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THE SELECTIVE MELTING OF FROZEN SOLUTIONS
BY RADIO-FREQUENCY POWER

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The Selective Melting of Frozen Solutions by Radio-Frequency Power

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Introduction

A number of selective melting and freezing techniques have been proposed for concentrating dilute solutions of heat sensitive materials because of the superior quality product produced by such processes as compared to that produced by the more conventional means of distillation, evaporation or precipitation. This is especially true if the product contains volatile flavor and aroma components in addition to nonvolatile constituents as is the case with fruit juices. The older techniques require careful control of the freezing and melting rates at all times if the desired crystal orientation and temperatures are to be obtained in the frozen solution.

The production of heat uniformly within a solid dielectric being subjected to a high frequency electric field is a phenomenon which is found useful for a variety of processes, from cooking hot dogs to the controlled drying of heat-sensitive materials. Previous applications of this unique heating process have been on uniform materials where the entire mass was to be melted or where moisture was to be removed from a uniform solid. In the present work dielectric heating has been applied to a non-uniform sample; a frozen mass of ice and salt crystals in which the salt crystals are congregated along the ice crystal boundaries. This permits selective melting along crystal boundaries, following which the solute can be removed with relatively little water. This method has obvious advantages over present methods of separating a solute from a frozen solvent. This paper reviews the previous work done on the concentration of heat sensitive materials by various freezing and melting techniques and describes a process utilizing the most desirable features of the prior art with the generation of heat inside of the frozen materials by radio-frequency power.

Review of Freezing Process Promotes Understanding of New Method

Several theories have been proposed as to the actual mechanism of the freezing process: Ostwald (Kirk),¹³ Miers,²² and Ross³⁴; however, since the equilibrium condition between frozen solvent and molten solution is of interest here and is not affected by the mechanism, this condition only will be considered.

Consider a typical system represented by Figure 1. The curve DE represents the freezing point curve and EF the solubility curve. For convenience, define a dilute solution as one in which the concentration of solution is less than the concentration of solute in the eutectic mixture, E.

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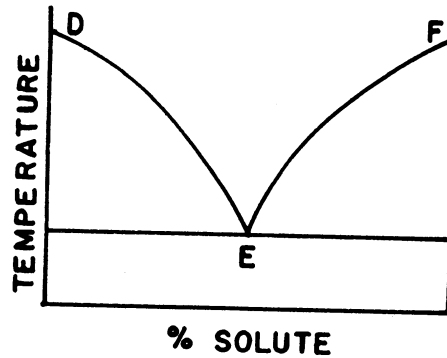


Figure 1. Typical Freezing Point - Solubility Curves

If heat is extracted from a dilute solution, its composition will remain constant until its temperature reaches the freezing point. In order for the solution to be in a state of equilibrium after further removal of heat, a portion of the solvent must solidify or freeze; thus leaving the remaining solution more concentrated. This process will continue until the eutectic or cryohydric point E is reached. Further removal of heat at this point results in the precipitation of an intimate mixture of very finely divided solvent and solute crystals.

The solute crystals freeze out from D to E in a definite crystalline form. As the quantity of solvent crystals increases, a solid mass of individual crystals is formed, each separated by a boundary region composed of solution in equilibrium with the solvent crystals.

Numerous Processes Have Been Used

Most investigators have attempted to use this type of process for concentrating heat-sensitive solutions such as fruit juices and pharmaceuticals; however, vaporization processes have generally proven cheaper, probably, according to Tressler, et al.,³⁹ because fluids are so much easier to handle than are solids and mixtures of solids and liquids.

Another serious problem which has troubled investigators using freezing processes has been the difficulties encountered in separating solvent crystals from the cold concentrated solutions, especially fruit juices and other aqueous solutions containing large quantities of sugar. These solutions are viscous and tend to cling to the crystals. Consequently, much effort has been expended toward the solution of this problem. The chief methods used to separate the crystals and the concentrated solution have been centrifugation, gravity draining, filtration, and pressing.

The maintenance of a high rate of freezing is also a serious problem in these processes. Except in certain limited applications, the refrigerant must be kept separated from the solution to be concentrated in order

to avoid loss of expensive refrigerant and product contamination. The isolation of refrigerant and solution introduces a static heat transfer surface which is subject to corrosion and ice formation on the surface, both of which drastically reduce the heat transfer coefficient. The problem of ice formation on the heat transfer surface has been met by freezing in such a manner that the water freezes out as free crystals in the bulk of the solution, or by removing the ice as fast as it is formed. The former is accomplished by close control over freezing conditions, and the latter by scrapers, flexible drums, etc.

The major difficulties encountered in any process for evaporation of the solvent from a heat-sensitive solution in general, and food juices in particular, have been the loss of volatile constituents other than solvent from the solution and maintenance of a high evaporation rate at low temperatures.

The problem of loss of volatile constituents has been attacked in several ways. One method currently used by several plants concentrating citrus juices consists of evaporating the juice beyond the desired concentration and diluting this concentrate with raw juice to obtain the desired concentration, McDowell, et al.¹⁹ The raw juice supplies sufficient amounts of the volatile materials lost during evaporation to produce acceptable flavor and aroma in the finished product.

In another scheme that has been used, the volatile constituents and a minimum quantity of water are evaporated in the first effect of a multiple effect evaporator. A certain amount of condensate from the first effect is then added to the concentrate leaving the last effect.

Attempts have also been made to utilize the economy of evaporation processes and the better quality of freezing processes by blending the concentrates of both to make the final product, Sperti.³⁸

Attempts to solve the problem of maintaining a high rate of vaporization at low temperatures have generally followed one or more of several methods:

- 1) Utilization of high-velocity flow over a heated surface to keep to a minimum the time of exposure to the heated surface and to raise the heat transfer coefficient to as high a value as possible.
- 2) Vaporization under high vacuum conditions to reduce the boiling point.
- 3) Utilization of radio-frequency power as the source of heat in order to keep temperature gradients to a minimum by generating the heat within the solution.

- 4) Means to obtain as great an evaporation and heat transfer area as possible.

Many Partial Freezing Processes Have Been Proposed

Processes for concentrating solutions by freezing are readily classified according to how the solution is frozen. For example: partially, completely, or as a continuously removed film on a chilled surface. Since most of the previous work has been done with partially frozen solutions, these will be considered first. These processes freeze a definite quantity of the solution and separate the resulting solvent crystals from the concentrate, generally by centrifuging. Depending upon conditions existing during the freezing process, the frozen solvent will take one of three different forms.

The first form, which is the most desirable from the standpoint of recovery of concentrate, is that of individual crystals floating on the surface of the concentrate. These crystals are easily skimmed off and centrifuged for maximum recovery of concentrate.

The principle processes utilizing this general method of attack are those of Gürber,¹⁰ Schuftan and Ranke,³⁶ Escher-Wyss Maschinenfabriken A.G.,⁸ and Cunningham as described by Olive.³²

The principle problems associated with this method of operating are the close control of the freezing temperature, low rate of heat removal, and the separation of the last fraction of the highly concentrated solution from the remaining ice crystals.

Probably the most effective method utilizing this method is that of Cunningham,³² who developed a countercurrent crystallizer from which the ice crystals are removed from the apparatus at the point of introduction of the dilute feed stock.

In the second type, the solvent crystals are distributed throughout the entire solution. The frozen mass appears to be a slush. This structure is more difficult to drain completely than the first, but by special techniques it can give fairly satisfactory results. This type of process is exemplified by those of Gore,⁹ Weber,⁴⁰ Morris,²⁵ Krause,^{15,5,3,25,39} and Schuftan.³⁵

The most successful of these appears to have been Krause and Schuftan. Krause took advantage of the fact that ice crystals tend to form as long needles oriented perpendicular to the freezing surface. He froze his solutions in a deep cylindrical vessel, fitted with a large concentric core. Thus the major area of the vessel is represented by the sides so that when the frozen solution was placed intact in a centrifuge,

a maximum number of crystals were oriented parallel to the flow of concentrate from the centrifuge.

Schuftan froze his solutions in smaller vessels and stacked the resulting blocks of frozen solution into the centrifuge basket so as to obtain the same effect, but at a much higher freezing rate.

In the third type, the solvent freezes as a clear solid block, generally containing some inclusions of concentrate which will not drain. The principle difficulty of this form of ice structure is that it forms on the heat transfer surface. When an appreciable thickness forms, the freezing rate is reduced to a low value. Except for inclusions of concentrate in the block of frozen solvent, the separation of concentrate and ice is readily accomplished. Examples of this type of process are those of Irish as reported by Tressler, et al.,³⁹ Johnson,¹² Whitney,⁴¹ and the conventional method of making ice on a commercial scale.

Complete Freezing Processes Have Also Been Used

Although refrigeration requirements are lower in a process in which the solution is only partially frozen, processes in which the solutions are entirely frozen require less careful control of freezing conditions. In common with bulk freezing processes in general, the heat transfer coefficients are poor.

One method of removing the concentrate from the completely frozen mass is to warm the frozen solution slightly above the eutectic temperature and remove the resulting concentrate from the remaining ice crystals by centrifuging or draining. Among the processes using this principle are those of Monti,²³ Burkhart,⁷ Noyes,^{28,29,30} Schwab and Wichers.³⁷ This type of process is characterized by very low production rates caused by the length of time required to heat the frozen mass to a uniform temperature without using excessive temperature gradients.

In a second type process, using completely frozen solutions, the concentrate is removed from between the solvent crystals by squeezing the frozen solution in rolls, screw presses, etc. Both Krause,^{16,17} and Mantle²¹ have reported recovery of about 99 percent of the concentrate.

Film Freezing Methods Increase Freezing Rates

While film freezing methods increase the rate of freezing markedly, they present other problems of their own. Bilham³ states that the separation of concentrate and solvent crystals from film-frozen solutions is much more difficult than from the frozen solutions produced by other freezing methods. In this type of process, the frozen solution is removed from the freezing surface by rotating a breezing drum past doctor knives or by

rotating scrapers inside of stationary drums. The former presents the difficulty of rotating refrigerant seals while producing a dry, easy to handle frozen solution while the latter produces a wet, hard to handle frozen solution. The processes of Monte,²⁴ and Malcolm²⁰ represent the former, while those of Johnson,¹² Heyman,¹¹ and Badger¹ represent the latter. All of these processes used centrifuges to separate the concentrate and solvent crystals.

Radio-Frequency Power Has Been Used to Concentrate Frozen Solutions

Radio-frequency power has been used to obtain even heating throughout solutions during evaporation of solvent, Brown, et al.,⁶ sublimation of solvent from frozen solutions, Bradbury,⁴ Nyrop,³¹ and Palmer.³³ Sperti³⁸ classed radio-frequency power as only another means along with steam, hot air, etc. for bringing his frozen solutions to a temperature slightly above their eutectic temperature without excessive temperature gradients.

Radio-Frequency Power is Preferentially Absorbed by the Crystal Boundary Material

Consider a unit cube of frozen solution of side length, t_0 , and volume, V_0 , located within a larger section of frozen solution so that edge effects are not present. The electrodes are located above and below the cube.

For the sake of simplicity assume that the cube of frozen solution is composed of cubic ice crystals of uniform dimensions, t_1/n and that the crystals are distributed in a uniform manner throughout the cube of frozen solution, each crystal separated from all other crystals by a distance, t_2/n_1 comprising the crystal boundary phase as shown in Figure 2a.

If n is the number of crystals along an edge of the unit cube, the total distance along this dimension occupied by the crystals and crystal boundary are t_1 and t_2 respectively.

Figure 2b assumes that all of the small crystals have been combined into one large cubical crystal located in one corner of the unit cube of material as illustrated by region I. The boundary material in planes perpendicular to the electrodes is considered as region III and the remaining portion in planes parallel to the electrodes is considered as region II.

This procedure yields a greatly simplified model of the system under consideration. This treatment permits each region to be considered separately and the separate results to be combined to give the final result. It is recognized that this is not an exact treatment of the problem, nevertheless the approximation is good enough to show the effect of the variables on the ratio of the power dissipated in the crystals to that dissipated in the crystal boundary.

The power absorbed in a right angled parallelogram is

$$P_o = E_o^2 a_o \frac{A_o}{t_o} \quad (1)$$

Combining the dimensions of the various regions and equation (1)

$$P_I = P_1 = E_1^2 a_1 x t_o \quad (2)$$

$$P_{II} = \frac{E_2^2 a_2 x^2 t_o}{(1-x)} \quad (3)$$

$$P_{III} = E_o^2 a_2 t_o (1-x)^2 \quad (4)$$

$$P_2 = P_{II} + P_{III} \quad (5)$$

$$P_o = P_1 + P_2 \quad (6)$$

The ratio of the power dissipated in the crystal, P_1 , to that in the total P_o is then

$$\frac{P_1}{P_o} = \frac{1}{1 + \left(\frac{E_2}{E_1}\right)^2 \left(\frac{x}{1-x}\right) \left(\frac{a_2}{a_1}\right) + \left(\frac{E_o}{E_1}\right)^2 \left(\frac{a_2}{a_1}\right) \left(\frac{1-x^2}{x}\right)} \quad (7)$$

Table I gives the data obtained by Maibaum¹⁸ for the dielectric constant and conductivity of potassium chloride solutions at 103 megacycles and 20°C. These values will not be correct for temperatures in the vicinity of -10°C but the order of magnitude should be similar.

