Normal Freezing of Eutectic Forming Organic Mixtures

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Normal freezing of several organic systems exhibiting simple eutectic behavior has been studied experimentally, and the occurrence of constitutional subcooling has been clearly established. This phenomenon, previously observed in systems of metallurgical interest, results in the instability of a planar solid-liquid interface and leads to solute trapping. This trapping mechanism quantitatively explains why eutectic forming systems exhibit solid phase concentration profiles identical to those expected of systems which form solid solutions. The onset of constitutional subcooling can be correlated and reliably predicted by theoretical equations.

Although the process of normal freezing with no liquid phase agitation would appear to be well described by a diffusion model, free convection induced by concentration gradients renders a boundary-layer model more appropriate when the liquid density of the solvent exceeds that of the solute and freezing is in an upward direction.

Normal freezing is a term applied to the progressive freezing of a liquid charge, and in terms of a theoretical analysis this process is equivalent to single-crystal pulling. The successful application of these processes and the related process of zone melting to the production of semiconductor materials has generated considerable interest in applications of the processes and has stimulated fundamental investigations of the concomitant transport phenomena. Much fundamental study has been devoted to systems forming solid solutions and ample experimental results are available for corroboration of theory. Only recently, however, has a theoretical analysis of normal freezing in eutectic forming systems appeared (*1*) and as yet no experimental investigations suitable for testing this analysis quantitatively have appeared in the literature. This study was undertaken to supply these necessary experimental results.

THEORY

In systems where solute is rejected by the freezing solid ($k_o < 1$) there is an accumulation of solute ahead of the advancing interface and hence a concentration gradient is established in the liquid. For eutectic forming systems ($k_o = 0$) two separate regimes must be recognized: the liquid phase solute concentration at the interface is less than the eutectic concentration and the solid formed is pure solvent; and as freezing progresses the solute concentration of the liquid at the interface reaches the eutectic concentration and the solid deposited thereafter is a mixture of pure solvent and solute. Here we are interested only in the first regime and cite Wilcox's analytical solution (*2*) for pure diffusional mass transport.

$$\frac{c}{c_o} = 1 - \frac{1}{2}\operatorname{erfc}\left(\frac{\eta+\tau}{2\sqrt{\tau}}\right) + \frac{1}{2}(1-\eta+\tau)e^{-\eta}\operatorname{erfc}\left(\frac{\eta-\tau}{2\sqrt{\tau}}\right) + \frac{\sqrt{\tau}}{\sqrt{\pi}}\exp\left[-\eta-\left(\frac{\eta-\tau}{2\sqrt{\tau}}\right)^2\right] \quad (1)$$

The problem is simplified considerably by postulating the existence of a boundary layer across which the liquid phase solute concentration changes from its maximum value at the interface to c_L, the bulk liquid concentration. It is further assumed that a quasi steady state condition is established because the solute transport rate through the boundary layer is large compared to the rate of concentration change within the boundary layer. Using this approach Burton et al. (*3*) obtained the liquid phase concentration profile for systems forming solid solutions; however their results are more conveniently expressed in terms of the effective distribution coefficient, k_E

$$k_E = \frac{k_o}{k_o + (1-k_o)e^{-R\,\delta/D}} \quad (2)$$

As in the case of the diffusion model, the two regimes must be considered separately when applying the boundary-layer model to eutectic forming systems. Wilcox (*1*) has obtained analytical solutions for both regimes. During the period when the solid is pure solvent, he obtained the following expression for the liquid phase concentration profile:

$$c/c_L = [e^{\frac{\delta R}{D}}]\,[e^{-\frac{zR}{D}}] \quad (3)$$

In the derivation of the preceding equations it is implied that the solid-liquid interface is planar and that there are no transverse concentration gradients. However, experimental observations with solid solution forming systems of metallurgical interest have revealed that the interface is not always planar, but that a cellular structure sometimes exists with transverse concentration gradients occurring within each cell. The phenomenon responsible for this nonplanar morphology has been analyzed (*4 to 7*) and is referred to as *constitutional subcooling*. The criterion for stability of the planar interface has been established and may be stated in terms of the temperature and concentration gradients at the interface and the slope of the liquidus line.

$$G \geqq -m\left.\frac{dc}{dz}\right|_{z=0} \quad (4)$$

Equations based on this criterion have been remarkably successful in predicting the onset of the cellular morphology for systems forming solid solutions. This phenomenon is believed to be responsible for the failure to obtain the expected purity of zone-melted organic compounds forming simple eutectic systems (*2, 8*).

