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Growth of Sucrose Crystals: Determination of Edge Energy from the Effect of Added Impurity on Rate of Step Advance

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Quantitative experiments to investigate the effect of added impurity on the growth of sucrose crystals are described. Rates of advance of growth steps were measured on crystals growing from pure solutions and from solutions to which raffinose was added. The temperature of the crystals was controlled at 30 °C. and the saturation ratio of the solutions was known. From the experimental results the diameter of the critical two dimensional nucleus at each saturation ratio was calculated and from this edge energy of a growth step.

Introduction

The mechanism of growth of sucrose crystals (Albon & Dunning, 1957, 1959) is the movement of steps which originate at screw dislocations (Frank, 1949). A study of the kinetics of this process was made by measuring the rate of advance of steps on crystals growing under controlled conditions (Dunning & Albon, 1958; Albon & Dunning, 1960). This paper describes an extension of the application of this method to examine the effect of an added impurity on the crystal growth process.

Earlier work (Dunning & Albon, 1958) showed that the addition of dextrose ($C_6H_{12}O_6$) is without appreciable effect on the rate of movement of growth steps on sucrose ($C_{12}H_{22}O_{11}$) crystals. When raffinose ($C_{18}H_{32}O_{16}$) was added to a sucrose solution in which crystals were growing the growth step ceased moving and on transferring to a pure sucrose solution normal growth was resumed. This indicated that raffinose molecules were adsorbed reversibly on to the growth steps. We describe here a quantitative investigation of the effect.

Experimental

Sucrose crystals were nucleated in a microscope cell which was enclosed in a thermostat. Pure solution of controlled saturation ratio was then pumped through the cell. A crystal having a well defined growth step system on the (100) face was selected and the position of a step advancing in the [010] direction measured at intervals with a micrometer eyepiece. The micrometer readings were plotted against time giving straight lines from which the rate of advance was determined. Each rate was obtained from ten or more readings over a time of from 10 to 150 min. This resulted in approximately the same accuracy for all rates as the measurements were taken for similar total distances of step travel.

Successive additions of weighed portions of raffinose were then made to the solution being circulated and the rate of step advance measured after each addition.

Table 1. *Rates of step advance at various raffinose concentrations and saturation ratios*

Raffinose		Rate of advance´divisions/minute			
% as hydrate	$C_0 \times 10^3$	$\alpha =$ 1·0065	$\alpha =$ 1·013	$\alpha =$ 1·015	$\alpha =$ 1·020
0·0		0·0148	0·0223	0·034	0·049
0·1	0·57	0·0115	0·0193	0·030	0·044
0·2	1·15	0·0035	0·0160	0·0245	0·0395
0·3	1·72	0·00090	0·0120	0·0193	0·0345
0·4	2·30	0·00035	0·0060	0·0147	0·0315
0·5	2·87		0·0027	0·0083	0·0267
0·6	3·45		0·0013	0·0040	0·0220
0·7	4·02			0·0020	0·0166
0·8	4·60				0·0125
0·9	5·17				0·0093
1·0	5·75				0·0071

The saturation ratio was held constant during an experiment and the whole procedure was then repeated at a different saturation ratio.

These experiments were all made with the crystal held at 30 °C. The rates of step movement in scale divisions/min. (8·17 divisions = 1 mm.) are given in Table 1 together with the corresponding saturation ratios and raffinose concentrations. Saturation ratio = concentration of sucrose/concentration at saturation = α.

Discussion of experimental data

A plot of step advance against raffinose concentration at four saturation ratios is shown in Fig. 1. This shows an exponential relation especially at low saturation ratios and increasing raffinose concentration. The experimental results are in quantitative agreement with the following simple model.

Growth of sucrose crystals from pure solutions at

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30 °C. is controlled by incorporation of the molecules into kinks on the steps (Albon & Dunning, 1960). Adsorption of raffinose at kinks lowers the rate of step movement and the relation between raffinose concentration and rate of advance at high saturation ratios is governed by the adsorption of raffinose on to the steps.

