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CHARACTERIZATION OF CRYSTAL POPULATIONS OF VITAMIN C BY HYPERBOLIC TANGENT DISTRIBUTION FUNCTIONS

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The four parameter hyperbolic tangent distribution family is used for characterizing the size distributions of vitamin C crystals. The crystals were obtained in batch experiments in a laboratory scale agitated crystallizer under different experimental conditions. It is demonstrated by the results of matching that hyperbolic tangent distribution functions describe the experimental data well thus the crystallization process of vitamin C can satisfactorily be characterized by means of these distribution functions.

Introduction

Of the primary quantifiable properties of crystals, crystal size and their distribution are probably the most important. Much attention was paid to the description of crystal size distribution (CSD)[1-5], and a variety of probability distributions can be used for this purpose.

The most widely used log-normal, gamma and Rosin-Rammler distributions, however, involve only two independent parameters, thus their matching to experimental crystal size distribution data, although it is not too difficult, sometimes leads to unsatisfactory results, especially in process design of solids processing systems [6].

Distributions having more parameters for fitting, although they need more computational efforts, usually provide a better mechanism for summarizing experimental data. Such distributions are either the three- and four-parameter JOHNSON [7] and PEARSON [8] distributions, or the recently developed hyperbolic tangent distribution family involving four free parameters [9]. It appeared that the hyperbolic tangent distribution functions can be used for describing particulate systems in a general manner since by means of them both, the particle size distributions by number and those by surface or by mass may be well approximated. In consequence, the hyperbolic tangent distribution functions were applied for describing such processes as granulation [10], grinding [11], or crystallization from solutions [12], and a family of methods for evaluation, analysis and design of fluid-solid disperse systems was developed on the basis of this distribution law [6].

The aim of the work is to present further data concerning the applicability of the hyperbolic tangent distribution functions for describing crystal size distributions. It is shown how crystal populations of vitamin C, obtained under different experimental conditions, can be characterized by means of distribution functions of this type.

Experimental

A series of batch experiments was performed in a 0.8 litre volume, mechanically agitated double jacketed vessel, schematically shown in *Fig.1*. All experiments were carried out with L-ascorbic acid (vitamin C)-water system which has a great application field in the chemical, pharmaceutical, cosmetic and food industry.

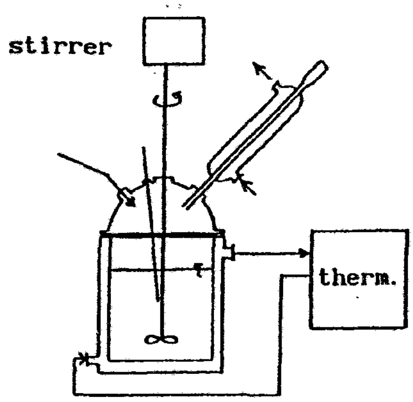

Fig.1 The mechanically agitated batch crystallizer

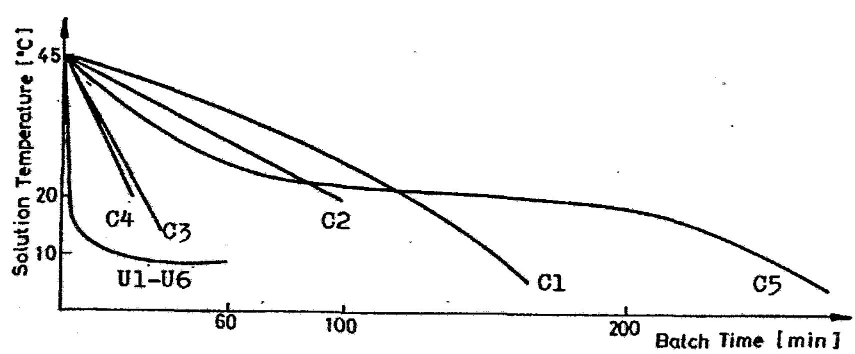

Fig.2 Cooling curves of batch crystallization experiments

Temperature control within the crystallizer was achieved by pumping water through the jacket at the maximum possible rate according to the given cooling programme. Different cooling programmes were applied without seed crystals, applying also ultrasonic irradiation at constant frequency 20 kHz and $1{\cdot}10^{-4}$ - $1.8{\cdot}10^{-4}$ m/s intensities, as it was described by BODOR et al. [13] in detail, generating in this way a great variety of different experimental conditions.