The concentration gradient appearing in Equation (4) can be evaluated from liquid phase concentration profiles

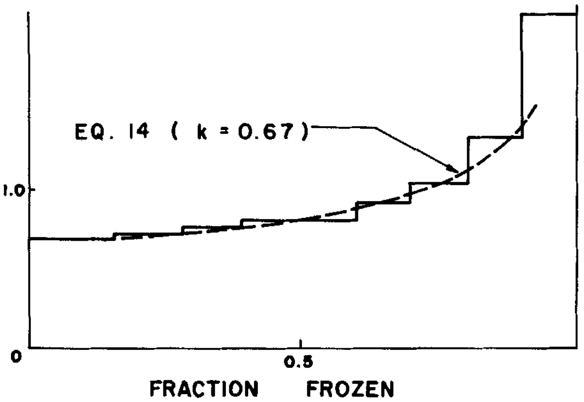

Fig. 1. A typical solid phase composition profile (run 5, benzene—hexadecane, freezing rate: 1.25 in./hr.).

for either the boundary-layer model or the diffusion model.

Use of the boundary-layer model [Equation (3)] results in

$$G \geq \frac{mc_L \, Re^{\delta R/D}}{D} \tag{5}$$

Up to the time constitutional subcooling occurs, the deposited solid is pure and hence the fraction frozen at the onset of subcooling is related to the bulk liquid concentration through a material balance

$$(1 - g_P) = c_o/c_L \tag{6}$$

Here one assumes that the liquid phase is well mixed except for the boundary layer and that the amount of solute contained within the boundary layer can be neglected. Elimination of c_L between Equations (5) and (6) yields the desired relationship among freezing rate, initial solute concentration, and fraction of pure solid obtained before the onset of constitutional subcooling

$$\frac{1}{1 - g_P} = \frac{DG}{Rmc_o} e^{-\delta R/D} \tag{7}$$

A corresponding stability analysis based on the diffusion model is obtained from Equations (1) and (4):

$$\frac{DG}{Rmc_o} \geq \left\{ \frac{\sqrt{\tau}}{\sqrt{\pi}} e^{-\tau/4} + \frac{2 + \tau}{2} \left[1 + \text{erf}\left(\frac{\sqrt{\tau}}{2} \right) \right] \right\} \tag{8}$$

Here the amount of pure solid obtained is expressed in terms of the time at which subcooling occurs. It should be noted that both Equations (7) and (8) contain the dimensionless group (DG/Rmc_o) which should be as large as possible to prevent constitutional subcooling.

Before the stability criteria expressed by Equations (7) and (8) can be applied, one must have some knowledge of the temperature gradient G. In the absence of convection, the following one-dimensional energy equation can be written for the liquid phase by using a moving coordinate system with the interface at $z = 0$ and the positive z axis extending into the liquid.*

$$\alpha \frac{d^2T}{dz^2} + R \frac{dT}{dz} - \beta(T - T_a) = 0 \tag{9}$$

The ambient temperature T_a is assumed constant, and the boundary conditions are

$$T = T_E \text{ at } z = 0 \tag{10}$$

$$T = T_a \text{ at } z = \infty \tag{11}$$

The solution to Equations (9) through (11) is

$$\frac{T - T_a}{T_E - T_a} = e^{-\left(\frac{R + \sqrt{R^2 + 4\beta\alpha}}{2\alpha}\right) z} \tag{12}$$

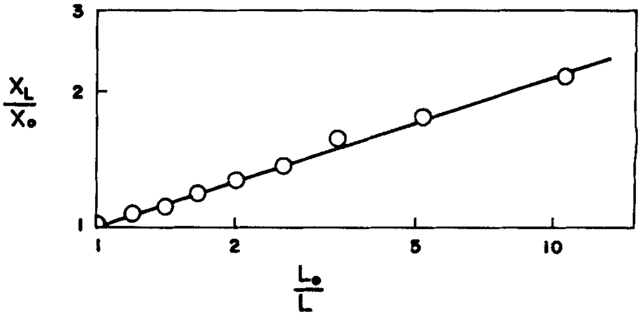

Fig. 2. Logarithm x_L/x_O vs. logarithm L_O/L for a typical run (run 5, benzene-hexadecane, freezing rate: 1.25 in./hr.).