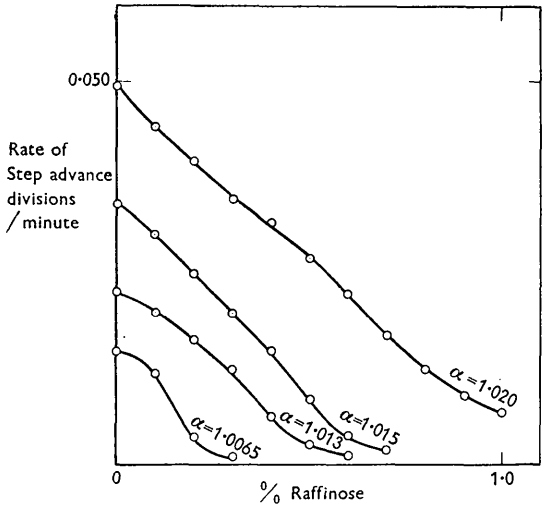

Fig. 1. Graph showing effect of raffinose on the rate of step advance.

When any two raffinose molecules are closer than the corresponding diameter of the critical two-dimensional nucleus (Burton, Cabrera & Frank, 1951) the advancing growth step will be held up between these molecules. This leads to an exponential relation between rate of step movement and raffinose concentration.

Let C = concentration of adsorbed raffinose molecules, the probability of finding a site along a step without an adsorbed raffinose molecule will be $1-C=p$. Then the probability of finding a gap of length m (molecules) is $p^m C^2$. The rate of step movement is proportional to the fraction of step length along which growth can still continue, that is the sum of all lengths greater than r times the probability of each. This leads to the relation:

$$R/R_0=(r-pr+p)p^r, \qquad (1)$$

where R_0 = rate of step movement in pure solution and R = rate of step movement in solution containing a molar fraction C_0 of raffinose. The concentration C of adsorbed raffinose molecules is related to the concentration of raffinose in solution and the results of the experiment at a saturation ratio of 1·020 fit a classical adsorption equation such as (2):

$$(R_0-R)=AC_0^{1/n}\,. \qquad (2)$$

We assume that R_0-R is proportional to C the concentration of adsorbed raffinose molecules. From a plot of $\log(R_0-R)$ against $\log C_0$ (Fig. 2) $A=81{\cdot}8$ and $1/n=0{\cdot}92$ for $\alpha=1{\cdot}02$ and raffinose concentrations of 0·1 to 0·5% by weight. Thus for concentrations of up to 0·5% raffinose and for $\alpha=1{\cdot}020$; $p=(1-C)=1-(R_0-R)$ and above 0·5% raffinose, equation (2) is used to give p.

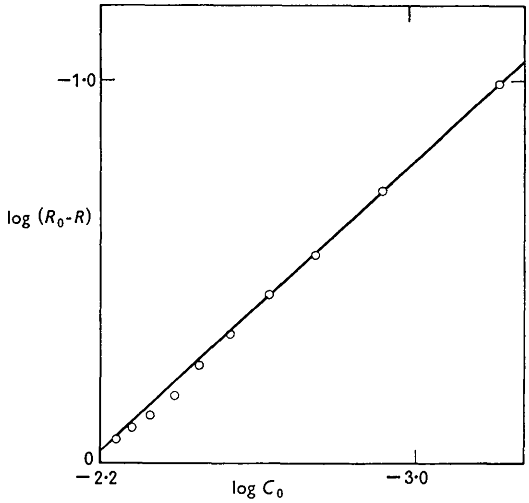

Fig. 2. Graph showing plot of $\log(R-R)$ against $\log C_0$ for $\alpha=1{\cdot}020$.

