ACKNOWLEDGMENT

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NOTATION

f_a, f_c = weight fraction of ash, carbon by proximate analysis
$F^o_{O_2}$ = molar feed flux of oxygen
IA, IO = Illinois coal with air, oxygen blast
M_c = atomic weight of carbon
t = time
t_l, t_a = lower, upper bound for transient following change of coal
t_r = coal residence time
v = coal velocity
v_t = velocity of position of maximum temperature
WA, WO = Wyoming coal with air, oxygen blast
z_h = position in reactor
Z = height of coal bed
z_m = position of maximum temperature

Greek Letters

ϵ = void fraction
$\theta_{0.9}$ = time for 90% approach to new steady state
θ_m = time for maximum temperature to reach middle of coal bed
ν = velocity of combustion zone in infinite coal bed
ρ_p = density of char
Φ_m = burning rate capacity, moles carbon processed/moles feed oxygen

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Growth of Ice in a Saltwater Drop Falling in an Organic Phase

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Data on the ice formation rate are presented for a saltwater drop suspended by drag forces in a flowing cold organic liquid. The effects of refrigerant undercooling, salt concentration, drop size, and time were studied. Ice formation rates in drops of 3 wt % sodium chloride solution were two to three times lower than in pure water drops. A parallel plate model was used to correlate the data and predict ice formation rates for other drops and refrigerants.

Dispersing drops of brine or fruit juices in a countercurrent cold organic refrigerant is a method of desalination (or freeze concentration) that deserves further study.

SCOPE

Direct contact freezing was reported by Wiegandt (1958) as an attractive method to desalt seawater. The main steps in the process are partial freezing, separating the ice from the brine and washing the ice crystals, and melting the ice. The present study concerns only the first step, wherein an organic refrigerant, for example a C_4 hydrocarbon, is normally dispersed in the precooled seawater. The very large number and the thin shape of the ice crystals formed make the ice brine separation and the washing very difficult. For this study, we reversed the phases in the crystallizer by dispersing the seawater in the cold organic liquid. Larger crystals could be produced most likely because of very limited collision breeding of nuclei for ice growing inside a drop of brine. A higher ΔT could be used, which would give both higher growth rates and larger crystals. The first objective of this study was to test this method of direct contact freezing. For convenience, the work was done with relatively large brine drops suspended by drag forces in flowing naphtha. The second objective was to develop a model which predicts the rate of freezing for other cases such as small drops in butane.

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CONCLUSIONS AND SIGNIFICANCE

Data for the ice formation rate were obtained for a single drop of saltwater suspended by drag forces in a flowing cold petroleum naphtha. Variables included were refrigerant undercooling, salt concentration, and drop size. Ice growth rates in drops of 3 wt % sodium chloride solution were two to three times lower than in pure water drops. Three minutes were required to form 30% ice in a 7.3 mm drop of 3 wt % sodium chloride with the naphtha temperature 2°C below the initial freezing point. The ice crystals were stacked plates of 1 to 3 mm diameter.

A parallel plate model satisfactorily correlated the experimental data. In the model, the drop contains a small number *n* of equidistant stacks of plates separated by brine pools. It was derived that the overall Sherwood number for the drop equals approximately 5 *n*. From very early in the growth, the mass transfer resistance becomes as important as the heat transfer resistance; later it is almost rate controlling.

Data on the freezing of saltwater drops have significance for water desalination and freeze concentration. Based on the observations for a single drop, large and relatively thick crystals can be obtained at a high rate by dispersing the water instead of the organic refrigerant. Big crystals make the subsequent separation and washing easier. Preliminary data for this new freezing concept are presented. The proposed parallel plate model applied to smaller drops dispersed in butane predicts that 33% of a 2 mm seawater drop could be frozen in 15 seconds at a nominal undercooling of 2°C. At this undercooling, the estimated production rate is about 1.8×10^{-3} g ice/cm^3, s, that is, 400 lb ice/ft^3, hr, twice the highest production rate reported for butane dispersed crystallizers.

Freezing processes have much potential for seawater desalting or for the concentration of other aqueous systems. They have a lower energy consumption than commercial evaporation processes, and there is no thermal degradation. Yet the very small size of the ice crystals formed is a major hurdle to commercialization. The thin shape of the crystals reflects the order of magnitude difference between the ice growth rate in the basal plane and the rate perpendicular to the basal plane.

In the past 15 years, many have studied the nucleation and growth of ice in stirred salt solutions, where a refrigerant is dispersed and vaporized. The literature is reviewed by Margolis (1969), Bustany (1970), and Barduhn (1975). A number of studies (Melia and Moffitt, 1964; Cayey and Estrin, 1967; Margolis et al., 1971; Clontz and McCabe, 1971; Strickland-Constable, 1972; Ottens et al., 1972; Kane et al., 1974; Estrin et al., 1975) have demonstrated that secondary nucleation (breeding) is the main factor accounting for the large number of tiny ice crystals that are formed at low undercooling. Secondary nucleation is due to the breaking of early dendrites, and the principal mechanism for nuclei removal is crystal-crystallizer collisions, followed by crystal-crystal collisions and fluid shear (Evans et al., 1974).

If these collisions can be minimized, larger crystals would be produced. This can be achieved by having the ice grow in a drop, the drop protecting the dendrites or platelets from collisions with the crystallizer and reducing the crystal-crystal collisions and the fluid shear. Another characteristic one might expect from crystal platelets growing in a drop is that once they reach the drop boundary or another crystal, they cannot grow in the *a* direction any longer and have no choice but to grow in the *c* direction alone, that is, to thicken. This thickening is highly desirable for a commercial process because it means easier separation and washing of crystals.