TABLE I. CONDUCTIVITIES AND DIELECTRIC CONSTANTS OF POTASSIUM CHLORIDE SOLUTIONS AT 20°C AND 3.1 METERS WAVELENGTH¹⁸

Concentration gms/100 ml H ₂ O	Wavelength meters	Dielectric Constant k	Conductivity a	
			$\frac{\text{mho}}{\text{cm}}$	$\cdot 10^2$
0.74	3.10	91	1.38	
1.48	3.10	137	2.72	
3.7	3.10	175	6.63	
7.4	3.10	240	10.4	
14.8	3.12	450	18.0	
22.2	3.11	860	28.3	

Murphy and Morgan²⁶ give a value of 2 for the dielectric constant of pure ice above 100 kilocycles between the temperatures of 0 and -94°C. They give the conductivity of pure ice above 50 kilocycles at -10°C as $1.7 \times 10^{-7} \frac{\text{mho}}{\text{cm}}$.²⁷

As indicated previously, the concentration of the solution comprising the crystal boundary is determined by the temperature of the frozen mass if C_2 and C_0 are the concentrations in the boundary phase and original solution respectively, and none of the solute is contained in the solvent crystals.

$$C_0 V_0 = C_2 V_2 \quad (8)$$

$$x = \left[1 - \frac{1}{C_2/C_0} \right]^{1/3} \quad (9)$$

Table II gives values of x computed by equation (9) assuming $C_2 = 23$ gms/100 ml solvent.

A summary of the system constants of a potassium chloride solution frozen to -10°C is as follows:

$$C_0 = 1 \text{ gm/100 ml solution}$$

$$C_2 = 23 \text{ gm/100 ml solution}$$

$$a_1 = 1.7 \times 10^{-7} \text{ mho/cm}$$

$$a_2 = 2.83 \times 10^{-1} \text{ mho/cm}$$

$$f = 1 \times 10 \text{ cycles/sec}$$

$$k_1 = 2$$

$$k_2 = 860$$

$$t_2/t_1 = (1 - x) = 0.015$$

Equation (7) can be simplified considerably by evaluating the magnitude of the quantities E_2/E_1 and E_0/E_1 . The impedance, Z_1 , of region I may be written as

$$\frac{1}{Z_1} = \frac{j2\pi f k_1 A_1}{t_1} + \frac{a_1 A_1}{t_1} = \frac{A_1}{t_1} (j2\pi f k_1 + a_1) \quad (10)$$

By a similar process an expression for the impedance, Z_2 , of region II may be written.

$$\frac{E_1}{E_2} = \frac{Z_1}{Z_2} = \frac{(j2\pi f k_1 + a_1) t_2}{(j2\pi f k_2 + a_2) t_1} \quad (11)$$

Evaluating equation (11) by means of the values given above $j2\pi f k_1 \gg a_1$ and $j2\pi f k_2 \gg a_2$. Therefore,

$$\frac{E_1}{E_2} = \frac{k_1 t_2}{k_2 t_1} = \frac{k_1}{k_2} \left(\frac{1-x}{x} \right) = m \left(\frac{1-x}{x} \right) \quad (12)$$

This evaluation also shows that $E_1 \gg E_2$, and therefore $E_0/E_1 \approx 1$.

Substitution of these results in equation (7) gives

$$\frac{P_1}{P_0} = \frac{1}{1 + \left(\frac{1-x}{x} \right) \frac{a_2}{a_1} \left[\frac{1 + m^2 + m^2 x}{m^2} \right]} \quad (13)$$

Noting that $m^2 = \left(\frac{860}{2} \right)^2 \gg 1$,

$$\frac{P_1}{P_0} = \frac{x}{x + (1-x^2) \frac{a_2}{a_1}} \quad (14)$$

Values of P_1/P_0 computed by means of equation (14) are given in Table II.

TABLE II. RESULTS FROM EQUATIONS (9) AND (14) FOR POTASSIUM CHLORIDE SOLUTIONS FROZEN TO -10°C .

C_0	x	P_1/P_0
0.01	0.9998	1.6×10^{-3}
0.1	0.9985	2.1×10^{-4}
1.0	0.985	2.1×10^{-5}
10.0	0.826	1.9×10^{-6}
20.0	0.50	8.3×10^{-7}

Thus it appears that for all practical purposes the power absorbed by the crystals, if the temperature is above the eutectic, is relatively negligible as compared to the power absorbed by the crystal boundary. This absorption of power causes the crystal boundary material to become warmed and to melt the surface of the solvent crystals. If a means for separating the liquid and solid phases is provided, considerable concentration and purification of the frozen solution should result.

Since the value of P_1 is negligibly small,

$$P_0 = P_2 = E_0^2 a_2 t_0 (1-x^2) + \frac{E_0^2 a_2 x^2 t_0}{(1-x)}, \quad (15)$$

but since E_2 and x are very small,

$$P_0 = E_0^2 a_2 t_0 (1 - x^2). \quad (16)$$

This equation indicates that for all practical purposes all of the power dissipated in the frozen solution is dissipated in the crystal boundary material lying in planes parallel to the applied electric field. Preparation of the frozen solutions for melting in such a manner that the highest possible fraction of the crystal boundary phase is parallel to the applied electric field is, therefore, very desirable. This is the same conclusion reached by Krause and his co-workers¹⁵ with regard to the orientation of the crystal boundary with respect to the centrifugal force used to effect the separation of the solution and the ice crystals. Therefore a combination of the effects of both the centrifuge and of the radio-frequency power in order to obtain the maximum efficiency is most desirable.

Feasibility of Dielectric Melting Shown by Preliminary Experiments

The preliminary experiments were carried out using clear commercial ice as the frozen solution. Blocks of ice measuring 1-1/2" x 3" x 3" were cut and placed between two 3" x 3" electrodes and 95 megacycle radio-frequency power applied. A beaker was located below the block to catch the melted portion. The block soon took on the appearance of Figure 3. This appearance is caused by the melted portion of the ice draining from the block and being replaced by air.

The block was then removed from the electrodes and crushed by squeezing. The result was a mass of individual crystals from the original block as shown in Figure 4.

The remaining crystals were drained on a screen, placed in a beaker and allowed to melt. A sample of the original ice was also melted

to serve as a control. When all three samples--original ice, melt, and residual crystals had melted and reached room temperature, their relative electrical resistivities were measured. Several similar experiments gave results similar to those given in Table III.

TABLE III. DATA FROM PRELIMINARY EXPERIMENTS

Sample	Approximate Volume Milliliters	Resistance ohms
Original Ice		30,000
Melt	60	18,000
Residue	400	60,000

Since the resistance varies inversely to the solute content, the above results indicate that a considerable concentration resulted. Accordingly equipment was constructed to permit further study of the process.

A Centrifuge was Constructed to Separate Concentrate

As mentioned earlier a review of the literature on concentration of solutions by freezing methods indicated that the chief problem to be solved would be that of separation of the liquid and solid phases of the frozen and partially melted solution.

Consideration of earlier attempts to use centrifuges for separating the liquid and solid phases indicated that a modification of the method of Krause and his co-workers¹⁵ discussed earlier, was the most promising. Accordingly, an underdriven basket type centrifuge was constructed.

To obtain a uniform distribution of radio-frequency energy throughout the ice mass, the arrangement of the material between the electrodes must be uniform, or specially shaped electrodes must be used. Since the ice mass was to be shaped into a hollow cylinder, the logical method of applying the radio-frequency power appeared to be to place the "hot" electrode inside the hollow core of the cylinder of ice and to utilize the basket as the outside grounded electrode.

Layers of copper screen, glass fiber cloth, and copper screen were placed on the inside of the basket to reduce heat conduction from the centrifuge basket to the ice. The center electrode also gave trouble in

this respect, so it was wrapped with two layers of Fiberglas cloth, soaked with silicone resin (General Electric Company, type 9989), cured overnight in an oven at 150°C, and sanded smooth. Graphite was then rubbed on the surface, and the post copper plated. This assembly is shown in Figure 5.

Radio-frequency power was supplied to the center electrode by means of two brass brushes bearing against the end of the electrode.

The drive for the centrifuge was a 1/4 hp., 1750 rpm ball bearing motor. The motor and basket spindle were fitted with step pulleys which allowed the basket to be driven at 1165, 1750, and 2630 rpm.

A cover had to be added to the basket to prevent small pieces of frozen solution from being thrown out. This cover was a 1/8 inch thick brass disc wedged onto the top of the basket. A 1-3/4 inch hole was cut in its center to prevent shorting the center electrode to ground.

While the glass cloth was used between the two layers of screen wire in melting the bulk-frozen solutions, consistent material balances could not be obtained on the runs made on the film-frozen solutions which were carried out with considerably more accuracy. The difficulties were traced to the amount of water absorbed in the glass cloth. Therefore, all runs on the film-frozen solutions were made without the glass cloth in the basket.

Bulk Frozen Solutions were Concentrated

Although a continuous film-freezing method is the most desirable as far as realizing a high rate of freezing, the necessary equipment for such operation was not immediately available whereas the equipment required for bulk-freezing was on hand. Therefore, the solutions shown on Figure 8 were frozen and selectively melted according to the following procedure.

The potassium permanganate solutions were prepared according to the procedure given by Kolthoff and Sandell¹⁴ for preparing standard solutions. The concentrations were measured by means of a colorimeter. Eight hundred milliliters of these solutions were placed in one liter Pyrex beakers previously cleaned with chromic acid cleaning solution. A 1-1/4" glass core was then centered in the beaker. The entire assembly was then frozen at -8°C to -9°C in a refrigerated water-isopropanol bath. The frozen mass was removed from the beaker by immersing the beaker in lukewarm water. The hollow cylinder of ice was then placed in the centrifuge and split in quarters to keep the centrifuge balanced. The centrifuge was then connected to the output of the radio-frequency heater.

The centrifuge was started and run at 1165 rpm throughout the experiment. Any liquid draining from the frozen mass before the radio-frequency power was turned on was collected as the first sample. The

radio-frequency power was turned on and the centrifuge tuning adjusted for a maximum indication of the plate current meter.

The melt was collected in 15-25 milliliter portions in 18 x 150 mm Pyrex test tubes. The melting was continued until the melt showed only a trace of color or until the rate of melting fell off markedly. The remaining ice crystals were allowed to melt in a liter beaker. All solutions were then analysed with a colorimeter.

The same procedure was followed for the sodium chloride and sucrose solutions. The solutions were allowed to stand until they reached room temperature. Ten milliliter portions were then pipetted into tared 50 ml Pyrex beakers, evaporated to dryness and weighed.

Examination of Figure 6 reveals that a considerable concentration of the original solution results when the frozen solutions are treated in this manner. However, the data are not believed to be accurate enough to permit conclusions to be drawn as to the effects of various solutes and concentrations upon the efficiency of the process.

A possible cause of this is the marked concentration gradient observed quite plainly in the frozen potassium permanganate solutions and presumably present in the other frozen solutions. The frozen potassium permanganate solutions were visibly much more concentrated near the glass core than in the other parts of the solution.

Solutions were Frozen Continuously in York Flakice Machine

The only changes made on the Flakice machine were the addition of an external 25 gallon feed tank and pump to permit the freezing of the desired solutions instead of city water and the substitution of a hand-operated needle valve for the automatic expansion valve. This last change was found to be necessary in order to permit lower drum temperatures than that for which the automatic valve was set, and because the automatic valve gave trouble by sticking or freezing.

A Briquetting Die was Made to Compact Flakice

For reasons to be given later the Flakice containing the desired solutes had to be compressed into a denser mass. For this a die was constructed of such shape and size as to produce a briquet which would fit snugly in the centrifuge basket. The briquets took the form of a hollow cylinder approximately 2-1/2 inches tall. The outside diameter was approximately 3.8 inches, and the inside diameter was approximately 1.2 in. Both the inside and outside surfaces were tapered slightly to facilitate the removal of the briquet from the die.

Film-Frozen Solutions were Concentrated

The external feed tank of the York Flakice machine was filled with 17 gallons of water, sufficient solute added to produce the desired concentration and the solution thoroughly mixed by means of the feed pump. The tank of the Flakice machine was filled, and the compressor and freezing drum started. The frozen solutions were collected and stored in wooden boxes and one gallon Seal-right containers. All were kept at -18°C in a freezer storage room.

The Flakice drum was operated at 15 psig for all solutions except the 1 percent sodium chloride and 10 percent sucrose which were frozen at 10 psig and 6 psig respectively. A uniform flake containing 5 to 10 percent sodium chloride could not be obtained even at 0 psig.

The use of Flakice introduces another factor which must be considered. If the Flakice is merely dumped into the centrifuge basket, the resulting large void areas severely limit the ratio of the applied voltage, $E_0 + E_3$, to the voltage which can be developed across the frozen solution, E_0 , according to the equation of Besser and Piret.²

$$\frac{E_0 + E_3}{E_0} = \left(\frac{1.8 d_3 a 10^6}{f d_0} \right)^2 + \left[\left(\frac{k_0 d_3}{d_0} + 1 \right)^2 \right]^{1/2} \quad (17)$$

Inspection of equation (17) indicates that unless the portion of the distance between the electrodes occupied by the sample, d_0 , is much greater than that of the air gap, d_3 , practically all of the voltage will appear across the air gap. The use of loose flakes, therefore, is not practical.

The frozen solutions were kept at -18°C for at least 12 hours before being formed into briquets by means of the die and hydraulic press, both of which were kept in the freezer storage room. The pressure on the die was measured by a pressure gage connected to the hydraulic jack of the press. After the frozen solutions were briquetted, they were stored in the freezing compartment of a refrigerator at -18°C .

The running time clock of the radio-frequency power generator was set to zero and numbered, tared beakers were placed in a position under the drain of the centrifuge.

Two briquets of frozen solution were removed from the refrigerator, weighed on a triple beam balance, placed in the centrifuge, quartered to keep the basket balanced, and the cover of the basket wedged in. The center electrode of the centrifuge was connected to the radio-frequency power source and the 93 megacycle radio-frequency power turned on. The entire

assembly was then quickly tuned to resonance by means of a tuning stub, and the radio-frequency heater plate supply voltage adjusted to 2,000 volts, in necessary.

