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EXPERIMENTAL STUDY OF RATES OF CRYSTAL GROWTH
FROM ORGANIC MELTS

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ABSTRACT

A new temperature-gradient microscope stage, suitable for the study of crystal growth from liquid mixtures of organic compounds, is described. The apparatus incorporates facilities for the optical determination of interfacial liquid and solid compositions and temperature through the use of light diffraction by a thin wedge of liquid. The imposed temperature gradient causes the profile of the solid-liquid interface to be more stable than in an isothermal liquid, despite compositional undercooling. Some results are presented for a binary system which forms a eutectic solution.

INTRODUCTION

Measurements of the rates of growth of crystals in molten mixtures of organic compounds can not be interpreted properly unless the composition and the temperature of the interface are known. Since the flux of material needed to form new solid phase sets up a diffusion gradient in the liquid and since the heat of fusion, released at the interface, has to be dissipated by heat conduction, use of bulk temperature and composition in the study of interface kinetic phenomena may lead to error. Consequently, Kirwan and Pigford (1969) and Berg (1938), Bunn (1949), Humphreys (1948), have employed optical interference methods for the observation of concentration patterns around crystals as they grow in supersaturated

solutions under microscopes. Similar methods have been used (Nishijima

and Oster, 1956, and Secor, 1965) for the determination of diffusion co-

efficients from the shapes of interference fringes observed during the

mixing of two liquids.

In most such work the liquid within which the crystals grow has

been kept at a uniform temperature, except for the usually small temperature

rise at the interface. By setting the temperature of the solution at a

value beneath the equilibrium liquidus temperature the growth rate can be

uniquely determined. Such measurements are very suitable for the study

of crystal nucleation rates but they have an important handicap when growth

of crystals, already present in the solution, is being observed. This is

for the reason that the profile of a crystal interface as it advances into

the adjacent liquid is often unstable at finite rates of growth. An inter-

face which may be flat initially may project sharp points or "dendrites"

into the undercooled liquid ahead, especially when that liquid is under-

cooled more than the interface liquid is. Thus, the shape of the liquid-

solid interface may change as growth proceeds, especially when the system

tends to grow rapidly even with small amounts of undercooling. In such

a situation, as with the components salol and thymol, the freezing inter-

face acts as a strong source of heat and the interface temperature rise,

ΔT_i, may be as much as 2 to 3 deg. C. above the temperature, T_s, of the

presumably isothermal microscope stage. A sharp pointed crystal, pro-

jecting itself into the adjacent liquid, will find even colder and more

concentrated liquid a short distance from the interface than it feels at

the interface itself.

To avoid such experimental problems during crystal growth studies Hunt, Jackson, and Brown (1966) introduced a temperature-gradient micro-scope stage (hereafter called TGMS) to study the growth behavior of certain pure organic substances, especially those for which the molecules are nearly spherical so that the freezing phenomena are like those for metals. By providing a flux of heat through the liquid within which the crystals were growing, the direction of the temperature gradient being normal to the interface, the shape of the interface was much more regular and more easily controlled. No provisions were made in their apparatus, however, for the measurement of bulk liquid or interfacial temperature. Furthermore, it is not easy to use their apparatus for observing the growth of crystals from solution because no means is provided for the determination of concentration patterns.

In the present work a new TGMS has been designed which provides not only a temperature gradient for the control of interface shape but also optical interference patterns for the calculation of temperature and concentration profiles near the crystal faces. The purpose of this paper is to describe this new equipment and to report a few results obtained with it using the binary systems salol-thymol. The bibenzyl-stilbene system is one in which undercooling is extremely slight, even at large rates of growth. Measurements for it were extremely difficult using an isothermal stage (Kirwan, 1967) and have been made possible with the aid of interface shape control. Details of the studies for this system will be reported in the future article.

## DESCRIPTION OF TEMPERATURE-GRADIENT MICROSCOPE STAGE

The new TGMS, shown in Fig. 1, is suitable for growth rate studies using not only pure materials but also binary mixtures. The main features of this apparatus include hot and cold stages made from aluminum blocks 3/8 in. thick. These are placed at the left and right of a stationary mount which can be adjusted in position with the microscope's mechanical stage. The liquid is placed inside an optical wedge formed by two half-aluminized glass slides, as in the previous microscope optical interference apparatus (Kirwan and Pigford, 1969, and Kirwan, 1967). The opposite ends of the lower microscope slide rest on the hot and cold stages, respectively, and the temperature of the glass and of the liquid contained in the wedge varies nearly linearly with position in the space above the gap between the two stages. The glass slides are held in position relative to each other by a Teflon boat which is connected to a lead screw turned by a variable speed motor. As the screw advances the boat is moved horizontally under the microscope objective, the boat advancing toward the cold stage. Thus, a point in the wedge encounters progressively lower temperatures and increasing undercooling is experienced by the liquid at that point. The growth rate is determined by the setting of the motor which drives the lead screw.

