ELECTRICAL PHENOMENA ACCOMPANYING THE PHASE CHANGE OF DILUTE KC L SOLUTIONS INTO SINGLE CRYSTALS OF ICE

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ABSTRACT. The Workman–Reynolds effect was investigated during the phase change of dilute (about $2 \times 10^{-4}$ N) KCl solutions into single crystals of ice. The ice crystals were oriented with the $c$-axes either parallel or perpendicular to the growth direction. The solute distribution in the liquid phase, near the interface (within 10 mm), was obtained with a wire-type conductivity cell. For a crystal growth rate of 8.8 $\mu$m/s the freezing potentials were $+10.0$ V and $+6.0$ V and the specific charge separations were $1.3\pm0.1 \times 10^{-6}$ C/g of ice and $1.4\pm0.1 \times 10^{-6}$ C/g of ice for growth parallel and perpendicular, respectively, to the $c$-axes of the ice crystals. The equilibrium solute distribution coefficient was found to be $4 \times 10^{-3}$ for KCl solutions. An “apparent” (because of convection in the liquid phase) distribution coefficient ranged from 0.031–0.074. The “apparent” diffusion coefficients ranged from $1.3\cdot4.9 \times 10^{-3}$ mm$^2$/s and varied linearly with growth rate. The ionic diffusion coefficients, $K^+$ and $K^-$, were approximately $K^+-K^- = -2 \times 10^{-5}$ and $K^++K^- = 8 \times 10^{-3}$ for the KCl solutions.

RéSUMÉ. Les phénomènes électriques accompagnant le changement de phase de solutions diluées de KCl dans des monocristaux de glace. L’effet Workman–Reynolds fut étudié durant le changement de phase de solutions diluées (c. $2 \times 10^{-4}$ N) KCl dans des monocristaux de glace. Les cristaux de glace furent orientés avec les axes $c$ soit parallèles, soit perpendiculaires à la direction de croissance. La distribution du solvant dans la phase liquide près de l’interface dans les 10 mm fut obtenue avec une cellule de conductivité à fil. Pour une vitesse de croissance du cristal de 8.8 $\mu$m/s, les potentiels de congélation furent de 10,0 V et $+6.0$ V et les séparations de charge spécifique de $1.3\pm0.1 \times 10^{-6}$ C/g de glace et de $1.4\pm0.1 \times 10^{-6}$ C/g de glace pour la croissance parallèle ou perpendiculaire respectivement aux axes $c$ des cristaux de glace. On trouvera le coefficient d’équilibre de distribution du solvant égal à $4 \times 10^{-3}$ pour les solutions KCl pour les deux orientations du cristal. Un coefficient de distribution “apparent” (du à la convection dans la phase liquide) s’étendait de 0.031 à 0.074. Les coefficients de diffusion “apparents” s’étendaient de $1.3\cdot4.9 \times 10^{-3}$ mm$^2$/s et variaient linéairement avec la vitesse de décroissance. Les coefficients de distribution d’ions, $K^+$ et $K^-$, étaient approximativement $K^+-K^- = -2 \times 10^{-5}$ et $K^++K^- = 8 \times 10^{-3}$ pour les solutions de KCl.

ZUSAMMENFASSUNG. Elektrische Erscheinungen bei der Zustandsänderung von wässerigen KCl-Lösungen in Ein­kristallen von Eis. Bei der Zustandsänderung von wässerigen (etwa $2 \times 10^{-4}$ N) KCl-Lösungen in Einkristalle von Eis wurde der Workman–Reynolds-Effekt untersucht. Die Einkristalle waren mit ihren $c$-Achsen entweder parallel oder senkrecht zur Wachstumsrichtung orientiert. Die Lösungsspannung in der Flüssigkeit nahe der Grenzfläche (innerhalb 10 mm) wurde mit einem Draht-Leitungsgefäße ermittelt. Für eine Kristallwachstumsgeschwindigkeit von 8.8 $\mu$m/s betrugen die Gefrierpotentiale $+10.0$ V und $+6.0$ V und die spezifischen Ladungstrennungen $1.3\pm0.1 \times 10^{-6}$ C/g Eis und $1.4\pm0.1 \times 10^{-6}$ C/g Eis für Wachstum jeweils parallel und senkrecht zu den $c$-Achsen der Einkristalle. Die Verteilungskoeffizienten der Lösung im Gleichgewicht wurden zu $4 \times 10^{-3}$ für KCl-Lösungen und beide Kristallorientierungen gefunden. Ein „scheinbarer“ (infolge von Konvektion in der Flüssigkeit) Verteilungskoeffizient reichte von 0.031–0.074. Die „scheinbaren“ Diffusionskoeffizienten reichten von $1.3\cdot4.9 \times 10^{-3}$ mm$^2$/s und änderten sich linear mit der Wachstumsgeschwindigkeit. Die Ionenverteilungskoeffizienten $K^+$ und $K^-$, waren annähernd $K^+-K^- = -2 \times 10^{-5}$ und $K^++K^- = 8 \times 10^{-3}$ für die KCl-Lösungen.

