[ x_i = \frac{\text{mass of specie } i}{\text{mass of solution}} = \frac{M_i}{\rho_l}. \]

- Molality, $$m_i$$ (mol [kg of solvent]$$^{-1}$$):
  \[ m_i = \frac{\text{mole of specie } i}{\text{mass of free solvant}} = \frac{n_i}{M_{solvent}}. \]
\* Supersaturation, \( S (\phi) \):
\[
S = \text{molality} = \frac{m}{m_{eq}}.
\]  

\( (E4) \)

**E.2. Useful relationships**

- We use the following relationship between the density of a NaCl solution and the salt mass fraction or mass concentration \[15\]:
\[
\rho_1 = \frac{\rho_w}{(1 - 0.7\%_s)} = \frac{\rho_w}{(1 - 0.7\%_s)} = \rho_w + 0.7c_s.
\]  
\( (E5) \)

where \( \rho_w \) is the density of pure water

- Relationship between solution density and solute mass concentration:
\[
\rho_1 = c_s + c_w.
\]  
\( (E6) \)

- Relationship between salt molality and salt mass concentration:
\[
m_c = \frac{n_c}{\overline{M}c_w} = \frac{M_s}{c_w} = \frac{M_c(h_1 - c_s)}{c_s} = \frac{\rho_w - 0.3c_s}{c_s}. \]  
\( (E7) \)

where \( M_s \) is the molar mass of salt. Conversely:
\[
c_s = \frac{m_cM_s}{1 + 0.3m_cM_s} \]  
\( (E8) \)

**Appendix F. Determination of the overall growth rate parameters reported in Table 1**

In order to compare values of the overall crystal growth rate parameter from different sources, we have expressed values of crystal growth found in other papers using the same convention as in the present study. Results are presented below: (see Tables F1–F4)

Ref \[17\]:

\[
c_s \text{ is obtained noting that } m_{eq} = \frac{x_{eq}}{100/M_s} \text{ and using } Eq. (E8) \text{ which gives:}
\]
\[
c_s = \frac{x_{eq}\rho_w}{100 + 0.3 \times x_{eq}} \]  
\( (F1) \)

\( J_c \) is obtained using Eq. \( (A2) \) and \( k_c \) using Eq. \( (3) \)

Ref \[12\]:

In this paper the mean kinetics of crystal growth during the first five minutes is equal to 1.6 \( \mu \text{m/s}. \)

Ref \[18\]:

Ref \[16\]:

Authors indicate that the growth rate is about 10 \( \mu \text{m/s} \) and the supersaturation is about 1.3. With these approximate values, one obtains the values reported in Table F4.

**Table F1**

Data from \[17\] used to determine \( k_c \).

<table>
<thead>
<tr>
<th>Article data</th>
<th>( x_{eq} - x_s ) (g/100 g H₂O)</th>
<th>( d(2\pi)/dt ) (m/s)</th>
<th>Result</th>
<th>( c_s ) (kg/m³)</th>
<th>( J_c ) (kg/m²/s)</th>
<th>( k_c ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>4.20 × 10⁻³</td>
<td>327.7</td>
<td>4.55 × 10⁻³</td>
<td>1.40 × 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>5.60 × 10⁻³</td>
<td>329.31</td>
<td>6.06 × 10⁻³</td>
<td>1.24 × 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>7.00 × 10⁻³</td>
<td>330.93</td>
<td>7.58 × 10⁻³</td>
<td>1.16 × 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>8.50 × 10⁻³</td>
<td>332.55</td>
<td>9.20 × 10⁻³</td>
<td>1.13 × 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>1.00 × 10⁻²</td>
<td>334.17</td>
<td>1.08 × 10⁻³</td>
<td>1.11 × 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>1.16 × 10⁻²</td>
<td>335.79</td>
<td>1.26 × 10⁻³</td>
<td>1.10 × 10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>1.31 × 10⁻²</td>
<td>337.41</td>
<td>1.41 × 10⁻³</td>
<td>1.09 × 10⁻⁵</td>
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<td></td>
</tr>
</tbody>
</table>

**Table F2**

Data from \[12\] used to determine \( k_c \).

<table>
<thead>
<tr>
<th>Article data</th>
<th>( S/m_{eq} )</th>
<th>( x(2\pi)/dt ) (m/s)</th>
<th>Result</th>
<th>( c_s ) (kg/m³)</th>
<th>( J_c ) (kg/m²/s)</th>
<th>( k_c ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.62</td>
<td>1.60 × 10⁻⁶</td>
<td>492</td>
<td>1.73 × 10⁻³</td>
<td>1.03 × 10⁻⁵</td>
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<td></td>
</tr>
</tbody>
</table>

**Table F3**

Data from \[19\] used to determine \( k_c \).

<table>
<thead>
<tr>
<th>Article data</th>
<th>( m ) (m/s)</th>
<th>( d(2\pi)/dt ) (m/s)</th>
<th>Results</th>
<th>( c_s ) (kg/m³)</th>
<th>( J_c ) (kg/m²/s)</th>
<th>( k_c ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.9</td>
<td>5.30 × 10⁻⁶</td>
<td>575</td>
<td>5.74 × 10⁻³</td>
<td>2.29 × 10⁻⁵</td>
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<tr>
<td>12.2</td>
<td>5.10 × 10⁻⁶</td>
<td>587</td>
<td>5.52 × 10⁻³</td>
<td>2.10 × 10⁻⁵</td>
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<td></td>
</tr>
<tr>
<td>11.36</td>
<td>5.60 × 10⁻⁶</td>
<td>554</td>
<td>6.06 × 10⁻³</td>
<td>2.64 × 10⁻⁵</td>
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</tr>
</tbody>
</table>

**Table F4**

Data from \[16\] used to determine \( k_c \).

<table>
<thead>
<tr>
<th>Article data</th>
<th>( M_s ) (mol/l)</th>
<th>( d(2\pi)/dt ) (m/s)</th>
<th>Result</th>
<th>( c_s ) (kg/m³)</th>
<th>( J_c ) (kg/m²/s)</th>
<th>( k_c ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.03</td>
<td>10 × 10⁻⁶</td>
<td>410</td>
<td>10.82 × 10⁻³</td>
<td>1.26 × 10⁻⁴</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
References