The liquid phase temperature gradient at the solid-liquid interface G can be obtained from Equation (12) and is

$$G = (T_a - T_E) \left[\frac{R + \sqrt{R^2 + 4\alpha\beta}}{2\alpha} \right] \tag{13}$$

This equation allows the estimation of G from the liquid thermal diffusivity, the system variables, and the heat transfer coefficient between the tube and the ambient air.

EXPERIMENTAL PROCEDURE

Details of the apparatus and experimental procedure are given elsewhere (9). Essentially the apparatus consisted of a refrigerated temperature bath serving as a heat sink and a drive mechanism to establish freezing rates. The bath temperature was adjustable but was usually set 10° to 20°C. below the freezing point of the liquid charge. At a given set point the temperature varied little. Two different drive mechanisms were used to provide freezing rates in the ranges of 0.065 to 0.25 in./hr. and 0.25 to 2.5 in./hr. These mechanisms were powered by 60-cycle synchronous motors and showed no variation in freezing rate during an individual run.

In a typical run a liquid charge was placed in a long, cylindrical, round-bottomed container made from Pyrex tubing and the tube was lowered vertically into the bath at a constant and predetermined rate. The majority of runs were made with a ¾-in. I.D. tube, although tubes of ½- and 1-in. diameter were also used. After the charge was completely frozen the tube was raised incrementally so that approximately ⅛ of the specimen melted each time. After each increment had melted the liquid was withdrawn, weighed, and analyzed. Compositions were determined from refractive index measurements with a previously established refractive index-composition relationship. The composition and weight of each increment were then used to construct the solid phase concentration profile such as shown in Figure 1. The initial concentration and the weight of the charge were determined before the normal freezing operation so that the profile could be checked for material balance consistency.

The normal freezing tubes were equipped with standard taper joints to enable degassing of the liquid sample before freezing. This was accomplished by a freezing, pumping, thawing cycle which was repeated until no gas bubbles were observed on thawing. After degassing the liquid was mixed by rocking the tube to ensure a uniform composition before the normal freezing operation.

A tube specially designed to produce a monocrystal was used for the study of constitutional subcooling. This tube was fabricated from 19-mm. Pyrex tubing and had a spiral capillary end as recommended by Spendiarov and Aleksandrov (*10*) for growing single anthracene crystals. For these runs the liquid charge was thoroughly degassed and then mixed before freezing. The temperature bath was maintained at −5°C. with little variation. Because of the rather low thermal driving force it was necessary to use a cold source to produce a small crystal in the capillary spiral before starting the normal freezing operation.

Temperature gradients during normal freezing were obtained from a copper-constantan thermocouple fabricated from 0.002-in. diameter wire and suspended in the liquid at a fixed posi-

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* In this problem the velocity v_z is negative. Here v_z has been replaced by $-R$. The solid growth rate R is always taken positive.

tion relative to the tube. As freezing progressed and the solid-liquid interface moved toward the thermocouple, readings were recorded at definite times so that the relative position of the thermocouple could be determined from the known freezing rate. The time at which the thermocouple touched the interface was also recorded. As a smooth interface was desirable, these runs were made in the spiral tipped tube with pure benzene. Temperature profiles were determined in both the liquid and solid phases. Photographic studies of the solid-liquid interface were made with a microscope with camera attachment mounted at an angle a few degrees from the horizontal. With this arrangement a profile photomicrograph of the interface could be obtained. For these runs a tube with flat polished sides was used to prevent distortion and the drive mechanism was stopped just prior to exposure to ensure against movement of the tube.

The benzene, cyclohexane, and *n*-heptane used in this study were Phillips Petroleum Company pure grade hydrocarbons, the hexadecane was Eastman Organic Chemicals practical grade; and the chloroform was Fisher Scientific Company certified reagent. The solutes were subjected to no special treatment before use. The refractive index of the solvents, benzene and cyclohexane, checked with literature values and chromatographic analyses, revealed no impurities. Normal freezing of these materials produced no change in refractive index; hence further purification was not deemed necessary.

RESULTS

Normal Freezing

Three systems were subjected to normal freezing at moderate freezing rates: benzene—cyclohexane, benzene—*n*-heptane, and benzene—hexadecane. Solid-liquid equilibria have been reported for all three systems (*11*, *12*) and each has been found to exhibit eutectic behavior with no solid solubility. At these freezing rates (0.25 to 2.5 in./hr.) solid phase composition profiles were obtained for all three systems with an initial charge composition of approximately 97 mole % benzene. Contrary to expectations, no pure solid was formed; rather all profiles possessed the characteristic shape of the solid solution boundary-layer model.