INTRODUCTION

In 1948, Workman and Reynolds (1950) investigated an electrical effect which accompanies the phase change of dilute aqueous solutions from the liquid to the solid phase. They observed large electrical potentials (200 V or more in some cases) and discharge currents on the order of 1 $\mu$A measured across the interface between the solid and liquid phases of the solutions during the freezing process. This effect has been termed the “Workman–Reynolds effect”, the “Costa Ribeiro effect”, and the “Thermodielectric effect” (Gross, 1954). In this paper we shall use the terminology of Gross (1958) in a recent review article and call the above effect the Workman–Reynolds (W–R) effect. The electrical potentials will be referred to as the “freezing potentials” and the electrical discharge currents as “the freezing currents”.

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A qualitative explanation of the W–R effect was offered by Workman and Reynolds (1950). Their explanation was based on pH differences between the unfrozen solutions and the melt water from the solid phase. These authors considered the effect to be due to selective incorporation of one solute ion into the solid phase during the freezing process. The ideas of Workman and Reynolds have been extended and refined, particularly by Gross (1965), LeFebre (1967), and Drost-Hansen (1967).

Although the W–R effect has been studied extensively, it appears that the effect of crystal orientation has not been studied in detail. The importance of crystal orientation is suggested by experience in crystal growth from the melt (Mullin and Hylme, 1960) and by some experiments with dielectrics in which a phenomenon similar to the W–R effect has been observed. Mascarenhas and Freitas (1960) found, for single crystals of naphthalene, that the charge separation for growth normal to the cleavage plane is about ten times greater than for growth in any other direction.

In the present investigation, the freezing potentials and the freezing currents have been measured during the phase change of dilute KCl solutions into single crystals of ice. The measurements were made for two growth directions, parallel and perpendicular to the c-axis. In addition, the distribution of solute in the liquid phase adjacent to the interface was determined.

**Theory**

LeFebre (1967) has derived an equation for the freezing potential

\[
V_s = \frac{I_0}{2RC_i} \exp \left( -\frac{t}{R_iC_i} \right) \int_0^t \exp \left( -\frac{t}{R_iC_i} \right) dt,
\]

where \( I_0 \) is the charging current due to the difference between the rates of incorporation of the positive and negative ions, \( z \) is a growth-rate constant, \( C_i \) is the interface capacitance, \( R_i \) is the interface resistance, \( R \) is the crystal growth rate and \( t \) is the time measured from the beginning of crystal growth. This equation for \( V_s \) does not apply to constant crystal growth rates which were used in the present experiments. LeFebre’s equation reduces to

\[
V_s = R [1 - \exp (-t/R_iC_i)],
\]

for the condition of constant crystal growth rates.

If the resistance of the ice can be neglected in comparison to \( R_i \), then

\[
R_i = V_m/I_m,
\]

where \( V_m \) is the maximum freezing potential and \( I_m \) is the maximum freezing current. The separate ionic distribution coefficients are defined to be

\[
K^+ = \frac{C_{s+}}{C_{L+}} \quad \text{and} \quad K^- = \frac{C_{s-}}{C_{L-}},
\]

where \( C_{s+} \) and \( C_{s-} \) are the positive and negative ion densities in the ice at the ice–liquid interface and \( C_{L+} \) and \( C_{L-} \) are the positive and negative ion densities in the liquid at the ice–liquid interface. These unequal ionic distribution coefficients and the separate ionic diffusion coefficients \( D^+ \) and \( D^- \) are related (LeFebre, 1967) to the freezing potential \( V_s \) through the charging current \( I \). In the case of identical ionic diffusion coefficients the freezing potential can be attributed to the difference between the ionic distribution coefficients