The time at which the first drop fell into the tared beakers was recorded. Eight numbered samples of approximately 25-35 milliliters were then collected in the tared beakers. The time at which the beakers were changed was recorded. After the eight samples were collected, the radio-frequency power and centrifuge were turned off, and the remaining ice crystals placed in a tared one-liter beaker and weighed. The ice crystals were then allowed to melt at room temperature and the resulting solution mixed well. A 35 milliliter sample was analysed along with the samples collected above and a sample of the original frozen solution.

The solutions were analysed by weighing the beaker and the solutions, evaporating the solutions to dryness in an oven at 100 to 105°C in the oven, after which they were placed in vacuum dessicators with controlled leaks. The dessicators were placed in the oven at 75-80°C, and a vacuum of 20 to 24 in. of mercury maintained until most of the water was removed, usually about 3 hours. The vacuum was then increased to 28 in. for another hour.

The solutions containing 0.096 percent sodium chloride in 0.96 percent sucrose were evaporated to dryness and weighed, as mentioned above, then redissolved in distilled water. The sodium chloride was then determined by titrating with silver nitrate using potassium chromate as the indicator.

Four Factors Evaluate Selective Melting

The effects of the several variables on the following factors evaluate this method of concentrating solutions.

1) Time:

The total time elapsed from the moment at which the radio-frequency power was turned on.

2) Percent of solution recovered:

The total weight of solution recovered at any time, multiplied by 100 and divided by the weight of the original charge to the centrifuge.

3) Percent of solute recovered:

The total weight of solute contained in all of the solution recovered at any time, multiplied by 100 and divided by the weight of solute in the charge to the centrifuge.

4) Concentration ratio:

The concentration of the solution which would result if all of the individual fractions of the solution recovered at any time were completely mixed, divided by the concentration of the charge to the centrifuge.

These data were plotted against both time and percent of the frozen solution recovered. Items 2, 3, and 4 were plotted against time in order to show the approximate rate at which the process occurred and, therefore, the rate at which the power was absorbed by the frozen solutions. Because of the difficulties involved in maintaining the voltage applied to the centrifuge tuning assembly constant, this type of plot is not useful for comparing the rates of melting of the runs made over a long period of time. This trouble was encountered several times in the course of this work as will be pointed out later.

When the percent of the solute recovered and concentration ratio is plotted against the percent of solution recovered, the difficulty encountered plotting against time disappears, since small changes in the voltage of the radio-frequency power merely change the rate of melting.

A few preliminary runs were made on sodium chloride solutions to determine the effect of varying the time during which the radio-frequency power was on and the effect of delaying the start of the centrifuge until some time after the radio-frequency power was turned on. None of these improved the concentration ratio or the speed of melting, so that even though a saving in power cost would result from such operation, it would needlessly complicate the operating procedure. Therefore, all subsequent runs were made with the radio-frequency power and centrifuge in operation continuously from beginning to end of each run.

During the melting of the frozen solutions, according to the procedure described previously, the following facts were observed in addition to the numerical data:

- 1) At the end of each run the space between the quarters of the briquets was greatly enlarged, probably because the centrifuge basket and the frozen solution acted as a centrifugal fan which circulated air down through the perforations, and back to the top of the basket.
- 2) The ice crystals remaining in the centrifuge basket after runs at varying centrifuge speeds were packed in a denser mass as the centrifuge speed was increased.

- 3) The solutions containing sodium chloride at -18°C could not be tuned until approximately the time the first drop of the solution was recovered. This difficulty was apparently caused by the low impedance presented to the radio-frequency transmission line by the partially frozen sodium chloride solutions, causing the centrifuge assembly to appear as a short circuit until a portion of the still fluid solution was removed from the central portion of the briquet. This effect was not noticeable during the run on the 0.84 percent sodium chloride solution cooled to -40°C .
- 4) The data often reveal inconsistencies in the first few samples of an experiment and the last sample of the experiment. Those obtained at the beginning of the experiment appear to have been caused by slight deviations and errors in starting up, tuning the load, etc. The sample obtained at the end of an experiment was often in error because of the unavoidable holdup of liquid on the centrifuge shell, particularly when the basket was run at 2630 rpm. When the centrifuge was stopped at the end of an experiment, this portion of the melt would run down into the tared beaker and be included in the last sample, thus giving a final sample of improper size and composition.

Solution Recovery Indicates Power Requirements

The curve obtained when the percent of the solution recovered is plotted against time is a nearly straight line, the slope of which slowly decreases with time. The slope is generally in the range of from 5 to 10 percent of solution recovered per minute, depending upon the conditions present. Since all of the liquid phase contained in the frozen solution cannot be recovered, the solution recovered is not the amount of the solution melted. The slope of the line, however, does give an estimate of the rate at which power is dissipated in the frozen solutions since the quantity of liquid held in the frozen solution should not vary greatly during a given experiment. If the above figures are assumed to represent the rate of melting, the power density in the frozen solutions varies from about 0.28 to 0.56 watts per gram of frozen solution.

One would not expect the centrifuge speed to affect the rate of recovery to any great extent since the rate of recovery is dependent upon the rate at which power is dissipated in the frozen solution. This in turn is dependent upon the conductivity and, therefore, upon the composition and concentration of the frozen solution.

In this respect the process behaved as expected. The results shown by Figure 7 are those obtained during the melting of a frozen solution containing 0.775 percent potassium nitrate in water. These results are quite similar to those obtained with approximately 1 percent solutions of sodium and sucrose melted at the same centrifuge speeds. The rate of melting of the potassium nitrate solutions is approximately 9 percent per minute for all runs, while the time required to recover 30 percent of the solution decreases regularly as the centrifuge speed increases from 1165 rpm to 2630 rpm from 4.5 to 2.5 minutes. Figure 7 also reveals that most of this decrease in the time required to recover 30 percent of the solution is accounted for in the time required to collect the first drop of solution. This decrease of time is to be expected since increasing the centrifuge speed increases the force on the solution between the crystals, thus reducing the time required to accumulate an excess of the solution at the periphery of the centrifuge where it is thrown off and collected in the receiver.

Briquetting pressure affects the rate of melting in much the same manner as centrifuge speed; increasing pressure having the same effect as reducing the centrifuge speed.

Typical effects of solute concentration on the selective melting of frozen solution containing the three solutes studied are shown by Figure 9 which shows the data obtained on approximately 0.1 percent, 1.0 percent, and 9.0 percent sucrose solutions. As can be seen the effects of concentration on the rates of melting are not so regular as the effects of the centrifuge speed and briquetting pressure. The rate of melting increases from the 0.1 percent to the 1 percent solutions, however, the rate of melting should increase still more for the 9 percent solutions since the value of x decreases as the concentration is increased. This may have been caused by the voltages applied to the centrifuge being different at the time the 1 percent solution and 0.1 percent and 9 percent solutions were melted. As indicated by the run numbers, 72, 47, and 48 respectively, these runs were made on different days, possibly a week or so apart, so that certain adjustments in the radio-frequency power supply may have changed, thus changing the voltage applied to the centrifuge.

Solute Recovery Indicates Efficiency of the Process

The curves which show the percent of the solute recovered, plotted against either time or percent of the solution recovered, are quite similar for all solutes and concentrations. The rate of solute recovery remains fairly constant until approximately 80 percent to 90 percent of the solute has been recovered. Typical values for the rate of solute recovery for the sodium chloride solutions, Figure 11, are: for less than 85 percent of the solute recovered, 40 percent per minute; more than 85 percent of the solute recovered, 1 percent per minute. For the potassium nitrate solutions the above values are 40 percent per minute and 1 percent per minute, and for

sucrose solutions, 30 percent per minute and 3 percent per minute, also taken from Figure 11. These figures show that the rate of solute recovery is much faster from ionic solutions than for non-ionic solutions. The rate of recovery of the solute undergoes this abrupt change at various percentages of the solute recovered within the limits indicated above. There is no orderly trend in this respect, however, and for this reason the differences are perhaps the result of experimental errors rather than any significant characteristic of the process. The time required to recover 85 percent of the solute in the above cases was two minutes for the sodium chloride and potassium nitrate solutions, and five minutes for the sucrose solution.

The percent of solute recovered varies with the percent of solution recovered in much the same manner as with time, which would be expected since the percent of solution recovered is essentially linear with time. Plotting against percent of solution recovered rather than time, however, has the advantage that the results are not affected by changes in the voltage applied to the centrifuge.

The ratios of the percent of solute recovered to the percent of solution recovered behave in the same manner as the rate of solute recovery. The change of the former, however, is not nearly so abrupt as the latter but occurs gradually between 75 to 95 percent of the solute recovered. Typical values for the ratios of the percent of solute recovered to the percent of solution recovered for 1 percent sodium chloride, potassium nitrate, and sucrose solutions respectively (from Figure 12) are 7 up to 85 percent of the solute recovered and 0.2 over 85 percent recovered; 4 up to 85 percent recovered and 0.2 over 85 percent recovered; and 3.5 up to 85 percent recovered and 0.4 over 85 percent recovered. In order to recover 85 percent of the solute, approximately 22 percent of the sodium chloride solutions, 26 percent of the potassium nitrate solutions, and 32 percent of the sucrose solutions must be recovered. These values are also from Figure 12.

In general, the rate of solute recovery is affected in much the same manner as the rate of solution recovery by centrifuge speed, and temperature. The chief effect is to change the time required to recover 85 percent of the solute without greatly affecting the rate of solute recovery. This is well illustrated by Figures 7 and 13. Figures 8 and 14 show that centrifuge speed and temperature have essentially no effect upon the relationships between the percent of solute recovered and the percent of solution recovered.

Figure 10 indicates that for sucrose concentrations of 0.1 percent, 1 percent and 10 percent, the percent of solution which must be recovered to obtain 85 percent of the solute is 20 percent, 38 percent and 42 percent respectively, with corresponding ratios of the percent of solute recovered to the percent of solution recovered of 6, 3.5 and 3. The results obtained

on potassium nitrate and sodium chloride solutions of similar concentrations while not shown here, are similar in behavior. Thus, it appears that within the limits of concentration of 0.1 percent to 10 percent, increasing the solute concentrations require that a greater portion of the total frozen solutions must be recovered in order to recover 85 percent of the solute.

Figure 15 indicates that the addition of approximately 0.1 percent sodium chloride to a 1 percent sucrose solution results in a marked decrease in the time required to recover 85 percent of the solute. The times required to recover 85 percent of the 1 percent sucrose, 0.1 percent sodium chloride and 1 percent sucrose, and 0.1 percent sodium chloride solutions are 5 minutes, 2 minutes, and 1.5 minutes respectively. The rate of melting of the mixture and of 0.1 percent sodium chloride solutions is about 50 percent per minute for each, while that of the 1 percent sucrose solution is about 35 percent per minute. Figure 16 shows that the percent of the solution which must be recovered to recover 85 percent of the solute for the 1 percent sucrose, 0.1 percent sodium chloride and 1 percent sucrose, and 0.1 percent sodium chloride solutions is 40 percent, 27 percent, and 22 percent respectively. A solution 0.1 percent sodium chloride and 1 percent sucrose resembles a 0.1 percent sodium chloride solution more than it does a 1 percent sucrose solution as far as this process is concerned.

The ratios of sucrose to sodium chloride in the various fractions of the solution recovered are at all times very nearly constant and equal to the initial value. No preferential concentration of either solute seems to occur. This is to be expected since both solutes are found together in the crystal boundary material. Small additions of ionic solutes to non-ionic solutions will considerably aid in the concentration of the non-ionic solutions.

Concentration Ratio Indicates the Maximum Concentration Attainable

The variation of concentration ratio with the percent of solution recovered followed two distinct patterns. For the type characterized by most sodium chloride solutions, Figure 12 for example, the concentration ratio of the first 5 percent of the solution recovered is about 7 or 8. This value decreases rapidly to a value of 4 by the time 20 percent of the solution is recovered, and to a value of 2 after 50 percent is recovered.

With the exception of the 0.1 percent solutions, the concentration ratios of all solutions of potassium nitrate and sucrose, Figures 12 and 10 for example, are between 2 and 3.5 after the first 5 percent of the solution has been recovered, and increase to a maximum value of 3 or 4 after between 20 to 30 percent of the solution has been recovered. When 50 percent of the solution has been recovered, the concentration ratios of all solutions are approximately 2.

All of the 0.1 percent solutions behave in a unique manner in that variation of the concentration ratio with the percent of solution recovered follows neither of the patterns described above, but combine certain features of both. As shown by run 47 of Figure 10 and run 49 of Figure 16 the concentration ratio of the first 5 percent of the 0.1 percent solutions recovered is generally between 6 and 7 instead of the 7 to 8 noted for the 1 percent sodium chloride solutions, or the 2 to 3 noted for the potassium nitrate and sucrose solutions. While following the same general trends as do the concentration ratios of the 1 percent sodium chloride solutions, the concentration ratios of the 0.1 percent solutions do not decrease as rapidly as do those of the 1 percent sodium chloride solutions.

Inspection of Figures 13 and 14, which show the results obtained on melting a 1 percent sodium chloride solution frozen to -40°C , reveals that the concentration ratio of this solution varied in a manner more nearly resembling the variation of the concentration ratios of the 0.1 percent solutions than the other 1 percent sodium chloride solutions.

Comparison of the eutectic temperatures of the three solutions, Figure 17, shows that at -18°C only the sodium chloride solutions still contain a liquid phase. At -40°C the sodium chloride solutions are also completely frozen. Thus, the major factor in determining whether or not the concentration ratio goes through a maximum, with certain exceptions, appears to be whether or not the solution is completely or only partially frozen, the former exhibiting the maximum. This is shown quite clearly by Figures 11 and 12.

The time required to reach a given value of the concentration ratio increases as the briquetting pressure is increased and the temperature, centrifuge speed and concentration decrease. These results are to be expected when the effects of these factors are considered.