Growth of ice in saltwater drops at temperatures close to the freezing point does not appear to have been previously studied. This is the main objective of this research, with emphasis on the ice formation rate and the heat and mass transfer.

In the case of a stirred crystallizer with evaporating refrigerant, the temperature difference between the refrigerant and the brine is 0.3° to 4°C, whereas the bulk undercooling (defined as the difference between the equilibrium freezing point at the bulk brine concentration and the bulk brine temperature) is less than 0.1°C. Unwanted nucleation may occur near the colder vapor refrigerant film which acts as a cold spot. Since there are no such cold spots in the proposed system, and since there is little chance for collision breeding of nuclei for ice growing inside a brine drop, higher ΔT's can be used, and thus the growth rates should be higher and the crystals larger.

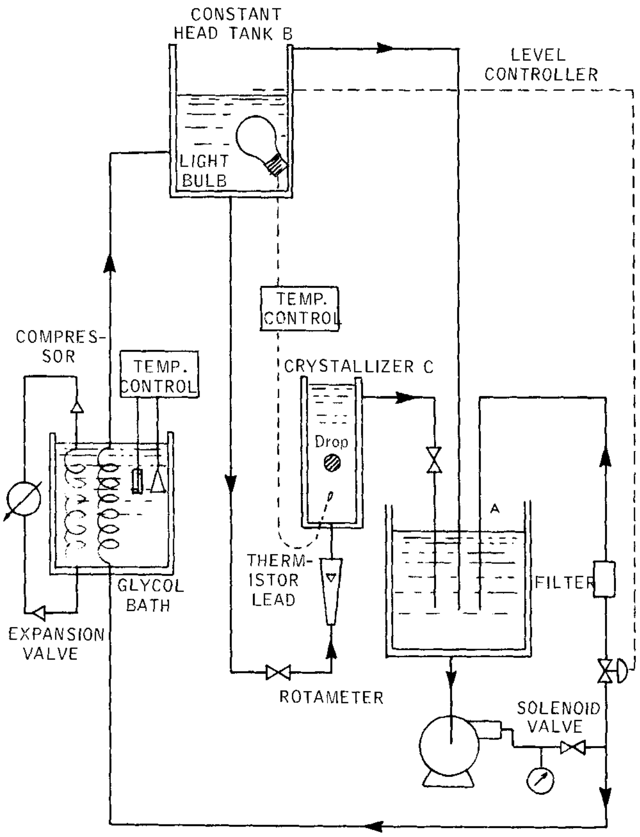


Fig. 1. Schematic diagram of apparatus.

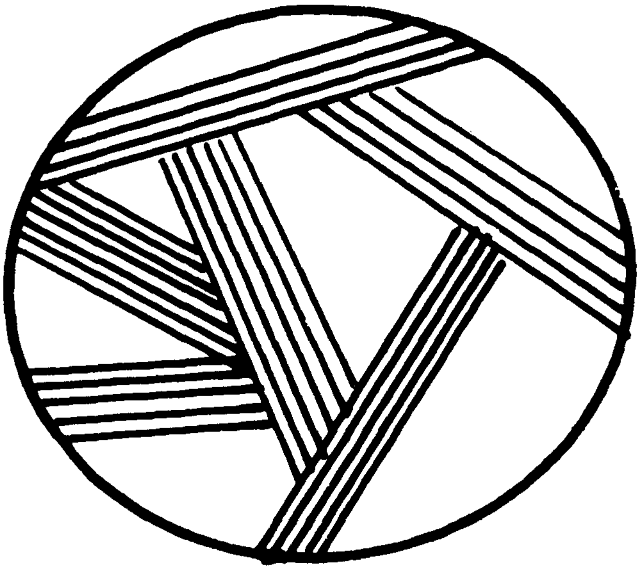


Fig. 2. Sketch of crystals in partially frozen drop $\Delta T_0 > 1°C$.

EXPERIMENTAL

A diagram of the apparatus is shown in Figure 1. The function of the circulating system is to provide a constant flow of refrigerant liquid at constant temperature past a drop. The organic liquid from lower tank A was pumped to an upper constant head tank B after going through a coil in a refrigeration bath. The constant head tank provided a constant flow to the crystallized tube C. The crystallizer C was a Plexiglas® tube of 3.7 cm ID. On a 15-mesh copper screen rested a Plexiglas® ring which supported a 15-mesh polyethylene screen which could be lifted out of the crystallizer. The drop was about 1.5 cm above this polyethylene screen. The organic liquid used was Mobil's "Sovasol"® No. 5, a highly purified naphtha of 0.80 specific gravity at −2°C. The temperature just below the drop was controlled and measured to 0.01°C.

When the organic temperature was constant within 1/100°C, a saltwater drop of a given size was injected into the crystallizer with a graduated pipette. The flow was adjusted until the drag force was equal to the gravity force, and thus the drop stayed freely suspended.

