Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Grushka, Eli , Guttel, Claudine and Sussman, M. V.(1983) 'Regelation Zone Melting of Ice', Separation Science and Technology, 18: 3, 195 — 204
To link to this Article: DOI: 10.1080/01496398308058330
URL: http://dx.doi.org/10.1080/01496398308058330

SEPARATION SCIENCE AND TECHNOLOGY, 18(3), pp. 195–204, 1983

Regelation Zone Melting of Ice

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Abstract

A thin layer of water surrounds a wire while passing through ice in a regelation experiment. The thickness of this layer is very small, around 10 nm. This is ideally suited for zone melting separation and purification. The present paper demonstrates the feasibility of regelation zone melting of ice. It is shown that wire passing through ice can remove a dye in proportion to its initial concentration. When the ice contains two solutes, the wire can remove one of them preferentially.

INTRODUCTION

The phenomenon of ice regelation has been known for a great many years. As early as 1872 Bottomley (*1*) has shown that a block of ice maintains its integrity after the passage of a wire through the ice. The explanation of the phenomenon has been a source of controversy until the present day (see, for example, the work of Gilpin in Ref. *2*). The two main explanations of regelation are: (*a*) in terms of pressure melting, and (*b*) in terms of the formation of a flowing water layer. Both schools of thought seem to agree that a layer of water surrounds the wire while passing through the ice. It is this layer of liquid water which is of importance for regelation zone melting (RZM) of ice.

0149-6395/83/1803-0195$3.50/0

The rejection of solute(s) from a solid into the melt during solidification is a well-studied phenomenon (*3*). Conventional zone melting techniques are based on this rejection, as clearly discussed by Pfann (e.g., Ref. *4*). The ice-water interface behaves in a similar manner to other solid–liquid interfaces, and salt rejection is known to occur (viz. Refs. 5 and *6*). There is little doubt that the water–liquid phase at the ice interface is rather concentrated in impurities. The thickness of the layer containing the concentrated solute, as well as its concentration, depends on the freezing rate. Typical thickness is between 50 to 500 μm. Gilpin (*2, 7*) has calculated the thickness of the layer of water surrounding a wire moving through ice to be between 1 to 14 nm, depending on various experimental conditions. It stands to reason, therefore, that a wire, when passed through ice containing impurities, will carry these impurities along in the liquid layer. Moreover, the concentration of the impurities in the liquid layer should be greater than in the ice. This, then, is the basis for RZM of ice. RZM is similar to conventional zone melting in its application to purification. It differs, of course, in the manner in which the molten zone is obtained.

The theoretical treatment of mass transfer in and out of the molten zone in RZM is complicated by the cylindrical symmetry and the presence of an annular liquid zone due to the wire. As a first (and certainly rough) approximation, we can use the models of conventional zone melting. Assuming complete mixing and a single zone pass, the classical theory shows that the amount of solute left in the solid (ice) is given by (*8*)

$$\frac{W_i}{W_o} = 1 - (1 - K) \exp\left[-K \frac{z\,\rho_i}{l\,\rho_w}\right] \tag{1}$$

where W indicates the weight fraction of solute, K is the partition coefficient of the solute between ice and water, z is the length coordinate traversed by the zone, l is the water layer thickness, ρ is the density, and subscripts o, i, and w represent, respectively, original, ice-, and water-related quantities. The assumption of complete mixing is not a bad one since the liquid layer is flowing (*2*). The equation points out that everything else being constant, decreasing the zone layer increases the amount of solute in the layer earlier during the pass:

$$\lim_{l\to\infty} \frac{W_i}{W_o} \to 1 \tag{2}$$

Since

$$W_w = W_i/K$$

and $K < 1$, the amount in the melt will be higher in zone melting. Thus, passing many extremely narrow zones in close proximity to one another will achieve optimum separation or purification. RZM of ice can be carried out with extremely narrow molten zones, the like of which are extremely difficult to obtain in conventionally heated systems.

It is somewhat surprising that RZM was not tried previously. That freezing could be used for partitioning and purification, as mentioned above, is well known. Some possible applications of freezing are enrichment of ^{18}O or D in water (*9, 10*) and concentration of proteins (*11*). Drake and Shreve (*12*), while studying regelation phenomenon, indicated that anomalous wire velocities through ice are a result of the concentration of impurities at the liquid layer. More recently Hanshaw and Hallet (*13*) have discussed the precipitation of $CaCO_3$ from glacier onto bedrocks in terms of a subglacial regelation mechanism. Yet, to our knowledge, no attempts have been made to employ regelation for separation and purification. The present work communicates initial results, demonstrating the feasibility of RZM.

EXPERIMENTAL

Since the aim of the work was to check the technique, the experimental setup was extremely simple.

