

## Research Article

# Sugar Industry: Effect of Dextran Concentrations on the Sucrose Crystallization in Aqueous Solutions

Abdelali Borji , Fatima-Ezzahra Borji , and Abdelaziz Jourani 

Laboratory of Physical Chemistry of Processes and Materials, Department of Applied Chemistry and Environment, Faculty of Sciences and Techniques, University Hassan I, B.P.: 577, Settat, Morocco

Correspondence should be addressed to Abdelali Borji; a.borji@uhp.ac.ma

Received 17 April 2019; Accepted 26 May 2019; Published 13 June 2019

Academic Editor: Runcang Sun

Copyright © 2019 Abdelali Borji et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Using the spectrophotometric method, as a new method, the influence of dextran on the sucrose solubility and metastable zone width has been studied. In agreement with the literature the experimental data show that the dextran has a negligible effect on the sucrose solubility. The results also show that this impurity decreases the sucrose metastable zone width. The study of the nucleation kinetics performed, using Nyvlt's approach, shows that the dextran accelerates the nucleation and that the nuclei are formed in the solution by instantaneous nucleation. The presence of dextran in the system causes a decrease in the growth rate of sucrose. The growth process of sucrose is governed by a Birth and Spread mechanism. The kinetic parameters of sucrose growth in aqueous solutions without and with dextran were estimated.

## 1. Introduction

Crystallization is an important process in industrial operations. In sugar manufacturing, crystallization is a crucial step that determines the quality of the final product, which requires control of its fundamental parameters. The presence of impurities (non-sugars) in the sugar solution may influence the sucrose crystallization. In fact, impurities in supersaturated solutions significantly affect the nucleation, growth rate, morphology, and also the agglomeration rate of the crystals [1]. Among these impurities, we find the dextran which has already been recognized as a serious problem in sugar processing [2]. Dextran is a branched polymer of dextrose (glucose) of very high molecular weight, belonging to the group of colloids. It is one of the exopolysaccharides excreted by various soil microorganisms, which play an important role at the molecular level in the formation and conservation of soils (dextran, xanthan, rhamosan, and succinoglycan). Dextran can be formed if sugar cane stays in the sun for too long before being treated in mills, which decreases the amount of sugar available.

The presence of dextran in the sugar juice causes certain problems at the level of the sugar treatment in particular in the crystallization process, in fact the presence of this impurity causes a significant increase in the viscosity, elongated

crystals, lower evaporation rates, longer wash and separation cycles in centrifuges, and loss of sugar to molasses [3–8]. However, there are few reports in the literature concerning the influence of dextran on the crystallization kinetics of sucrose.

Consequently, the aim of this work is to study the effect of dextran on the fundamental parameters of sucrose crystallization in particular the solubility, the metastable zone width, the nucleation rate, and the growth rate.

## 2. Theory

*2.1. Nucleation Modeling.* According to Nyvlt's approach [9], the nucleation rate  $N_m$ , during a constant cooling speed ( $R = \Delta T / \Delta t$ ), is linked to the supersaturation  $\Delta C$  by a power law relation given by

$$N_m = K_m (\Delta C)^m = K_m (C - C^*)^m \quad (1)$$

where  $C$  and  $C^*$  are the solution concentration and the solubility, respectively.

On the other hand, Nyvlt [9] assumes that nucleation rate corresponds to the rate of generation of supersaturation for a limited time period.

The supersaturation rate during cooling is given by the following relation:

$$\frac{d(\Delta C)}{dt} = R_s \left( \frac{dC^*}{dT} \right) \quad (2)$$

The MSZW is related to the maximum supersaturation  $\Delta C_{max}$  developed during cooling by the following relation:

$$\Delta C_{max} = \left( \frac{dC^*}{dT} \right) \Delta T_{max} \quad (3)$$

From Eqs. (1) and (2) one obtains

$$K_m (\Delta C)^m = K_m \left[ \frac{dC^*}{dT} \Delta T_{max} \right]^m \quad (4)$$

Taking logarithms on both sides of Eq. (4), Eq. (5) is obtained as follows:

$$\ln R = m \ln \Delta T_{max} + (m - 1) \ln \left( \frac{dC^*}{dT} \right) + \ln K_m \quad (5)$$

From the slope of the linear relation between  $\ln b$  and  $\ln \Delta T_{max}$ , the values of  $m$  and  $K_m$  can be deduced because  $dC^*/dT$  may be determined from solubility data.