The effects of the variables on the manner in which the concentration ratios vary are considered in relation to the percent of the solution recovered. However, as the percent of the solution recovered is nearly linear with time, the same considerations in general apply to the variation of the concentration ratios with time. This solution-time relationship will be assumed in the future unless otherwise stated.

Figure 8 indicates that increasing centrifuge speed increases the maximum concentration ratio obtainable by the process, the maximum value increasing from 3.2 to 3.8 as the speed is increased from 1165 rpm to 2650 rpm. This behavior is similar to that observed for the sodium chloride solutions except that instead of increasing the maximum value of the concentration ratio, the initial values of concentration ratio were

increased. The sucrose solutions, however, behaved in the reverse manner--increasing centrifuge speed decreasing the maximum concentration ratio. The reason for this behavior is not known.

The results obtained by varying the briquetting pressure are inconsistent. Their differences, however, are small (about 5 percent) and so are within the experimental error of the experiments. Thus pressure appears to have little effect on the concentration ratios obtained.

Figure 10 indicates that increasing the original concentration of the solution markedly decreases the maximum value of concentration ratio obtained for 0.11 percent, 0.96 percent and 9.4 percent sucrose solutions. Similar behavior was noted for the potassium nitrate solutions.

The results obtained on the 0.086 percent and 0.84 percent sodium chloride solutions, run 49, Figure 16, and run 41, Figure 14, respectively, show just the opposite. The concentration ratio of the first 5 percent recovered increasing from 6.4 to 7 as the concentration increased.

While more data is required to confirm the sodium chloride results it appears that for solutions frozen below their eutectic temperature, an increase in original concentration will cause the maximum concentration ratio to decrease. For solutions not frozen below their eutectic temperatures, an increase in concentration increases the concentration ratio of the first 5 percent of the solution recovered. After 30 percent of the solution has been recovered all of the ionic solutions behave alike, the concentration ratios dropping steadily from a value of 3 when 30 percent of the solution has been recovered to a value of 2 when 50 percent of the solution has been recovered. The concentration ratios of the non-ionic solutions approach 1.7 when 50 percent of the solution has been recovered.

Figure 16 shows that the addition of 0.1 percent of sodium chloride to a 1 percent sucrose solution increases the concentration ratio from 3.4 to 4.7, and at the same time decreases the percent of the solution recovered, required to obtain the maximum concentration ratio, from 12 percent to 7 percent. While the concentration ratio of the solution containing the mixture did not reach the value of the concentration ratio of 6.5 observed for the 0.1 percent sodium chloride solution, its value is considerably greater than that of the 1 percent sucrose solution. No preferential concentration of either solute occurs as mentioned earlier.

Figure 14 shows that decreasing the temperature of the frozen 1 percent sodium chloride solution to -40°C , which is below the eutectic temperature of the sodium chloride solution, -23°C (Figure 17) decreases the value of the concentration ratio, after the first 5 percent of the solution has been recovered, from about 8 to about 6.9, and changes the manner in which this value decreases as more of the solution is melted to resemble the behavior of the 0.1 percent solutions. The trend is therefore

in the direction which would be predicted from a comparison of the results obtained on potassium nitrate and sodium chloride solutions.

A comparison of the results from the selective melting of bulk and film-frozen solutions reveals that the results obtained on 0.1 percent sodium chloride solutions are about the same for both methods of freezing, Figures 6 and 16, while those of the film-frozen sucrose solutions are markedly better than those for bulk-frozen solutions, Figures 6 and 10. The observed differences between the two sucrose solutions may have been caused by the fact that the bulk-frozen solution was made up from distilled water and frozen in a clean Pyrex beaker, while the film-frozen solutions were made up with city water and frozen in the York Flakice Machine.

Since sucrose is a non-conductor of electricity, the conductivity of its solutions will probably be controlled by the conductivity of the water used in their preparation and by any impurities in the sucrose. The conductivities of sodium chloride solutions, on the other hand, are controlled by the concentration of sodium chloride; thus it appears that the freezing process does not markedly affect the results obtained.

Numerous Industrial Applications are Possible

The salient characteristics of the new process of concentrating solutions by freezing the solution substantially completely and subsequently selectively melting the frozen mass by means of radio-frequency power are as follows:

- 1) The type of freezing process used has little effect upon the process.
- 2) Either ionic or non-ionic solutions may be concentrated.
- 3) The concentration of non-ionic solutions may be speeded up and the concentration ratio increased by the addition of traces of ionic materials.
- 4) Close control of any operating conditions is not necessary to obtain satisfactory results.
- 5) Higher concentration ratios result if the temperature of the frozen solution is above the eutectic point.
- 6) Increased briquetting pressure and decreased centrifuge speed, temperature, and conductivity of the crystal boundary material slow the rate of melting.

- 7) Less than 1 percent of the original ionic solute and about 5 percent of non-ionic solutes remain in the last unmelted 50 percent of the original frozen solutions.

Heat generated by radio-frequency currents flowing in a material is much more expensive than heat obtained from condensing steam; thus the main value of this process will be in concentrating solutions of materials which are unstable when exposed to elevated temperatures. The widespread use of frozen fruit juice concentrates has intensified the search for economical means of producing these products with no sacrifice of quality. The use of this process may reduce the excessive solute losses of the older freeze concentration processes to such a point that the process could compete economically with high vacuum evaporation processes and produce a product which is admittedly superior. Obviously the percentage of the frozen solution to be melted must be determined by an economic balance involving the value of the solute, the cost of freezing and melting, and the solute concentration desired in the concentrated solution. It is also possible to take two or more separate fractions of concentrate and reprocess the more dilute fractions until desired concentration is achieved.

SYMBOLS USED

A = area of a surface perpendicular to the applied electric field in cm^2

C = concentration of solution in grams of solute per 100 ml of solution

E = potential drop across the material in volts

P = power absorbed by the material in watts

Q = weight of solute in the solution in grams

V = volume in cm^3

Z = impedance

a = conductivity in mho/cm

f = frequency in megacycles/sec

k = dielectric constant

m = k_2/k_1

n = number of ice crystals along one edge of the unit cube of frozen solution

t = thickness of material parallel to the applied electric field

x = t_1/t_0

SUBSCRIPTS

o = the unit cube taken as a single unit

1 = the solvent crystal phase

2 = the crystal boundary phase

3 = air gap

I = region I of Figure 2b

II = region II of Figure 2b

III = region III of Figure 2b

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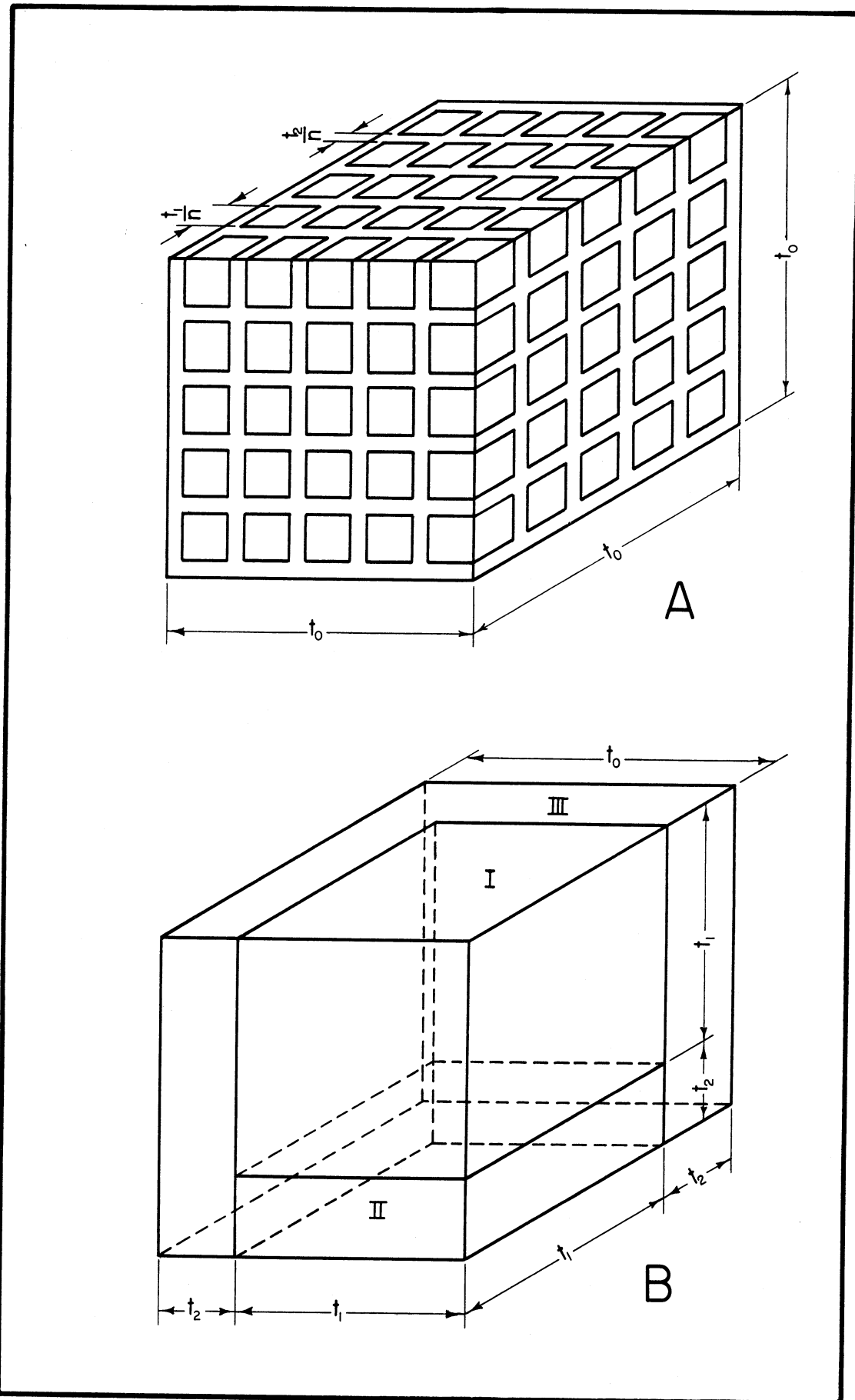