In Fig. 2, the picture at the left shows the Teflon boat, used to move the diffraction assembly slowly toward the cold stage. The lead screw from the drive motor fits into the yoke at the left. The partially aluminized slides are at the right. The larger slide fits into the boat from below and forms the bottom of the wedge. The smaller slide is held at an angle to the longer slide by the adjustable lever on the boat.
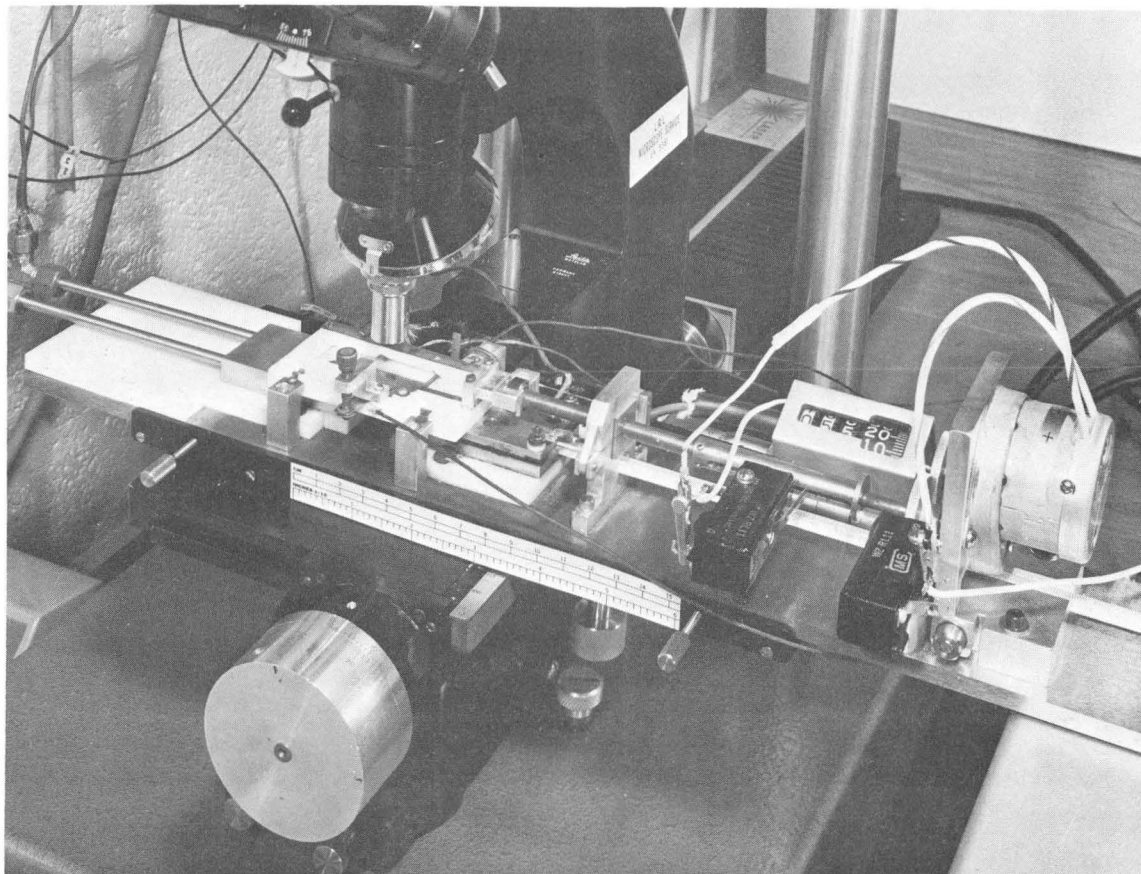
XBB 693-1781

Fig. 1. Temperature-gradient microscope stage.
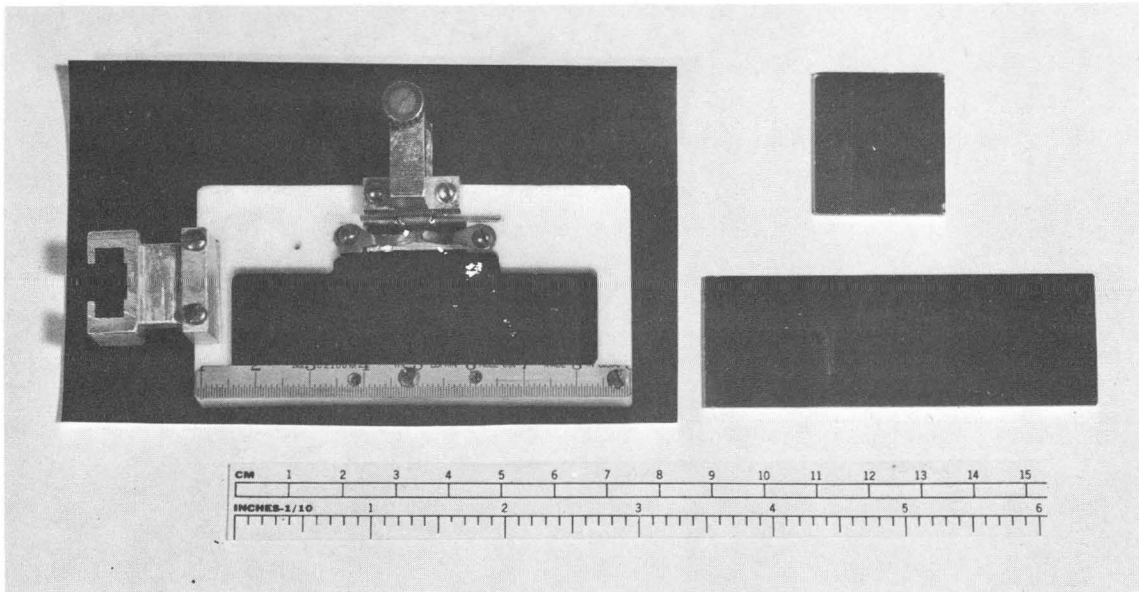
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Fig. 2. Optical wedge for crystal growth measurements.

