ELECTRICAL CONDUCTIVITY AND RELAXATION IN ICE CRYSTALS WITH KNOWN IMPURITY CONTENT

By Gerardo Wolfgang Gross, Iris Cox Hayslip, *and* Roberta N. Hoy

(New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, U.S.A.)

Abstract. Three-terminal dielectric bridge measurements (in the range 20 Hz to 100 kHz between $-5°C$ and -90 to $-120°C$) have been made of ice doped with (a) conductivity-enhancing ionic impurities (HCl, HF, $NaCl$, KF, NH_4F) and (b) conductivity-depressing solutes (NH_4OH, NH_4Cl, NH_5CO_3, $NaHCO_3$). Blocking electrodes were used for the first group. The true ice parameters were extracted from linearized plots of the Debye equations. Chlorides and fluorides showed very similar characteristics in their spectra and static conductivity. The results suggest that static conductivity is controlled by extrinsic protons. On the other hand, bases, or solutes that impart a positive freezing potential to the ice, suppress extrinsic protons. In this case, the static conductivity was not, or only weakly, temperature dependent and lower than in the first group. A conductivity cross-over was observed in neither case. The dielectric conductivity contribution is strongly dependent on impurity concentration but apparently less affected than the static conductivity by the nature of the solute. The principal relaxation time is reduced by most solutes, exceptions are pure (bicarbonate-free) bases, sodium bicarbonate, and carbon dioxide.

Résumé. *Conductivité et dispersion électrique de cristaux de glace dopés avec des impuretés en concentration connue.* Nous avons effectué des mesures électriques à la méthode du pont (de 20 Hz à 100 kHz entre $-5°C$ et -90, $-120°C$) dans le cas de glace dopée avec: (a) des impuretés ioniques augmentant la conductivité (HCl, HF, $NaCl$, KF, NH_4F), et (b) des impuretés diminuant la conductivité (NH_4OH, NH_4Cl, NH_5CO_3, $NaHCO_3$). Des électrodes bloquantes ont été utilisées dans le premier cas. Les paramètres propres à la glace ont été obtenus à partir des formes linéarisées des équations de Debye. Les chlorures et les fluorures entraînent des caractéristiques très semblables dans les spectres et la conductivité statique. Les résultats suggèrent que la conductivité en courant continu est contrôlée par des protons extrinsèques, c'est-à-dire introduits par les impuretés. Au contraire, les hydroxydes et les sels qui conduisent la glace à présenter un potentiel positif lors de la congélation, suppriment les protons extrinsèques. Dans ce cas la conductivité en courant continu n'est pas, ou seulement faiblement, dépendante de la température; elle est, en outre bien plus faible que pour le premier groupe d'impuretés. Le "cross-over" de conductivité n'a été observé dans aucun des cas. La contribution diélectrique à la conductivité dépend fortement de la concentration en impuretés mais est beaucoup moins affecté par la nature des impuretés que la conductivité en courant continu. Le temps de relaxation principal est diminué par toutes les impuretés sauf les hydroxydes purs (sans CO_2), le bicarbonate de sodium et le dioxyde de carbone.

Zusammenfassung. *Elektrische Leitfähigkeit und Relaxation in Eiskristallen mit bekanntem Gehalt an Fremdstoffen.* Dielektrische Brückenmessungen (Frequenzbereich 20 Hz bis 100 kHz; Temperaturbereich $-5°C$ bis $-90°C$ bzw. $-120°C$) wurden ausgeführt an Eis, das dotiert war mit (a) Spurstoffen, welche die Leitfähigkeit erhöhen (HCl, HF, $NaCl$, KF, NH_4F) und (b) solchen, welche die Leitfähigkeit vermindern (NH_4OH, NH_4Cl, NH_5CO_3, $NaHCO_3$). Die erste Gruppe wurde mit blockierenden Elektroden gemessen. Die Eiswerte wurden aus linearisierten Auftragungen der Debyegleichung ermittelt. Chloride und Fluoride zeigten sehr ähnliche Merkmale in ihren Spektren und ihrer statischen Leitfähigkeit. Die Ergebnisse legen nahe, dass die statische Leitfähigkeit von Fremdprotonen bestimmt wird. Andererseits unterdrücken Basen oder Salze, die dem Eis ein positives Gefrierpotential verleihen, Fremdprotonen. In diesem Fall war die statische Leitfähigkeit nicht oder nur wenig temperaturabhängig und kleiner als in der ersten Gruppe. Ein *cross-over* der Leitfähigkeiten wurde in keinem Falle beobachtet. Der dielektrische Leitfähigkeitsbeitrag ist stark von der Konzentration des Fremdstoffes abhängig, aber weniger als die statische Leitfähigkeit von seiner chemischen Beschaffenheit. Die meisten Lösungsstoffe verkürzen die Hauptrelaxationszeit. Ausnahmen sind reine, bikarbonatfreie Basen, Natriumbikarbonat und Kohlendioxid.

Introduction

This work reports on three-terminal dielectric bridge measurements of ice doped with different ionic impurities.

We emphasize the chlorides in this paper. Other solutes are discussed primarily to point out similarities and contrasts. Space limitations prevent us from presenting graphs of all the dispersion parameters that have been computed, nor can we adequately discuss or cite earlier investigations of several impurities studied in this paper.

The purpose of this work was to define specific impurity effects on the electrical properties of ice. Interest in the chlorides stems from the fact that the distribution coefficient (Gross and others, 1975[a], [b], 1977) is (1) only about one-tenth in magnitude of that typical for fluoride

in ice; (2) in contrast to the fluoride, the coefficient is nearly concentration independent; thus, differences in the electrical parameters of these two species in ice were expected on theoretical grounds (Seidensticker, 1972; Bilgram, 1974); (3) compounds tagged with [36]Cl are readily available and can be measured very precisely with a scintillation counter in the concentration range $10^{-3}M$ to $10^{-8}M$.

The chloride and fluoride of ammonium enter the ice lattice in proportions much higher than the corresponding alkali salts. Why is this so and how does it affect the electrical properties?

From freezing-potential studies (Cobb and Gross, 1969) it is known that certain ("proton-enhancing") solutes (e.g. alkali-metal halides) attract hydrogen ions into the ice while others, the "proton-suppressing" solutes (e.g. NH_4Cl, NH_5CO_3) require hydroxyls for neutralization. How do these processes affect the electrical parameters?

When ice containing proton-enhancing solutes is subjected to a polarizing electric field, it exhibits electrode space-charge effects that mask the dielectric characteristics of the bulk more or less completely. This difficulty was avoided by using a blocking-electrode technique with these solutes. Proton-suppressing solutes, by contrast, cause only minor space-charge effects or none at all. Stainless-steel guard electrodes were used with satisfactory results.

With this observation as a starting point, we propose a classification of the investigated solutes according to their effects on the electrical properties of ice.

METHODS

If differential ion separation occurs during ice growth into a dilute solution, solute stoichiometry is not conserved, the deficit being made up by hydrogen and hydroxyl ions respectively. All of our crystals were grown under near equilibrium conditions when ion separation is most efficient. In alkali-halide solutions the cation is preferentially excluded from the ice. Its concentration in the ice is typically orders of magnitude lower than the anion. For this reason, in the present work we do not differentiate whether an ice sample was doped with a hydrogen halide or with its alkali-metal salt.