The following equation gives the relation between the mass of formed nuclei and the number of nuclei formed:

$$\frac{dN}{dt} = K_m (\Delta C)^m = k \alpha \rho r^3 (\Delta C)^m \quad (6)$$

where  $r$  is the detectable nuclei size at the maximum supersaturation, which is generally supposed to be  $10 \mu\text{m}$  [7, 8].

**2.2. Growth Modeling.** The increase in the mass of crystals with time, in the case of isothermal seeded crystallization, may be expressed by the following expression [10]:

$$R_g = \frac{1}{a_c} \frac{dm_s}{dt} = 3 \frac{\alpha}{\beta} \rho \frac{dL}{dt} = 3 \frac{\alpha}{\beta} \rho G \quad (7)$$

where  $R_g$  is the rate of solute consumption per unit,  $a_c$  is seed area, and  $G$  is the linear growth rate for sucrose crystals. A spherical shape for the sucrose crystal is assumed ( $\alpha = 0.75$ ,  $\beta = 5.02$ , and  $\rho = 1580 \text{ Kg.m}^{-3}$ ).

From Eq. (8), giving the expression of the linear growth rate  $G$ , the evolution of  $m_s$  versus time can be estimated according to Eq. (9):

$$G = \frac{dL}{dt} = K_g \sigma^g \quad (8)$$

$$\left. \frac{dm_s}{dt} \right|_{t=0} = 3 a_c \frac{\alpha}{\beta} \rho K_g \sigma_0^g \quad (9)$$

In Eqs. (8) and (9)  $a_c$  is the overall seed area,  $\rho$  is the density of the crystals,  $m_s$  is the mass of crystals,  $\alpha$  and  $\beta$  are the volume shape factor and the area shape factor, respectively,  $K_g$  is the constant of growth kinetics, and  $g$  is the growth kinetics order.

One can assume constant initial seed area  $a_c$  which leads to the following expression:

$$\ln \left( \left. \frac{dm_s}{dt} \right|_{t=0} \right) = \ln \left( 3 a_c \frac{\alpha}{\beta} \rho K_g \right) + g \ln (\sigma_0) \quad (10)$$

### 3. Experimental Section

**3.1. Materials.** Sucrose and dextran employed are "of analytical" quality to avoid any other impurities which may influence the measurements. Distilled water is used as solvent.

**3.2. Solubility and Metastable Zone Width.** The experimental setup used for the determination of the sucrose solubility and metastable zone width consists of a jacketed reactor with a mechanical stirrer, a cryothermostat for temperature control, and a digital thermometer for temperature measurement (accuracy  $\pm 0.1^\circ\text{C}$ ) (see Figure 1). The cooling is carried out by the cryothermostat and the determination of the solubility and the supersaturation limit is achieved using the spectrophotometric method [11]. This method consists of following the evolution of the absorbance of a sucrose solution during its cooling. The first jump of the absorbance corresponds to the sucrose solubility. The second jump corresponds to the supersaturation limit. The metastable zone width is the difference between the solubility temperature and the limit supersaturation temperature.

**3.3. Nucleation Kinetics.** The experimental setup is identical to that presented in Figure 1. The cooling is carried out by the cryothermostat and the determination of the metastable zone width is achieved using the spectrophotometric method [11].

To determine the nucleation kinetics of sucrose, water-sucrose solutions were prepared by dissolving known masses of sucrose in 100 ml of distilled water at temperatures higher than those of the solubility. The metastable zone widths for different cooling rates (0.2, 0.5, 1, and  $1.5^\circ\text{C}/\text{min}$ ) were measured. Based on Eq. (5) the nucleation kinetic parameters can be calculated.

**3.4. Crystal Growth Kinetics.** The experimental setup is identical to that presented in Figure 1. Seeded isothermal growth experiments of sucrose are performed in a batch cooling crystallizer starting with an initial known concentration solution (200g/100g of water) and for three concentrations of dextran (500, 1000, and 1500). Three relative supersaturations, 10, 15, and 20%, were selected for the measurements. In this study, the size of the sucrose seeds, prepared before by sieving, is between 0.5 and  $1\text{mm}$ . The variation of the crystallized mass of sucrose is monitored as a function of time by a refractometer (repeated tests have shown the good reproducibility of measurements). This mass variation as a function of time is plotted and the growth rate is deduced according to Eq. (10).

