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# Nucleation Kinetics of Freeze Crystallization with Various Aqueous Solutions

The nucleation kinetics of ice were investigated with four different types of aqueous solutions. The studied aqueous solutions, i.e., sucrose solution, ionic liquid (IL) solution, pyrolysis oil extract (PO) solution, and acetone-1-butanol-ethanol (ABE) solution, were concentrated by batch suspension freeze crystallization. The nucleation kinetics were investigated using a temperature response method which results in data on nucleation rate per crystal. The obtained nucleation rate per crystal value can be used when dimensioning continuous crystallization processes: the nucleation rate per crystal is inversely proportional to the residence time in continuous crystallization. The subcooling degrees for different solutions were in the range of 0.33 °C to 1.89 °C. Aqueous sucrose solutions had the fastest nucleation kinetics. Ice crystallization from non-ideal aqueous [DBNH][OAc] ionic liquid solutions required higher subcooling degrees and the nucleation rates per crystal were higher as well. Nucleation of ice formed from aqueous pyrolysis oil extract and aqueous ABE solutions occurred at a lower subcooling degree and the obtained nucleation rate per crystal values were lower.

**Keywords:** Acetone-1-butanol-ethanol solutions, Ice nucleation, Ionic liquid, Pyrolysis oil, Suspension freeze crystallization

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## 1 Introduction

Biorefinery is a key industry for the production of sustainable and green bioproducts, biochemicals, and biofuels. The common bioprocessing methods for biomass are based on pyrolysis and fermentation. Organic solutions obtained by these methods are multicomponent aqueous solutions that need further treatment in order to separate and purified produced biochemicals. Moreover, a novel concept in bioprocessing, ioncell, based on the dissolution of cellulose-based materials with ionic liquid solvents offers a potential solution for the recycling of waste lignocellulose materials and the production of a new type of sustainable fibers. The current challenge in the biorefinery field is the development and application of appropriate downstream processing units that enable efficient recycling of the used solvent, concentration of the organic aqueous solutions generated, and separation and purification of the biochemicals produced [1–3].

Melt crystallization is an industrial separation and purification technology that enables high purity of final products crystallized at a temperature close to their melting point [4]. Freeze crystallization is a type of melt crystallization that consumes less energy in comparison with evaporation-based separation technology because water's latent heat of freezing is around seven times lower than the latent heat of vaporization. The freeze crystallization method, namely suspension freeze crystallization, is defined as the formation and growth of ice crystals dispersed in a stirred aqueous solution. Freeze crystallization has been extensively studied as a concentration method in food processing [5,6]. Moreover, recently freeze crystallization has been reported as a potential and efficient wastewater treatment method [7,8].

Ice nucleation kinetics was investigated by a temperature response method [9,10] and induction time measurements. This work investigates the nucleation kinetics of ice crystallization obtained by suspension freeze crystallization from four different aqueous solutions related to different processes typical of a biorefinery. Freeze crystallization was conducted with aqueous solutions of sucrose, [DBNH][OAc] ionic liquid, pyrolysis oil extract, and ABE. The influence of different solutes present in different aqueous solutions on ice nucleation was assessed based on the temperature response method. The nucleation kinetics model was used by collecting data on the maximum slope of the temperature response curve apparent upon ice crystal seeding as a function of subcooling degree.

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## 2 Materials and Methods

Different aqueous solutions were prepared by dissolving different solutes in deionized water and mixing them on a magnetic stirrer for 60 min.

Thus, an aqueous sucrose solution was prepared by dissolving 10 wt % food grade sucrose (equivalent to 0.994 water mole fraction) and an aqueous [DBNH][OAc] ionic liquid solution was prepared by dissolving 6 wt % of [DBNH][OAc] ionic liquid (0.994 water mole fraction). The ABE solutions were prepared by dissolving acetone, butanol, and ethanol in the range of 3.68–19.2 wt % of the total amount of solutes (equivalent to 0.932–0.988 water mole fraction) in deionized water inside a closed Wheaton reactor to reduce solvent evaporation during mixing.