The cooling programmes always were started at temperature 45 °C as it is illustrated in *Fig.2* since here the solution was saturated. Data on solubility of vitamin C have also been presented elsewhere [13].

The final product size distribution was measured by a MALVERN Series 2600 laser-analyser in the crystal suspension. The size distribution data produced by the instrument were elaborated by a computer programme fitting hyperbolic tangent distribution functions to the experimental data.

The Hyperbolic Tangent Distribution Function

The distribution function of the hyperbolic tangent distribution has the form

$$F(L)=\begin{cases}0, & \text{if } a+bL\le 0\\ \tanh^{m}(a+bL)^{n}, & \text{if } a+bL>0\end{cases}\tag{1}$$

where $m > 0$, $n > 0$, $-\infty < a < \infty$ and $b > 0$ are independent parameters of the distribution, and $L > 0$ denotes some characteristic size of the particles.

Since F is continuous, the density function f also exists and takes the form:

$$\frac{dF(L)}{dL}=f(L)=$$
$$=\begin{cases}0, & \text{if } a+bL\le 0\\ mnb(a+bL)^{n-1}\tanh^{m-1}(a+bL)^{n}\cdot & \\ \cdot(1-\tanh^{2}(a+bL)^{n}, & \text{if } a+bL>0\end{cases}\tag{2}$$

It is easy to show [14] that

$$\lim_{L\to -a/b} f(L)=\begin{cases}0\,, & \text{if } mn>1\,,\\ 1\,, & \text{if } mn=1\,,\\ \infty\,, & \text{if } mn<1\,,\end{cases}\tag{3}$$

thus the hyperbolic tangent distribution function, depending on the values of parameters, may represent different types of probability distributions.

The hyperbolic tangent distribution function has some advantageous properties:

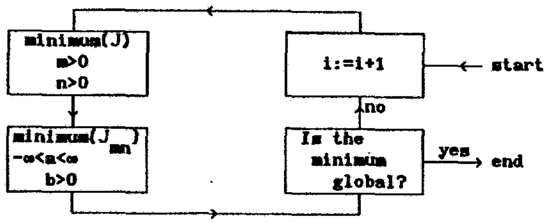

Fig.3 The algorithm of fitting the hyperbolic tangent distribution functions to measurement data

- its four parameters allow for good matching to experimental crystal size distribution data;
- with inreasing L, it approaches asymptotically to the value of 1 very quickly [9], thus

    1) the moments can be computed numerically conveniently, which appears to be important in case of estimating the parameters by the moments method,
    2) truncated distributions (in essence, all distributions in practice are truncated) are shown to be approximated very well by means of hyperbolic tangent functions;

- some other distribution functions, often used for describing crystal size distributions (lognormal, Rosin-Rammler, gamma) can also be approximated well by hyperbolic tangent functions [9], providing in this way a convenient method for comparing measurement data described in different ways.

Evaluation of CSD Measurements

Based on the observation that parameters m, n, a and b can be divided into two groups, a two-level method of least squares was developed for fitting the hyperbolic tangent distribution function to experimental particle size distribution data.

The method is based on the minimization of the objective function

$$J=\sum_{i}\left[\frac{s_i-\tanh^{m}(a+bL_i)^{n}}{s_i}\right]^2, \qquad (4)$$

where s_i denotes the measured size fraction at crystal size L_i, with respect to parameters m, n, a and b. This is performed in two steps:

$$\underset{\substack{-\infty<a<\infty\\ b>0}}{\text{minimum}}\left[\underset{\substack{m<0\\ b>0}}{\text{minimum}}(J)\right] \qquad (5)$$

where the inner minimization is inherently a nonlinear problem, while the outer one can be reduced into linear regression. The algorithm is summarized in *Fig.3.*

For minimization with respect to parameters m and n, an algorithm without calculating the derivates of the objective function is used. The local minima are sought on a grid of variable size in a given region of the parameters from which the global minimum is selected in each iteration step. At this partial minimum, denoted by J_{mn}, the parameters a and b are fitted to the data by using linear regression, based on the solution of the transformed problem

$$\underset{\substack{-\infty<a<\infty\\ b>0}}{\text{minimum}}(J_{mn})=\sum_{i}\left[\sqrt[n]{\operatorname{arctanh}\sqrt[m]{s_i}}-(a+bL_i)\right]^2. \qquad (6)$$

which is equivalent to the solution of the set of linear algebraic equations

$$a\sum_{i}+b\sum_{i}L_i=\sum_{i}\sqrt[n]{\operatorname{arctanh}\sqrt[m]{s_i}}\,, \qquad (7)$$

$$a\sum_{i}L_i+b\sum_{i}L_i^2=\sum_{i}L_i\sqrt[n]{\operatorname{arctanh}\sqrt[m]{s_i}}\,. \qquad (8)$$

The iteration process is stopped if the difference between the values of minima of two successive steps becomes smaller than the given error tolerance.