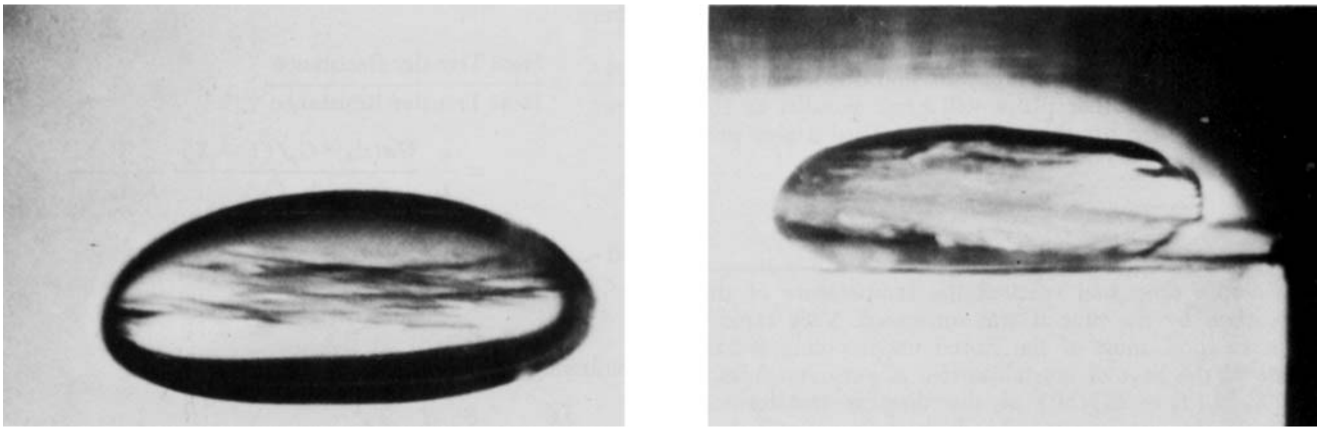
If the undercooling was larger than 2°C, all drops spontaneously nucleated within 2 min. On the other hand, if the undercooling was 0.1°C or less and the organic liquid was relatively clean, no drop ever nucleated spontaneously. In most of the runs, the undercooling was between 0.1° and 2°C, and the drop was nucleated by throwing a little frost in tank A. These tiny crystals were entrained, and 15 s later they were seen entering the crystallizer and one or more crystals impacted the drop. Other nucleation techniques were used at times. Zero time was set when the first crystals were observed in the drop. Runs were made for different ice growth durations, 1 to 80 min.

At the end of a run, a large part of the brine in the partially frozen drop was sucked off rapidly with a micropipette. No crystals passed through the micropipette. The mixture of brine and organic liquid thus obtained was separated by centrifugation. The sodium chloride concentration was determined by conductivity measurement and the conversion calculated. What was left of the frozen drop was withdrawn by lifting a polyethylene screen. More details of the equipment and procedure can be found elsewhere (Bustany, 1970).

DESCRIPTION OF ICE GROWTH

To justify the choice of the mathematical model, it is necessary to describe briefly the way ice grew in the suspended saltwater drops. The outside surface of the drop is its coldest part, and one might think that ice would first form an outside shell which would grow symmetrically inward. In saltwater drops, no initial ice shell was ever observed, and ice grew as crystals within the drop.

Drops were generally nucleated by an external polycrystalline seed impacting the drop. The early fast ice growth at $\Delta T_0 > 1°C$ was generally characterized by dendrites. Soon after, the dendrites filled in to form plates. The crystals entrained by the drop shear stresses rotated around a horizontal axis as they rapidly grew in the direction of the basal plane until the platelets reached the drop boundary or another platelet at about 9% ice; then the platelets stopped rotating, merely oscillated, and slowly thickened. This thickening should be the growth in the *c* direction. Compared to a conventional crystallizer, the system was now practically stationary, with no crystal-crystal or crystal-crystallizer collisions and low fluid shear. The crystals did not break and appeared to agglomerate in many instances. Because of the combination of favorable circumstances, the number of platelets obtained was smaller and their size larger (1 to 3 mm diameter) than those obtained in stirred or draft tube



(a) (b)

Fig. 3. Low undercooling ($\Delta T_0 = 0.5°C$) and nucleation by monocrystal. (a). Single ice plate. (b). Same drop several minutes later. 2 mm thick laminated disk.

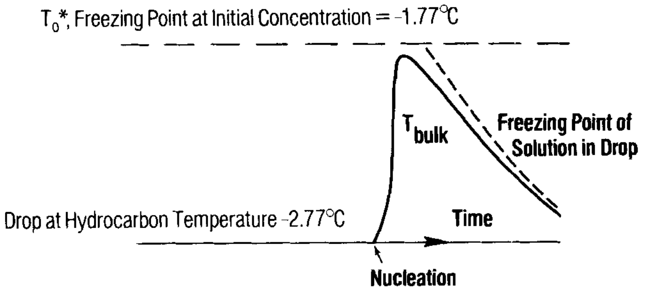


Fig. 4. Average drop temperature as function of time.

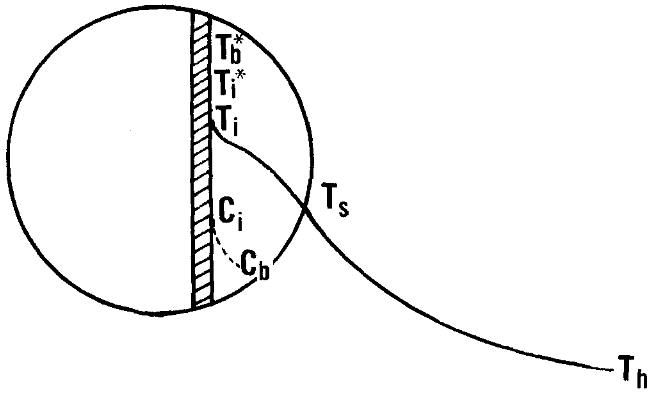


Fig. 5. Driving forces.

crystallizers with the organic phase dispersed (Campbell, 1977; Denton et al., 1973; Gibson et al., 1972; Margolis, 1969).