The diameters of the critical two dimensional nucleus (r) are obtained from a plot of $\log(R/R_0)$ against $\log p$ as shown on Fig. 3. These values are given in Table 2 together with the saturation ratios and the edge free energy γ calculated from the relation $\gamma=rkT/n\alpha$.

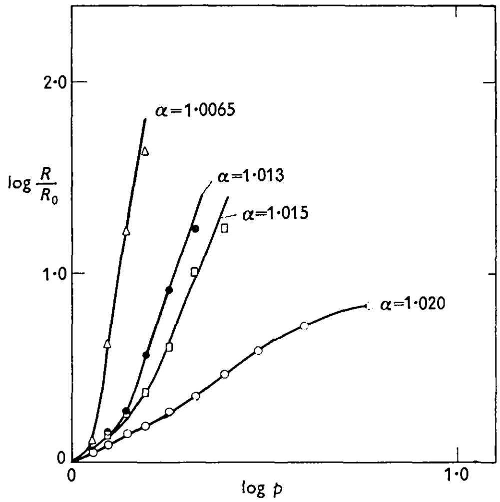

Fig. 3. Graph showing plot of $\log(R/R_0)$ against $\log p$.

At high raffinose concentrations there is a slight deviation from a straight line for the plot of $\log(R/R_0)$ against $\log p$. This deviation is only appreciable for

$\alpha = 1{\cdot}020$ and at raffinose concentrations of 0·9% and 1·0% and arises from the effect of raffinose in reducing the edge energy. The magnitude of this effect is indicated by the values of γ given in Table 2. Possibly the use of equation (2) to calculate p is inaccurate at higher concentrations, but this only applies to the values for $\alpha = 1{\cdot}020$.

Table 2. *Diameters of critical two-dimensional nucleus for various saturation ratios and the calculated edge energies*

		Edge energy		
r Molecules	Saturation ratio	Molecule ergs × 10^{15}	cm. ergs × 10^{8}	Raffinose % hydrate
11·8	1·0065	3·12	4·02	0·1–0·4
5·42	1·013	2·92	3·78	0·3–0·6
4·52	1·015	2·80	3·61	0·4–0·7
(1·6)	1·020	1·33	1·71	0·6–0·8

A source of uncertainty in the calculation of γ arises from the value used for the solubility of sucrose which is difficult to measure accurately. A figure of 68·70 parts by weight of sucrose per 100 parts by weight of solution is used here. There are no other published measurements of γ but our figures are consistent with the surface free energy obtained by Dunning & Shipman (1956) from nucleation experiments.

General discussion

When discussing the effect of impurities on crystal growth Wells (1949) urged that it was first desirable to obtain reproducible growth rates during normal growth. The procedure described here shows that reproducible quantitative measurements of normal growth are possible and that the effect of an impurity can be measured.

Using the value obtained for the edge energy at a low saturation ratio ($\alpha = 1{\cdot}0065$) a simple calculation shows that for a pure sucrose solution containing 0·1–0·4% raffinose $r = 1$ when $\alpha = 1{\cdot}078$. At higher saturation ratios than 1·078 the growth process does not require an existing step or a crystal containing screw dislocations. Under normal conditions of growth the saturation ratio is less than 1·078 except sometimes at nucleation. An extension of these measurements to the other crystal faces and higher temperatures would be of interest.

A low concentration of raffinose exerts a considerable effect on the growth rate especially at low saturation ratios. Using simple apparatus an alteration in growth rate resulting from a change in raffinose concentration of less than 1 part in 10^4 could be detected. This sensitivity could be increased considerably by refinements in technique. The measurement of rates of step movement can therefore be used as indicator of the presence of traces of active impurities. A molecule larger than raffinose may be adsorbed more strongly or irreversibly so that the effect on step movement would be greater. The rate of step movement on sucrose crystals growing from solutions of high purity varies slightly at the same saturation ratio (Albon, unpublished work). This is probably due to traces of impurity which arise during preparation of the solutions.

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