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Size dependency of citric acid monohydrate growth kinetics

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Abstract

An experimental study concerned with the growth kinetics of citric acid monohydrate crystals is presented. Due to the properties of the system, which is very soluble, with low solid–liquid density difference and high liquid viscosity, two different techniques were used: large crystals (710–850 μm) were grown in a fluidized bed crystallizer; small crystals, belonging to three size ranges from 90 to 355 μm, were grown in the cell of a laser light diffraction granulometer. A first order growth kinetics resulted in both cases; a comparative analysis of both the present data and those reported in the literature relevant to larger or smaller crystals, indicates that the system exhibits size-dependent growth, which increases linearly with the crystal size. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Growth kinetics; Citric acid monohydrate; Size dependency

1. Introduction

Citric acid monohydrate (CAM), stable below 36.6°C, is a compound with many interesting industrial uses, especially in the food and pharmaceutical fields.

A number of studies concerning crystallization of CAM have been reported in the literature. Laguerie et al. [1] determined some physicochemical data on MCA solutions in water: at 25°C the solubility is about 0.675 kg kg^{-1} solution, the viscosity 0.022 Pa s, and the density of the saturated solution is 1309 kg m^{-3}, rather close to that of the solid (1540 kg m^{-3}). Nývlt and Václavu [2] investigated the importance of diffusive and superficial reaction resistance during the growth of a CAM monocrystal at 32 and 12°C. The growth order ranged from 1.9 to 2, and, depending on the operating conditions (temperature, and possible addition of sulfuric acid) the growth process was controlled by the diffusive resistance, or no controlling resistance existed. Sikdar and Randolph [3] obtained a growth order equal to 0.65 for small crystals (<70 μm) from mixed crystallizer experiments in the temperature range 16–24°C. They indicated that the growth process was controlled by the particle integration step. Laguerie et al. [4,5], using large seeds (>1.4 mm) in a fluidized bed crystallizer at 25°C, determined a growth order equal to 1.04. They showed that the kinetics depended on the crystal size and on the superficial velocity of the solution. Berglund and Larson [6,7] studied the growth kinetics of nuclei (<20 μm) deriving from contact nucleation at 30°C. They suggested that the system exhibited growth rate dispersion, rather than size dependent growth. Ulrich and Stepanski [8] studied the growth of hurt and unhurt citric acid crystals in a fluidized bed crystallizer. The differences in the kinetics being negligible, the system was assumed to be diffusion controlled.

It can be noticed that the agreement between the available growth kinetics data appears quite limited; moreover, either small or rather large crystals were used for the experiments, and no data refer to sizes representative of the commercial product.

The present work investigates the growth kinetics of CAM using seed sizes intermediate between those adopted by previous researchers, gives information immediately useful for design purposes, and provides a critical comparison of the available data.

2. Experimental

CAM was supplied by Carlo Erba at 99.5% purity: the commercial crystals were preliminarily sieved and the size fractions 90–106, 180–212, 300–355, and 710–850 μm were separately collected.

The growth experiments, consisting in seeded batch runs, were carried out using two different techniques for the large (>710 μm) and the small (<355 μm) crystals. In the first

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case, the equipment consisted of a fluidized bed crystallizer, and in the second of the cell of a laser light diffraction granulometer.

2.1. Fluidized bed crystallizer

The fluidized bed crystallizer, described in detail elsewhere [9], is 50 mm in internal diameter and 1 m high; all the parts contacting the solution are made of glass, stainless steel or acid resistant plastic.

At the beginning of each run 13 l of solution at concentration corresponding to saturation temperatures in the range 31–34°C were prepared by dissolving the required amount of CAM in water in the feed tank. The solution, pumped by a Jabsco-type volumetric pump through a cooler, entered the bottom of the crystallizer and escaped from its top, returning to the tank which was maintained at 35°C. Before the cooler, the flow rate was adjusted to the set value of $5.6 \cdot 10^{-6}$ m^3 s^{-1}: the measurements were made by means of a suitably recalibrated flowmeter. The coolant temperature and flow rate were controlled so that the crystallizer temperature could be adjusted in the range 28.3–30.8°C, corresponding to the desired range of supersaturation values (0.005–0.02 kg kg^{-1} solution).