Procedure

Methyl orange or methyl violet (or both) were dissolved in triply distilled water and then poured into plastic cups. These were put into a freezer at −7°C for several hours. The ice was then removed from the cups. The height of the block of ice was 5 cm and its cross-section 25 cm^2. A block of ice was put in a cold room (4°C) on a wire shelf supported by two chairs. A fuse wire, 0.25 mm o.d., was passed through the ice by attaching 2 kg weights to each end of the wire.

Under the conditions described here, the passage of the wire through the ice took about 20 min.

To more clearly demonstrate RZM, the following experiment was prepared. Triply distilled water was frozen as discussed above. Once frozen, a thin layer of methyl violet containing water was added to the top of the ice and the cup was put back in the freezer. A block of clear ice with a thin, colored layer on top was thus obtained. The wire was put on the colored end of the ice and passed through.

Measurement of the Dye Carried by the Wire

After passing through the dye containing ice, the portion of the wire emerging from the ice was cut and immersed in 5.00 mL of ethanol or water: ethanol solution. The concentration of the extracted dye was determined with a Perkin-Elmer 137UV or Cary 14 spectrophotometer. For this experiment, four blocks of ice were prepared containing 100, 200, 300, and 400 ppm methyl violet respectively. Measurements were made at 585 nm for methyl violet and 453 nm for methyl orange.

Controlled experiments were done by immersing for 20 min the same length of wire as above in solutions containing the same concentrations of dye as in the ice blocks. This was done in the cold room. The wires were then put into ethanol or water:ethanol solution and treated as above. The same experiment was repeated with a solution containing 1000 ppm of methyl violet.

RESULTS AND DISCUSSION

Figure 1, which is a photograph of the block of ice on the shelf and the wire passing through the ice, shows several points which need to be discussed.

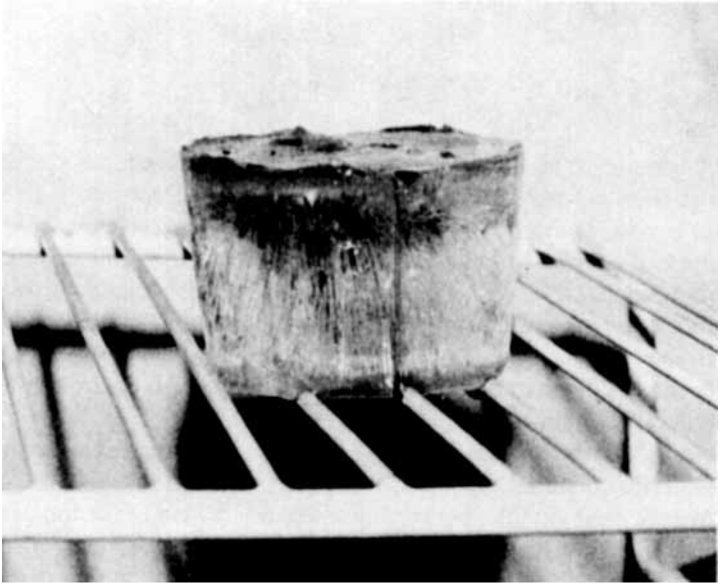

FIG. 1. A photograph of the experimental setup of RZM in ice. The dye is methyl violet.

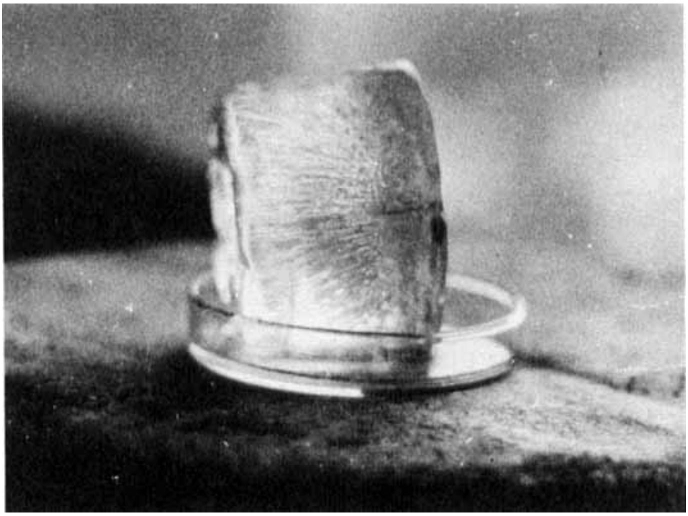

FIG. 2. Methyl violet tracks left by the wire passage.

The ice in this figure contains methyl violet. The distribution of the dye in the ice is not uniform due to the fast freezing rate. The top of the block is more concentrated in methyl violet. We have noticed, however, that different dyes were distributed differently in the ice. We are now looking into this aspect of freezing rejection for separation purposes.