Figure 2. Idealized Arrangement of Solvent Crystals in a Frozen Solution

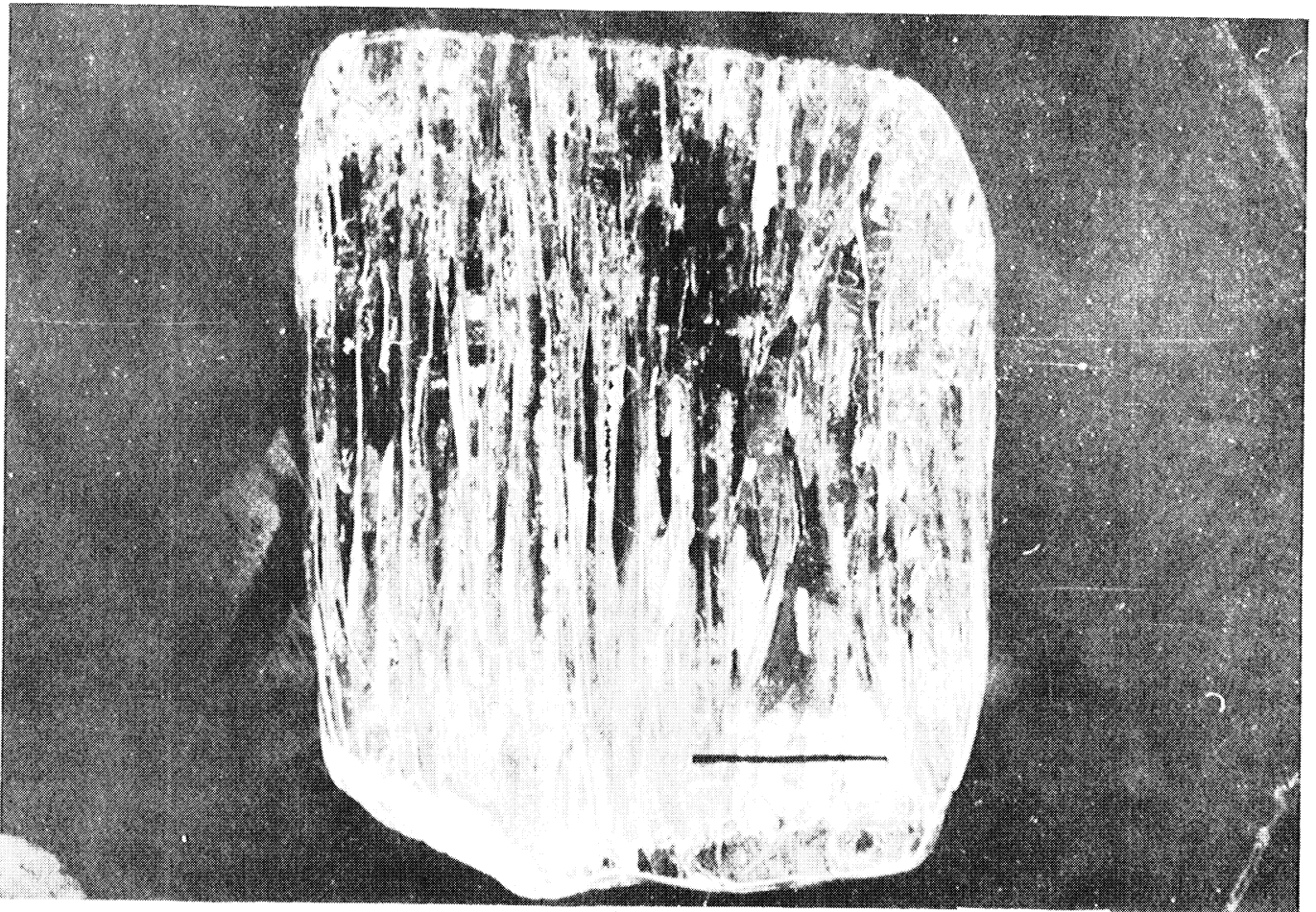
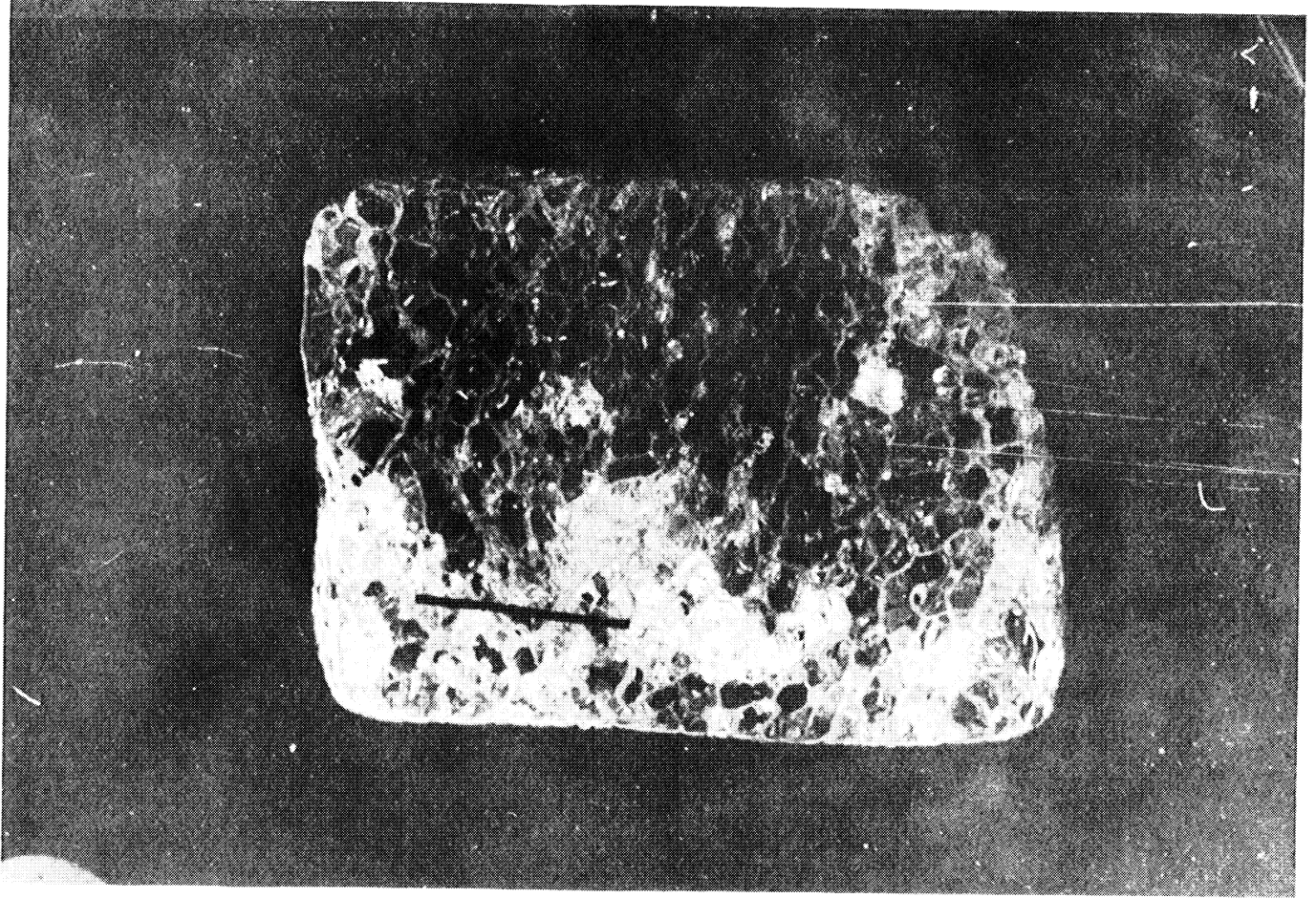


Fig. 3. Top and side views of clear commercial ice after several minutes in radio-frequency field. (Dark horizontal line = 1 inch.)



Fig. 4. Ice crystals from block of figure 3.