\[
K^+ - K^- \approx \frac{I'}{G_L},
\]

where \( I' \) is the charge parameter defined by LeFebre (1967). The equilibrium solute distribution coefficient is approximately

\[
K_0 \approx \frac{1}{2}(K^+ + K^-).
\]
The data for the solute distribution in the liquid phase have been analyzed using the equation of Tiller and others (1953):

\[
\frac{C_L(x)}{C_0} - 1 = \frac{1 - K_o}{K_o} \exp \left( -\frac{R \cdot x}{D_0} \right),
\]

where \( C_L(x) \) is the solute concentration in the liquid at a distance \( x \) ahead of the ice–liquid interface, \( C_0 \) is the solute concentration in the bulk liquid, \( K_o \) is the equilibrium solute distribution coefficient, \( R \) is the crystal growth rate and \( D_0 \) is the solute diffusion coefficient in the liquid phase. Equation (7) is valid provided (1) a steady-state solute distribution has been established in the liquid; (2) diffusion in the solid is negligible; (3) the value of \( K_o \) is constant and \( K_o < 1 \); (4) convection in the liquid is negligible (i.e., no mixing of the solute in the liquid phase).

Experimentally, a steady-state solute distribution was established in the liquid phase after a 40 mm thickness of solid had formed at a growth rate of 5.5 \( \mu \)m/s (Osterkamp, unpublished). It should be emphasized that this result is valid only for the growth conditions of the present investigation. Somewhat different results (Gross, 1968) have been obtained under different growth conditions. According to Gross (1968), diffusion of solute in the solid phase is extremely low. Jaccard and Levi (1961) have found a concentration dependence of the distribution coefficients of \( \text{NH}_3 \) and \( \text{NH}_4\text{F} \) in ice, but it does not appear that an investigation has been made for KCl in ice. Since the present investigation was primarily concerned with a small concentration range \((2.2-2.4 \times 10^{-4} \text{ N})\), condition (3) was satisfied.

The experimental conditions maintained in the present investigation indicate the presence of convection in the liquid phase. Thus, convection in addition to diffusion caused the transfer of solute away from the interface and Equation (7) was not strictly valid for the system. However, the data have been analyzed under the assumption that diffusion was the primary means of solute transport away from the interface. The distribution and diffusion coefficients were obtained from a semi-logarithmic plot of Equation (7). These were called "apparent" distribution and diffusion coefficients because of the presence of convection in the liquid phase.

The solidification of dilute aqueous solutions during small crystal growth rates results in the formation of clear, glass-like ice with a smooth or planar interface (Harrison and Tiller, 1963; Weeks and Lofgren, 1967). At larger crystal growth rates the ice changes to a cloudy or milky appearance and the planar interface becomes unstable and breaks down into a cellular interface. A necessary condition for the formation of a cellular interface is the presence of a constitutionally supercooled layer ahead of the advancing solid–liquid interface. Tiller and others (1953) have derived the expression

\[
\frac{G}{R} \leq \frac{mC_0}{D_0} \left( \frac{1 - K_o}{K_o} \right),
\]

where \( G \) is the temperature gradient in the liquid and \( m \) is the slope of the liquidus line. Equation (8) is a criterion for the presence of constitutional supercooling in the liquid phase and was used to obtain estimates of \( K_o \) since the change from clear to cloudy ice was observed experimentally.

At a cellular interface, the concentration of solute in the ice cells is relatively small and the solute tends to accumulate between the ice cells. The length of the cells is given (Harrison and Tiller, 1963) as

\[
d \approx \frac{-2mC_0}{G_sK_0[\phi \delta/a + K_0/(1 - K_0)]},
\]

where \( G_s \) is the average temperature gradient in the solid, \( \phi \) is a geometrical factor and \( \delta/a \) is the ratio of the distance between cells to the cell diameter. The value of the term \( \phi \delta/a \approx 0.5 \) for ice.
Experimental Details

Pure water (conductivity $\approx 10^{-5} \, \Omega^{-1} \, \text{m}^{-1}$) was obtained by processing ordinary tap water. The tap water was doubly distilled and then passed through a mixed-bed ion exchange resin and a 3 $\mu$m filter. The conductivity measurements were made in a Jones-type conductivity cell with an A.C. Wheatstone bridge consisting of a General Radio 1605 AH comparator and General Radio 510 resistors. This pure water was used for the solutions and also as a rinse and soak water.