Light for the diffraction patterns was provided by a helium-neon gas laser. The spacing between adjacent interference fringes and their sharpness are governed by the angle of the optical wedge, by the reflectivity of the metallic coating on the slides, and by the refractive index of the liquid in the wedge. The quantitative measurements depend on knowing the value of the wedge thickness corresponding to each position on the plan view of the slide. Thus, it is necessary to have some way for setting the wedge angle at a desired value and of adjusting it slightly. For this purpose a lever mechanism with a thumb screw was attached to the Teflon boat.

In most of the work done with this apparatus the gap between the opposed aluminum coatings varied from zero at the thinner edge of the wedge, where the edges of the slides touched, to about 0.25 mm. at the thicker edge some 2.5 cm. away. In some measurements involving thicker cyrstals, however, a modification was made to increase the gap while using the same wedge angle. In every case, however, the thickness values were checked by observing scratches in the upper and lower coatings and reading the corresponding positions of the vertical fine adjustment scale of the Leitz Ortholux microscope.
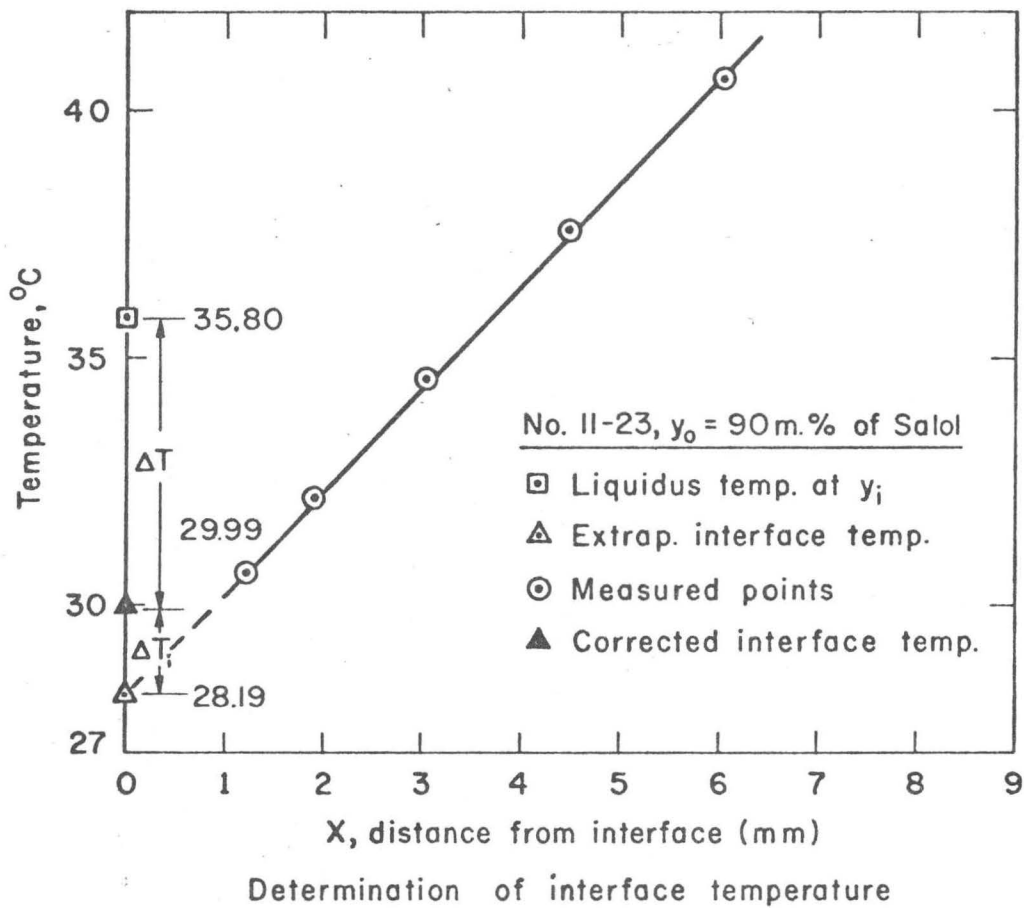
Liquid temperatures near the advancing crystal faces were observed with a very fine, calibrated copper-constantan thermocouple made from wire only 0.004 in. in diameter. This was inserted into the optical wedge perpendicular to the direction of motion. Since the thermocouple junction moves with the wedge while, at steady state, the crystal interface was fixed relative to the microscope objective temperature measurements at

different times corresponded to different distances from the interface. A last measurement of the thermocouple's position was made just as the junction touched the crystal itself. By using a linear least-squares fit of the observations the interface temperature could be computed accurately and its standard error estimated. The temperature gradient through the bulk of the liquid could also be determined. Fig. 3 shows the typical temperature distribution.

In some measurements trouble was encountered owing to the volatility of both solid and liquid components. When the hot stage had to be very hot and when the composition of the high-melting component was large it was not possible to complete measurements with the open-sided optical wedge just described. In these situations an optical wedge having a fixed angle was employed. This was prepared by closing all four sides of the wedge, except for small holes for injection of the sample and for the thermocouple. The loss of liquid was reduced to tolerable levels.