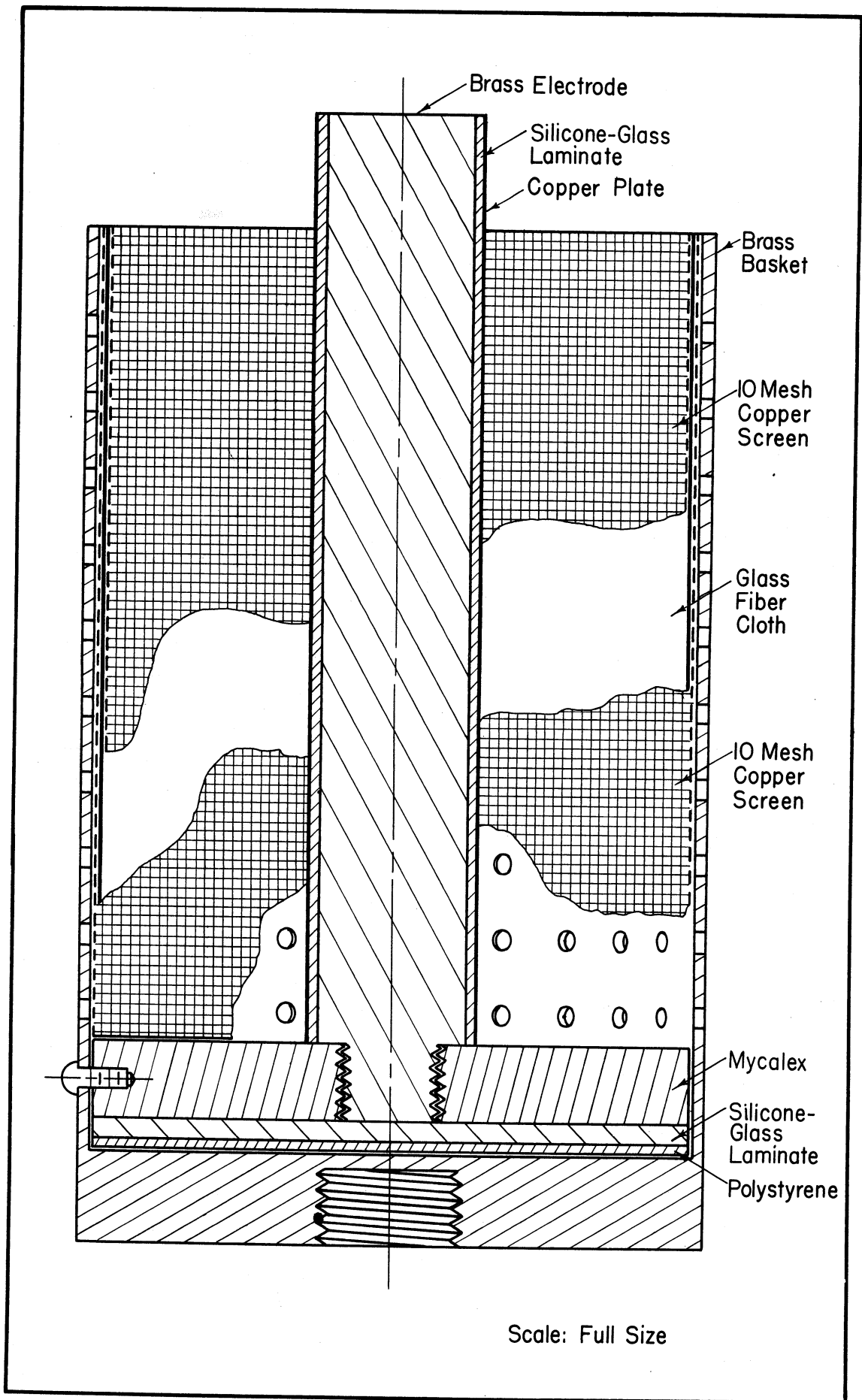


Figure 5. Cross Section of Centrifuge Basket

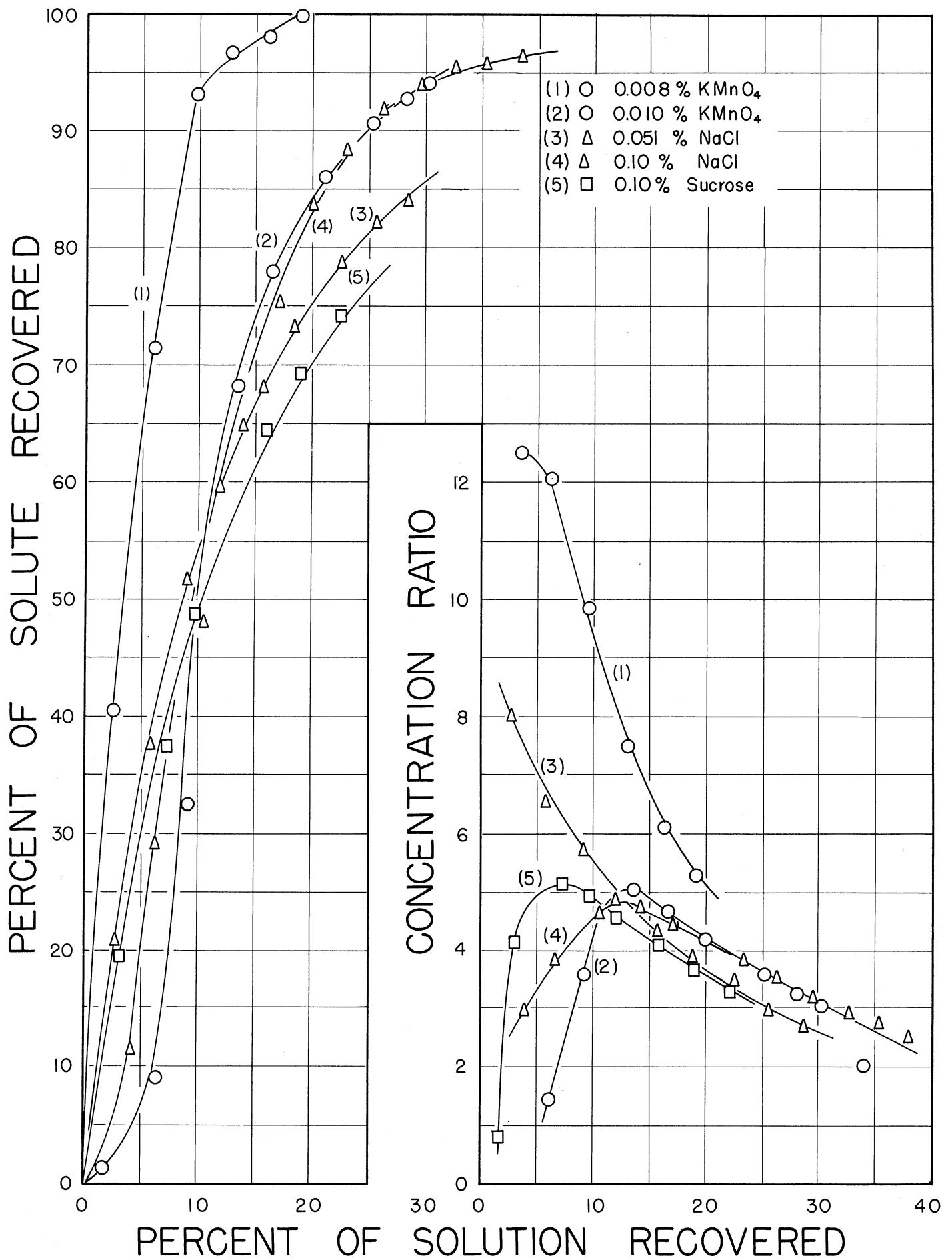


Figure 6. Results of Selective Melting of Various Bulk-Frozen Solutions

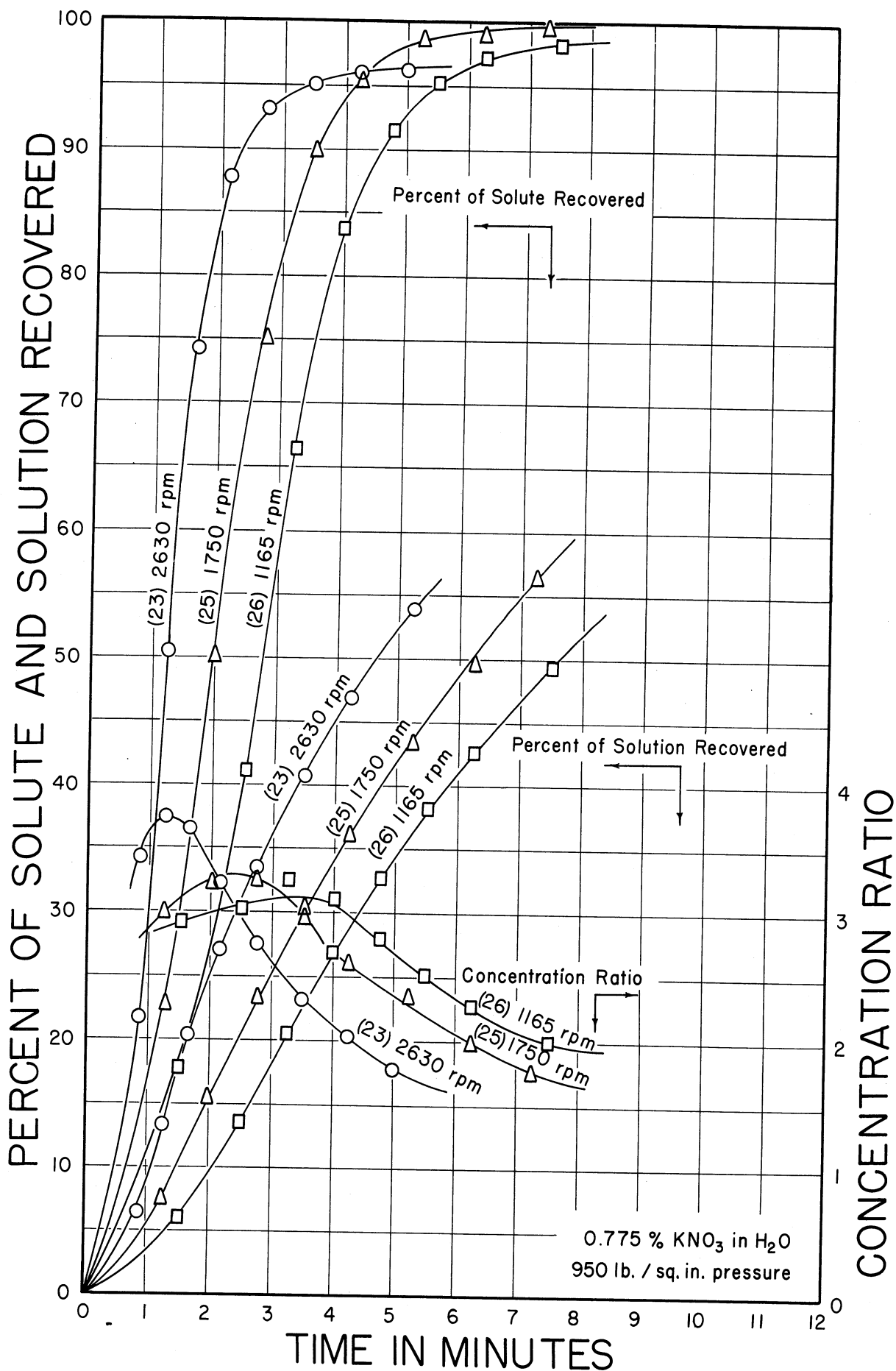


Figure 7. The Effects of Centrifuge Speed on Selective Melting as a Function of Time

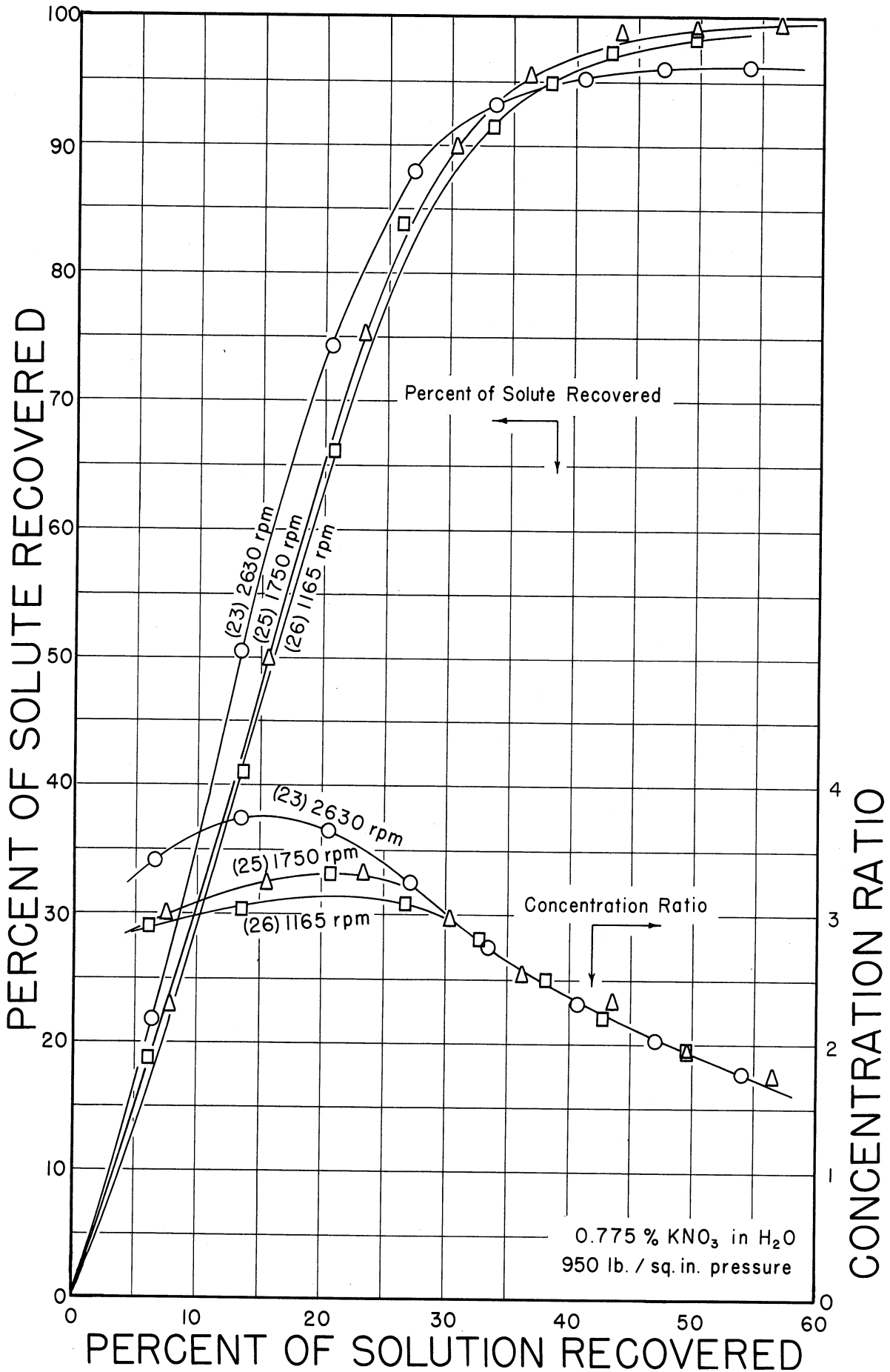


Figure 8. The Effects of Centrifuge Speed on Selective Melting as a Function of Solution Recovered

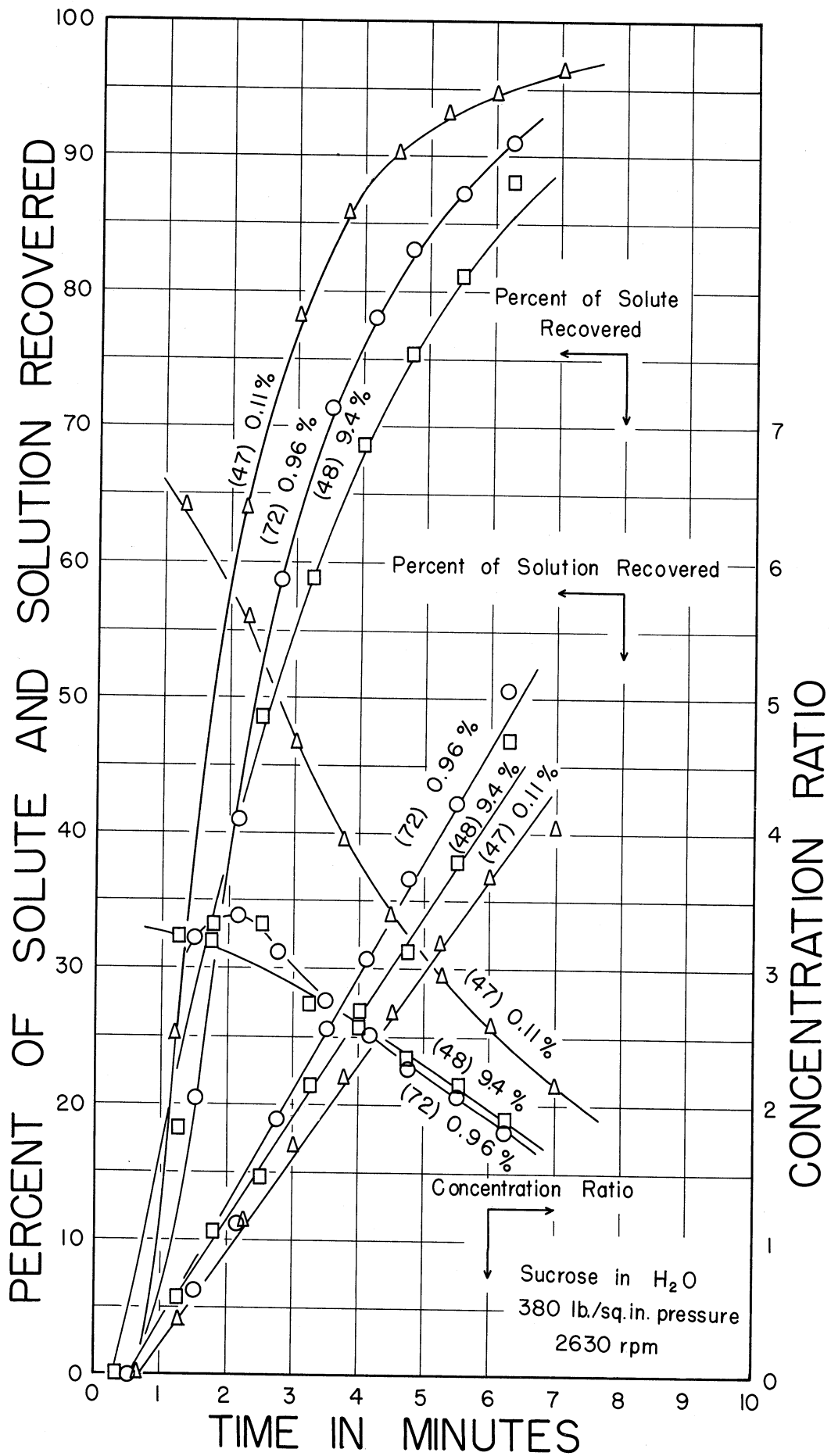


Figure 9. The Effects of Concentration on Selective Melting as a Function of Time

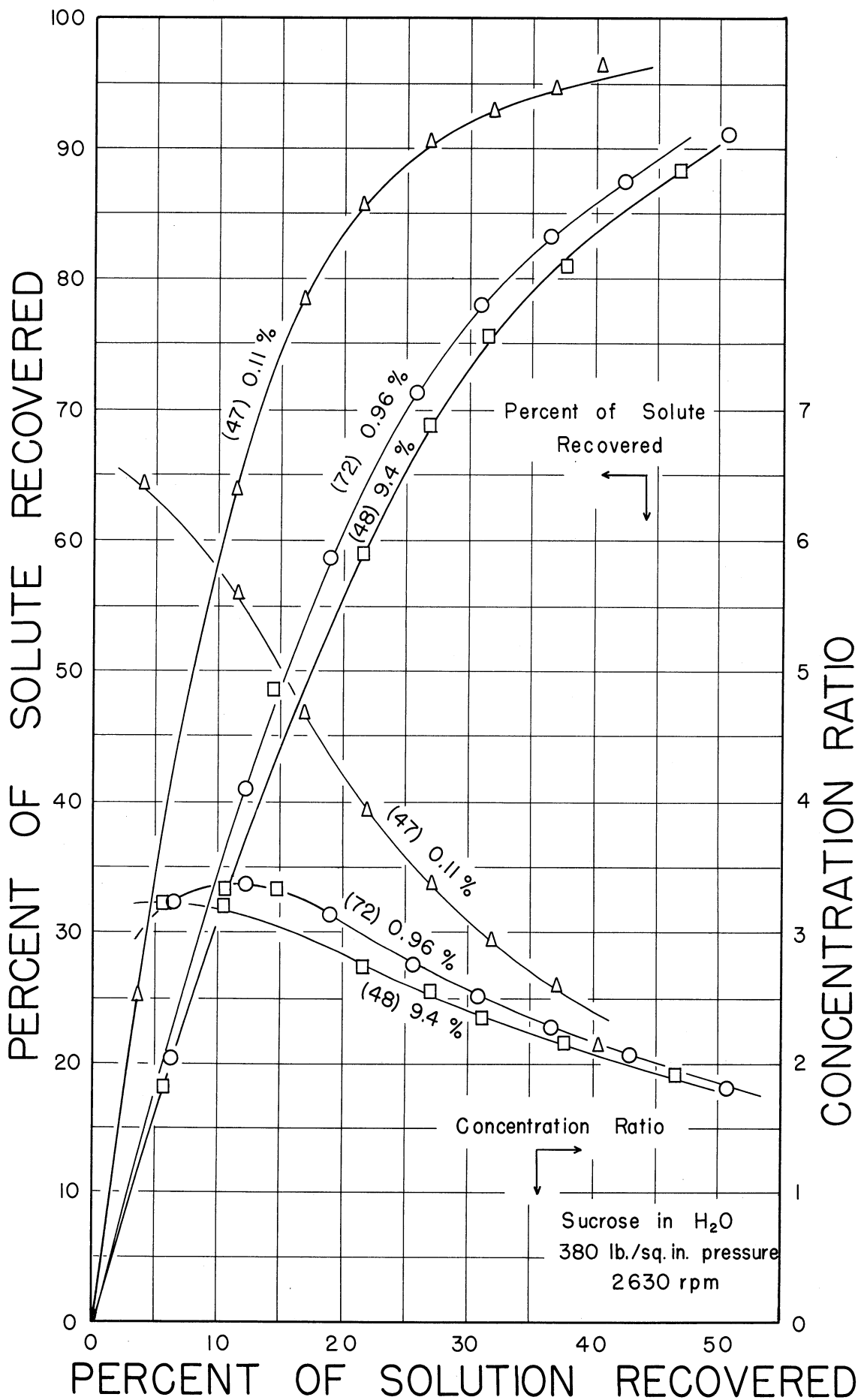


Figure 10. The Effects of Concentration on Selective Melting as a Function of Solution Recovered