Large single crystals of ice (26 mm O.D.) were grown in the “Lucite” (polymethyl methacrylate) tubes shown in Figure 1 and were examined optically between crossed polaroids to determine their crystalline perfection. The crystal orientation was determined with a universal stage of the same design as employed by Langway (1958). The electrodes were platinum wires (0.36 mm O.D.) placed perpendicular to the axis of the tube. The two lower electrodes were 2–3 mm apart and 18 mm from the single upper electrode. A forepump vacuum connection to the “Lucite” tube allowed the dissolved gases in the solution to be pumped off prior to freezing the solution.

The “Lucite” tubes containing the seed crystal in the desired orientation and a suitable solution were lowered into a cold bath ($-50^\circ\text{C} \pm 1^\circ\text{C}$) with a constant-speed motor. The cold bath consisted of an ethanol and water mixture in a metal container which was placed inside a deep-freeze unit. The freezing potentials were measured with a Keithley 610A electrometer and recorded with a Bausch & Lomb VOM-5 chart recorder.

![Fig. 1. Sketch of the “Lucite” tubes and the associated electrical apparatus used for growing single crystals of ice. A, thermistor probe; B, electrical connections to the platinum wire electrodes.](image-url)
The solute distribution in the liquid phase was obtained by measuring the resistance between the two lower electrodes in the freezing tube as a function of time as the ice–liquid interface advanced toward these electrodes from below. When the two lower electrodes were frozen into the ice, a switching arrangement allowed measurement of the freezing potential between the single upper and two lower electrodes while the ice–liquid interface was in that region. Thus, both the solute distribution in the liquid phase and the freezing potentials were measured for each crystal specimen.

The freezing currents were obtained by shunting the interface with a high impedance resistor ($1.00 \times 10^8 \Omega$) and measuring the potential drop across the resistor. The specific charge separation $Q$ was calculated from the curve of freezing current against time.

The solute concentrations in the present experiments were determined to within $\pm 1\%$ for constant concentrations. However, the solute concentration gradient near the ice–liquid interface resulted in an estimated error of $\pm 8\%$ because of changes in the cell constant of the wire-type conductivity cell. The position of the ice–liquid interface was determined to within $\pm 0.2$ mm from the lowering rate of the sample and the resistance change between the lower two electrodes as these were grown into the ice phase.

**Results and Discussion**

Single crystals of ice were grown from dilute ($2.2 \times 10^{-4}$ N) KCl solutions with their $c$-axes oriented either parallel or perpendicular to the growth direction. The results are summarized in Table I and typical solute distribution curves in semi-logarithmic form are shown in Figures 2 and 3. Equation (7) was used to obtain the apparent distribution and diffusion coefficients in Table I. The values for $K$ are larger for growth parallel to the $c$-axes of the ice crystals and $K$ increases as $R$ increases although the specific dependence of $K$ on $R$ is not clear. The values for $D$ are approximately the same for both crystal orientations and $D$ increases linearly with $R$ as shown in Figure 4. Extrapolation of the curve to $R = 0$ indicates a value of $D \approx 1 \times 10^{-3}$ mm$^2$/s. This is in excellent agreement with the known value (Gross, 1968) of $D_0 = 1.00 \times 10^{-3}$ mm$^2$/s.

### Table I. Average Values of the Apparent Distribution and Diffusion Coefficients and Maximum Freezing Potentials for the Phase Change of $2.2 \times 10^{-4}$ N KCl Solutions