At 1° to 5°C initial undercooling, a typical 30% frozen drop looked like Figure 2. Several groups of parallel plates are stacked together randomly and separated by brine pools. Sea ice is made of similar stacked plates.

In a few runs at 0.2° to 5°C undercooling, the drop was nucleated by a monocrystal, and a single medial plate was observed. Several minutes later the ice structure developed into a single 1½ to 2 mm thick stack of parallel plates (laminated disk) as shown in Figure 3.

One possible mechanism to explain the parallel plates is:

1. A dendrite forms in the basal plane.
2. Soon after, it is filled in to form a plate; there is a concentration boundary layer next to the interface.
3. At some point of the plate, there is a dislocation, an imperfection of some sort, and the growth in the c direction is enhanced.
4. At a certain distance from the first crystal, where the salt concentration is not too high, the liquid is more ready to solidify, and another plane will grow parallel to the first one because it has the same c axis. Then a new protrusion occurs, then another plate, and so forth.

THEORY

Temperature Profiles and Driving Forces

The entire drop had reached the temperature of the hydrocarbon by the time it was nucleated. Very rapidly after nucleation, most of the stored undercooling is lost because of the heat of crystallization. A very small fraction $[X_1 = (T_1 - T_h)/80]$ of the drop is transformed into ice in this rapid step. The drop is then just below its freezing point (Figure 4), and the growth is controlled by the heat transfer rate.

As an ice crystal grows, salt is rejected at the ice brine interface and must diffuse through a concentration boundary layer into the bulk of solution of concentration C_b (Figure 5). The salt concentration at the interface is C_i, and the mass transfer driving force $C_i - C_b$ can be converted into a change in freezing point by multiplying by α ($\alpha = 0.59$°C/% sodium chloride):

$$\Delta T_{M.T.} = \alpha(C_i - C_b) = T_b{}^* - T_i{}^* \qquad (1)$$

Salt Diffusion Driving Force

The ice brine interface temperature T_i must be slightly below the equilibrium freezing point $T_i{}^*$ (based on C_i) so that ice can grow. $T_i{}^* - T_i$ is the intrinsic growth driving force or the interface kinetics driving force; it depends on growth rates in the a and c directions. Intrinsic growth is very rapid. At 0.1°C undercooling, the intrinsic growth rates in the a and c directions are, respectively, 3×10^{-3} and 2×10^{-4} cm/s (Sperry, 1965). From the ice formation rates of this study, $T_i{}^* - T_i$ can be shown to be less than 0.1°C. T_i was assumed equal to $T_i{}^*$ in developing the model. Further assumptions made were:

1. The ice brine interface is considered at uniform temperature T_i.
2. The change in sensible heat in the drop is insignificant compared to the latent heat of crystallization.

The overall growth of ice is controlled by the transfer of the heat of crystallization out to the organic liquid:

$$L\frac{dm}{dt} = UA\Delta T = UA_d(T_i - T_h) \qquad (2)$$

The heat transfer coefficient U is defined by the above equation where the area is arbitrarily chosen as A_d, the area of a spherical drop of the same volume.

Since the salt concentration in ice is negligible, the salt mass balance equation for a partially frozen drop is

$$X \equiv \frac{m_{ice}}{m_o} = \frac{C_b - C_o}{C_b} \qquad (3)$$

If we modify Harriott's (1967) equation for the growth of a spherical ice crystal in saltwater, the effective driving force is

$$T_i - T_h = \frac{1}{1 + \frac{\alpha}{L} U \frac{\pi(d_d)^2}{k_c A_{M.T.}} \frac{C_b}{\rho_o - C_b}} (T_b{}^* - T_h)$$

$$= \frac{1}{1 + \frac{R_{M.T.}}{R_{H.T.}}} (T_b{}^* - T_h) \qquad (4)$$

where

$$\frac{R_{M.T.}}{R_{H.T.}} \equiv \frac{\text{Mass Transfer Resistance}}{\text{Heat Transfer Resistance}}$$

$$= \frac{\alpha}{L} \frac{U\pi(d_d)^2 C_o/(1-X)}{\rho_o - \frac{C_o}{1-X}} \frac{1}{k_c A_{M.T.}} \qquad (5)$$

and

$$T_b{}^* = \frac{T_o{}^*}{1-X} \qquad (6)$$

Combining Equations (2), (4), and (6), we get

$$\frac{dX}{dt} = \frac{6}{\rho_o d_d L}\left(\frac{T_o{}^*}{1-X} - T_h\right) U \frac{1}{1 + \frac{R_{M.T.}}{R_{H.T.}}} \qquad (7)$$

The rate could be calculated from Equations (5) and (7), but U, k_c, and $A_{M.T.}$ are not known and must be obtained by testing the model with experimental data.

Table 1. Overall Heat Transfer Coefficients

10^{-2} cal/(cm^2, s, °C)

	Theoretical*		Experimental
Drop diameter mm	Stagnant drop	Circulating drop	
5.8	0.9	2.6	2.7
7.3	0.8	2.2	1.9
9.5	0.6	1.7	1.35

* Elzinga and Banchero (1959).