For this model Pfann (*13*) has derived the expression for the solid phase composition profile

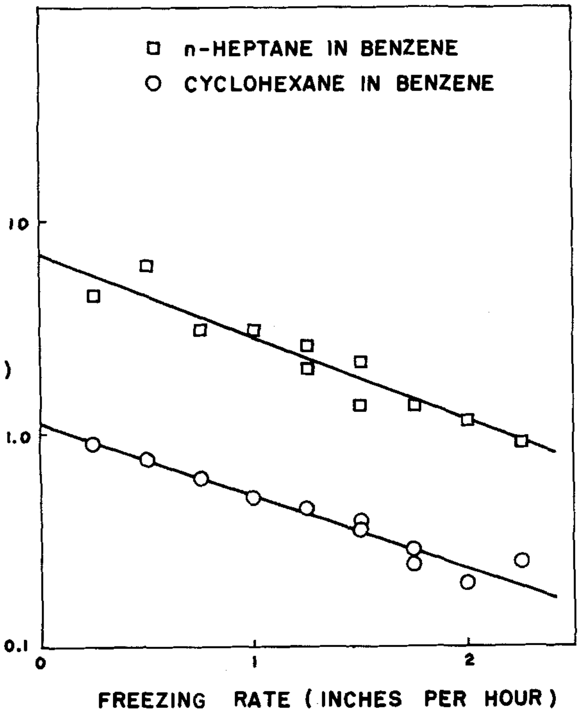

Fig. 3. Logarithm $1/(k_E - 1)$ vs. freezing rate.

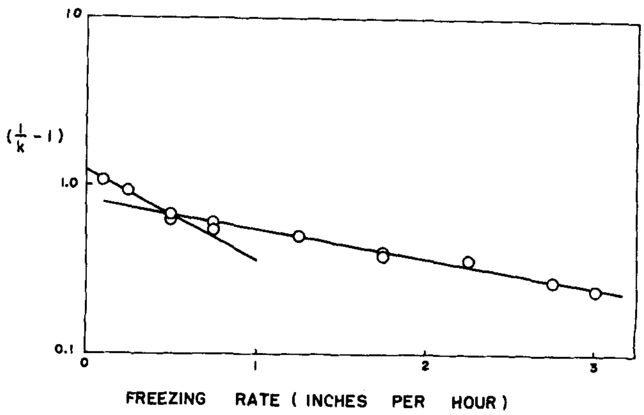

Fig. 4. Logarithm $1/(k_E - 1)$ vs. freezing rate for hexadecane in benzene.

$$c_s/c_o = k(1-g)^{k-1} \tag{14}$$

This equation is based on the integration of a differential material balance with constant k assumed, and applies either to the case of complete mixing ($k = k_o$) or partial mixing ($k = k_E$) in the liquid phase. For the purpose of evaluating k from the profile data, it is convenient to restate this equation in terms of liquid phase concentration.

$$\ln x_L/x_o = (1-k) \ln L_o/L \tag{15}$$

This form was found superior to Equation (14) for the correlation of profile data and determination of the effective distribution coefficient. When plotted as $\ln x_L/x_o$ vs. $\ln L_o/L$, all runs yielded straight lines such as shown in Figure 2. Values of x_L needed for use in Equation (15) were obtained from the profile data by cumulative material balance calculations based on the assumption that the bulk liquid was well mixed. This calculation procedure tends to damp out possible errors in the profile data, particularly at small values of g, and hence values of k determined from application of Equation (15) were used in Equation (14) so that the experimental and calculated profiles could be directly compared. Such a comparison is shown on Figure 1. The substitution of mole fraction ratio for concentration ratio seems quite reasonable here because of the small range of concentrations involved.

The effective distribution coefficients determined from Equation (15) were found to depend upon freezing rate in the manner prescribed by the boundary-layer theory of Burton et al. [Equation (2)]. Figure 3 shows that two of the systems yield the required linearity of $\ln(1/k_E - 1)$ with freezing rate, and Figure 4 shows that the benzene-hexadecane system exhibits two regions of linearity. For this system profile photomicrographs of the interface, Figures 5 and 6, reveal that each of the regions is associated with a distinct type of interface morphology. At freezing rates up to 0.5 in./hr. the interface has a corrugated or saw-toothed appearance, whereas at freezing rates of 1.0 in./hr. and greater it displays a highly irregular dendritic appearance. Within each range of freezing rates there is no discernable change in interface morphology with freezing rate.