<table>
<thead>
<tr>
<th>Growth rate $R$</th>
<th>Apparent distribution coefficient $K$</th>
<th>Apparent diffusion coefficient $10^3 D$ mm$^2$/s</th>
<th>Maximum freezing potential $V_m$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>0.068</td>
<td>4.9</td>
<td>*</td>
</tr>
<tr>
<td>2.1</td>
<td>0.033</td>
<td>1.5</td>
<td>*</td>
</tr>
<tr>
<td>3.3</td>
<td>0.040</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>5.5</td>
<td>0.031</td>
<td>2.0</td>
<td>+1.0</td>
</tr>
<tr>
<td>8.8</td>
<td>0.047</td>
<td>3.2</td>
<td>+5.0</td>
</tr>
<tr>
<td>14</td>
<td>*</td>
<td>*</td>
<td>+5.0</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>Growth rate $R$</th>
<th>Apparent distribution coefficient $K$</th>
<th>Apparent diffusion coefficient $10^3 D$ mm$^2$/s</th>
<th>Maximum freezing potential $V_m$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>0.035</td>
<td>1.3</td>
<td>*</td>
</tr>
<tr>
<td>2.1</td>
<td>0.039</td>
<td>1.5</td>
<td>*</td>
</tr>
<tr>
<td>3.3</td>
<td>0.046</td>
<td>1.9</td>
<td>0.5</td>
</tr>
<tr>
<td>5.5</td>
<td>0.031</td>
<td>2.0</td>
<td>+1.0</td>
</tr>
<tr>
<td>7.1</td>
<td>0.055</td>
<td>4.3</td>
<td>+2.0</td>
</tr>
<tr>
<td>8.8</td>
<td>0.074</td>
<td>3.5</td>
<td>+10.0</td>
</tr>
<tr>
<td>12</td>
<td>*</td>
<td>*</td>
<td>+8.0</td>
</tr>
<tr>
<td>14</td>
<td>*</td>
<td>*</td>
<td>+9.0</td>
</tr>
</tbody>
</table>

* Insufficient data for these values.
† Freezing potential of the liquid with respect to the ice.
Larger freezing potentials were associated with phase change when the c-axes of the ice crystals were parallel to the growth direction (Table I). The average maximum freezing potentials are shown plotted against growth rate in Figure 5. The vertical bars in Figure 5 represent the spread in the data. The largest spread was 4.0 V for a crystal growth rate of 8.8 μm/s with the c-axes of the crystals parallel to the growth direction.

The freezing potentials were small (± 1 V or less) when \( R \leq 5.5 \text{ μm/s} \) and large (± 6 V or more) when \( R \geq 8.8 \text{ μm/s} \). These growth rates bracket the transition from clear ice (planar interface) to cloudy ice (cellular interface) as shown by Figure 5. The transition region was not always as sharply defined as shown in Figure 5. However, a large number of experiments indicated that it was usually within the region shown for the solute concentration and growth

![Graphs showing solute distribution](image)

*Fig. 2. Typical semi-logarithmic plots of the solute distribution in the liquid phase (cf. Equation (7)) obtained during the phase change of \( 2.2 \times 10^{-4} \text{ N KCl solutions. The c-axes of the ice crystals were oriented perpendicular to the growth direction.} \)*

conditions used in the present experiments. The length of the cells \( d \) can be calculated from Equation (9). If \( K_0 \approx 10^{-3} \), then \( d \approx 2 \text{ mm} \) for a \( 2 \times 10^{-4} \text{ N KCl solution. This } d \text{ is of the same order as the depth of the charged layer in the ice (1 mm) as determined experimentally by LeFebre (1967). Thus, the possibility exists that the larger freezing potentials may be associated with the formation of a cellular interface.}

The transition from a planar to a cellular interface (as indicated by the change from clear to cloudy ice) was visually observed and Equation (8) was used to calculate the equilibrium distribution coefficient \( K_0 \). The value of \( K_0 \) for KCl solutions was calculated to be \( 4 \times 10^{-3} \) for both crystal orientations; however, the method of visual observation is not sufficiently sensitive to determine small differences (20% or less) due to crystal orientation. Some experiments were also performed with dilute (about \( 2 \times 10^{-4} \text{ N} \) NaCl and LiCl solutions (Osterkamp,
The values of $K_0$ were calculated to be $9 \times 10^{-3}$ and $3 \times 10^{-3}$, respectively, for these solutions. The value of $K_0$ for NaCl solutions has been estimated by Weeks and Lofgren (1967) at about $10^{-3}$, while Harrison and Tiller (1963) state that $K_0 < 10^{-4}$. There does not appear to be any data available for the KCl and LiCl solutions.