EXPERIMENTAL PROCEDURE

1. Sample Preparation: Salol (phenyl salicylate) and thymol (3-p-cymenol) system, which forms a single eutectic system for which the phase diagram is given by Timmermans (1959), was selected for the growth rate experiments. All the chemicals were obtained from the Eastman Kodak Company as "Reagent Grade." Salol was used as received after it had been degassed. Thymol was sublimed several times. The melting points of the purified samples were: salol, 42.14°C.; thymol, 49.60°C. These values compare favorable with the higher values accepted in the literature.

Determination of interface temperature

XBL 6910-3997

Fig. 3

Fringe pattern at interface
during crystal growth

XBL 6910-3998

Fig. 4

2. <u>Experimental Method</u>: After the temperatures of the hot and
cold stages had become steady, crystallization was started by introducing
a small seed crystal into the opening at the colder side of the optical
wedge, in which the solution had been injected earlier. Then the drive
motor was turned on to push the Teflon boat farther toward the cold stage.
Eventually the crystal interface assumed a position that was apparently
steady as viewed through the microscope such that the growth rate was equal
to the velocity of the boat. If the crystal interface being observed
through the microscope was not perpendicular to the direction of movement
of the boat the velocity of the interface was computed from the motor speed
by multiplying the boat's velocity by $\cos \gamma$, where γ is the appropriate
angle.

Thermocouple readings were recorded for the junction immersed in
the liquid within the wedge and Polaroid pictures were taken to record
the interference patterns. Figure 5 shows a typical photograph of such
fringe patterns. A small correction was applied to the computed temperature
of the interface, extrapolated from measurements in the adjacent liquid,
owing to the heat release there caused by freezing. The corrections were
based on measurements of temperature rise using the interference method
to observe diffraction with the pure substances on the isothermal stage.
The diffraction effects corresponded to temperature rises of 1.5 deg. C.
for thymol at a growth rate of 1.0×10^{-3} cm./sec. and 2.0 deg. C. for
salol at 1.5×10^{-3} cm./sec. At other growth rates the temperature rise
at the interface above the straight line through the points observed a
few mm. away in the liquid was assumed to be proportional to the growth
rate.
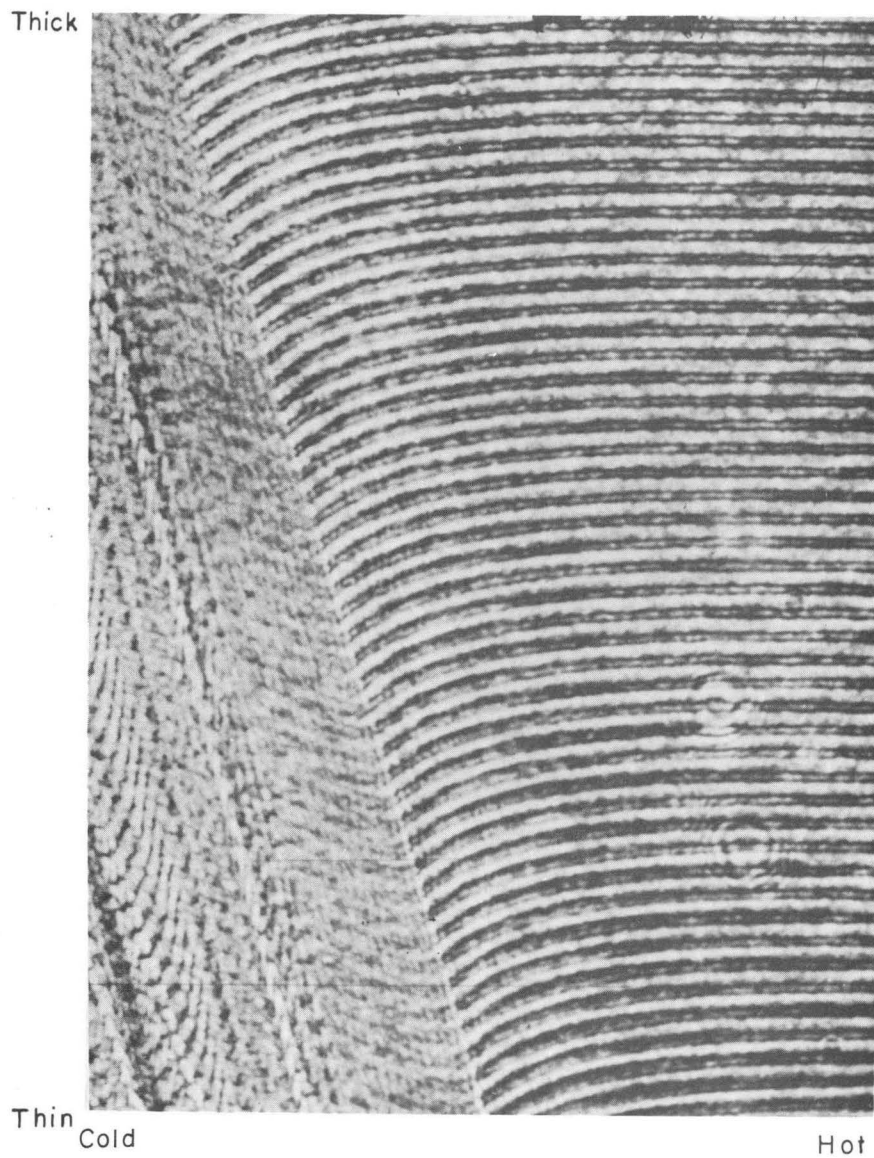
XBB 6910-6867

Fig. 5a. Fringe pattern at interface during crystal growth of thymol
   in 10 mole % salol solution.