TABLE I. EFFECT OF SOLUTES ON ELECTRICAL PROPERTIES, COMPARED TO PURE ICE

Solute	Maximum concentration studied M	Approximate lowest temperature studied °C	σ_0	E kcal/mol	$\Delta\sigma_D$	E kcal/mol	τ_2	E kcal/mol	$\Delta\epsilon_D$	Thermoelectric power Warm end $(-)$ or $(+)$ [†]	Maximum freezing potential Ice sign [‡] V
None		-75	Figure 3	<5	Figure 7	12–13	Figure 9	12–13	Figure 7	$(-)$	o
I. Proton enhancing											
a. Interacting HF, NaF, HCl, NaCl	1×10^{-3}	-80	Increases	5–6	Increases	Less	Shorter	Less	Increase or decrease depending on concentration and temperature	$(-)$	-40 to -90*
b. Non-interacting CO$_2$	10^{-4}	-100	Increases	5–6	Same (above $-40°C$)	Same (above $-40°C$)	Same	Same	Slight increase?	$(-)$?	o
c. NH$_4$F	7×10^{-3}	-120	Increases	5–6	Increases	Less	Shorter at high concentration	Less	Increases	$(-)$	-20
II. Proton depressing											
a. Interacting NH$_4$Cl	7×10^{-6}	-100	Much less	o?	Increases	Less	Shorter	Less	Same?	$(+)$	$+92$
NH$_5$CO$_3$	1×10^{-3}	-120	Much less	o?	Increases	Less	Shorter	Less	Same?	$(+)$	$+95$
b. Non-interacting NaHCO$_3$	$<1\times10^{-5}$	-60	Much less	o?	Same	Same	Same	Same	Same?	$(-)$?	-55
NH$_4$OH	5×10^{-6}	-85	Much less	o?	Same (above $-50°C$)	Same	Same (above $-50°C$)	Same	Same?	$(+)$?	o

* HF, HCl show zero freezing potential.
† Data in part from Bryant and Fletcher (1965).
‡ From Cobb and Gross (1969) and other observations by the authors.

In the ammonium chloride and fluoride, stoichiometry is not conserved but concentrations of the two ion constituents are comparable in magnitude. The concentrations given are those of the anion; both ions were measured for ammonium fluoride.

Chloride solutions tagged with [36]Cl (as well as ice grown from them) were measured with a scintillation counter. This procedure was used for all but the most concentrated solutions; these were determined by conductivity and pH measurements (Cobb and Gross, 1969).

Concentrations of the fluorides, the bicarbonates, and of the bases in ice were determined by conductivity and pH measurements of the melted ice at room temperature in a CO_2-free glove box. Ammonium-hydroxide ice contained the solute near the solubility limit ($5 \times 10^{-6}M$, see Gross and others, 1975[b]). The incorporation of sodium bicarbonate in ice is so small that we can only give an upper limit ($1 \times 10^{-5}M$) for the concentration of this solute in the ice samples we have studied.

Concentrations are given as moles of solute per liter of melted ice or of solution at room temperature (M). Concentration and temperature ranges for different impurities are summarized in Table I.

Slices were taken from the center portion of monocrystalline ice columns of 200 to 250 mm length and 35 mm diameter. The crystallographic c-axis was perpendicular to the cylinder axis. Because the solute redistributes itself unequally between the phases when an ice crystal
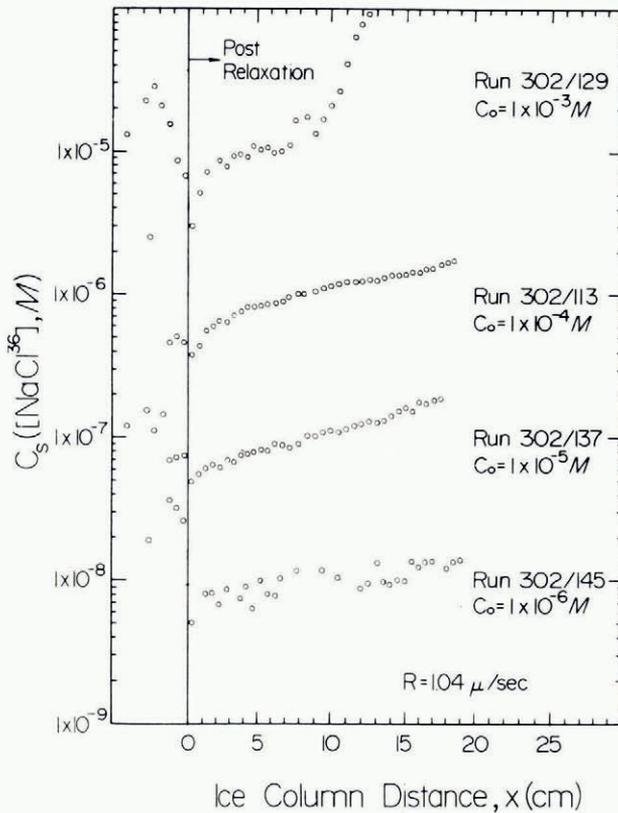
Fig. 1. *Typical concentration profiles of ice columns used in this work. Crystals were grown by a modified Bridgman method (Gross and others, 1975[b]). After a crystal had grown through the conical end section of the crystal holder, the growth was stopped for 48 h to allow solute transient to decay. For calculations (e.g. Gross and others, 1977), crystal growth was reckoned from this point ($x = 0$). C_o = concentration in the liquid prior to start of crystal growth. R = growth rate. C_s = solute concentration in the ice.*

freezes from an initially homogeneous solution, a complete solute-concentration profile was measured for each column in 5 mm intervals (Fig. 1). For this purpose, a melting apparatus was especially designed (Fig. 2).

The dielectric parameters were determined with a General Radio Model 1615-A capacitance bridge in the range 20 Hz to 100 000 Hz and between temperatures $-5°C$ and -90 to $-120°C$.

Limiting conductivities, relaxation times, and polarization strengths of partly overlapping ranges were computed from linearized plots of the Debye equation. In agreement with earlier investigators (e.g. Von Hippel and others, 1971; Camplin and Glen, 1973) it was assumed that dielectric relaxation in ice is best described by a small number (2–4) of discrete relaxation ranges, exclusive of space-charge ranges, each characterized by a single relaxation time.
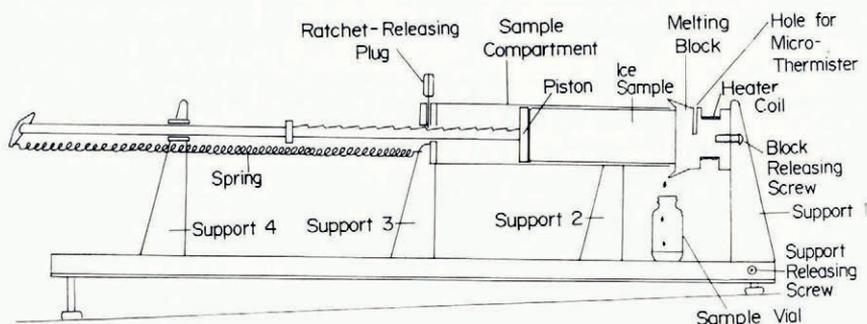
Fig. 2. Ice-melting apparatus.