The freezing currents were measured during the phase change of $2.4 \times 10^{-4} \text{N KCl}$ solutions. Single crystals of ice were grown with the $c$-axes oriented either parallel or perpendicular to the growth direction at a growth rate of 8.8 $\mu$m/s. The specific charge separation

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Typical semi-logarithmic plots of the solute distribution in the liquid phase (cf. Equation (7)) obtained during the phase change of $2.2 \times 10^{-4} \text{N KCl}$ solutions. The $c$-axes of the ice crystals were oriented parallel to the growth direction.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Apparent diffusion coefficient versus growth rate (see Table I) for growth parallel (□) and perpendicular (○) to the $c$-axes of crystals formed from $2.2 \times 10^{-4} \text{N KCl}$ solutions.}
\end{figure}
Fig. 5. Average maximum freezing potentials versus growth rate (see Table I) for growth parallel (□) and perpendicular (○) to the c-axes of crystals formed from $2.2 \times 10^{-4} \text{N KCl}$ solutions. The vertical bars represent the spread in the data.

$Q$ was calculated to be $1.3 \pm 0.1 \times 10^{-6} \text{C/g}$ of ice and $1.4 \pm 0.1 \times 10^{-6} \text{C/g}$ of ice when the c-axes were oriented parallel and perpendicular, respectively, to the growth direction. These values of the specific charge separation are of the same order of magnitude as found by other investigators (Pruppacher and others, 1968).

The interface parameters, $R_i$, $C_i$ and $I'$ of LeFebre's model have been calculated from Equations (2)–(6), and the results are shown in Table II. It appears that data are not available in the literature for the ice–liquid interface parameters for KCl, NaCl and LiCl solutions. However, LeFebre (1967) has found that $C_1 = 2 \times 10^3 \text{pF}$, $R_i = 2.8 \times 10^{10} \Omega$ and $I' = 1.0 \times 10^{-1} \text{C/m}^3$ for a $2 \times 10^{-5} \text{N KF}$ solution which may be compared with values for the same parameters determined in the present investigation (Table II).

**Table II. Ice–liquid interface parameters for the solutes shown as a function of crystal orientation**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Maximum freezing potential $V_m$ (V)</th>
<th>$10^{-3}C_i$ (pF)</th>
<th>$10^{-3}R_i$ (Ω)</th>
<th>$I'$ (C/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl $2.2 \times 10^{-4}$ N</td>
<td>$+6.0$</td>
<td>$1.9 \pm 0.2$</td>
<td>$8 \pm 1$</td>
<td>$2.1 \pm 0.3$</td>
</tr>
<tr>
<td>NaCl $2.4 \times 10^{-4}$ N</td>
<td>$+9.0$</td>
<td>$2.2 \pm 0.5$</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>LiCl $2.1 \times 10^{-4}$ N</td>
<td>$+9.0$</td>
<td>$2.4 \pm 0.2$</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>KCl $2.2 \times 10^{-4}$ N</td>
<td>$+10.0$</td>
<td>$2.8 \pm 0.3$</td>
<td>$10 \pm 1$</td>
<td>$2.3 \pm 0.3$</td>
</tr>
</tbody>
</table>

* Insufficient data for these values.
† The separate values of $R_i$ and $I'$ were computed for a crystal growth rate of 8.8 μm/s only.

The difference between the separate ionic distribution coefficients for the KCl solutions may be calculated by Equation (5). Since the negative ion density in the solution $C_L \approx 1.4 \times 10^{-1} \text{C/m}^3$, then $K^+ - K^- \approx -2 \times 10^{-5}$. The sum of the separate ionic distribution coefficients for the KCl solutions may be calculated by Equation (6). Since the equilibrium distribution coefficient $K_o = 4 \times 10^{-3}$, then $K^+ + K^- \approx 8 \times 10^{-3}$. 
CONCLUSIONS

A wire-type conductivity cell may be used to determine the solute distribution in the liquid phase near an advancing ice-liquid interface. The theory of Tiller and others (1953) describes the solute distribution in the liquid phase near the interface (within 4 mm) provided apparent distribution and diffusion coefficients are used in place of the equilibrium distribution coefficient and the usual diffusion coefficient. The apparent distribution coefficients and the maximum freezing potentials are larger for growth parallel to the c-axes of the ice crystals. It appears that significant freezing potentials may be associated with a cellular interface structure; however, additional experimental work is needed to test this hypothesis.

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