Trapping of liquid at the interface appears to be a reasonable explanation for the failure of these systems to exhibit the expected eutectic type of solid phase composition profile. This explanation is supported by the photomicrographs for one system. Furthermore the following simplified analysis shows that this trapping mechanism can produce in a eutectic system a profile identical to that for a solid-solution system.

When trapping occurs in eutectic systems the composite solute concentration in the solid at the interface is given in terms of the surface void fraction f and the solute concentration at the interface

$$\bar{c}_s = f\, c\Big|_{z=0} \tag{16}$$

Thus, Equation (16) is analogous to the equilibrium distribution relation for systems forming solid solutions with the surface void fraction f corresponding to the equilibrium distribution coefficient. Because our experimental technique is incapable of distinguishing trapped liquid from equilibrium solid, the solid phase composition profile can be correlated in terms of an effective distribution coefficient.

This effective distribution coefficient can be shown to depend upon freezing rate in the manner prescribed by the equation of Burton et al. If one retraces their derivation and everywhere substitutes Equation (16) for the distribution relationship, the following expression is obtained

$$k_E = \frac{f}{f + (1-f)e^{-R\delta/D}} \tag{17}$$

One observes that this equation is identical in form with Equation (2), with the equilibrium distribution coefficient replaced by the surface void fraction. The fact that the two systems shown in Figure 3 can be correlated in terms of this equation implies that the boundary-layer thickness δ and the surface void fraction f are independent of freezing rate. The two regions of linearity exhibited by the benzene-hexadecane system in Figure 4 correspond quite closely to the two distinct regions of interface morphology. This suggests that a constant or average value of f can be assigned to each region.

Equation (17) may be used to obtain estimates of the surface void fraction from the effective distribution coefficients. For the benzene-hexadecane system one obtains a value of 0.48 for the region associated with the corrugated interface and a value of 0.59 for the dendritic region. Considering the known interface morphology, these surface void fractions do not appear unreasonable. Thus they support the foregoing analysis, for one would certainly expect more trapping with the dendritic interface.

In the case of the benzene-cyclohexane and benzene-*n*-heptane systems, the bath temperature was considerably above the eutectic temperature, and hence trapping seems to offer the only reasonable explanation for their observed behavior. For the benzene-hexadecane system, however, the bath temperature was maintained below the eutectic temperature (−3°C.), and hence the possibility that eutectic freezing could account for the behavior of this system needs to be explored. The liquid phase concentration profile for the boundary-layer model (3) in terms of the trapping mechanism is

$$c/c_L = \frac{f + (1-f)e^{-zR/D}}{f + (1-f)e^{-\delta R/D}} \tag{18}$$

At the interface the concentration is

$$c\Big|_{z=0} = c_L\left[\frac{1}{f + (1-f)e^{-\delta R/D}}\right] \tag{19}$$

The second term in the denominator can only be positive and hence

$$c\Big|_{z=0} \leq c_L/f \tag{20}$$

The eutectic composition for this system is about 15 mole % hexadecane and if f is taken as 0.5, eutectic freezing would not be expected until the bulk liquid concentration approached 7.5 mole % hexadecane. When the profile data are examined in the light of this result, there seems to be little likelihood that eutectic freezing is responsible for the behavior of this system.

The effect of tube diameter on segregation efficiency was studied with the benzene-hexadecane system. As before, the composition profiles were correlated well by Equation (15) and it was found that at the same freezing rate the segregation efficiency increased (a decrease in the value of k_E) with increasing tube diameter. This observation is certainly expected and can be explained in terms of reduction of the boundary-layer thickness due to natural convection effects which intensify as the tube diameter is increased.

Constitutional Subcooling

The results of normal freezing experiments at moderate freezing rates strongly indicated that the phenomenon of constitutional subcooling was producing a nonplanar interface with subsequent liquid trapping. As an experimental investigation of this phenomenon seemed desirable, a series of normal freezing runs was performed with dilute solutions at very low freezing rates (0.065 to 0.1 in./hr.).