Heat Transfer Coefficient

Upper and lower limits of the overall heat transfer coefficient U can be estimated from available correlations of the heat transfer coefficient to circulating and stagnant drops. Elzinga and Banchero (1959) showed that

$$U_{\text{rigid drop}} = \frac{2}{3} (\psi_1)^2 \frac{K_d}{d_d^2} \tag{8}$$

where the eigenvalue ψ_1 is given in Table 3 of Elzinga and Banchero.

Similarly

$$U_{\text{circulating drop}} = 32 \frac{\lambda_1 K_d}{3 d_d} \tag{9}$$

where the eigenvalue λ_1 is given in Table 2 of Elzinga and Banchero.

U can also be calculated from the experimental data for ice formation in almost pure water drops. For pure water or very low salt concentration, Equation (7) simplifies to

$$U = \frac{dX}{dt} \frac{\rho_0 d_d L}{6\,|T_h|} \tag{10}$$

dX/dt is the slope of Figure 8. The initial slope (up to 15% ice) was used to get U from Equation (10).

Table 1 shows that the initial experimental heat transfer coefficient U is close to the theoretical coefficient for a circulating water drop. This coefficient U decreased with time by 20 to 40%. A decrease is expected as the plates reaching the drop boundary hinder the circulation inside the drop. The increase in thermal conductivity with increasing ice content only partially offsets the effect of decreasing circulation. The data for both the very dilute and the concentrated solutions were correlated satisfactorily using the experimental U's listed in Table 1 for the initial period and coefficients two-thirds as great for ice conversions beyond 9%. At approximately 9% conversion, the ice plate(s) reached the drop boundary.

Mass Transfer

In the previous section, a typical freezing drop is described as having stacks of crystals randomly dispersed in the drop, as sketched in Figure 6*a*. The diffusion of salt is allowed for by using a parallel plate model, shown in Figure 6*b*.

In this model, the drop contains a small number of equidistant stacks of plates separated by brine pools. Ice grows mainly in the space between the stacks, and the different ice fronts stay parallel. Diffusion is assumed to be the only mechanism of salt transfer, and the concentration profiles are similar in each brine pool (Figure 7).

The diffusion of salt is treated assuming a constant interface concentration C_i and a driving force $(C_i - C_b)$, where C_b is the bulk or average salt concentration in the pool between stacks of crystals. Crank's (1956) solution for diffusion in a slab with constant C_i is used to get the effective mass transfer coefficient. For moderate times

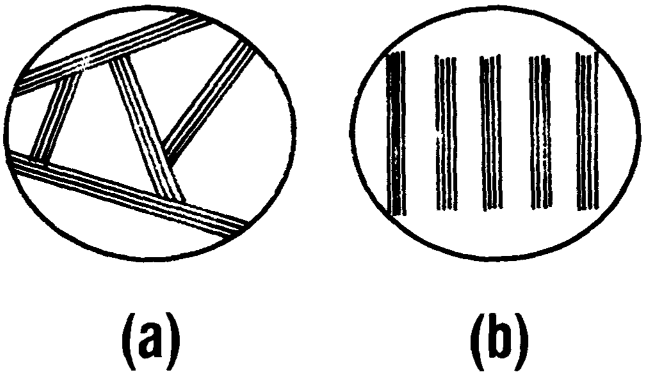


Fig. 6. Actual crystal configuration and mathematical model. (a) Actual configuration. (b). Parallel plate model.

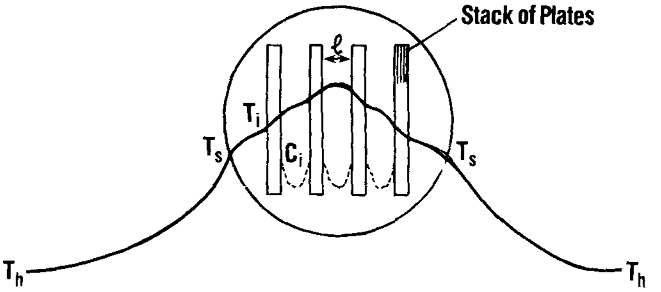


Fig. 7. Temperature and concentration profile in parallel plate model.

$$C_i - C_b \cong \frac{8}{\Pi^2} \exp\left(\frac{-\Pi^2 D t}{l^2}\right) \tag{11}$$

or

$$\frac{dC_b}{dt} \cong (C_i - C_b)\, \frac{\Pi^2 D}{l^2} \tag{12}$$

since

$$\text{salt flux} \equiv 2\,k_c(C_i - C_b) = l \frac{dc_b}{dt} \tag{13}$$

$$k_c = \frac{l}{2}\left(\frac{dC_b}{dt}\right) \frac{1}{(C_i - C_b)} \tag{14}$$

and

$$k_c = \frac{\Pi^2}{2} \frac{D}{l} \cong 5 \frac{D}{l} \tag{15}$$

In freezing drops, C_i increases with time, but the value of k_c does not change very much, judging from the solution for other unsteady-state diffusion problems. Since the stack spacing

$$l \cong \frac{d_d}{n} \tag{16}$$

$$k_c \cong 5n \frac{D}{d_d} \tag{17}$$

or Sherwood number

$$N_{Sh} \cong \frac{k_c d_d}{D} \cong 5n \tag{18}$$

Therefore, the Sherwood number is proportional to the number of plates but independent of the drop diameter. It is to be noted that this Sherwood number is for ice plates inside the drop, not for the outer surface of the drop.