The aqueous phase of pyrolysis oil was extracted from pyrolysis oil by adding water to the pyrolysis oil (volume fraction 10:1 water: pyrolysis oil) and mixing then on the shaker for an hour at 178 rpm. The aqueous pyrolysis oil extract contained between 92.4 % and 95.7 % water and the other major compounds present were formic acid, acetic acid, and levoglucosan.

The suspension freeze crystallization experimental setup is shown in Fig. 1.

Experiments were performed inside a 250 mL jacketed glass crystallizer (2) connected to a Lauda ECO RE 1050 thermostat (1) that pumped coolant through the jacket. The coolant (50 wt % aqueous ethylene glycol solution) circulated through the jacket with a flow rate of 1.64 L min$^{-1}$. The internal temperature in the Lauda coolant pool was the parameter for the coolant temperature adjustment. Solution temperature was measured with a thermometer (4) connected to real-time temperature data acquisition (6) and data collection was performed with LabView software (7). The solutions were stirred with a rotating stirrer (3) at a speed of 18 rpm in order to prevent ice encrustation.

The nucleation kinetic parameter, $\beta$, was calculated by Eq. (1) derived by Shirai et al. [9]:

$$\frac{\beta}{\left[\frac{1}{s}\right]} = \frac{5.93\left(\frac{\mu_2^0}{[1/\mathrm{m}]}\right)^{0.027}}{\frac{\Delta T}{[^\circ\mathrm{C}]}} \left\{ \frac{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\max}}{\left[\frac{^\circ\mathrm{C}}{\mathrm{s}}\right]} \right\} \tag{1}$$

Where $\beta$ is the nucleation rate per crystal, which is inversely proportional to the average residence time $t$ in a continuous crystallizer, $\beta = 1/t$, $\Delta T$ is the subcooling degree, $\mu_2^0$ is the the second moment of the seed crystal size distribution (assumed to be equal to 1 m$^{-1}$), and $\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\max}$ maximum slope of temperature response curve.

The solutions fed to the crystallizer were cooled down to temperatures that corresponded to the desired subcooling temperature. The subcooling degree (difference between solution subcooling temperature and its freezing point) was in the range of 0.33 °C to 1.89 °C. The freeze crystallization was initiated with ice seeding. Ice seeding was performed when the solution temperature reached a stable and constant value. Upon seeding, the temperature of the solution gradually rose to its freezing point due to the release of the latent heat of freezing. The obtained response curves from the measured solution temperature were analyzed in order to collect data on the maximum slope of temperature over time as a function of subcooling degree.

## 3 Results and Discussion

Temperature response curves for three different types of solutions are shown in Fig. 2. The cooling time necessary for the solution to reach a certain subcooling temperature varies for different solutions, which is a result of different thermophysical properties and the different initial temperature of the solutions.

Fig. 2 shows that the freezing times were 60 min for the aqueous ABE solution and 40 min for the aqueous pyrolysis oil extract (PO) and the aqueous [DBNH][OAc] ionic liquid (IL) solutions. The cooling region, seeding, and crystallization region shown in Fig. 1b can be similarly seen in Figs. 1a and 1c. The slope of the temperature response upon seeding differs for