Preliminary tests showed that the concentrations of dextran studied do not influence the refractive index of sucrose and therefore the refractive index measured in the impure mediums corresponds to that of sucrose.

### 4. Results and Discussion

**4.1. Solubility and Metastable Zone of Sucrose in Presence of Dextran.** The influence of dextran on the sucrose solubility and the metastable zone width of its aqueous solutions

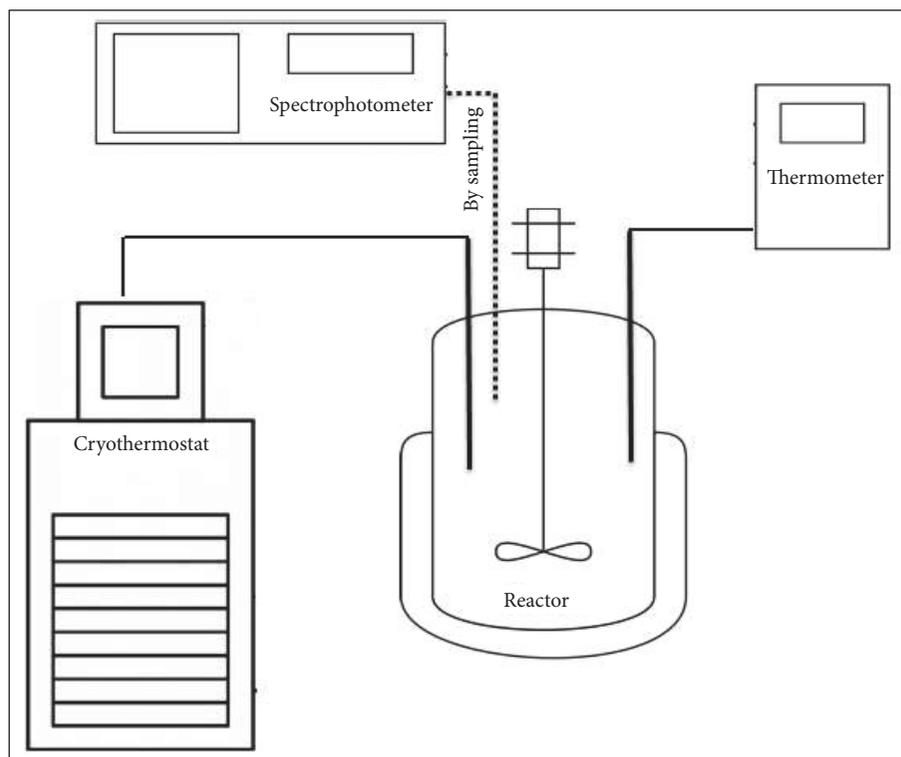


FIGURE 1: Experimental setup.

has been studied. Three concentrations of this impurity (500, 1000, and 1500 ppm) and for different concentrations of sucrose were selected for the measurements. Figure 2 illustrates the influence of this polysaccharide on the sucrose solubility according to the temperature. As seen from this figure, in agreement with the literature [12], the addition of dextran causes a slight decrease in sucrose solubility (negligible effect for the range of studied concentrations). The results also show that the presence of dextran causes a decrease in MSZW of sucrose (see Table 1). For example, for a sucrose concentration of 240 g/100 g of water, the metastable zone widths decrease from 7.4°C in the case of the pure system to 5.8°C in the presence of 1500 ppm of dextran.

**4.2. Estimated Nucleation Kinetics.** The measured MSZWs as a function of cooling rate in aqueous solutions without and with dextran are illustrated in Figure 3 indicating that the MSZW depends closely on the cooling rate. It widens significantly with increasing cooling rate as predicted by Eq. (5), and this behavior has been observed for many investigated systems [13–15]. Thus, the maximum supercooling always increases with increasing cooling rate.