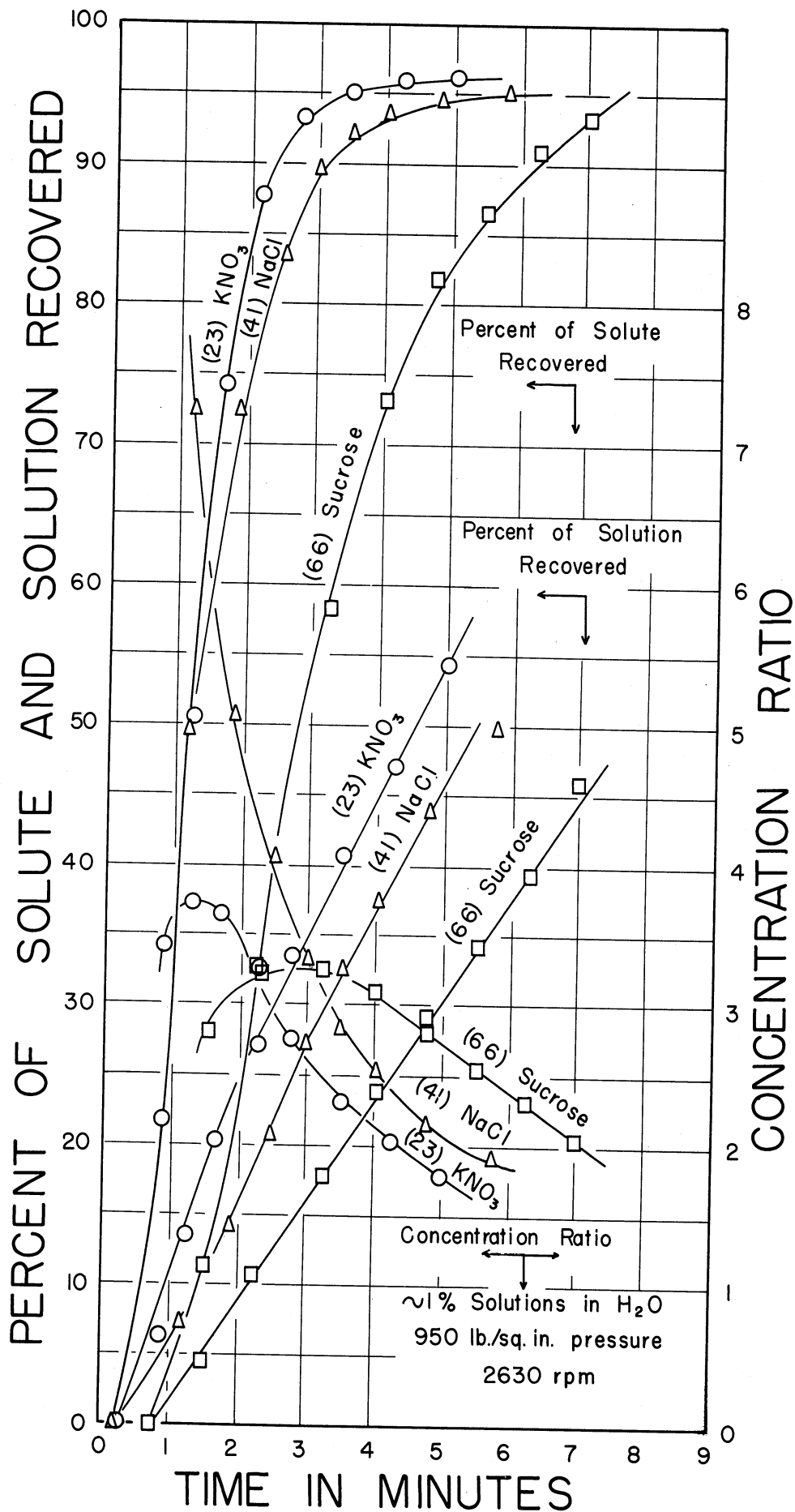


Figure 11. The Effects of Solute on Selective Melting as a Function of Time

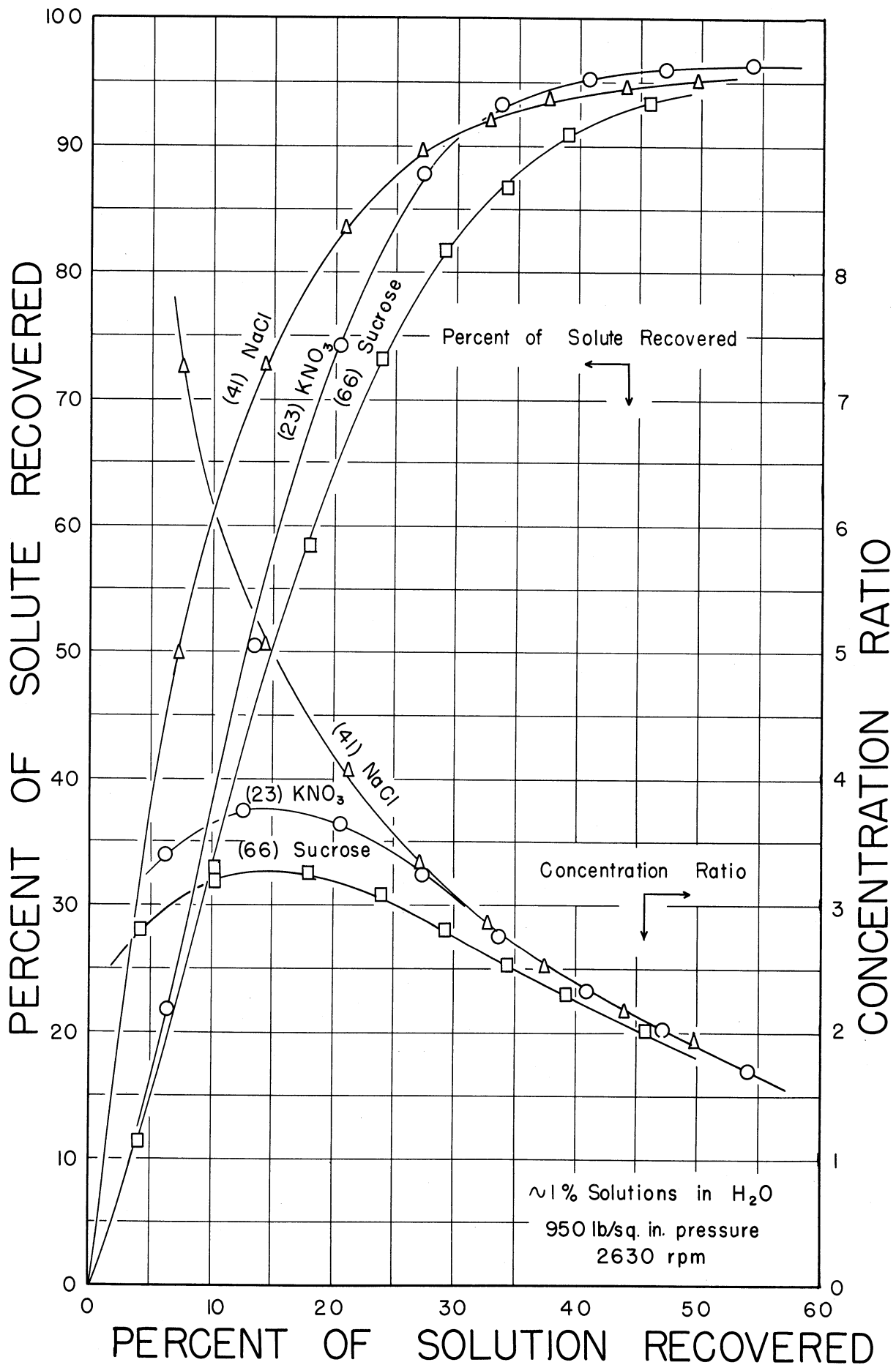


Figure 12. The Effects of Solute on Selective Melting as a Function of Solution Recovered

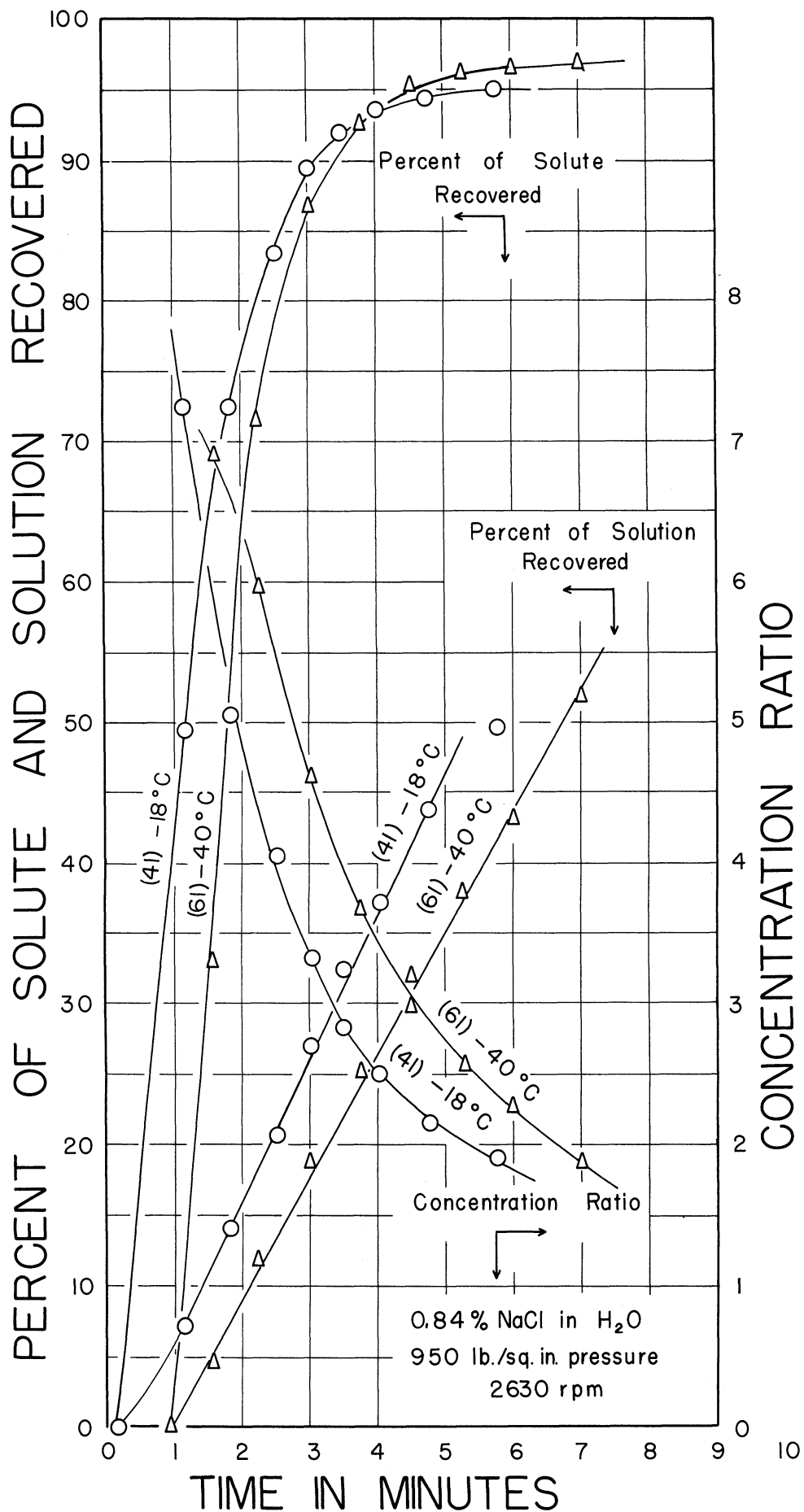


Figure 13. The Effects of Temperature on Selective Melting as a Function of Time

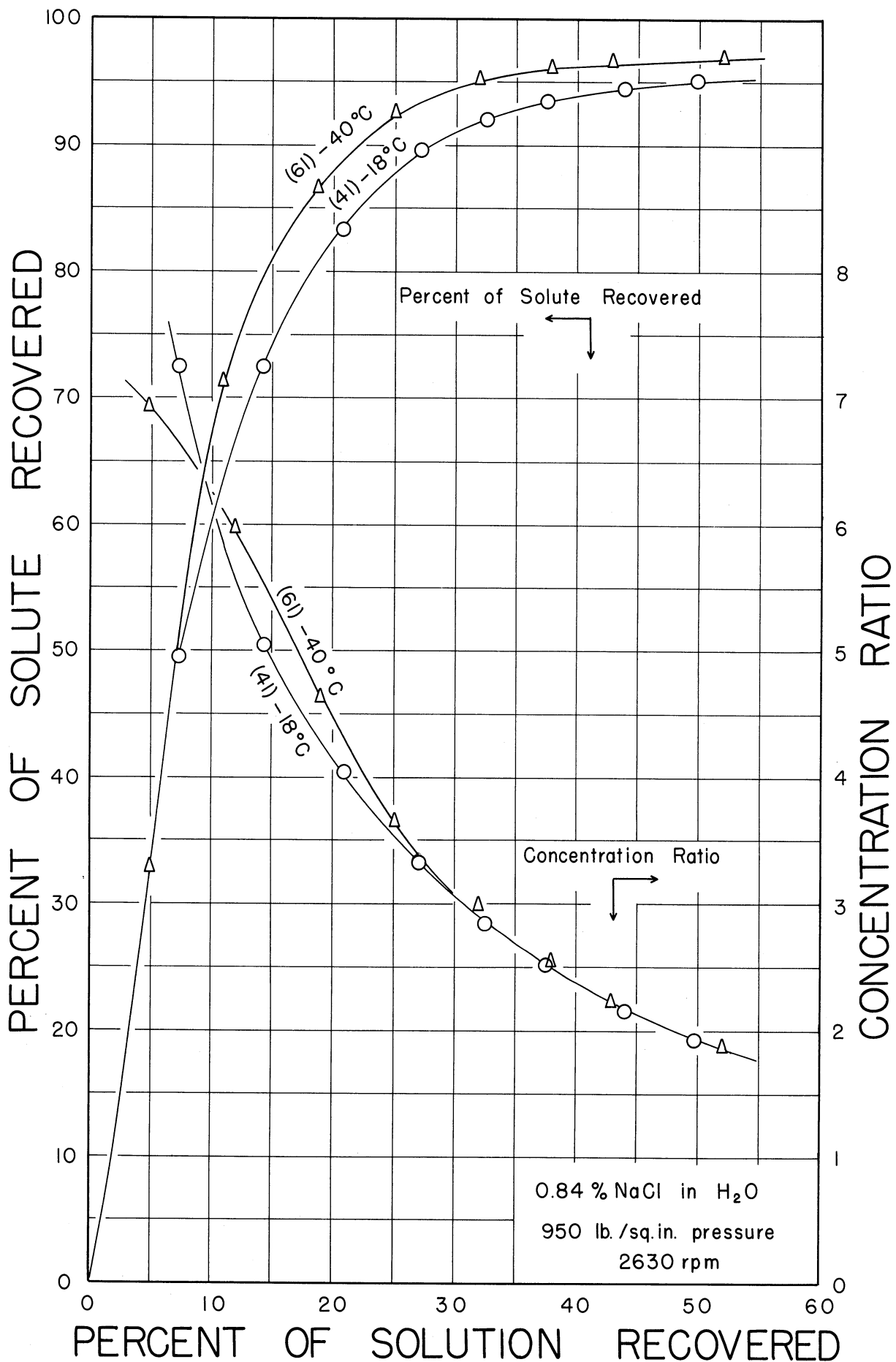


Figure 14. The Effects of Temperature on Selective Melting as a Function of Solution Recovered