The concentration of the methyl violet dye is much higher in the track of the wire. This can be seen in Fig. 1 where the regeled ice has a darker shade. In fact, we were hoping to show the opposite, namely a region devoid of color past the position of the wire. However, the concentration of the dye on top of the ice is so high that it is dragged along with the wire and is depleted into the ice with lower dye concentration. To demonstrate this effect more clearly, we prepared ice with a thin top layer containing methyl violet. The track left by the wire passing through the ice is shown in Fig. 2. The block of ice in Fig. 2 is on its side and the colored top layer is on the right. The track is quite obvious in the background of the dye-free ice. The track is darkest on the right-hand side. On the left-hand side, the side from which the wire emerged, the track is barely visible. This is a result of the fact that the wire started to move from the end containing the dye and, as the wire passed through ice not containing methyl violet, the dye in the liquid layer around the wire partitioned between the two phases. This partitioning, the exact mechanism

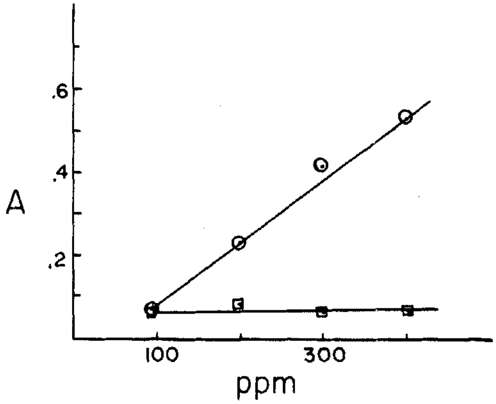

FIG. 3. The relation between the absorbance of methyl violet extracted from the wire and the concentration of the solution: (○) wire passed through ice, (□) wire immersed in solution.

of which is being investigated now, tends to even out the distribution of the dye. A similar phenomenon is observed with other dyes.

It should be pointed out that the water was frozen quite rapidly without stirring. As a result, the ice contains trapped air bubbles as can be seen in Figs. 1 and 2. Moreover, the dye distribution in the ice was uneven. As a consequence, it is important to try and ascertain the amount of dye carried along with the wire. The easiest method of determination (but perhaps not the most accurate) was to extract the dye from the wire as it emerges from the ice.

Figure 3 shows the relation between the absorbance, A, of methyl violet extracted from the wire after passing through the ice versus the concentration of the solution from which the ice was prepared. The increase in A with the dye concentration is clearly evident in Fig. 3. What makes this result startling relates to the amount extracted from the wire immersed in the solution from which the ice was made. As seen in Fig. 3, the amount extracted is independent of the concentration in solution. The wire passing through the ice carries with it more dye than the wire immersed in the solution having the same concentration of methyl violet. A possible explanation for this phenomenon may be related to the very thin layer of liquid which surrounds the wire passing through the ice. Due to the rejection of the dye from the ice, its concentration in the liquid layer is very high. Moreover, the concentration in the liquid layer is a function of that in the ice. As the wire emerges from the ice this thin layer, concentrated in the dye, is carried along. On the other hand, the dye in the solution is adsorbed on the immersed wire and the concentration of the solution, in the range studied here, is of little importance, since the adsorption sites on the wire are saturated. The effect of the liquid layer carried along with the wire from the solution is negligible since it contains a very small amount of dye. To check this hypothesis, a wire was immersed in a solution containing 1000 ppm of the dye. The absorbance of the amount extracted from the wire was only about 0.15, a value below that obtained from ice with 200 ppm dye.

The argument developed here is now being investigated further.

From the absorbances, the amount of dye carried along with the wire from the ice can be calculated. It was found that the amounts vary from about 4 μg to about 16 μg when the concentration of the solutions from which the ice was prepared changed from 100 to 400 ppm.

For RZM to be useful as a separation or purification technique, the effect of passing a wire through ice containing more than one solute should be studied. Regelation experiments were repeated on ice blocks containing equal weights of methyl violet and methyl orange. Invariably, the results showed that more methyl violet was carried out by the wire. Figure 4A shows a typical spectrum of the solution containing the dyes before freezing. Figure 4B shows a typical spectrum of the two dyes extracted from the wire after passing through the ice. The decreases in methyl orange concentration is obvious. As an example, when the original solution contained 500 ppm of each dye, the amounts removed by the wire were 6.4 μg methyl orange and 20.6 μg methyl violet. These experiments were repeated several times and in each case the amount of methyl violet removed from the ice was far greater than that of methyl orange. It is worthwhile to point out that the amount of methyl violet removed from the ice containing 500 ppm of each dye agrees