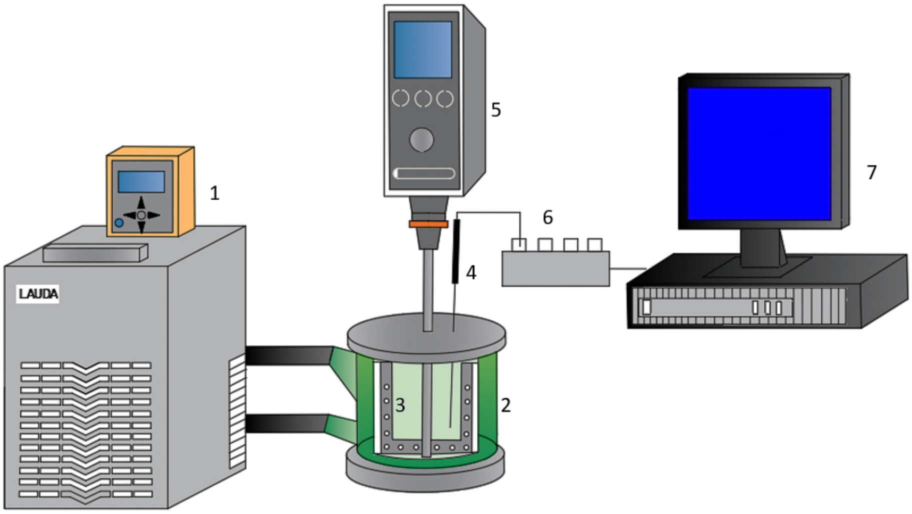

**Figure 1.** Suspension freeze crystallization setup: (1) thermostat, (2) jacketed crystallizer, (3) stirrer, (4) thermometer, (5) mixer, (6) data acquisition, (7) data storage.

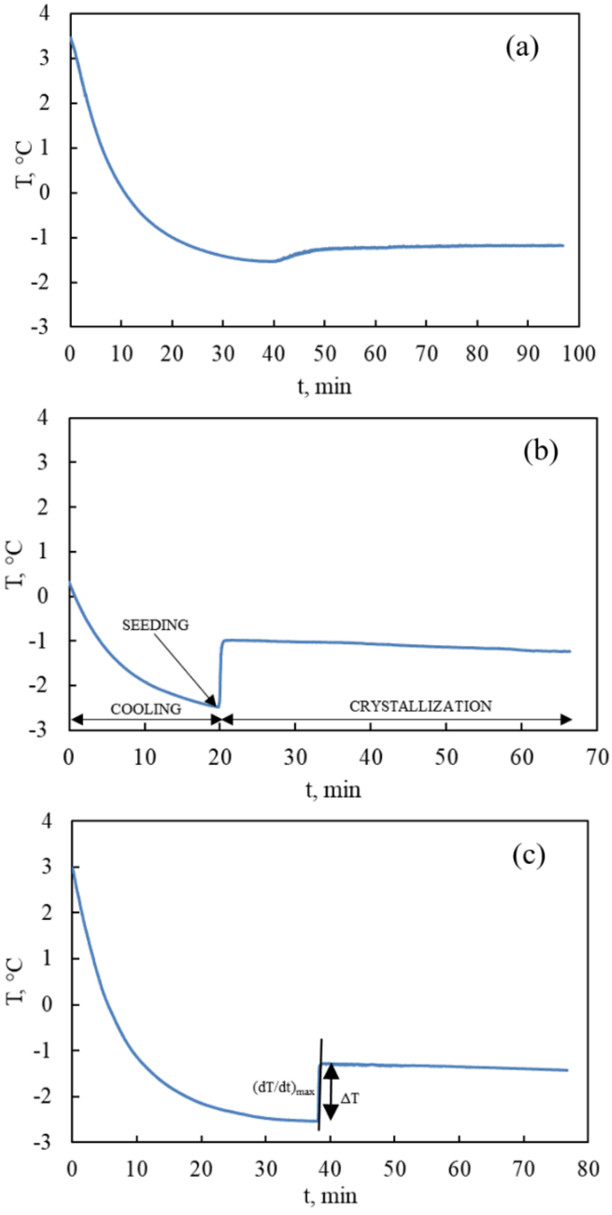

**Figure 2.** Cooling curves for: (a) aqueous ABE solutions (ABE), (b) aqueous pyrolysis oil extract (PO), and (c) aqueous [DBNH][OAc] ionic liquid solutions (IL).

the different solutions as a result of the different subcooling degree, $\Delta T$, as well as the ice crystallization kinetics for the various solutions.

The freezing points of the aqueous sucrose, aqueous [DBNH][OAc] ionic liquid, and aqueous ABE solutions as a function of water mole fraction are shown in Fig. 3. The freezing points of the [DBNH][OAc] and ABE solutions had been determined experimentally in previous studies [11, 12] and, in the case of sucrose, temperature data were taken from the literature [13]. The freezing point depression of pyrolysis oil extract is not shown as a function of mole fraction due to the complexity of its composition.

The aqueous sucrose and ABE solutions are ideal solutions with an activity coefficient value of water almost equal to unity, whereas the [DBHN][OAc] solutions are non-ideal with attractive forces between the water molecules and ionic liquid molecules.