RESULTS

Measurement of the Growth Rates of Pure Substances: The observed growth velocities of salol and thymol using the TGMS are shown in Figs. 6 and 7, along with similar data reported by Kirwan and Pigford (1969). The new data appear to be in good agreement with the previous results, and also with the results obtained in this work on isothermal stage, despite the presence of the thermal gradient in the new measurements. Although the points on the figures are scattered the growth rates are seen to follow the empirical formula

$$V = K(\Delta T)^2 , \tag{1}$$

indicating, as suggested previously (Hillig and Turnbull, 1956), that the growth mechanism involves the presence of spiral screw dislocations on the advancing interface. The lines shown on Figs. 6 and 7 are based on this equation.

Growth from Binary Mixtures: Salol and thymol form a eutectic system with the equilibrium phase diagram shown in Fig. 8. On the assumptions that equilibrium is established instantly between the interfacial liquid and the solid, and that diffusion in a binary melt having the bulk composition, y_0 will deposit pure solid thymol when cooled to the liquidus temperature, T_0. If cooling continues until the temperature falls to T_i the liquid composition should move to point F. However, owing to the finite rates of diffusion and of interfacial kinetic reaction for the phase transformation the interfacial composition will shift from y_0 to y_i. The finite thermal driving force, $T_e - T_i = \Delta T$, is needed to
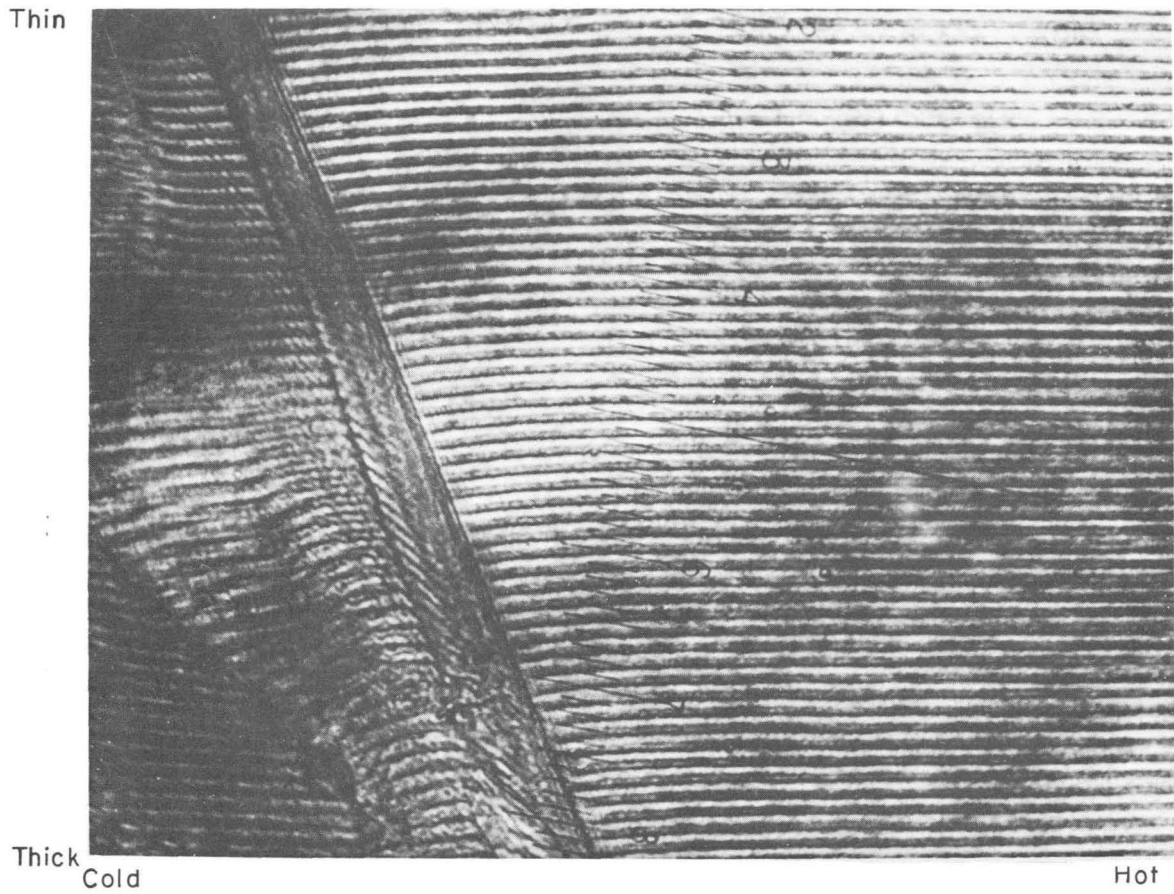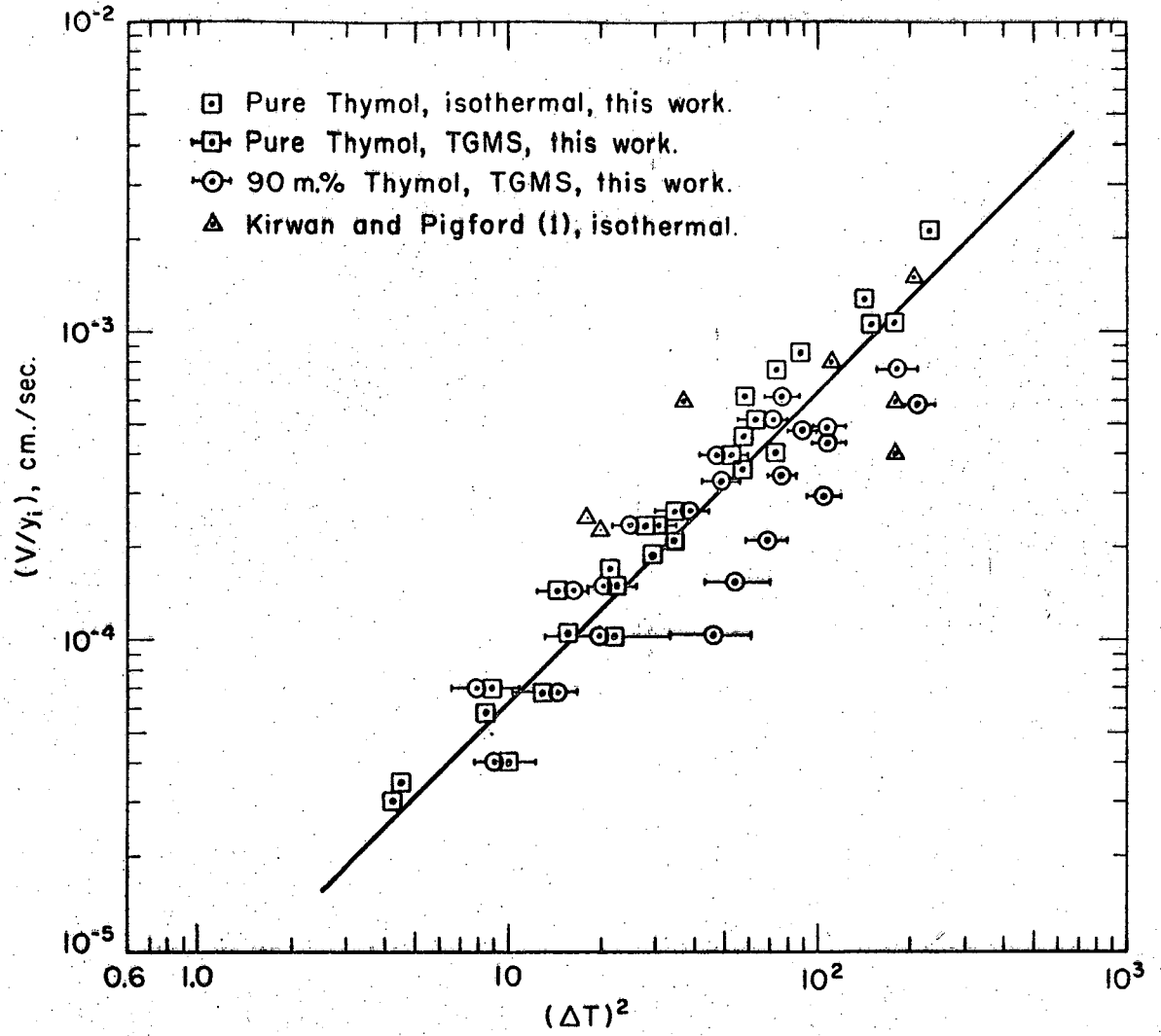
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Fig. 5b. Fringe pattern at interface during growth of mixed crystal
          in 15 mole % stilbene solution.
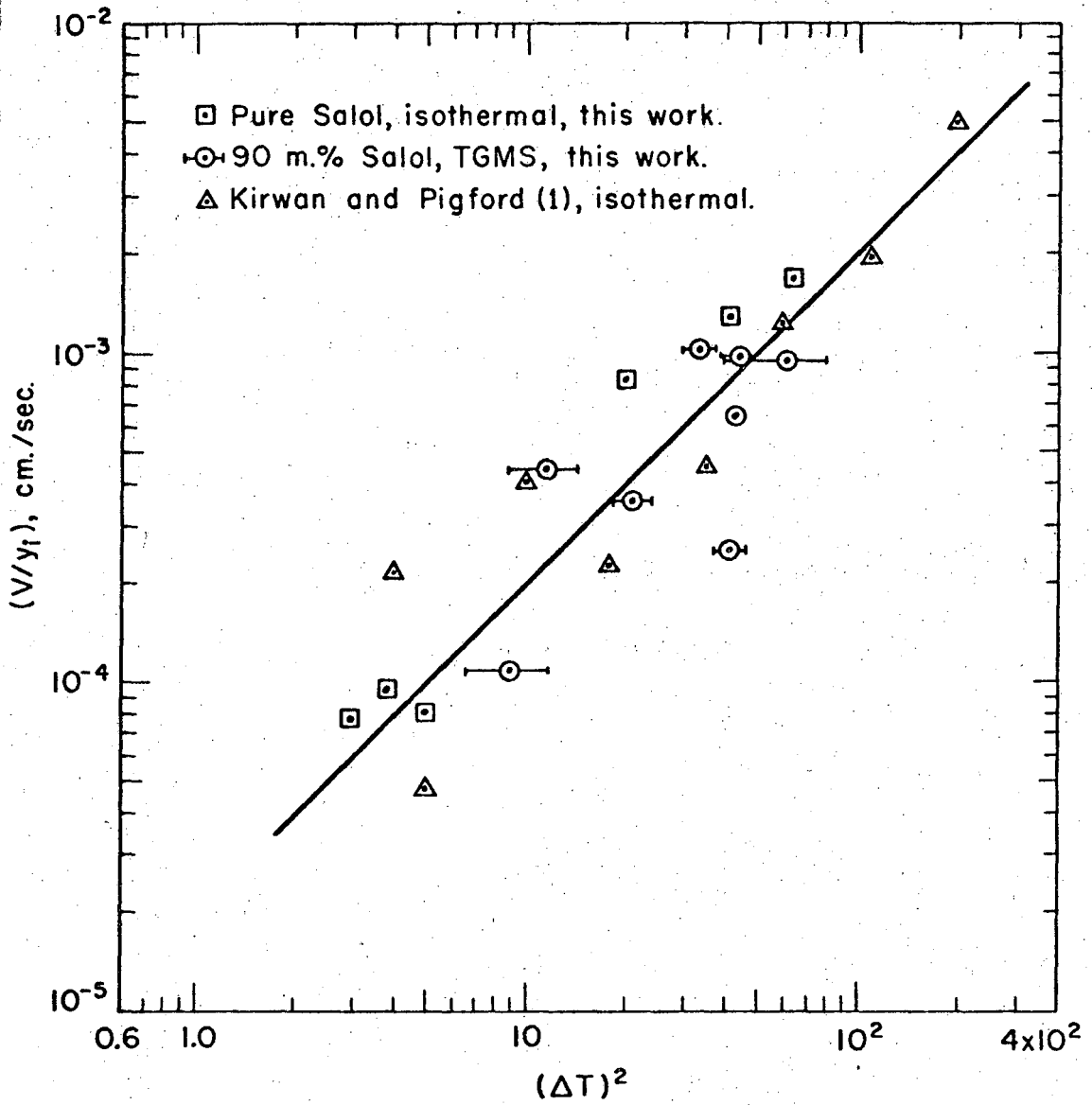
Growth rates of Salol crystals in undercooled liquids