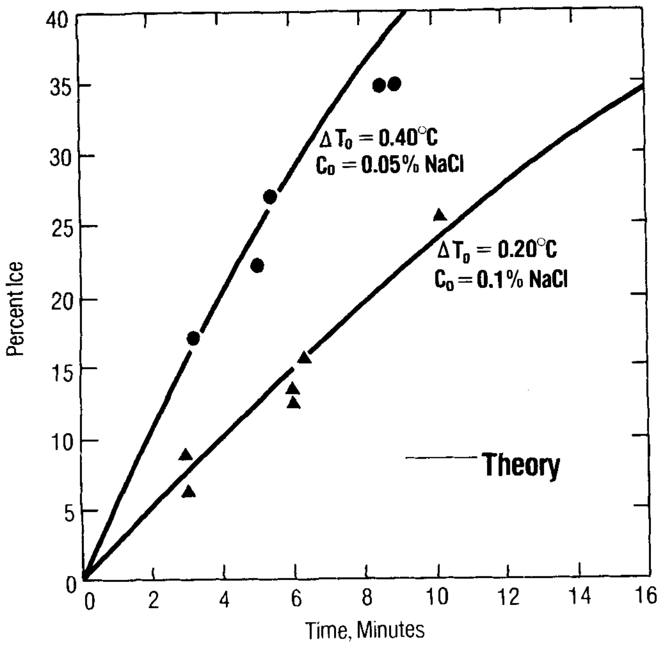


Fig. 8. Runs at low salt concentration.

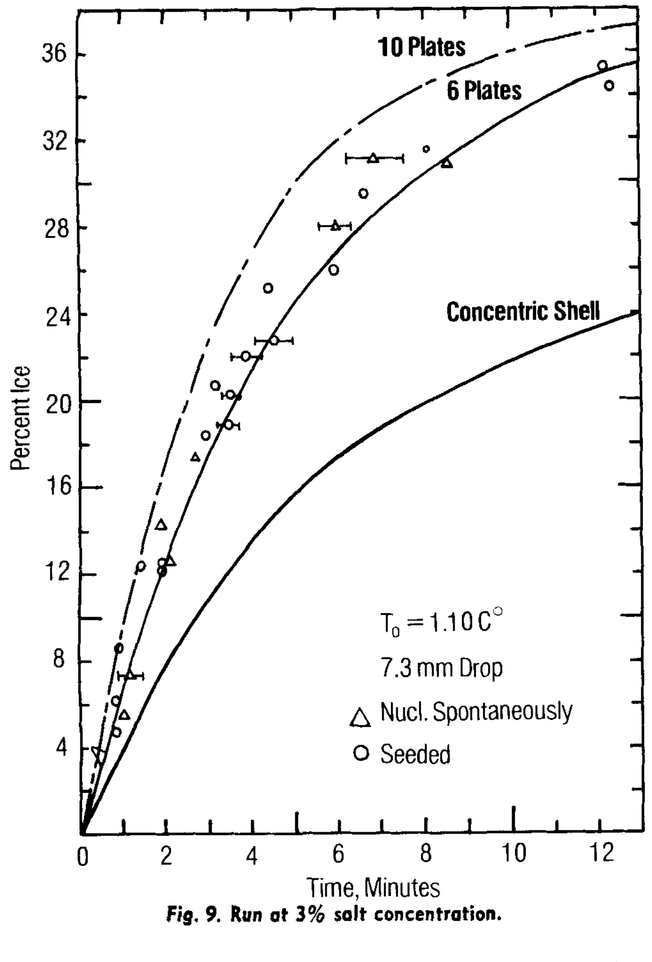


Fig. 9. Run at 3% salt concentration.

The area for mass transfer $A_{M.T.}$ depends on the plate diameter d, which should be a bit smaller than the drop equivalent diameter d_d. d was chosen to be equal to $0.8 d_d$. Therefore

$$A_{M.T.} = 2n \frac{\Pi d^2}{4} = 0.32\, n\, (\Pi d_d^2) \qquad (19)$$

TABLE 2. EFFECT OF SALT CONCENTRATION ON FREEZING RATES

7.3 mm drop

Initial NaCl concentration, wt %	0.05	1	3	4
$\frac{\text{Initial rate}}{\text{Initial undercooling}}$, $\frac{\%\ \text{ice}^*}{\text{min, °C}}$	12.5	8.8	6.2	4.8
$\frac{\text{Rate at 25\% ice}}{\text{Nominal undercooling } \Delta T_n}$ $\frac{\%\ \text{ice}}{\text{min, °C}}$	9.8	6.1	4.5	3.7

$$\Delta T_n = \frac{-0.59\, C_o}{1 - X} - T_h$$

[*] For the 7.3 mm drop, 1% ice corresponds to a little over 2 mg of ice.

If we substitute Equations (5), (17), and (19) into Equation (7), the ice growth rate can be calculated for the different runs and for different values of n. The model was tested by integrating Equation (7) and comparing the calculated conversions with the experimental values. The details of the computer algorithm can be found elsewhere (Bustany, 1970).

ICE GROWTH RATE RESULTS AND DISCUSSION

The three variables studied were; salt concentration, 0.05 to 4 wt % sodium chloride; drop size, 5.8 to 9.5 mm equivalent diameter; and initial undercooling, 0.2 to 2.0°C. Most runs were made at constant refrigerant temperature. As ice is formed, the undercooling decreases from its initial value ΔT_o to eventually reach zero at equilibrium. For example, the equilibrium conversion X^* is 38% ice if $C_o = 3$ wt % sodium chloride and $T_h = -2.87°C$:

$$X^* = 1 - \frac{0.59\, C_o}{-T_h} \qquad (20)$$

Two of the runs at very low salt concentration are shown in Figure 8. The ice growth rate for drops with low salt concentration decreases slightly with time. A typical conversion curve for 3% sodium chloride is shown in Figure 9. The decrease in rate with time is caused mainly by the change in driving force and partly by a reduction in circulation inside the drop. The initial growth rate per unit undercooling is 6.2% ice/min, °C compared to a rate of 4.5% ice/min, °C at 25% ice content. Rates for other salt concentrations are given in Table 2. It is apparent in this table that the growth rate at some nominal undercooling decreases not only with time but also with initial salt concentration.