Teflon (polytetrafluoroethylene) foil was used for blocking electrodes (Mounier and Sixou, 1969; Gross, 1975). In this case, further calculation was required to extract the parameters of bulk ice from the computed values (Gross, 1975). Consistency and correctness of results were tested in two ways: (1) Measurements on the same specimens were made with two foil thicknesses (0.05 mm and 0.24 mm, respectively); the corrected ice values were close in most cases. (2) Spectra of pure ice obtained with conventional (non-blocking) guard electrodes and with blocking layers, respectively, were compared; satisfactory agreement was achieved.

Furthermore, the principal relaxation time and principal dielectric conductivity of a number of samples of pure ice measured as a function of temperature either with stainless-steel guard electrodes or with blocking electrodes showed excellent agreement with the data published by Auty and Cole (1952). The straight lines described by Auty and Cole's data for the principal relaxation time, and for the principal dielectric conductivity, are reproduced on several of our graphs to serve as reference.

For samples measured with blocking electrodes, the static conductivity was derived from a.c. data with the method proposed by Mounier and Sixou (1969). In the present paper, this applies to all samples doped with alkali halides and ammonium fluoride. However, the static conductivity of ice doped with proton-depressing solutes (NH_4OH, NH_4Cl, NH_5CO_3, $NaHCO_3$) was so low that it could not be resolved with the blocking-electrode technique and our bridge. In these cases, an indirect method was used to estimate the static conductivity, viz. complex conductivity plots (Grant, 1958) taken with stainless-steel electrodes. In some cases, the a.c. conductivity at 20 Hz provided an upper-limit estimate of the static conductivity.

RESULTS

Static bulk conductivity σ_0 in chlorides: HCl, NaCl

The static bulk conductivity shows a strong and concentration-dependent enhancement (Fig. 3). At concentrations below $10^{-7}M$ (in the melted ice), the static conductivity is temperature independent above about $-50°C$. A sharp transition to a temperature dependent domain (5–6 kcal/mol, 1.2–1.4 kJ/mol) occurs below this temperature. A similar transition was observed in pure ice (Fig. 3); however, above the transition point a weak temperature dependence is noticeable in this case. The nature of the transition is not clear at present. Camp and others (1969) first observed this phenomenon in pure ice.

Since the conductivity plateau changes elevation with doping, it is probably controlled by extrinsic charge carriers rather than by thermal dissociation of the undisturbed ice lattice. A similar observation was made for HF-doped ice (Camplin and Glen, 1973).

Hobbs (1974, p. 100) suggested that the plateau may be caused by proton injection from the electrodes. However, our measurements show that the phenomenon also occurs with blocking electrodes where proton injection is excluded. Maidique and others (1971) suggested that it is the result of unspecified "extrinsic charge carriers" (whose sources are impurities or lattice faults).
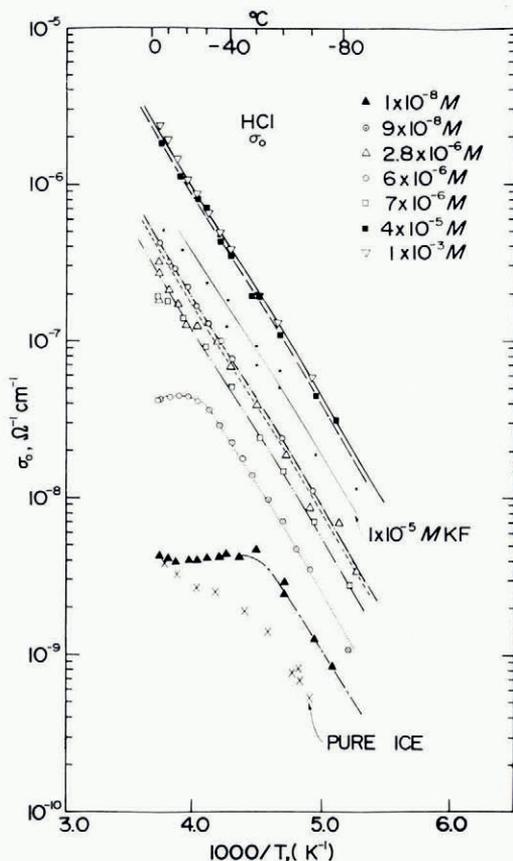
Fig. 3. *Static conductivity of ice grown from dilute HCl and NaCl solutions. Pure ice and KF-ice for comparison. Samples containing $9 \times 10^{-8}M$, $6 \times 10^{-6}M$, and $7 \times 10^{-6}M$ were actually grown from NaCl solutions of $1 \times 10^{-5}M$, $2.5 \times 10^{-4}M$, and $1 \times 10^{-4}M$, respectively. Remaining samples were grown from HCl solutions.*

With the exception of the plateau at very low doping levels and high temperature, the static conductivity in our data is temperature dependent with a rather uniform activation energy of 5–6 kcal/mol (1.2–1.4 kJ/mol, 0.2–0.3 eV) regardless of concentration (Fig. 3).

The conductivity is also concentration dependent

$$\sigma_0 \propto C^{0.4},$$

where C is the impurity concentration in the ice (Fig. 4). The relation found by earlier investigations for HF, HCl, and KCl in ice (Jaccard, 1959; Gross, 1962; Gross, 1965; Young and Salomon, 1968; Maeno, 1973) was

$$\sigma_0 \propto C^{0.5}.$$

Given the small number of points used for computation, and experimental uncertainty, further work is required to ascertain whether this difference is significant.
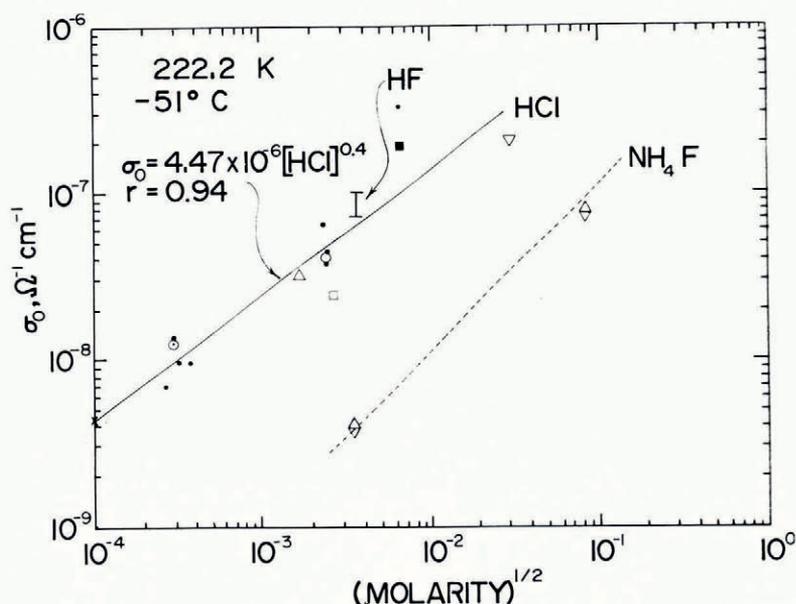
Fig. 4. Static conductivity of ice containing HCl as a function of concentration. HF and NH₄F for comparison. Symbols correspond with those of Figure 3 but fat dots are additional samples (not shown in Fig. 3) used for the correlation. The lower conductivity of ammonium fluoride ice appears related to its lower content of extrinsic protons (see Fig. 5). Dotted line of slope 0.5 is drawn close to the two data points in order to suggest a possible trend.