Results and Discussion

The evaluated mesurements are summarized in *Table 1*, where the cooling curves are as presented in *Fig.2*. In case of experiments with ultrasonic irradiation (u.irr.) different intensities and time-intervals of radiation were applied according to the following notation:

u.irr.: a - intensity=$1\cdot10^{-4}$ m/s, time= 5 s;
u.irr.: b - intensity=$1\cdot10^{-4}$ m/s, time=10 s;
u.irr.: c - intensity=$1.8\cdot10^{-4}$ m/s, time= 5 s;
u.irr.: d - intensity=$1.8\cdot10^{-4}$ m/s, time=10 s;
u.irr.: e - intensity=$1.8\cdot10^{-4}$ m/s, time= 5 s;
u.irr.: f - intensity=$1.8\cdot10^{-4}$ m/s, time=10 s.

Table 1 Data of measurements used for illustrating the fitting of hyperbolic tangent distribution function to CSD

Cooling curve	Process	Agitation r.p.m	S	Estimated parameters			
				m	n	a	b
Fig.1 - C1	nonlin.; u.irr.:no	250	1.34	0.5	3.8	0.01	0.007
Fig.1 - C2	linear; u.irr.:no	450	1.33	0.7	3.9	0.21	0.005
Fig.1 - C3	linear; u.irr.:no	100	2.00	0.2	3.7	-0.08	0.007
Fig.1 - C4	linear; u.irr.:no	450	1.66	1.5	3.8	0.49	0.004
Fig.1 - C5	nonlin.; u.irr.:no	450	1.10	3.9	1.0	0.24	0.006
Fig.2 - U1	nonlin.; u.irr.: a	100	1.50	2.0	0.5	-0.59	0.012
Fig.2 - U2	nonlin.; u.irr.: b	100	1.50	2.3	1.2	0.11	0.004
Fig.2 - U3	nonlin.; u.irr.: c	100	1.50	3.7	1.0	-0.19	0.019
Fig.2 - U4	nonlin.; u.irr.: d	100	1.50	3.7	1.0	-0.19	0.018
Fig.2 - U5	nonlin.; u.irr.: e	50	1.50	3.9	0.9	0.24	0.010
Fig.2 - U6	nonlin.; u.irr.: f	100	1.50	2.6	0.7	-0.42	0.023

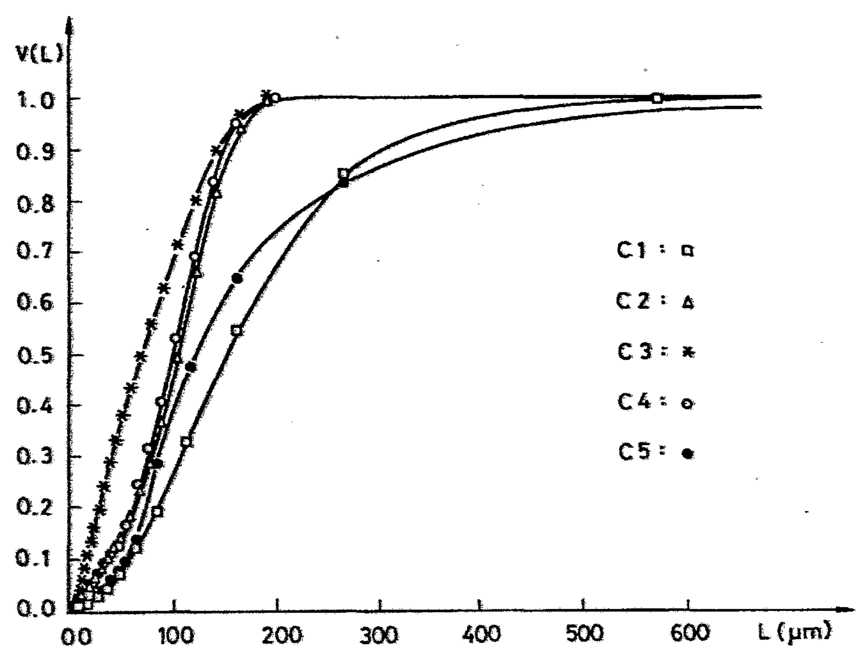

Fig.4 Fit of the hyperbolic tangent distribution functions to CSD data of runs referred in *Table 1*

In *Table 1*, linear means linear cooling rates, while in case of notion nonlin. the programmed cooling rates were nonlinear (convex - C1, concave -U1, general - C5) as it is shown in *Fig.2*.