Growth in 3 and 4% sodium chloride solutions was two to three times slower than in 0.5% sodium chloride solutions. Therefore, for these solutions, the mass transfer resistance was one to two times the heat transfer resistance. There was no evidence of a peak in growth rate of the type Vlahakis and Barduhn (1974) found for the a axis growth in 0.5 to 1% sodium chloride solutions.

The drop in rate with concentration was noticed from very early in the growth. A salt boundary layer forms very quickly, and the mass transfer resistance becomes as important as the heat transfer resistance, but it never becomes completely controlling. The six-parallel plate

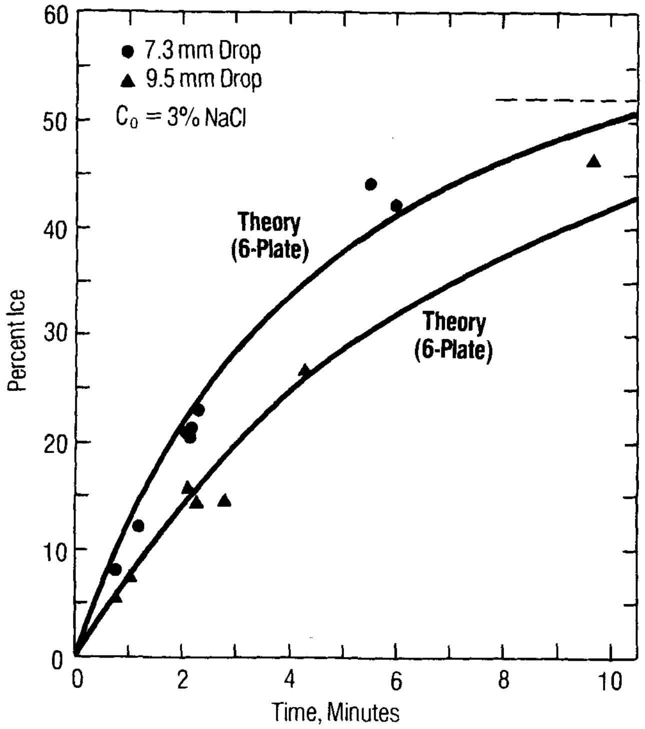


Fig. 10. Runs at high driving force ($\Delta T_0 = 2°C$).

model predicts that for $C_o = 3\%$ sodium chloride the effective driving force is half the nominal driving force at only 6% ice. For a quick calculation of the rate, one can take the effective undercooling

$$T_i - T_h \cong (T_b^* - T_h)/2.3 \qquad (21)$$

Figure 9 gives the data at undercooling of 1.10°C and 3% sodium chloride along with the curve based on the semitheoretical model. It shows that the parallel plate model with six plates correlates the data within 10%. The model with a constant and small number of plates fits the data reasonably well, even though a larger number of crystals was observed. This can be explained. From the salt diffusion standpoint, a stack of thin crystals is equivalent to one thicker crystal, and adjacent crystals can also be equivalent to a single longer crystal. A concentric shell model, where ice forms an outside shell which grows symmetrically inward, predicted growth rates that were much too low (Bustany et al., 1971).

For runs with other drop sizes and driving forces, the model gave good fits to the data, though the overall best value of n was about five for 5.8 mm drops, six for 7.3 mm drops, and seven for 9.5 mm drops. Some runs at a high initial driving force are shown in Figure 10. The freezing was quite rapid, but the six-plate model fitted the data quite well.

Figure 11 is a cross plot of the data which shows the lines of equal conversion for a given time and hydrocarbon temperature (T_h is assumed constant during a run). The lines go through both the computed (six-parallel plate model) and the measured values.

Extrapolation to Butane Continuous Phase

In order to predict the freezing rate of drops of saltwater in another liquid, butane for example, the outside heat transfer coefficient is calculated from the Boussinesq (1913) equation and the overall heat transfer coefficient U_o from Elzinga and Banchero's equation [Equation (9)]. An overall coefficient of 3.6×10^{-2} cal cm^{-2} s^{-1} (°C)$^{-1}$ was calculated for a 5.8 mm drop in butane vs. 2.6×10^{-2} cal cm^{-2} s^{-1} (°C)$^{-1}$ for the same drop in Sovasol. The coefficient is higher in butane because of lower viscosity. Figure 12 shows the results of the computer calculations of the freezing rate of saltwater drops in a butane continuous phase. The parallel plate model with five plates was assumed.