Static bulk conductivity σ_0 of ammonium compounds: NH_4F, NH_4Cl, NH_5CO_3

Two curves for NH_4F are shown in Figure 5. From Figure 4, they appear roughly to obey the relationship

$$\sigma_0 \propto C^{0.5},$$

but the conductivities are at least one order of magnitude lower than those for HCl and HF at comparable concentrations.

The conductivities for NH_5CO_3 (Fig. 6) and NH_4Cl are also lower by several orders of magnitude. The data show either a lack of temperature dependence or even an increase with decreasing temperature.
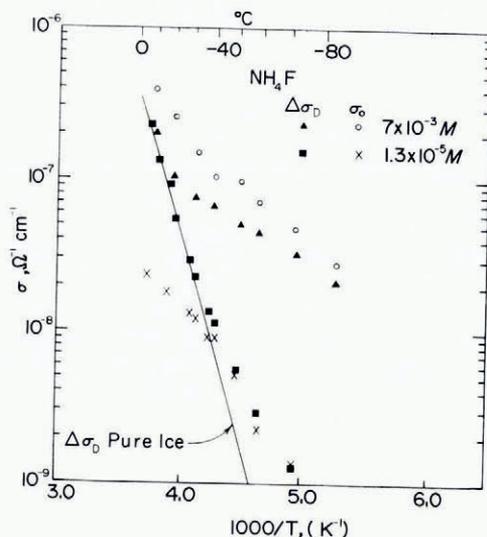
Fig. 5. Static (σ_0) and principal dielectric ($\Delta\sigma_D$) conductivities of two ice samples with NH_4F. The deficit of NH_4^+ with respect to F^- was less than 1% for the concentrated, and about 10% for the dilute sample (cf. Noll and Käss, 1969). The deficit is made up by hydrogen ions. The lower proton content is proposed as the cause for the lower static conductivities of these samples compared to HF or HCl (cf. Fig. 4). The dielectric conductivity is roughly comparable to NH_5CO_3 samples of similar concentration (Fig. 8), although the curve shapes differ in detail.
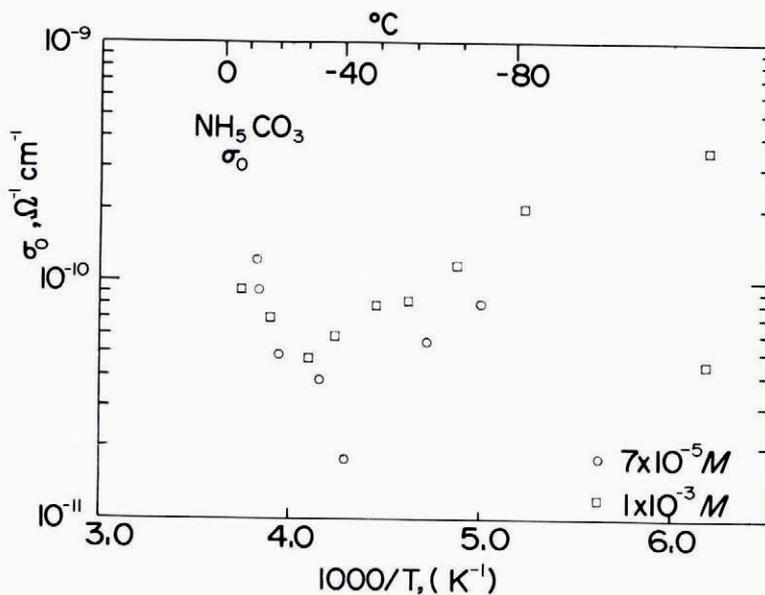
Fig. 6. Static conductivity of two ice samples containing NH_5CO_3. Derived from complex conductivity plots.

Principal dielectric conductivity $\Delta\sigma_D$

This is the conductivity contribution of the principal or Debye relaxation range. Conventionally one plots curves of σ_0, the static conductivity, versus $1000/T$, and $\sigma_{\infty D}$ versus $1000/T$, where

$$\sigma_{\infty D} = \sigma_0 + \Delta\sigma_D,$$

the high-frequency limiting conductivity of the Debye dispersion range.

From the Debye theory, $\Delta\sigma_D$ is functionally related to polarization strength and relaxation time by

$$\Delta\sigma_D = \frac{\epsilon_0 \Delta\epsilon_D}{\tau_2},$$

where $\Delta\epsilon_D$ is the polarization strength and τ_2 is the relaxation time of the "principal" range. Those solutes that depressed the principal relaxation time (compared to pure ice) increased the dielectric conductivity. Certain solutes ($NaHCO_3$, NH_4OH, CO_2) did not affect the principal relaxation time, at least in a certain temperature range (see Table I), and the principal dielectric conductivity was then also that of pure ice. It follows that the polarization strength should also be unaffected by these solutes (Fig. 7).
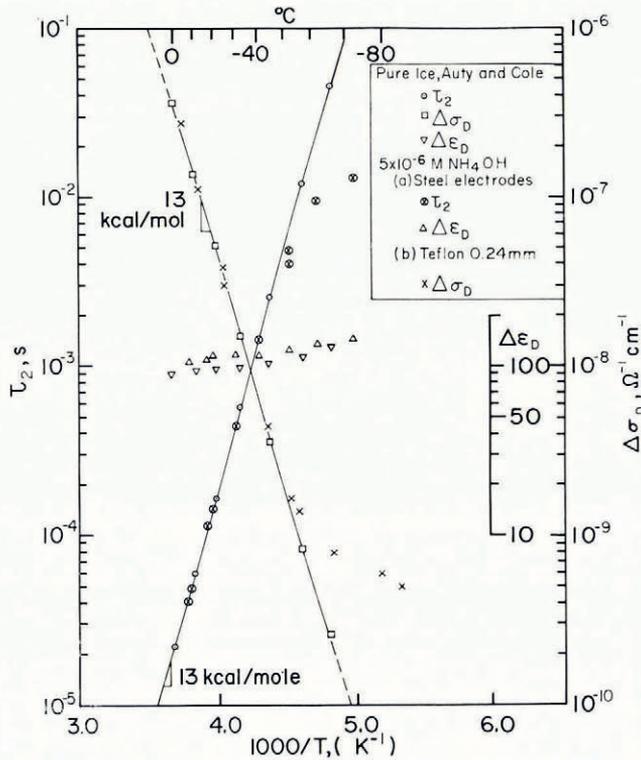
Fig. 7. *Dielectric conductivity, relaxation time, and polarization strength of the principal range in pure ice (after Auty and Cole, 1952) and in ice containing $5 \times 10^{-6} M$ NH_4OH, the solubility limit (cf. Fig. 15). A high-frequency dispersion range (Range 3) was absent in ammonium-hydroxide ice. Space-charge effects were minimal. The principal relaxation range was determined with stainless-steel guard electrodes because the Teflon correction could not be computed (the static conductivity was below instrumental sensitivity, and the associated low-frequency relaxation enters in the correction). The dielectric conductivity was the same with either stainless-steel or Teflon blocking electrodes. At low temperatures, both $\Delta\sigma_D$ and τ_2 deviate from the pure ice lines. This may indicate an incipient lattice interaction as defined in this paper. The polarization strength is about 10% higher than Auty and Cole's pure-ice values. This may simply represent experimental uncertainty.*