The nucleation of ice crystals formed from four different aqueous solutions was compared. Thus, the nucleation kinetic factor as a function of subcooling degree for the different solutions is shown in Fig. 4. Nucleation kinetics per crystal was investigated in our previous studies with other type of solution samples [10]. In the present work the viscosity effect via the presence of sucrose was compared as well.

It is apparent that the nucleation of ice from aqueous sucrose solutions proceeds with faster kinetics than the other solutions. Ice nucleation from [DBNH][OAc] ionic liquid solutions proceeds faster than ice nucleation from aqueous ABE solutions and aqueous pyrolysis oil extract solutions because it has the highest initial water content. Moreover, the maximum slope of the temperature response curve that is dependent on the subcooling degree applied is also a factor to consider regarding this trend.

A [DBNH][OAc] ionic liquid solution as a non-ideal solution with attractive forces between the water and ionic liquid molecules [11] and with a similar water content to sucrose solution, demonstrate a slightly slower ice nucleation than aqueous sucrose solution. In comparison with aqueous ABE solutions as another type of ideal solution, ice nucleation is much faster for [DBNH][OAc] ionic liquid solutions, since a much higher driving force, subcooling, is applied. In contrast, for the ideal aqueous ABE solutions a lower subcooling degree had to be applied to prevent spontaneous ice nucleation.

For ideal solutions, aqueous sucrose solutions, and aqueous ABE solutions, for the same subcooling degree, the ice nucleation from sucrose solutions occurs with higher kinetics than ice nucleation for aqueous ABE solutions because aqueous sucrose solutions contain more water than aqueous ABE solution in terms of the mole fraction of water. When comparing ABE and PO solutions, the ice crystallization kinetic for ideal ABE solutions is slightly faster than for PO solutions with similar initial water content.

In summary, Fig. 4 shows the overall trend for the nucleation rate per crystal over a range of subcooling degrees for the four different aqueous solutions under the same mixing conditions.

Induction time, t, is defined as the time between the moment of seeding and the moment when the solution temperature measured by the thermometer starts to change. The induction time is related to thermometer sensitivity in different types of solutions. The induction times for the different solutions and for the maximum and minimum subcooling degree are presented in Tab. 1.

The induction time values for maximum and minimum applied subcooling degrees for the different solutions correspond well to the solutions' ice crystallization kinetics. This is clear for the aqueous ABE solutions that have the longest induction times and slow crystallization kinetics, as well as for aqueous sucrose solutions with short induction times and high crystallization kinetics. However, pyrolysis oil extract solutions have very slow crystallization kinetics in applied subcooling range, but very short induction times due to the presence of the produced organic compounds soluble in water. [DBNH][OAc] ionic liquid solution with high kinetics achieved by high driving force has relatively long induction time due to solution's ionic conductivity.

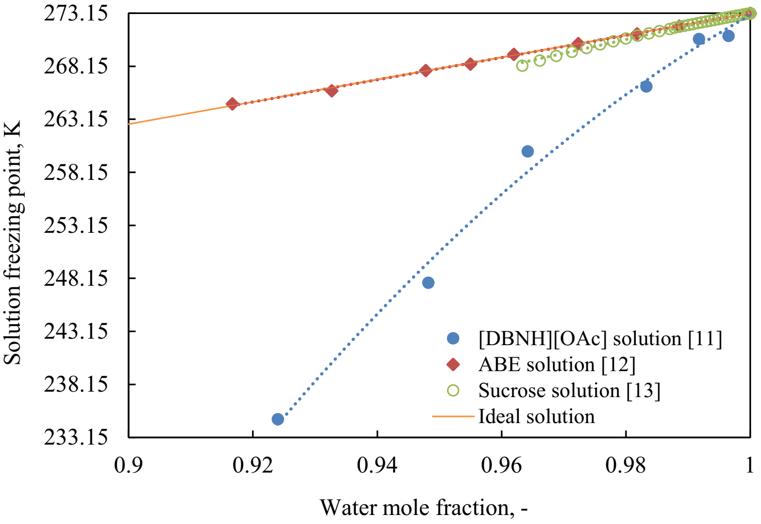

**Figure 3.** Freezing point depression of aqueous sucrose solutions, aqueous IL solution, aqueous ABE solutions and ideal solution.