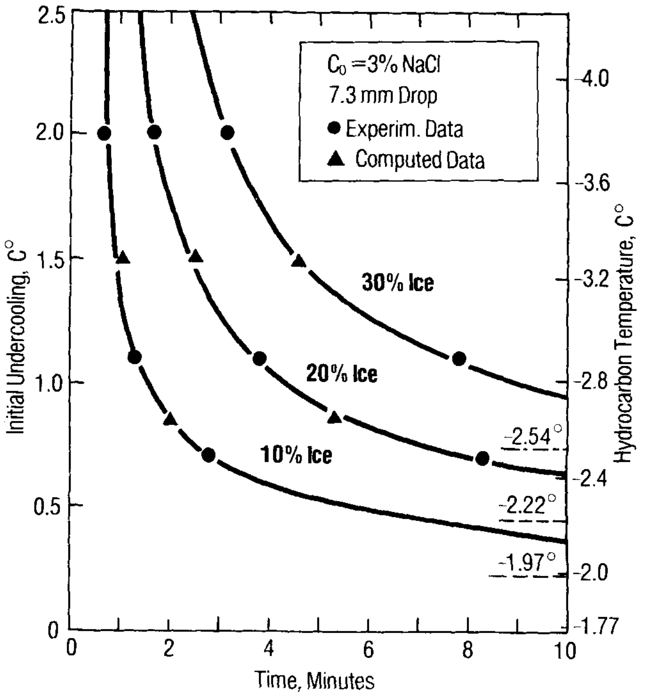


Fig. 11. Time to get 10, 20, and 30% ice.

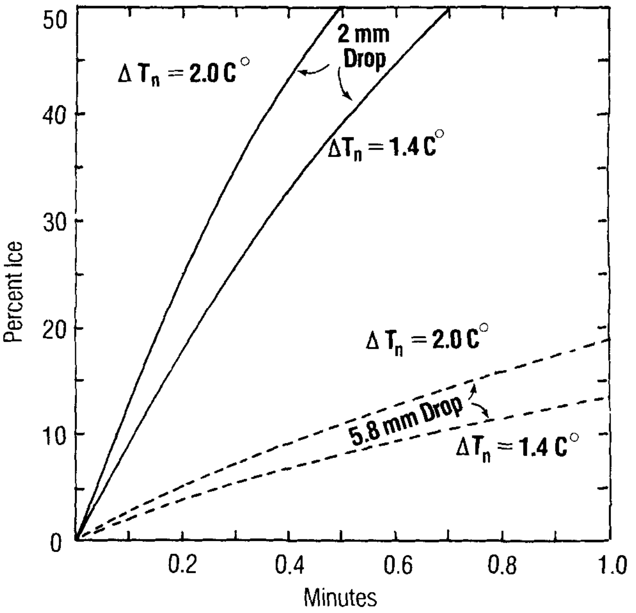


Fig. 12. Freezing of saltwater drops in butane.

If brine drops as small as 2 to 3 mm can be used as the dispersed phase, the volumetric production rate for ice can be calculated. Assume that a 2 mm drop is circulating freely at the start. The overall coefficient U_o for a 2 mm drop in butane is 6.4×10^{-2} cal cm^{-2} s^{-1} (°C)$^{-1}$, and the conversion curve is shown in Figure 12. It would take only 15 s for a 2 mm drop to reach 30% conversion at 2°C constant nominal undercooling. For a crystallizer in which dispersed seawater falls as 2 mm drops through upflowing continuous phase butane at an approximately constant nominal undercooling of 2°C, no backmixing, and one-tenth of the total crystallizer volume occupied by the drops, a production rate of

$$1.8 \times 10^{-3} \frac{\text{g ice}}{\text{cm}^3 \text{ crystallizer, s}}$$

$$\left(\text{that is, } 400 \frac{\text{lb ice}}{\text{ft}^3 \text{ crystallizer, hr}} \right)$$

is calculated. This is more than four times the production rate reported by Ganiaris et al. (1969) of Struthers and by Campbell (1977) of Avco for sparged type of crystallizers, or twice the highest production rate reported for butane dispersed crystallizers (Denton, 1973). At this production rate and with crystals of the size observed experimentally, this freezing method seems attractive for seawater conversion.

There could be some serious problems to be overcome in this freezing concept. Drop coalescence could decrease the production rate. Simultaneous nucleation of a large number of drops forming at the same time might be difficult to achieve, but perhaps it would not be necessary for satisfactory operation; for example, ice could be added to the aqueous phase before drop formation. Finally, washing of the mother liquor occluded within the stacks of crystals might be a matter of concern; preliminary experiments in our laboratory indicate that agglomerates of ice crystals can be washed essentially free of mother liquor in a moving bed. All this requires testing on a larger scale. Further study with a multidrop system is worthwhile.

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NOTATION

A = area
$A_{\mathrm{M.T.}}$ = area for mass transfer
C = salt concentration
C_o = initial salt concentration
C_i = salt concentration at ice brine interface
C_b = salt concentration of bulk brine
d = diameter
d_d = diameter of drop
D = diffusivity of salt in water
K_d = heat conductivity of drop
k_c = mass transfer coefficient
L = latent heat of crystallization
l = crystal stack spacing
m = mass
n = number of plate stacks
$R_{\mathrm{H.T.}}$ = heat transfer resistance
$R_{\mathrm{M.T.}}$ = mass transfer resistance
T = temperature, °C
T_h = temperature of hydrocarbon
t = time
U = overall heat transfer coefficient
X = fractional conversion or fraction ice in drop
ΔT = difference in temperature or temperature driving force
ΔT_n = nominal driving force $\equiv T_b^* - T_h$
ΔT_o = initial undercooling $\equiv T_o^* - T_h$
α = $-\,\delta T^*/\delta C = 0.59°\mathrm{C}/\%$ sodium chloride
ρ = density
N_{Sh} = $k_c d/D$, Sherwood number

Subscripts

b = bulk solution
d = drop
i = ice brine interface
o = initial

Superscript

$*$ = in equilibrium

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