XBL6910-3999

Fig. 6

Growth rates of Thymol crystals in undercooled liquids

XBL6910-4000

Fig. 7

force the solid to form at the prescribed rate. Furthermore, the solid

which forms may not be the pure thymol phase which is expected at equili-

brium from the phase diagram instead, it may have a mole fraction, x_i, greater

than zero. The interferometric apparatus makes it possible to determine

the quantities y_i, x_i and T_i.

The interference fringes pattern is characterized by the equation

$$\frac{2nt}{\lambda_0} = N , \qquad\qquad (2)$$

where N is an integer and is constant along each line in the pattern.

In this equation $n = n(T,y)$ is the composition of temperature-dependent

refractive index of the liquid, t is the local thickness of the liquid in

the wedge, and λ_0 is the wavelength of the monochromatic light source

used. The determination of y_i is based on the fact that the displacement

of the fringes from their straight-line projections from the unaffected

liquid to the interface implies a certain change in n. Part of this may

be owing to the interfacial temperature rise; the residual part is owing

to the difference in composition, $y_0 - y_i$.

The solid composition, x_i, is harder to find but can be computed

from the same interference pattern. This is based on an interfacial

diffusion flux balance. This leads to the equation

$$x_i = y_i + \frac{D}{V(\rho_s/\rho_L)} \left(\frac{dy}{dz}\right)_{z=0} \qquad\qquad (3)$$

where D is the binary liquid diffusion coefficient, V is the measured

growth velocity, z is the coordinate perpendicular to the interface, and

the ρ's are densities of liquid and solid phases. The computation of the

composition derivative depends on the geometry of the fringe pattern and

upon Eq. (2). In Fig. 4 the X-axis is drawn parallel to the vertex of the

optical wedge. The thickness, t, is assumed to vary linearly in the Y

direction. Far away from the interface the fringes are straight but are

at the angle α from the X-axis, owing to the temperature gradient. The

v-w coordinate system has its origin in the interface and the v-axis is

parallel to the distant fringes. Coordinates of several fringe lines were

measured in the v-w system using a precise instrument designed originally

for locating particle tracks in photographic negatives. By considering the

geometry involved it can be shown that the interfacial composition gradient

is given by

$$\left(\frac{dy}{dz}\right)_{z=0} = \frac{\lambda_0 (dw/dv)_{v=0}}{2 \, s \, t_i \, \cos\alpha \, [\sin\beta + (dw/dv)_{v=0} \cos\beta] \, (\partial n/\partial y)_T} , \quad (4)$$

where s is the fringe spacing measuring in Y direction. A detailed

derivation of Eq. (4) can be found elsewhere (Cheng, 1969).