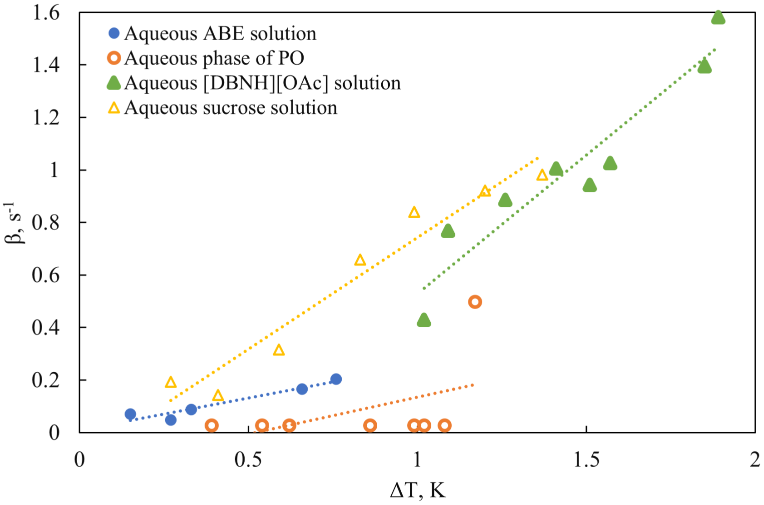

**Figure 4.** Nucleation rate per crystal as a function of subcooling degree for aqueous sucrose solutions, aqueous ABE solutions (ABE), aqueous pyrolysis oil extract (PO), and aqueous [DBNH][OAc] ionic liquid solutions (IL).

## 4 Conclusions

Suspension freeze crystallization was applied as a concentration method for four types of aqueous solutions, namely sucrose solution, ABE solution, pyrolysis oil extract solution, and [DBNH][OAc] ionic liquid solution. This investigation can be summarized as follows:

1. Ice crystallization kinetics are affected by the applied subcooling degree, initial water content, ideality of solution, and different types of organic compounds present in aqueous solutions.
2. The overall influence of these factors leads to the conclusion that the nucleation rate of ice crystallization is the highest from sucrose solutions, followed by ionic liquid solutions, ABE solutions and pyrolysis oil extract.
3. Aqueous sucrose solution is an ideal solution with the highest initial water content and consequently has the fastest ice crystallization kinetics.
4. The ice crystallization kinetics for non-ideal [DBNH][OAc] ionic liquid solutions proceed faster in comparison with ideal ABE solutions and at a similar level to ideal sucrose solutions because the subcooling degree applied as a driving force is higher.
5. Induction times for maximum and minimum subcooling degrees shows a similar trend as the kinetics for different solutions, even though it is also dependent on solution composition and ionic conduction in case of pyrolysis oil extract and ionic liquid solutions.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Table 1.** Induction times for maximum and minimum subcooling degrees for different solutions.

| Solution type | Maximum subcooling degree $\Delta T_{\max}$ [°C] | Induction time $t$ [s] | Minimum subcooling degree $\Delta T_{\min}$ [°C] | Induction time $t$ [s] |
|---|---|---|---|---|
| Sucrose solution | 1.37 | 14 | 0.27 | 71 |
| PO extract solution | 1.17 | 29 | 0.39 | 56 |
| IL solution | 1.89 | 72 | 1.25 | 79 |
| ABE solution | 0.66 | 157 | 0.33 | 192 |

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*The authors have declared no conflict of interest.*

## Symbols used

### Greek letters

| | | |
|---|---|---|
| $\beta$ | [$s^{-1}$] | nucleation rate per crystal |
| $\mu_2^0$ | [$m^{-1}$] | the second moment of the seed crystal size distribution |

### Sub- and Superscripts

| | |
|---|---|
| max | maximum |
| min | minimum |

### Abbreviations

| | |
|---|---|
| ABE | acetone-1-butanol-ethanol |
| IL | ionic liquid |
| PO | pyrolysis oil |

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