The effects of solutes on the dielectric conductivity are illustrated in Figures 5, 7, 8. Alkali-metal halides and ammonium fluoride increased both the static and dielectric conductivities. Ice doped with ammonium chloride and ammonium bicarbonate exhibited a strongly increased, and concentration dependent, dielectric conductivity while the static conductivity was reduced.
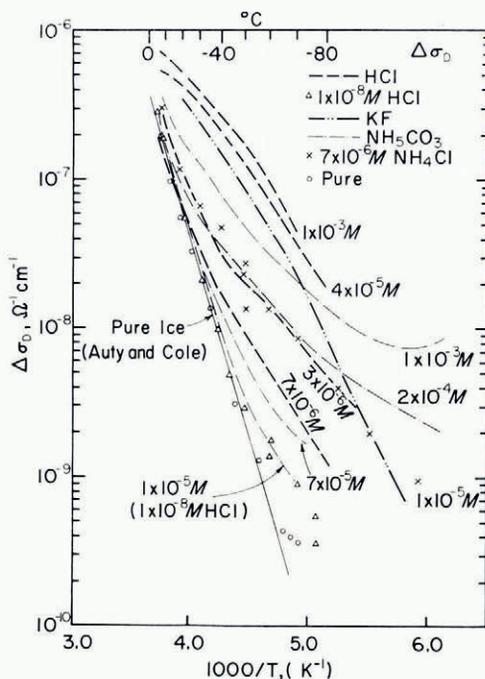
Fig. 8. *Composite diagram of principal dielectric conductivities determined for this study. The HCl curves correspond to those of Figures 3 and 9. A few are omitted because of crowding. The apparent reversal in sequence of the curves for $3 \times 10^{-6}M$ and $7 \times 10^{-6}M$ is unexplained. It is not due to an error (at least an obvious one) either in concentration measurement or in assignment of relaxation ranges. NH_5CO_3 curves are those corresponding to Figures 6 and 11.*

In ice moderately or highly doped with an alkali-metal halide or its acid, σ_0 is an appreciable component of $\sigma_{\infty D}$. The blocking-electrode method gives σ_0 and $\Delta\sigma_D$ separately with the same set of a.c. readings.

The composite graph of Figure 8 suggests that HCl, a proton-enhancing solute, ion for ion increases the dielectric conductivity more than NH_5CO_3, a proton-depressing solute. The effect of NH_4Cl, however, another proton-depressant, appears roughly comparable to HCl. This matter requires further investigation.

Impurity effects in ice have been compared with color centers in alkali halides (Von Hippel, 1971). Dryden and Meakins (1957) found that in alkali halides doped with a divalent cation, dielectric relaxation time and static conductivity had the same activation energy. It was concluded from this that both processes were due to the motion of the impurity. In ice, therefore, the two processes must be different (as is generally accepted).

Principal relaxation time τ_2 (Figs 9, 10, 11)

The principal relaxation time was unaffected by NH_4OH, $NaHCO_3$ ($< 1 \times 10^{-5}M$), and CO_2. For these solutes, it coincided with those measured for pure ice (solid line on figures). Below about $-50°C$ we observed a flattening of the slope for NH_4OH, $NaHCO_3$, CO_2, and

for pure ice. This was perhaps due to accidental impurities or lattice faults or to an incipient extrinsic effect (see below).

All solutes other than those named, shortened the principal relaxation time, and a strong concentration dependence is evident.
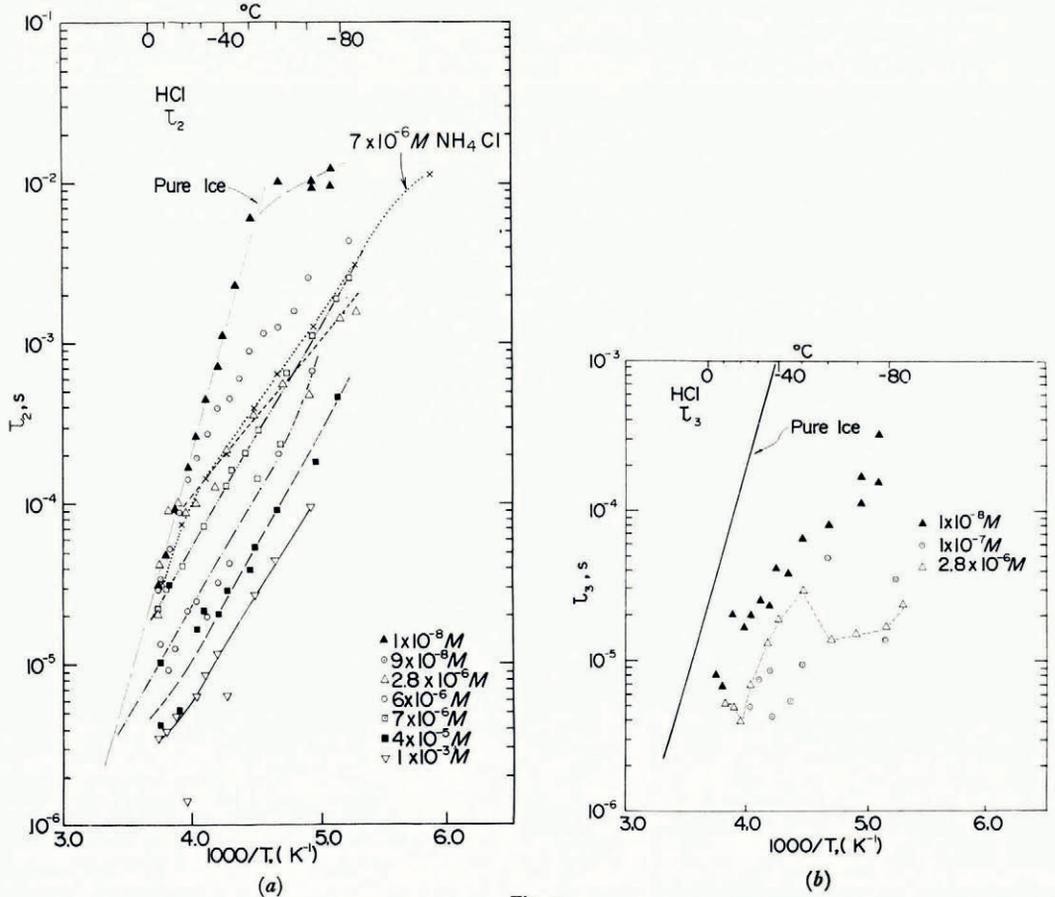
Fig. 9

(a) Principal relaxation time of ice samples with several concentrations of HCl (or NaCl). Same samples as Figure 3. Pure-ice values for comparison. ($1 \times 10^{-5} M$ KF omitted because of crowding. It falls where expected if solute concentration is the only independent variable. $7 \times 10^{-6} M$ NH$_4$Cl shown instead.)

(b) High-frequency relaxation time τ_3 measured in ice containing traces of HCl. This range could only be resolved below $3 \times 10^{-6} M$. Solid line: principal values of pure ice.

Polarization strength of the principal range $\Delta\epsilon_D$ (Figs 12, 13)

Ammonium salts of chloride and bicarbonate gave reproducible values similar to those of pure ice, and those for pure ice were consistent with those found by other investigators (e.g. Auty and Cole, 1952).