Equations (2), (3), and (4) were used to compute the interfacial

compositions and temperatures for the salol-thymol system. Some of the

results have been included in Figs. 6, and 7, where growth rates of the

salol phase and the thymol phase from the solution are shown. Figure 9

shows the computed solid compositions of the thymol phase and indicates

that the solid phase which grew at a finite velocity apparently contained

as much as 10 mole percent salol. The interfacial liquid contained about

85 mole percent thymol in the same experiments.

Phase diagram of Salol - Thymol system

XBL6910-3995

Fig. 8
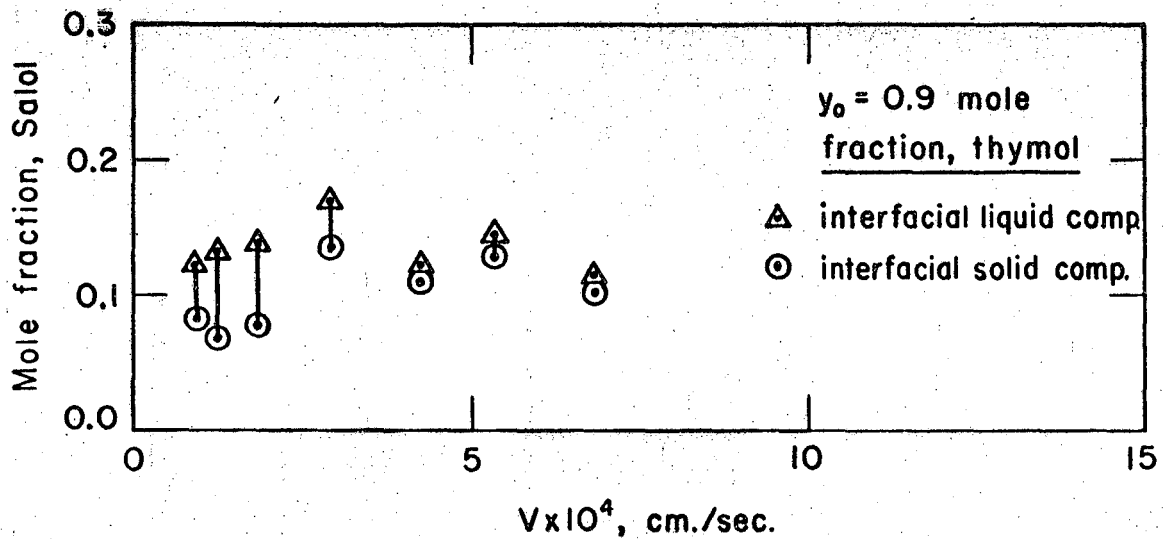
Compositions of Salol-thymol crystals growing
in thymol-rich liquid mixtures

XBL 6910-3996

Fig. 9

The accuracy of the computed interface solid composition depends
not only on the accuracy of the fringe measurements and on the composition-
derivative of the refractive index. It depends also on the liquid diffusion
coefficient, which was not measured directly in this work and may be in
error. The value used 0.74×10^{-6} sq. cm./sec. at $29.5°C$, based on a few
measurements by Kirwan (1967) and on the empirical correlation of Wilke
and Chang (1955). It is believed that the probable error in this coef-
ficient may account for the 10 percent deviation of x_i from the expected
value.

For solutions, as for pure compounds, the growth velocity is ap-
proximately proportional to the square of the temperature driving force,
indicating that the same spiral growth mechanism applies as before. The
growth velocity on the ordinate of Figs. 6 and 7 is divided by the inter-
facial liquid mole fraction of the substance which is being deposited.
Although it is not possible to prove that the velocity is proportional to
the interface composition because of the scatter of the data, and because
of the small variation of y_i, this quantity is included on the basis of
a theory of crystal growth from solution which forms a eutectic system
(Kirwan and Pigford, 1969).

CONCLUSIONS

The presence of an imposed constant temperature gradient is a
decided advantage in measurements of the rate of growth of crystals in
undercooled melts of organic substances, especially when mixtures are used
and constitutional undercooling can occur. This is owing to the improve-
ment in the stability of the interface as it advances, permitting

measurements of temperature and diffraction to be carried out long enough for repeat observations to be taken during periods of nearly steady state. The addition of facilities for quantitative measurement to the apparatus previously used by Jackson et. al. (1966) makes it possible for the first time for interfacial rate phenomena to be studied successfully for organic substances.

The results indicate that deviations of interfacial compositions and temperatures from the phase diagram values can be considerable, even at small growth rates and suggests that designs of crystallization equipment which are based on the assumption of instantaneous phase equilibrium may be considerably in error.

NOTATION

D = liquid phase diffusion coefficient, sq. cm./sec.

K = constant

n = refractive index of liquid

N = integer

s = fringe spacing, mm.

t = thickness of optical wedge, mm.

T = temperature, °C.

V = freezing velocity, cm./sec.

v,w = coordinates for interference fringe

x = mole fraction in solid phase

y = mole fraction in liquid phase

X,Y = coordinates for optical wedge

z = distance perpendicular to growing crystal face

GREEK LETTERS

α = angle, degree

β = angle, degree

γ = angle, degree

λ_0 = wave length of monochromatic light, 6328 Å. for He-Ne gas laser

ρ = molar density, g. mole/cc.

SUBSCRIPTS

e = equilibrium condition

i = interfacial condition

L = liquid phase

s = stage condition, or solid phase

0 = initial condition

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