Each run consisted of seeding about 13 g of CAM crystals, 710–850 μm in size, and allowing them to grow for 30 min, yielding a final mass around 25 g. Then, the pump was stopped and the crystallizer was rapidly discharged from the bottom, separating the crystals from the mother liquor by means of a sieve-like device with 0.5 mm openings that can easily be disassembled. The crystals, immediately recovered from the mesh, were gently rubbed on filtering paper, to rapidly remove the entrained solution. This procedure allowed to minimize further deposition of crystalline material from the solution, which has a very high content of citric acid, on the recovered crystals. The crystals were dried in air, weighed and then sieved to determine their final size distribution.

Due to the high viscosity of the solution and to the small crystal-solution density difference, the fluidisation velocity had to be kept below $3 \cdot 10^{-2}$ m s^{-1} to avoid crystals entrainment. This caused the seed settling velocity to be so low that they required some minutes to escape from the seeding tube and move to the growing zone in the crystallizer. To overcome this inconvenience, the column was partially emptied and the seeds were dropped directly in the growth zone for expediency: this was performed successfully. The low velocity of the solution also caused non negligible temperature gradients (up to 0.3°C) to be established along the bed. The temperature was measured at 1 min intervals at the top and at the bottom of the bed, giving the average temperature in the crystallizer. The temperature fluctuations during the run were within 0.5°C: all the observed deviations of the temperature with respect to the average value caused inaccuracies in the estimated supersaturation of about $\pm 1.3 \cdot 10^{-3}$, very similar to that of the solubility measurements.

2.2. Laser granulometer cell crystallizer

The fluidized bed crystallizer could not be used to investigate the growth kinetics of crystals smaller than about 0.6 mm, due to the difficulty of properly selecting the solution velocity for fluidization. In fact, the flow regime is laminar, and the velocity profile parabolic, so that the crystals close to the wall move downwards, while those on the axis are entrained by the upward solution flow. Moreover, the small crystals offer a large specific surface for the deposition of solute from the mother liquor during the time necessary to separate them from the mother liquor, and this may substantially affect the growth measurements.

In order to measure the growth kinetics without separating the crystals from the solution, a technique which uses as the crystallizer the measuring cell of a laser light diffraction was adopted. This method, described in detail elsewhere [10] could not be applied to measure the growth rate of large crystals, since the upper limit of size measured by the available instrument (Malvern 3600) was 564 μm.

The cell, 15 ml in volume, was temperature controlled, magnetically stirred and fitted with a high accuracy thermometer (± 0.02°C). The experiments consisted of filling the cell with a weighted quantity of supersaturated solution, adding a very small amount of seeds belonging to the selected size range, and measuring their transient size distribution and volume concentration. The measurements were taken at 90 s intervals, and the run was generally stopped upon occurrence of spontaneous nucleation: an average of 15 measurements were performed on each run, with a size increment around 10%.

The saturation temperatures of the used solutions were 22, 23 and 24°C, while the cell was kept at 21°C. Some difficulties were encountered when operating with highly supersaturated solutions, because of their strong tendency to nucleation. Conversely, slightly supersaturated solutions gave rise to instability of the basic obscuration reading which, in some cases, forced a halt of the run at its very beginning.

3. Results

3.1. Fluidized bed crystallizer

A total of 13 runs were carried out with the fluidized bed crystallizer.

First of all, the balance of the crystal number was carried out, based on the mass and the size of the seeds and of the recovered product: it matched satisfactorily for all the runs, showing that crystal entrainment was negligible. The influence of secondary nucleation could not be assessed, since the crystal were recovered using a device with 0.5 mm openings. However, no generation of nuclei was observed and, due to the low magma density, secondary nucleation can be assumed to be negligible.

The mass growth rate, R_G, was then calculated, for each run, from the difference between the final and the initial and mass of the crystals, referred to their average surface (calculated from the initial and final values of the Sauter diameter), and to the duration of the run.

The actual value of the supersaturation, Δw, was estimated as the difference between the concentration of the solution entering the bed and that corresponding to saturation at the average temperature in the crystallizer. The latter was calculated from the following relationship, which was demonstrated to accurately describe the solubility of the used CAM in pure water [11]:

$$\ln w_s = 2.094 - \frac{741}{T} \quad (1)$$

The obtained mass growth rates are shown in Fig. 1 vs. the supersaturation. The data appear scattered along a straight line, suggesting a first order growth kinetics. The value of the mass growth rate constant, derived by fitting the data according to the least squares method, was $4.74 \cdot 10^{-3}$ kg m^{-2} s.