When a pure substance was subjected to normal freezing at low freezing rates in the specially designed tube, a translucent solid was formed. Normal freezing of a dilute solution under identical conditions, however, produced a solid specimen which was initially translucent, but very abruptly became and remained opaque. This opaqueness was characteristic of the solid formed during all normal freezing runs at moderate freezing rates. Analysis revealed that the translucent material was pure

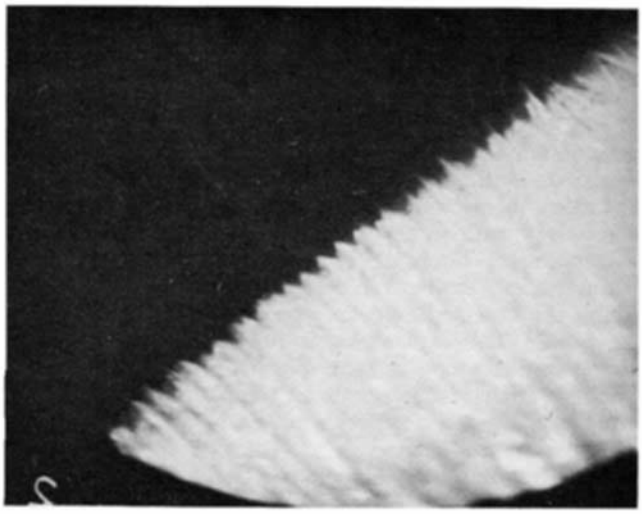

Fig. 5. Profile photomicrograph of solid-liquid interface for the benzene-hexadecane system at a freezing rate of 0.5 in./hr. 14×.

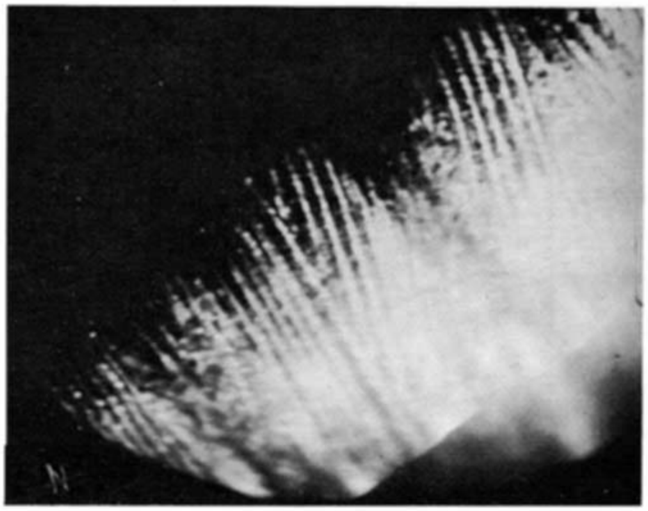

Fig. 6. Profile photomicrograph of solid-liquid interface for the benzene-hexadecane system at a freezing rate of 2.5 in./hr. 14×.

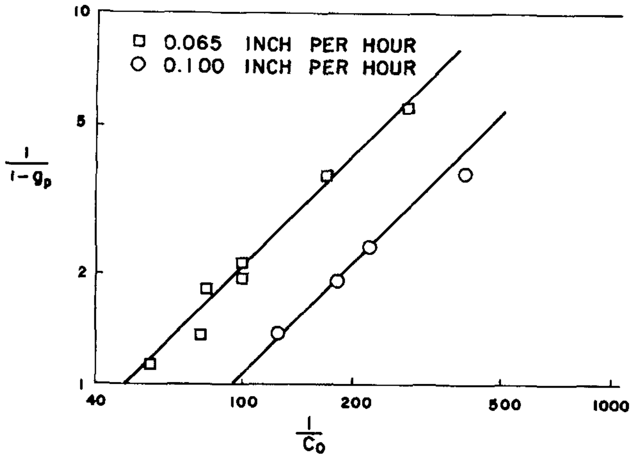

Fig. 7. Logarithm $1/(1 - g_p)$ vs. logarithm $1/c_o$ for cyclohexane solute in benzene solvent.

solvent and that the opaque material contained solute. The amount of pure solid solvent formed was found to depend upon the freezing rate and the initial solute concentration. Because the bath temperature was considerably above the eutectic temperature, the presence of solute can only be explained in terms of trapping due to constitutional subcooling.

In this series of experiments three simple eutectic systems were studied: (1) cyclohexane solute in benzene solvent, (2) benzene solute in cyclohexane solvent, and (3) chloroform solute in benzene solvent. The results from these experiments show that constitutional subcooling can be quantitatively predicted and that systems 2 and 3 are described by the diffusion model, while system 1 is described by the boundary-layer model.