No clear trend could be discerned in the chlorides of hydrogen and sodium (Fig. 12). Among the factors that may be responsible, individually or collectively, are: The polarization strength is more severely affected by uncertainties in the assignment of spectral ranges than the parameters τ_2 and σ_0. Doping with these proton-supplying impurities causes a closer overlap between ranges thus increasing the uncertainty of spectral separation. In particular
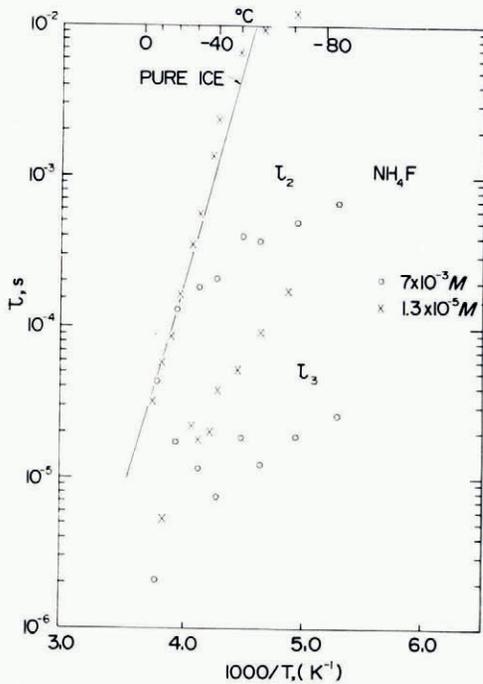
Fig. 10. τ_2 and τ_3 of ice with two concentrations of NH_4F. Pure ice values of τ_2 for comparison.
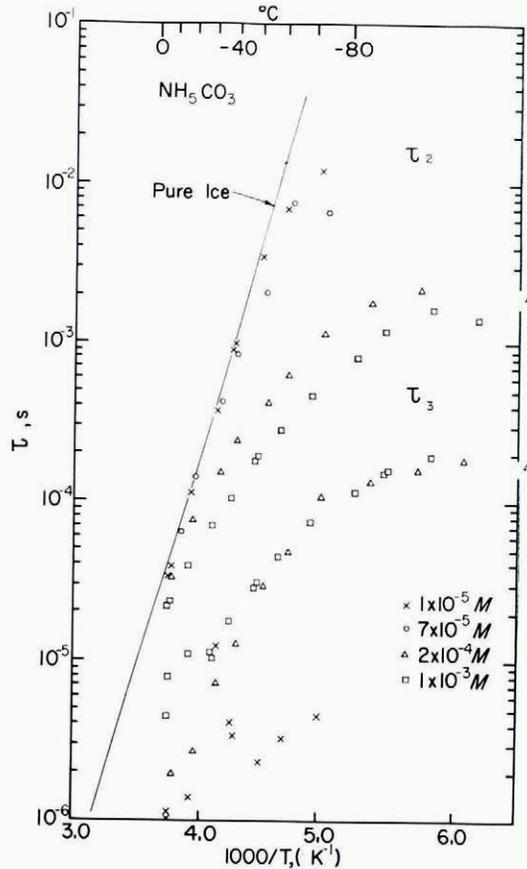
Fig. 11. Ice doped with NH_5CO_3. Relaxation times of the principal and high-frequency range as a function of concentration and temperature. τ_3 increased with concentration, in contrast with the other solutes studied for this paper (cf. Fig. 13).

the proton-supplying impurities apparently produce a strongly overlapping additional range. We have not always been able to separate it from the principal range. If these two ranges are seen as one, the combined polarization strength could easily be doubled.

However, there is also evidence that for certain doping levels and temperatures the principal polarization strength may drop to very low levels ($\leqslant 10$). The existence of such minima in HF-doped ice was reported by earlier investigators (Steinemann, 1957; Von Hippel and others, 1972; Camplin and Glen, 1973), but the systematic shift of these minima with temperature and concentration is missing from our data.

The high-frequency dispersion ranges (3 and 4)

Range 3 was well developed in chloride ice at the lower concentrations, in ammonium fluoride, ammonium chloride, and in ammonium bicarbonate ice (Figs 9(b), 10, 11). It came progressively into the frequency range ($\leqslant 100$ kHz) as the temperature dropped. Camplin and Glen (1973) show this range for hydrogen fluoride in ice. Range 4 could not always be resolved. The polarization strength corresponding to Range 3 was generally of the order of 10 (Figs 12, 13, 14), and Range 4 stayed around one.
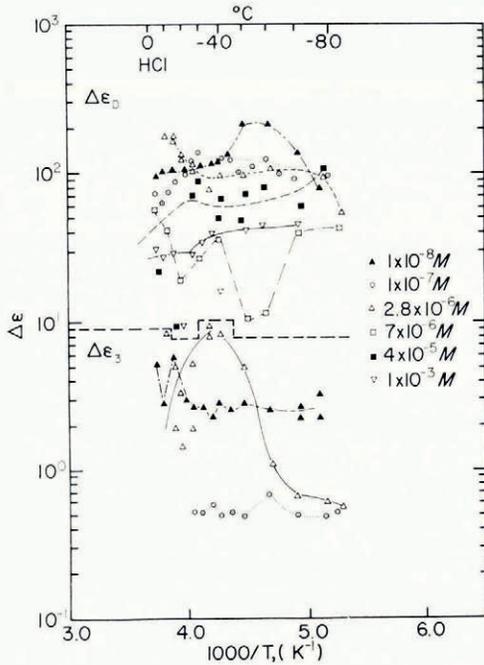
Fig. 12. *Principal and high-frequency polarization strength of ice with several concentrations of HCl (or NaCl). These are the same samples as in Figures 3 and 9.*
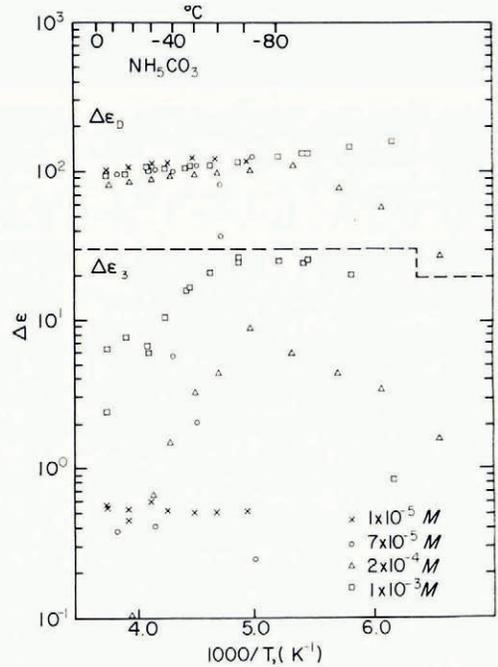
Fig. 13. *Ice doped with NH_5CO_3. Principal and high-frequency polarization strength (cf. Fig. 11).*
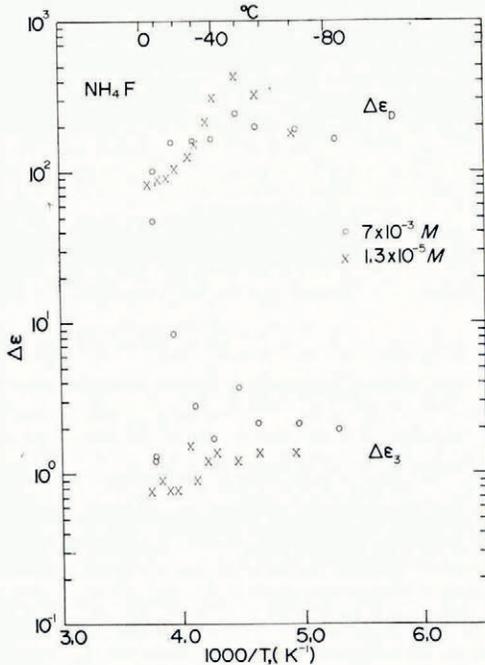
Fig. 14. *Principal and high-frequency polarization strength of ice samples with two concentrations of NH_4F.*
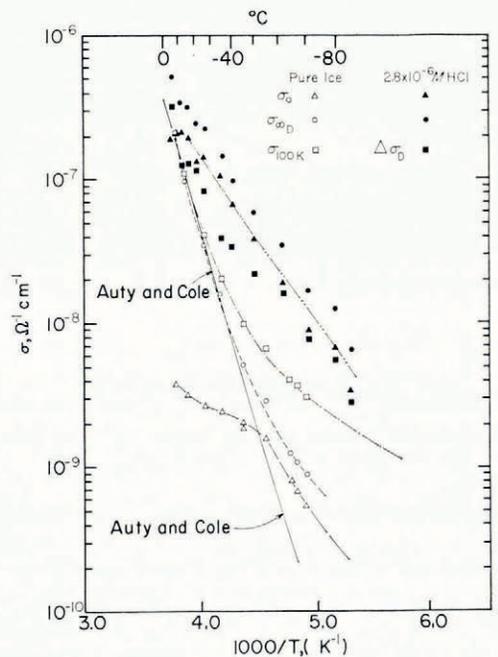
Fig. 15. *Comparison of conductivities. Pure ice: static conductivity σ_0, limiting conductivity of the principal range $\sigma_{\infty D}$, and conductivity at 100 kHz (which includes Range 3) for a sample of pure ice. $2.8 \times 10^{-6} M$ HCl: σ_0, $\Delta\sigma_D$, and $\sigma_{\infty D}$. A cross-over is absent in either case.*