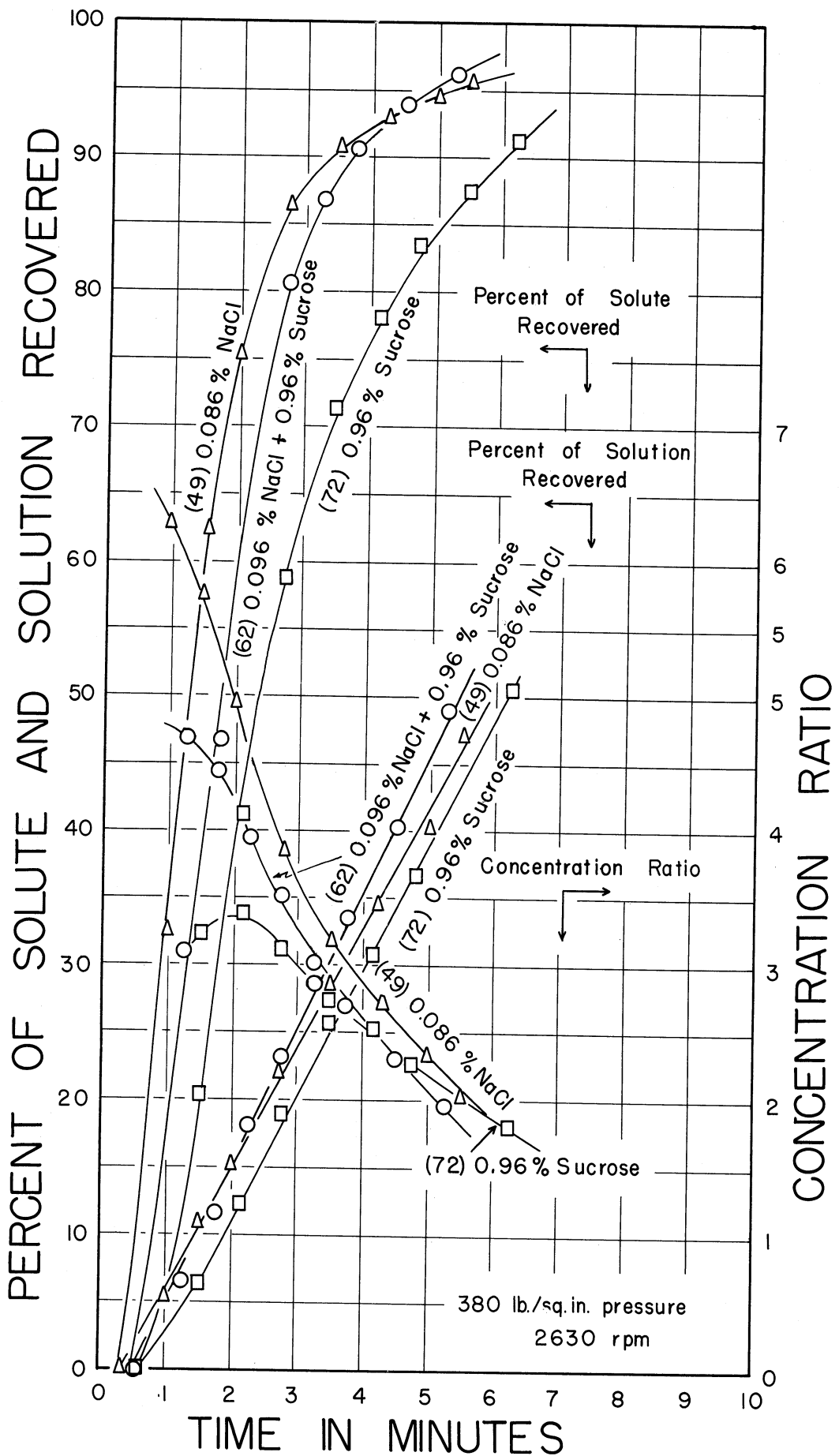


Figure 15. The Effects of a Trace of Ionic Solute in a Non-Ionic Solution as a Function of Time

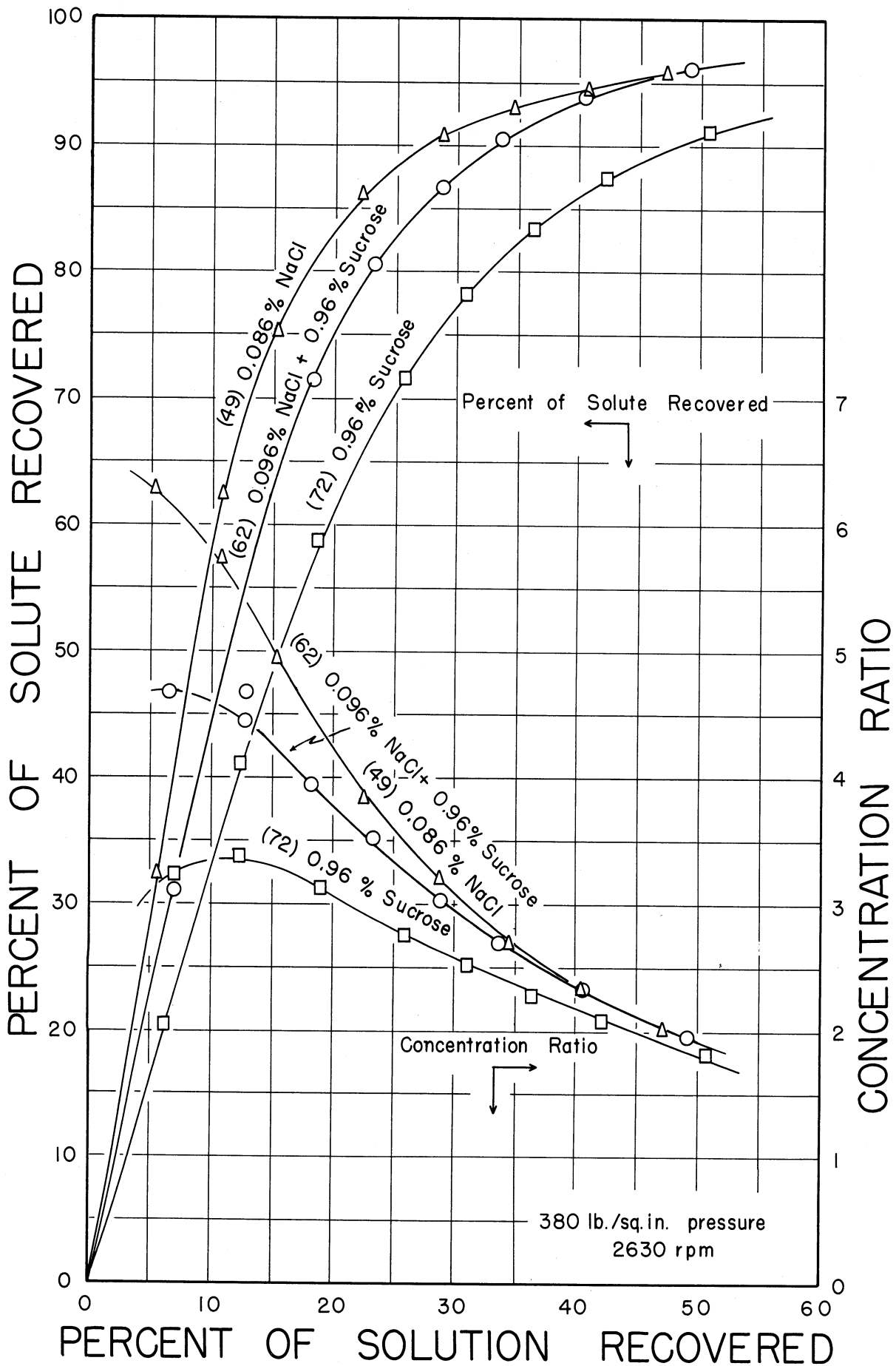


Figure 16. The Effects of a Trace of Ionic Solute in a Non-Ionic Solution as a Function of Solution Recovered

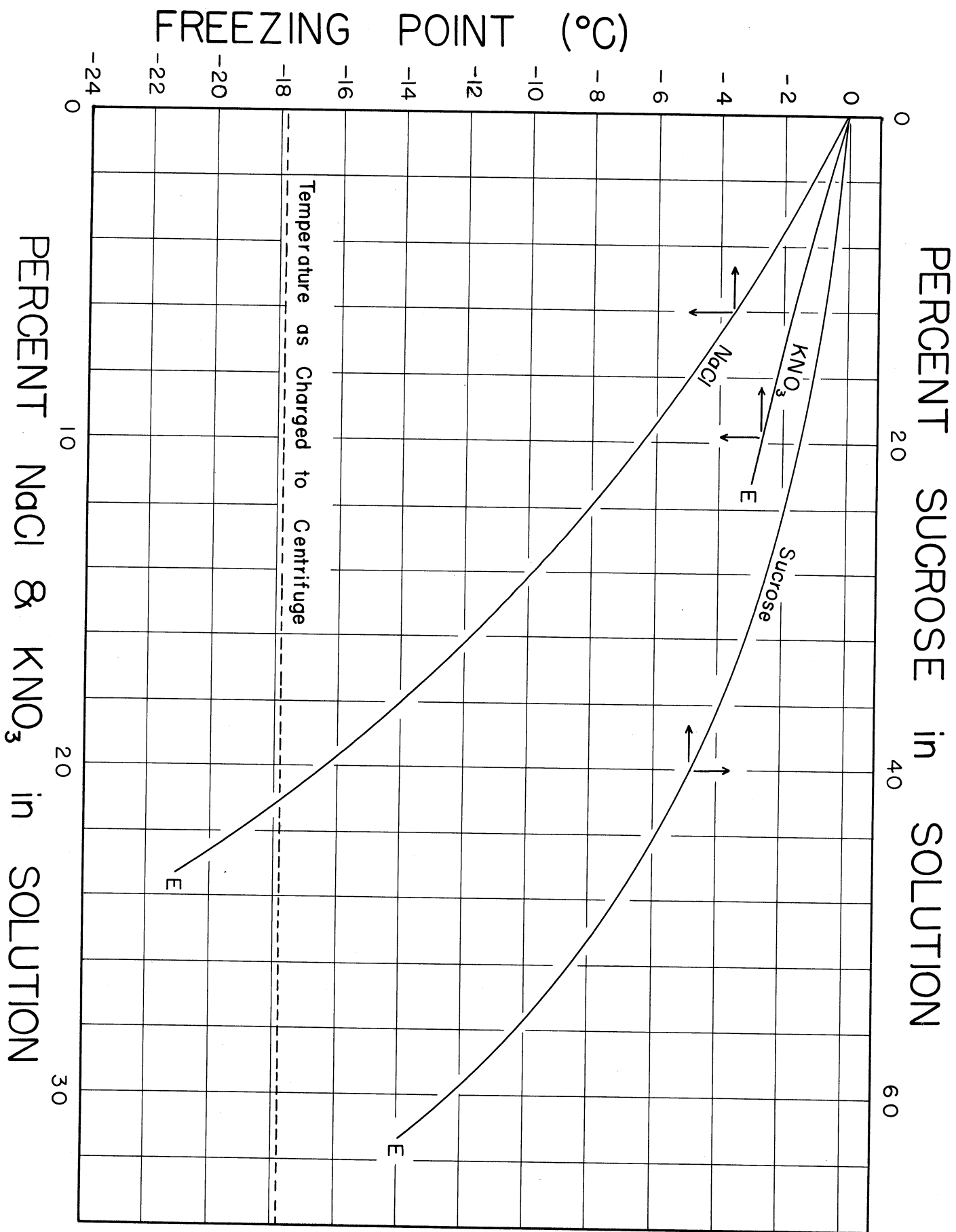


Figure 17. Freezing Point Curves of Solutions Used