Equation (7), derived from the boundary-layer model, suggests that at a constant freezing rate the amount of pure solvent obtained from normal freezing before constitutional subcooling occurs can be correlated by plotting $\ln 1/(1 - g_P)$ vs. $\ln 1/c_o$. Equation (13) indicates that G should be constant and hence such a plot should result in a straight line of unit slope. The results for system 1, plotted in this manner in Figure 7, do indeed yield straight lines of unit slope.

If the term G in Equation (7) is eliminated by use of Equation (13), then the resulting equation in effect contains two parameters: the boundary-layer thickness and the heat transfer coefficient. A further test of the boundary-layer model would be to evaluate these two parameters from the two lines in Figure 7 and determine if they are realistic. This was done by using the known system variables, and physical properties [the slope of the freezing curve m was calculated on the assumption that the solution behaved ideally, and the diffusivity was estimated by the method of Wilke and Chang (*14*)]. The parameters so determined were $\delta = 0.20$ cm. and $h = 0.19$ B.t.u./(hr.)(sq.ft.)(°F.). The value of δ is somewhat larger than the range of 10^{-3} to 10^{-1} cm. quoted by Chalmers (*15*), but is well within the range of 0.05 to 1.0 cm. obtained by Wilcox (*16*) from an experimental study of zone melting of organic systems. The calculated heat transfer coefficient is slightly lower than the normal range expected for free convection. This apparent discrepancy, however, might be due to the restriction of convection currents in the air surrounding the tube by the surface of the temperature bath which was located only a short distance below the solid-liquid interface. When this heat transfer coefficient is used in Equation (13), the gradients are calculated to be 8.7 and 8.9°C./cm. for freezing rates of 0.065 and 0.10 in./hr., respectively. These values are within the range 6 to 10°C./cm. obtained by graphical differentiation of the experimental temperature profile data. The fact that these calculated parameters have reasonable values seems to strengthen the argument for the boundary-layer model.

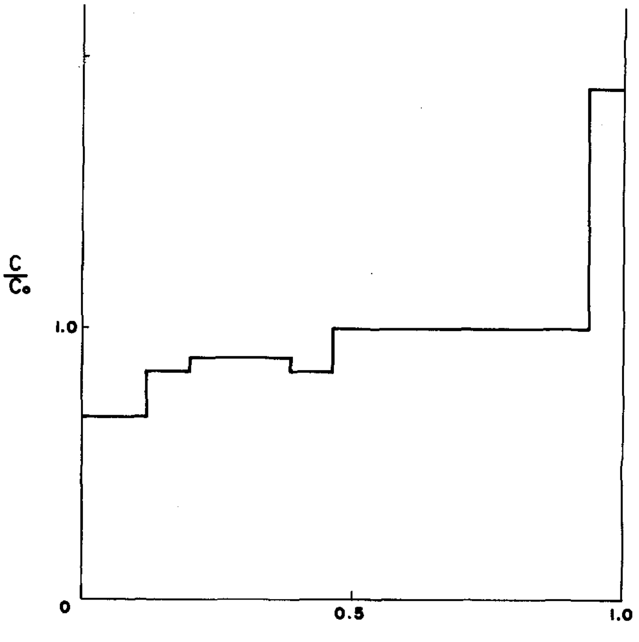

Fig. 8. A typical solid phase composition profile for benzene solute in cyclohexane solvent.

Although constitutional subcooling in this system appears to be explained quite well in terms of the boundary-layer model, the experimental data were also compared with the diffusion model. This model, however, predicts yields of pure benzene much less than were observed.

Because of the uncertainty in analyzing the dilute solutions required for the production of pure cyclohexane, it was not possible to test Equation (7) and (8) with system 2. However, several solid phase composition profiles were obtained at various freezing rates and initial concentrations. All profiles were similar to that shown in Figure 8 and exhibited the characteristic steady state region ($c/c_o = 1.0$) required by the diffusion model.