The size measurement data with the hyperbolic tangent distribution functions obtained in the fitting process are presented in *Fig.4* for experiments without ultrasonic irradiation, and in *Fig.5* for experiments in which ultrasonic irradiation of suspension was applied. The best values of the parameters are presented in *Table 1*, too.

The measurement data are described by the resulting curves acceptably illustrating well the applicability of the hyperbolic tangent distribution functions for characterizing crystal size distributions of vitamin C.

We should note here, however, that the results of fitting appeared to be satisfactory only for unimodal distributions. In case of multimodal distributions, measured in batch crystallizers under certain circumstances, only the fitting of composite hyperbolic tangent distribution functions would lead to acceptable results.

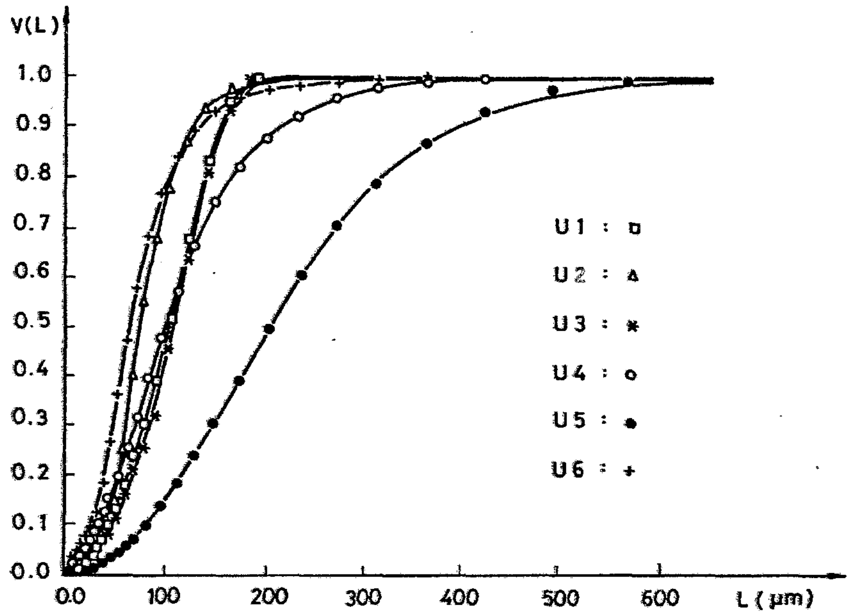

Fig.5 Fit of the hyperbolic tangent distribution functions to CSD data of runs referred in *Table 1*

Conclusions

The hyperbolic tangent distribution appears to be well applicable for characterizing size distributions of crystals of vitamin C, obtained by crystallization from aqeous solutions, thus similar sets of data of crystals of this important chemical species can be analyzed in the automated data analysis based on the method of distribution functions of this type.

A method of matching the distribution functions to experimental data has been presented which can be used for evaluating the quality of crystalline products of crystallization processes, as well as for comparing results obtained by different crystal size measurement methods.

The four parameters of the hyperbolic tangent distribution family can be corresponded to the first four ordinary moments of the crystal size distributions equivalently, thus these two methods seem to be well suited to each other.

Because of the good fitting results obtained in this work,the hyperbolic tangent distribution functions are expected to be suitable also for characterizing crystallization processes by themselves.

Acknowledgement

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SYMBOLS

a	parameter of the hyperbolic tangent distribution family
b	parameter of the hyperbolic tangent distribution family
f	hyperbolic tangent density function
F	hyperbolic tangent distribution function
J	objective function of parameter fitting
J_{mn}	minimum of J with respect to parameters m and n
L	characteristic size of crystals
L_i	value of the i-th size interval
m	parameter of the hyperbolic tangent distribution family
n	parameter of the hyperbolic tangent distribution family
S	supersaturation ratio
s_i	size fraction of the i-th size interval

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