Based on data analysis and Nyvlt's theory, the linear dependence expressed by Eq. (5) permits to calculate the values of the nucleation order  $m$  and the nucleation constant  $K_m$ .

The slopes of the curves, shown in Figure 3, give the nucleation orders and the intercept gives the nucleation constants, according to Eq. (5). The correlation equations obtained

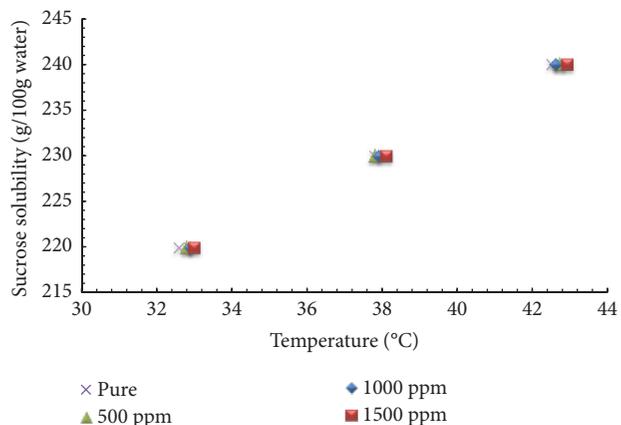


FIGURE 2: Sucrose solubility in water for different concentrations of dextran.

with their correlation coefficients for different systems were presented in Table 2. Table 3 shows the calculated parameters of sucrose nucleation in aqueous solutions without and with dextran.

After estimating kinetic parameters for given systems, the estimated nucleation rates as a function of supersaturation based on Nyvlt's theory, as given by Eq. (5), are shown in Figure 4.

Depending on Nyvlt's approach evaluated, the nucleation orders  $m$  were found between 3.21 and 3.53 for different systems. These values are in good agreement with published data for organic materials. Moreover, the apparent nucleation

TABLE 1: Saturation temperature  $T_{sat}$ , crystallization temperature  $T_{max}$ , and MSZW for aqueous sucrose solutions of different concentrations  $C_s$  containing different content  $C_{im}$  of dextran.

system	$C_s$ (g/100g water)	$C_{im}$ (ppm)	$T_{sat}$ (°C)	$T_{max}$ (°C)	MSZW (°C)
Water-Sucrose	220	0	32.7	22.9	9.8
	230	0	37.9	28.9	9.0
	240	0	42.6	35.2	7.4
Water-sucrose-dextran	220	500	32.8	23.1	9.7
		1000	32.9	23.9	9
		1500	33	25	8
	230	500	37.8	29	8.8
		1000	37.9	29.8	8.1
		1500	38.1	31	7.1
	240	500	42.7	35.5	7.2
		1000	42.6	35.8	6.8
		1500	42.9	37.1	5.8

TABLE 2: Correlation equation between  $\ln(R)$  and  $\ln(\Delta T_{max})$ .

System	Correlation $\ln(R) = f(\ln \Delta T_{max})$	$R^2$
water-sucrose	$\ln(R) = 3.5212 \ln(\Delta T_{max}) - 4.5543$	0.9987
water-sucrose-dextran (500 ppm)	$\ln(R) = 3.3915 \ln(\Delta T_{max}) - 4.1981$	0.9981
water-sucrose-dextran (1000 ppm)	$\ln(R) = 3.2526 \ln(\Delta T_{max}) - 3.7501$	0.9999
water-sucrose-dextran (1500 ppm)	$\ln(R) = 3.1976 \ln(\Delta T_{max}) - 3.1642$	0.9969

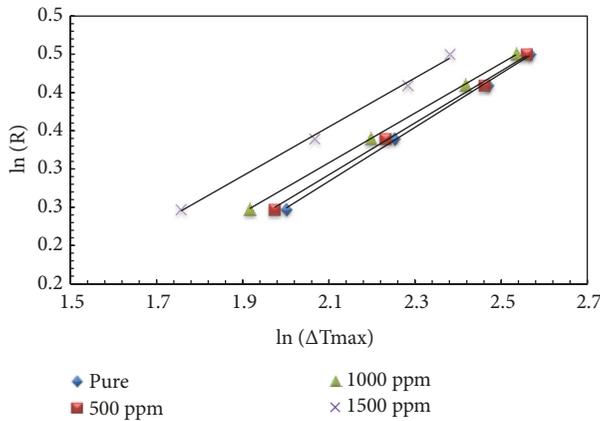


FIGURE 3: Plot  $\ln(R)$  versus  $\ln(\Delta T_{max})$  for sucrose aqueous solutions without and with dextran.