3.2. Laser granulometer cell crystallizer

A total of 18 runs were carried out, using seeds belonging to the sieve classes 90–106, 180–212 and 300–355 μm.

The results given from the Malvern instrument (volume percentage per size class, plus total solids volume fraction data) were submitted to a procedure similar to that reported by Söhnel et al. [10]. For each size range the instrument readings were converted into cumulative number oversize; the first measure, immediately after seeding, gave the value of the total number of seed crystals. Then, the size corresponding to this value of the cumulative number oversize was calculated for each size distribution measured at subsequent time intervals, thus following the size evolution of the seed crystals population with time. This procedure allowed to overcome the influence of crystals that might be generated by nucleation, which are much smaller than the seeds. The mechanism of nuclei generation by attrition was unlikely to occur, given the extremely low magma density, and the run was stopped upon occurrence of massive secondary nucleation. The instantaneous solute concentration at each time was determined by subtracting the magma density at that time from the known initial solute concentration.

The typical trends of the transient seed size and concentration vs. time are shown in Fig. 2.

The linear growth rate G is calculated as the ratio between the size increment between two given instants and the elapsed time. The corresponding supersaturation is estimated as the difference between the actual concentration and the solubility of CAM at the cell temperature, calculated from Eq. (1).

The results, shown in Fig. 3, indicate again that the growth kinetics can be regarded as linearly dependent on the supersaturation, for each seed size. The values of the linear growth rate constant, determined by applying the least squares method to each data set, were: $1.50 \cdot 10^{-6}$, $2.63 \cdot 10^{-6}$ and $2.91 \cdot 10^{-6}$ m s^{-1} for the seeds of average size 98, 196 and 327.5 μm, respectively.

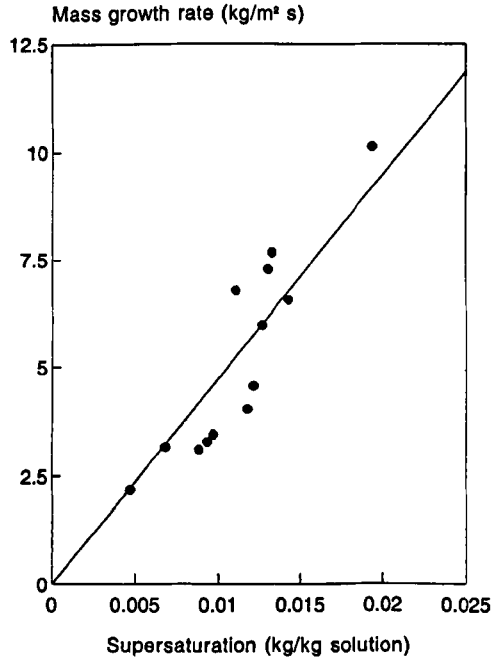

Fig. 1. Mass growth rate of CAM vs. supersaturation from the fluidized bed experiments.

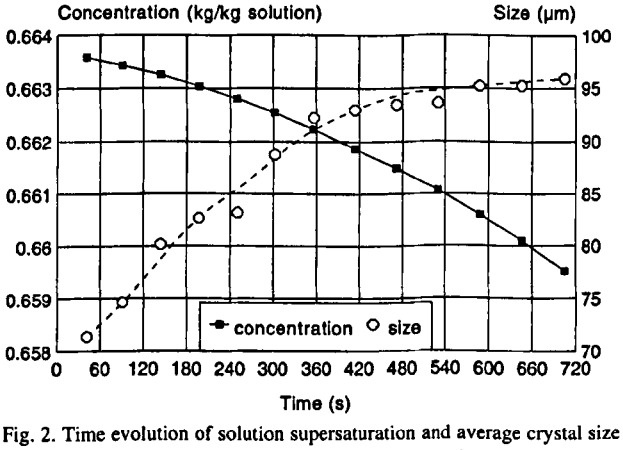

Fig. 2. Time evolution of solution supersaturation and average crystal size during a typical run in the laser granulometer cell experiments.

4. Discussion

The present results indicate that CAM growth kinetics is first order and size-dependent, increasing with crystal size.