The fluorides

A systematic study of the fluorides has not been completed as of this writing. Nonetheless, it appears that the spectra are similar to those for the chlorides. In particular, the respective laws of concentration dependence of σ_0, τ_2, and $\Delta\sigma_D$ are probably identical for both anions. For the static conductivity, this had been found experimentally by Gross (1965) and it was assumed by other investigators who studied only the fluorides.

DISCUSSION

The effect of solutes on the static conductivity is related to both the amount and the kind of impurity in the ice. Thus, e.g. for identical concentrations in the ice of HCl and NH_4Cl, the latter exhibits a conductivity in ice which is typically from one to three orders of magnitude lower than that of the former. This characteristic can be directly related to processes of selective ion incorporation taking place during solidification (Workman and Reynolds, 1950; Gross, 1968; Cobb and Gross, 1969). The solutes that were found to increase the static conductivity are either acids (HF, HCl, H_2CO_3) or those salts in which the anion is preferentially incorporated (NaF, NaCl, etc.). In these cases, the growing ice surface acquires a negative charge and attracts protons from the liquid for neutralization. Fluoride ice, although it rejects ammonium, does so to a much lesser extent than with other cations. Consequently, the extrinsic proton population in ice with NH_4F is reduced compared to ice grown from an alkali metal fluoride solution, and this is strongly reflected in the static conductivity (Fig. 4).

Figures 5 and 10 show that dielectric relaxation time and dielectric conductivity of ice with ammonium fluoride show little or no impurity effects at temperatures above $-20°C$, even for a doping level of $7 \times 10^{-3}M$. The (fluoride) distribution coefficient of NH_4F in ice is about ten times that of hydrogen fluoride (Gross and others, 1975[b]). Taken together, these results seem to indicate (a) that ammonium fluoride fits into the ice lattice better than most other solutes, and (b) that it generates fewer electrical point defects (ionic and orientational defects). The foregoing reconciles to some extent apparently conflicting measurement results reported by Dengel and others (1966) and by Levi and Lubart (1968), respectively.

The ammonium salts of chloride and bicarbonate generate a high positive potential difference between the growing ice surface and the water because the cation is preferentially incorporated. Since they require hydroxyl groups for neutralization, these solutes (as well as bases such as NaOH, NH_4OH) suppress protons and depress the static conductivity. This depression of the static conductivity is probably the reason why the ice-positive freezing potential difference of most ammonium salts is higher than that of the ice-negative alkali-halide solutions. On the other hand, the effects of ammonium chloride on the dielectric conductivity (Fig. 8) and on the principal relaxation time (Fig. 9) are comparable to those of hydrogen chloride at a similar concentration. Thus, ammonium chloride does not seem to be an exact counterpart of ammonium fluoride.

Our results indicate that static conductivity in ice is controlled by extrinsic protons.

Our curves of static conductivity versus $1\,000/T$ for both chloride- and fluoride-doped ice differ from those published by other investigators (for HF-doped ice) by the absence of an S-shape (see, e.g. Von Hippel and others, 1972, fig. 12; Camplin and Glen, 1973). This point requires further study. However, the results are consistent with our own measurements of the static conductivity of both HCl- and HF-doped ice done a number of years ago with a direct-current technique (Gross, 1962, 1965). Maeno (1973, fig. 11) shows curves similar to ours for ice single crystals doped with KCl. An S-shape could be due to electrode space-charge effects. Space-charge effects are minimized by our blocking-electrode technique.

Bullemer and others (1969) measured the static bulk and surface conductivity of ice with a gold anode and a palladium cathode. Gold is characterized as a poor proton injector,

palladium is a good proton injector and acceptor. They obtained straight-line plots similar to ours but with a higher activation energy (8 kcal/mol, 1.9 kJ/mol compared with our 6 kcal/mol, 1.4 kJ/mol). Proton injection with a Pd or Pd–H anode (Engelhardt and others, 1969) led to a reduction of the activation energy. This reduction became more pronounced with increasing voltage. Applying the same reasoning to our results, it is likely that the very small (alternating) voltages used (3–100 V), in conjunction with the blocking electrodes, minimized proton injection and electrode space-charge effects. This could account for our straight-line plots.

A second possible explanation for the discrepancy in curve shapes is the fact that with a blocking-electrode technique the static conductivity is derived from a circuit analog. In the work of previous investigators with conventional gold foil or evaporated gold electrodes, the static conductivity was taken from the limiting low-frequency conductivity of the principal relaxation range. Gränicher (1969, p. 532) has pointed out that in the presence of space-charge effects this may lead to error, although this factor should be minimized with the correction procedure used by Von Hippel and others (1971), and by Camplin and Glen (1973).

A third possibility is that it may be due to the fact that most of our samples were aged from four months to as long as two years before the measurements were made. This was the result of the lengthy procedures required and a large stock of crystals we had accumulated. Although the crystals were stored at −25°C to −30°C, some annealing of defects may have occurred. With possibly one exception (CO_2-doped ice) no evidence of appreciable outward migration of solutes was observed.