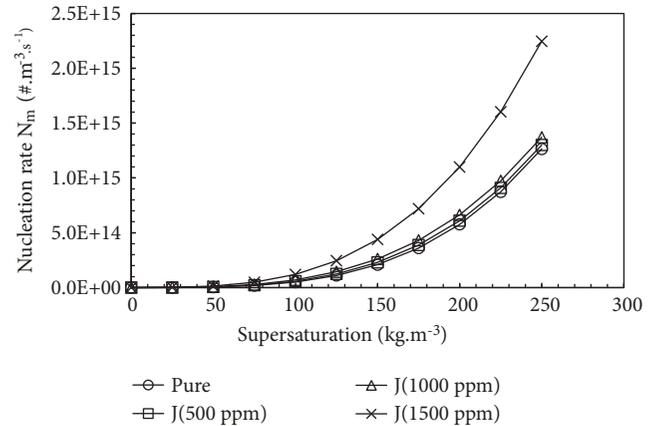


FIGURE 4: Nucleation rate as a function of supersaturation in aqueous solutions without and with dextran.

TABLE 3: Nucleation kinetic parameters estimation.

System	m	k
water-sucrose	3.53	$4.55 \times 10^6$
water-sucrose-dextran (500 ppm)	3.39	$9.58 \times 10^6$
water-sucrose-dextran (1000 ppm)	3.25	$2.17 \times 10^7$
water-sucrose-dextran (1500 ppm)	3.21	$4.83 \times 10^7$

order values ( $< 4$ ) reveal that nuclei in the solution are formed by instantaneous nucleation [16, 17].

According to the results obtained, the presence of dextran accelerates the nucleation. This acceleration can be explained by the fact that the increase of the concentration of this polysaccharide reduces the amount of free water molecules available for solvation of sucrose and, hence, the collisions probability between the solute molecules becomes more important.

4.3. *Estimated Growth Kinetics Parameters.* The effect of dextran on the kinetics of sucrose growth has been studied.

TABLE 4: Estimation of growth kinetic parameters.

System	$\ln(dm_s/dt) = f(\ln(\sigma_0))$	$R^2$	$K_g$	g
water-sucrose	$\ln(dm_s/dt) = 0.990 \ln(\sigma_0) - 0.9495$	0.9928	$2.38 \times 10^{-3}$	1.0
water-sucrose-dextran (500 ppm)	$\ln(dm_s/dt) = 1.0339 \ln(\sigma_0) - 0.9531$	0.9969	$2.37 \times 10^{-3}$	1.0
water-sucrose-dextran (1000 ppm)	$\ln(dm_s/dt) = 1.0226 \ln(\sigma_0) - 1.2013$	0.9951	$1.85 \times 10^{-3}$	1.0
water-sucrose-dextran (1500 ppm)	$\ln(dm_s/dt) = 1.0138 \ln(\sigma_0) - 1.4905$	0.9999	$1.38 \times 10^{-3}$	1.0

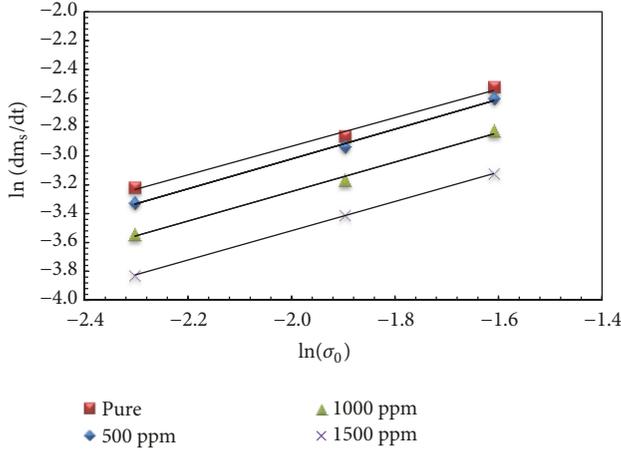


FIGURE 5: Evolution of mass sucrose crystal over time as function of supersaturation in aqueous solutions without and with dextran.