Not all the authors who investigated the growth of CAM determined the relevant kinetics as well. Berglund and Larson [6,7] focused on growth dispersion phenomena of contact nuclei (<20 μm), determining a mean growth rate. Ulrich and Stepanski [8] compared the growth performances of crystals whose surface was fragmented (hurt) or perfect (unhurt). No appreciable deviations in the growth rate were

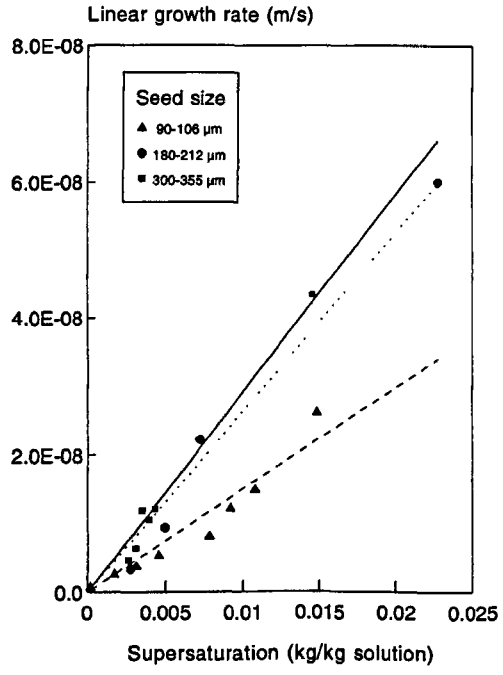

Fig. 3. Linear growth rate of CAM vs. supersaturation from the laser granulometer cell experiments.

observed and the process was regarded as diffusion controlled, since, in case of surface reaction control, the hurt crystals grew faster than the unhurt ones. Nývlt and Václavu [2] studied the growth kinetics of monocrystals suspended in an agitated solution at 12 and 32°C. At 12°C the integration into the crystal lattice was very slow and the diffusion rate was not determined, while at 32°C, diffusion and surface reaction constants were comparable. However, the growth orders approached 2 in both cases (2.0 at 12°C and 1.90 at 32°C) which, generally speaking, suggests surface reaction control (while a value close to 1 indicates diffusion control). Laguerie et al. [4,5] suspended large crystals (1.42–2.60 mm) in a fluidized bed at 25°C, varying the solution velocity from $1.5 \cdot 10^{-3}$ to $4.4 \cdot 10^{-3}$ m s^{-1}. They obtained growth orders close to the unity [4,5] and finally suggested the following kinetic expression [5]:

$$R_g = 5.37\, U^{0.20} L^{0.11} \Delta c^{1.04} \qquad (2)$$

where the mass growth rate R_g is expressed as kg m^{-2} h, the supersaturation Δc as g g^{-1} water, the velocity U in cm s^{-1} and the size L as cm. The dependency of the growth kinetics on both the crystal size and the solution velocity indicates that the process is diffusion controlled.

Sikdar and Randolph [3] studied transient and quasi steady state nuclei population in a mixed crystallizer at temperatures ranging from 16 to 24°C, with the main aim of investigating secondary nucleation kinetics. However, they also determined the growth rate, for nuclei smaller than 70 μm, obtaining an unusual value of the growth order (0.65), which may arise on a poor correlation of the data (linear correlation coefficient = 0.535). The growth kinetics were insensitive to stirring rate variations in the range 452–576 rpm, indicating that the diffusion resistance was not important for the growth process.

In conclusion, it appears that the use of mechanical agitation [2,3] improves diffusion to a much greater extent than the use of fluidized bed devices [4,5,8]: this is also confirmed by the present experiments, carried out under gentle agitation. Moreover, the growth rate seems either surface reaction controlled or diffusion controlled depending on the agitation modalities. This behaviour may arise from the hydrodynamic characteristic of the solution, which is highly viscous, and from the limited density difference between the crystals and the mother liquor.

The quantitative comparison of the available growth kinetics requires the available data to be expressed in the same units. To this end, the mass growth rates were preliminarily converted into linear ones, according to the usual expression:

$$G = \frac{R_g}{3\, \varrho_{MCA}} \frac{k_s}{k_v} \qquad (3)$$

where the value of the CAM density, ϱ_{CAM}, is equal to 1542 kg m^{-3} [1], and those of the surface and volume shape factor, k_s and k_v, were determined by Laguerie [12] for different crystal sizes.

To overcome the difficulty arising from the different definition of supersaturation used from the various authors, reference was made to the equilibrium conditions at 25°C, which is an average value among those adopted in all the experiments, and to a fixed value of supersaturation, 0.01 kg kg^{-1} solution (corresponding to 0.099 kg kg^{-1} water) which falls in the range selected by all the researchers.