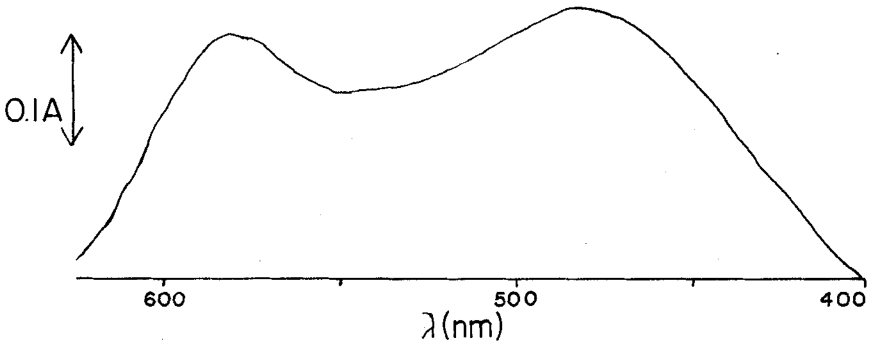

FIG. 4A. A spectrum of solution containing equal weights of methyl violet and methyl orange.

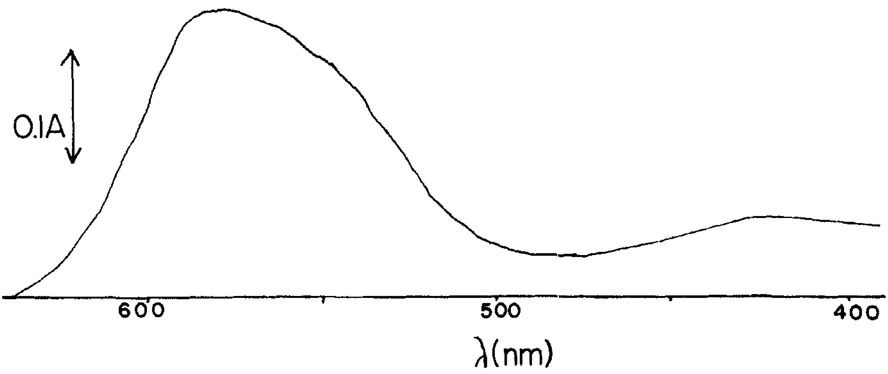

FIG. 4B. A spectrum of the dyes extracted from the wire after passing through the ice.

with the trend of the results in Fig. 3; extrapolation of the line in that figure to 500 ppm indicates that about 20 μg should be removed.

One of the factors which should affect the amount of dye removed from the ice by the wire is the mass of the weights attached to the wire. This is because the velocity of the wire passing through the ice is related to the mass of the weights. Figure 5 shows the relationship between the absorbance of the solution extracted from the wire after passing through the ice and the mass of the weights. As expected, the heavier the weights, the lower is the amount of dye removed from the ice. This is so since with heavier weights the wire

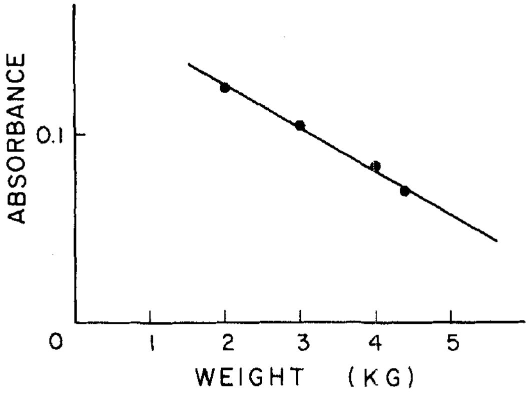

FIG. 5. A plot of the absorbance of dye solution extracted from the wire versus the weights attached to the wire.

moves faster through the ice, and the partitioning process is far from equilibrium. This result is similar to that found in conventional zone melting where the purification is a function of the zone velocity.

The results indicate that RZM can be used for the separation of different solutes in the ice or for the purification of ice.

CONCLUSION

We have demonstrated in this paper that RZM can cause redistribution of solutes in ice as well as their separation. To study the efficiency of RZM, factors such as wire diameter, wire velocity, chemical nature of the wire, temperature of the ice, and initial concentration of solute in the ice need to be checked. The thickness of the water layer around the wire on the ice, which is a function of some of the above parameters, affects the efficiency of the separation process. Consequently, all the experimental parameters and their influence on the separation should be studied.

To increase the capacity of the RZM process, several mesh screens stacked in parallel with a few millimeters of space between them should be passed through the ice. We are now in the planning stages of such a system. We plan to employ RZM for the separation and purification of biopolymers. We also envisage utilization of the method for D_2O and ^{18}O enrichment in natural water.

One of the attractive features of RZM in ice is the very narrow molten zone. Purification achieved should be much better with the passing of many very narrow molten zones, since then advantage can be taken of the high interface concentration of the solutes. From that viewpoint, RZM of ice has great prospects.

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Received by editor June 8, 1982
Revised October 13, 1982