Three concentrations of this impurity (500, 1000, and 1500 ppm) and for different supersaturations were selected for the measurements. In order to estimate the growth kinetic parameters, the variation of the mass as a function of time for different supersaturations is plotted as shown in Figure 5. From the intercept, the growth kinetic constant can be calculated and the growth rate order can be estimated from the slope. Table 4 shows the growth kinetic parameters for different systems studied.

The results show that the orders obtained from the experimental data for the different systems are found close to 1 indicating that the growth process of sucrose is governed by a Birth and Spread mechanism (B+S) [18]. The fitting results indicate that growth kinetic constant ( $K_g$ ) decreases with the increase in the concentration of dextran, which confirms that this impurity reduces the growth rate as shown in Figure 6.

The decrease in the sucrose growth rate in the presence of dextran can be explained by the fact that this polysaccharide causes an increase in viscosity [2]. This affects the transfer step of the sucrose molecules by diffusion to the crystalline surface.

## 5. Conclusion

In this work, solubility of sucrose in aqueous solutions without and with dextran and their metastable zone width have been investigated using the spectrophotometric method, as a new method. In agreement with the literature, the addition of dextran causes a slight decrease in sucrose solubility.

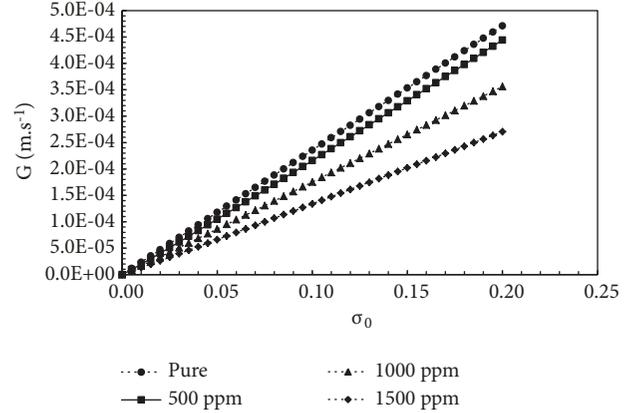


FIGURE 6: Growth rate versus supersaturation in aqueous solutions without and with dextran.

The results also show that the presence of dextran causes a decrease in the sucrose metastable zone width.

The nucleation study of sucrose, using Nyvlt's theory, shows that the presence of dextran accelerates the nucleation of sucrose and that nuclei in the solution are formed by instantaneous nucleation.

The kinetics of sucrose growth in aqueous solutions without and with dextran was also studied. The results show that this impurity reduces crystal growth rate and that the growth process of sucrose is governed by a Birth and Spread mechanism (B+S).

## Nomenclature

$a_c$ :	Overall seed area, $m^2$
$C$ :	Concentration, $Kg.m^{-3}$
$C^*$ :	Solubility concentration, $Kg.m^{-3}$
$\Delta C$ :	Supersaturation, $Kg.m^{-3}$
$\Delta C_{max}$ :	Maximum supersaturation, $Kg.m^{-3}$
$G$ :	Linear growth rate, $m.s^{-1}$
$g$ :	Order of growth, dimensionless
$N_m$ :	Nucleation rate, $\#.m^{-3}.s^{-1}$
$K_m$ :	Mass nucleation constant, $Kg^{-n}.m^{3n-3}.s^{-1}$
$k$ :	Number nucleation constant, dimensionless
$K_g$ :	Crystal growth rate coefficient, $m.s^{-1}$
$L$ :	Characteristic length, $m$
$m_s$ :	Solid mass, $kg$
$m$ :	Apparent nucleation order, dimensionless
$N$ :	Number of formed nuclei, dimensionless
$R$ :	Cooling rate, $^{\circ}C.h^{-1}$
$r$ :	Critical nucleus radius, $m$

$R_g$ : Rate of solute consumption per unit seed area,  $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$   
 $R^2$ : Correlation coefficient, dimensionless  
 $T$ : Temperature,  $^{\circ}\text{C}$   
 $t$ : Time, s  
 $\Delta T$ : Supercooling,  $^{\circ}\text{C}$   
 $\Delta T_{\text{max}}$ : Metastable zone width or MSZW,  $^{\circ}\text{C}$ .