The growth rates calculated at this supersaturation from the available kinetic expressions are compared in Fig. 4 vs. the average initial size of the crystals.

Since Nývlt and Václavu [2] did not specify the size of the used monocrystal, it was assumed to fall in the usual range for this type of the experiments (0.5–1 mm), giving a segment in the graph. The data of Laguerie et al. [5], calculated from Eq. (2) refers to the average size of the seeds (1.455 mm) and is represented by a segment, since, in their experiments the solution velocity ranged from 0.24 to 0.44 cm s^{-1}. Finally, the data of Berglund and Larson [7] refers to what they defined as the actual mean growth rate.

The growth rate values shown in Fig. 4, although partially dispersed at the small sizes, clearly indicate that larger crystals exhibit faster growth rates. Based on the trend indicated by the data, the growth constant was assumed to depend linearly on the crystal size; this type of dependency was already observed, for example, in the case of potassium sulphate [13,14]. By fitting the present data, determined from both the fluidized bed and the laser granulometer cell experiments, in terms of linear growth rate, the following overall expression of CAM growth kinetics is obtained:

$$G = 1.13 \cdot 10^{-2}\, L\, \Delta w \qquad (4)$$

which is shown as a dotted line in Fig. 4.

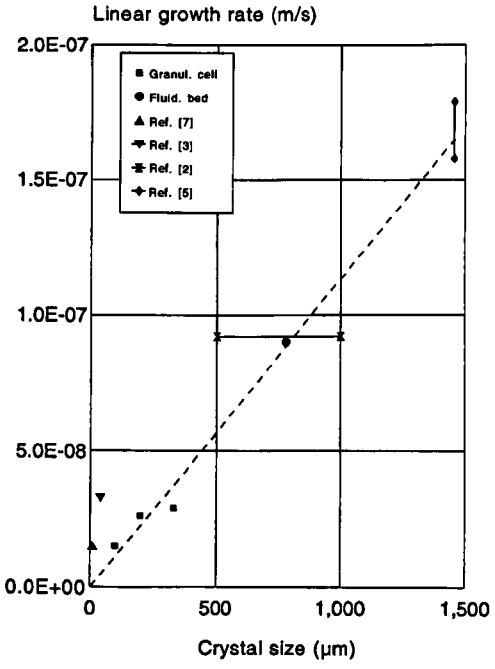

Fig. 4. CAM growth rate data vs. crystal size at the supersaturation of 0.01 kg kg^{-1} solution.

It can be observed that this line also crosses the ranges where the data of Laguerie et al. [5] and of Nývlt and Václavu [2] fall, and that it is not far from the data of Berglund and Larson [7], being quite distant from the sole data of Sikdar and Randolph [3]. It is worth noticing that the data reported in the graph refer to a number of different experimental techniques and that the good agreement obtained is independent of the selected value of the supersaturation and of the temperature (which influences the value of the supersaturation expressed on solvent basis).

A size dependency of CAM growth kinetics is not surprising, since the relative solid–liquid velocity, which influences the diffusional step, is strongly dependent on the crystal size, due to the small density difference between the solid and the liquid phase, and to the high viscosity of this latter. However, Laguerie et al. [4,5] who also observed an influence of the crystal size on the growth rate determined for this variable the exponent 0.1 (see Eq. (2)) which is lower than that here obtained. Indeed, the cited authors showed that, by treating differently their data, the exponents of the crystal size in their kinetic expression (Eq. (2)) assumes the value 0.91, that of the solution velocity being equal to -0.06.

5. Conclusion

On the basis of experiments carried out in two different devices and using crystals belonging to four size ranges of commercial interest, the growth kinetics of CAM appears to be first order with respect to the supersaturation and linearly dependent on the crystal size. This size dependency is confirmed by a comparative analysis of the published data, which also shows that the growth kinetics of this system may be diffusion controlled, under gentle mixing conditions, or surface reaction controlled, under intense mixing conditions.

6. Nomenclature

G	Linear growth rate (m s^{-1})
k_s	Surface shape factor (surface l^{-2})
k_v	Volume shape factor (volume l^{-3})
L	Crystal size (m)
R_G	Mass growth rate (kg m^{-2} s^{-1})
t	Time (s)
w	Concentration (kg kg^{-1} solution)
Δw	Supersaturation (kg kg^{-1} solution)
ϱ_c	Crystal density (kg m^{-3})

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