The area enclosed by $c/c_o = 1.0$ and the solid phase concentration profile from $g = 0$ to the steady state region is a measure of the segregation obtained by normal freezing. An analytical expression for this area can be obtained by using the solid phase profile equation derived by Tiller et al. (*17*) for systems with nonzero distribution coefficients:

$$\int_0^{g_{ss}} \left(1 - \frac{c_s}{c_o}\right) dg = \frac{(1-k_o)}{k_o(Rl/D)} \left[1 - e^{-k_o g_{ss}(Rl/D)}\right] \tag{21}$$

The left-hand side of Equation (21) is easily evaluated from the experimental solid-phase composition profiles, and thus a value of k_o may be calculated for each run. These

TABLE 1. VALUES OF k_o CALCULATED FROM EQUATION (21) FOR BENZENE SOLUTE IN CYCLOHEXANE SOLVENT

Run No.	c_o, mole % benzene	R, in./hr.	k_o
II-11	1.00	0.065	0.085
II-12	1.85	0.130	0.080
III-1	2.00	0.100	0.080
III-2	2.00	0.100	0.085
III-3	2.00	0.163	0.085

calculated values of k_o are listed in Table 1 where it is observed that essentially the same value of k_o is obtained for each run. As before, the significance of a nonzero distribution coefficient for a eutectic system is expressible in terms of the trapping mechanism.

When two dilute solutions of chloroform in benzene were subjected to normal freezing at the lowest attainable freezing rate (0.065 in./hr.), the yields of pure benzene were found to be in agreement with the predictions of the diffusion model. A 0.42 mole % solution yielded 42% of the charge as pure benzene, while a 15% yield was obtained from a 0.55 mole % solution. With the range of observed temperature gradients (6 to 10°C./cm.), Equation (8) predicts yields of 24 to 43% and 16 to 30%, *respectively*, for these solutions. The boundary-layer model predicts much larger yields for this system.

CONCLUSIONS

It has been shown that the boundary-layer model is applicable to normal freezing of the benzene-cyclohexane, benzene–*n*-heptane, and benzene-hexadecane systems and that the diffusion model is applicable to the cyclohexane-benzene and benzene-chloroform systems. Because these two groups of systems can also be classified on the basis of the variation of liquid density with solute concentration, for the case of freezing in the upward direction, it is concluded that when the liquid density of the solute is less than that of the solvent, free convection will occur and the boundary-layer model is appropriate. Conversely, when the liquid density of the solute exceeds that of the solvent, no free convection is possible and the diffusion model is appropriate. This mechanism was also invoked by Wilcox *(16)* to explain results obtained from zone melting mixtures of organic compounds.

With the appropriate model the onset of constitutional subcooling can be correlated and reliably predicted by means of theoretical equations. Although equations have been applied only to normal freezing here, equations based on the same stability criterion can be derived easily for the related process of zone melting. The most striking manifestation of this phenomenon is the severity of operating conditions required to produce pure material from eutectic forming organic systems. No doubt this severity of operating conditions could be reduced considerably by providing some means of agitation for the liquid phase.

Where conditions are such that constitutional subcooling exists, liquid is trapped by the resulting irregular interface as freezing occurs. The results from several systems show that under these conditions normal freezing of eutectic systems produces solid phase composition profiles characteristic of systems forming solid solutions. The effective distribution coefficient for such systems can be explained in terms of a surface void fraction.

ACKNOWLEDGMENT

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NOTATION

c = solute concentration in liquid
c_o = solute concentration of charge
c_L = solute concentration in bulk liquid (boundary-layer model)
c_s, $\bar{c}_s$ = solute concentration in solid
$\hat{C}_p$ = heat capacity
d = diameter of tube
D = diffusivity
f = void fraction of irregular solid-liquid interface
g = fraction frozen
g_P = fraction of charge obtained as pure solvent
g_{ss} = fraction frozen when steady state region is reached (diffusion model)
G = liquid phase temperature gradient at the solid-liquid interface
h = heat transfer coefficient between the tube and the ambient air
k_o = equilibrium distribution coefficient defined as $k_o = c_s/c$
k_E = effective distribution coefficient defined as $k_E = C_s/C_L$
l = distance from beginning of solidification to steady state region (related to g_{ss})
L = moles of liquid present at any time
L_o = moles of charge
m = slope of freezing curve of solvent
R = freezing rate
t = time
T = temperature
T_o = freezing point of solvent
T_a = ambient air temperature
T_E = equilibrium freezing temperature
v_z = velocity in the z direction ($v_z = -R$)
x_o = solute mole fraction of charge
x_L = solute mole fraction of bulk liquid (boundary-layer model)
z = distance from solid-liquid interface

Greek Letters

α = thermal diffusivity
β = $4h/d\rho\hat{C}_p$
δ = boundary-layer thickness
η = dimensionless distance from solid-liquid interface, zR/D
ρ = liquid density
τ = dimensionless time, tR^2/D

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