#### Greek Letters

$\alpha$ : Volume shape factor, dimensionless  
 $\beta$ : Area shape factor, dimensionless  
 $\rho$ : Density,  $\text{kg}\cdot\text{m}^{-3}$   
 $\sigma_0$ : Initial relative supersaturation, dimensionless  
 $\sigma$ : Relative supersaturation, dimensionless.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

#### References

- [1] K. Sangwal, *Additives and Crystallization Processes: From Fundamentals to Applications*, John Wiley & Sons, 2007.
- [2] E. A. Abdel-Rahman, Q. Smejkal, R. Schick, S. El-Siyad, and T. Kurz, "Influence of dextran concentrations and molecular fractions on the rate of sucrose crystallization in pure sucrose solutions," *Journal of Food Engineering*, vol. 84, no. 4, pp. 501–508, 2008.
- [3] F. K. E. Imrie and R. H. Tilbury, "Polysaccharides in sugar cane and its products," *Sugar Technology Reviews*, vol. 1, no. 4, pp. 291–361, 1972.
- [4] S. C. Jolly and C. Prakash, "Removal of dextran from cane juice," *International Sugar Journal*, 1987.
- [5] D. Kim and D. F. Day, "Determination of dextran in raw sugar process streams," *Food Science and Biotechnology*, vol. 13, pp. 248–252, 2004.
- [6] R. A. McGinnis, *Beet-Sugar Technology*, Beet Sugar Development Foundation, Fort Collins, Colo, USA, 1982.
- [7] V. Singleton, "Advances in techniques of dextran analysis: a modern day perspective," *International Sugar Journal*, vol. 104, no. 1239, pp. 132–136, 2002.
- [8] V. Singleton, J. Horn, C. Bucke, and M. Adlard, "A new polarimetric method for the analysis of dextran and sucrose," *American Society of Sugar Cane Technologists*, vol. 22, pp. 112–119, 2001.
- [9] J. Nývlt, "Kinetics of nucleation in solutions," *Journal of Crystal Growth*, vol. 3-4, pp. 377–383, 1968.
- [10] A. Myerson, *Handbook of Industrial Crystallization*, Butterworth-Heinemann, 2002.
- [11] A. Borji and A. Jourani, "Spectrophotometry as a method for the determination of solubility of sucrose in water and metastable zone width of its aqueous solutions," *Crystal Research and Technology*, vol. 53, Article ID 1700123, 2018.
- [12] I. Khaddour, A. Ferreira, L. Bento, and F. Rocha, "Sucrose crystal growth in the presence of dextran of different molecular weights," *Journal of Crystal Growth*, vol. 355, no. 1, pp. 17–25, 2012.
- [13] N. Lyczko, F. Espitalier, O. Louisnard, and J. Schwartzentruber, "Effect of ultrasound on the induction time and the metastable zone widths of potassium sulphate," *Chemical Engineering Journal*, vol. 86, no. 3, pp. 233–241, 2002.
- [14] H. Gürbüz and B. Özdemir, "Experimental determination of the metastable zone width of borax decahydrate by ultrasonic velocity measurement," *Journal of Crystal Growth*, vol. 252, no. 1-3, pp. 343–349, 2003.
- [15] O. Sahin, H. Dolas, and H. Demir, "Determination of nucleation kinetics of potassium tetraborate tetrahydrate," *Crystal Research and Technology*, vol. 42, pp. 766–772, 2007.
- [16] K. Sangwal, "Recent developments in understanding of the metastable zone width of different solute-solvent systems," *Journal of Crystal Growth*, vol. 318, no. 1, pp. 103–109, 2011.
- [17] D. Kashchiev, A. Borissova, R. B. Hammond, and K. J. Roberts, "Effect of cooling rate on the critical undercooling for crystallization," *Journal of Crystal Growth*, vol. 312, no. 5, pp. 698–704, 2010.
- [18] T. N. P. Nguyen and K.-J. Kim, "Kinetic study on hemipenta hydrate risedronate monosodium in batch crystallization by cooling mode," *International Journal of Pharmaceutics*, vol. 364, no. 1, pp. 1–8, 2008.