A "cross-over" (Bilgram and Gränicher, 1974) of static and high-frequency conductivity was not observed, although a slight flattening of the high-frequency conductivity with decreasing temperature was observed in some cases (Figs 7, 8, 15).

If a high-frequency dispersion range exists above the principal range, then two high-frequency conductivities can be considered for the purposes of the "cross-over", the upper limiting conductivity of the principal range and the high-frequency limiting conductivity (Fig. 15). The above comment applies to both.

A tentative classification of solutes and their effects on the dielectric relaxation spectrum (Table I)

Based on their chemical effects, the investigated solutes are divided into *proton-enhancing* and *proton-suppressing*. Each of these groups is further subdivided into *interacting* and *non-interacting* solutes, depending on whether the principal relaxation range is altered with respect to pure ice. Since the electrical effects of a solute are, in general, both temperature and concentration dependent, this classification is only valid for the narrow temperature and concentration domains investigated for this study. Thus, for example, at the low-temperature end "non-interacting" solutes may begin to interact (e.g. NH_4OH, Fig. 7). Furthermore, this classification is only valid for the small number of solute species actually investigated. It is based on a crude, and probably naïve, picture of the relation between impurities and lattice.

Proton-enhancing solutes introduce extrinsic hydrogen ions into the ice lattice and, as a result, greatly increase the static conductivity. In addition, the alkali halides and their acids *interact* with the lattice polarization, that is, the dielectric conductivity is increased (and the principal relaxation time is reduced). A possible reason is that these solutes introduce lattice (L-) defects, or, alternatively, lower the energy required for the thermal formation of lattice defects in their neighborhood (Von Hippel, 1971). These effects are absent in the *non-interacting* solutes. For example, CO_2 increases the static conductivity but (at least above −40°C) does not affect the principal relaxation. $NaHCO_3$ and NH_4OH suppress protons and do not interact with the lattice as defined above. The work of Kelly and Salomon (1969)

suggests that NaOH belongs with this group also. NH_4F represents a sort of transition between proton-enhancing and proton-suppressing solutes. It interacts weakly with the lattice. Ammonium chloride and bicarbonate are solutes that reduce the static conductivity but strongly interact with the lattice polarization.

Distribution coefficients and dielectric relaxation

Based on the work of Seidensticker (1972), who linked concentration dependence of the distribution coefficient with the creation of electrical point defects in the ice lattice, Bilgram (1974) has suggested that hydrogen fluoride and chloride should show similar or identical dielectric relaxation spectra, except perhaps at very high concentrations (Bilgram and Gränicher, 1974). While the present work seems to bear out the prediction, the premise apparently does not hold (Gross and others, 1977). The distribution coefficient of hydrogen fluoride is strongly concentration dependent while that of hydrogen chloride is not and is lower by about a factor of ten. Bilgram's argument, therefore, should be re-examined because of its bearing on widely accepted notions about electrical point defects in ice.

SUMMARY OF CONCLUSIONS

The blocking-electrode technique is especially well suited for the study of solutes that increase the static conductivity of ice. A model based on a few (2 to 4) discrete relaxation frequencies seems to fit the solutes investigated for this study.

Hydrogen fluoride and hydrogen chloride in ice show very similar electrical properties but very unlike distribution coefficients. This feature is not satisfactorily explained by present concepts.

No cross-over has been observed between the static and the high-frequency conductivities, with any of the solutes investigated. Neither did the static conductivity of conductivity-enhancing solutes (HCl, HF, NaCl, KF, CO_2) show the S-shaped Arrhenius plots reported by other investigators.

On the other hand, bases, or solutes that impart a positive freezing potential to the ice suppress extrinsic protons by attracting hydroxyls to the nascent ice surface. In this case, the static conductivity is only weakly temperature dependent and much lower.

The results suggest that the static conductivity is controlled by extrinsic protons in both doped and "pure" ice.

The dielectric conductivity contribution is strongly dependent on impurity concentration but appears to be less affected than the static conductivity by the nature of the solute.

Most solutes depress the principal relaxation time but carbon dioxide and pure bases leave it unchanged above a threshold temperature of typically $-40°C$ to $-60°C$.

REFERENCES

Auty, R. P., *and* Cole, R. H. 1952. Dielectric properties of ice and solid D_2O. *Journal of Chemical Physics*, Vol. 20, No. 8, p. 1309–14.

Bilgram, J. H. 1974. Phase equilibria and point defects in ice. *Physics of Condensed Matter*, Vol. 18, No. 4, p. 263–73.

Bilgram, J. H., *and* Gränicher, H. 1974. Defect equilibria and conduction mechanisms in ice. *Physics of Condensed Matter*, Vol. 18, No. 4, p. 275–91.

Bryant, G. W., *and* Fletcher, N. H. 1965. Thermoelectric power of ice containing HF or NH_3. *Philosophical Magazine*, Eighth Ser., Vol. 12, No. 115, p. 165–76.

Bullemer, B., *and others.* 1969. Protonic conduction of ice. Part I: high temperature region, [by] B. Bullemer, H. Engelhardt, N. Riehl. (*In* Riehl, N., *and others*, ed. *Physics of ice: proceedings of the international symposium on physics of ice, Munich, Germany, September 9–14, 1968. Edited by N. Riehl, B. Bullemer, H. Engelhardt.* New York, Plenum Press, p. 416–29.)

Camp, P. R., *and others.* 1969. Electrical conduction in ice, [by] P. R. Camp, W. Kiszenick, D. Arnold. (*In* Riehl, N., *and others*, ed. *Physics of ice: proceedings of the international symposium on physics of ice, Munich, Germany, September 9–14, 1968. Edited by N. Riehl, B. Bullemer, H. Engelhardt.* New York, Plenum Press, p. 450–70.)

Camplin, G. C., *and* Glen, J. W. 1973. The dielectric properties of HF-doped single crystals of ice. (*In* Whalley, E., *and others*, ed. *Physics and chemistry of ice: papers presented at the Symposium on the Physics and Chemistry of Ice, held in Ottawa, Canada, 14–18 August 1972. Edited by E. Whalley, S. J. Jones, L. W. Gold.* Ottawa, Royal Society of Canada, p. 256–61.)

Cobb, A. W., *and* Gross, G. W. 1969. Interfacial electrical effects observed during the freezing of dilute electrolytes in water. *Journal of the Electrochemical Society*, Vol. 116, No. 6, p. 796–804.

Dengel, O., *and others.* 1966. Messungen der Dielektrizitätskonstanten von reinem und NH_4F-dotiertem Eis, [von] O. Dengel, N. Riehl und A. Schleippmann. *Physik der kondensierten Materie*, Bd. 5, Ht. 2, p. 83–88.

Dryden, J. S., *and* Meakins, R. J. 1957. Dielectric relaxation processes in lithium, sodium, and potassium halides. *Discussions of the Faraday Society*, No. 23, p. 39–49.

Engelhardt, H., *and others.* 1969. Protonic conduction of ice. Part II: low temperature region, [by] H. Engelhardt, B. Bullemer, N. Riehl. (*In* Riehl, N., *and others*, ed. *Physics of ice: proceedings of the international symposium on physics of ice, Munich, Germany, September 9–14, 1968. Edited by N. Riehl, B. Bullemer, H. Engelhardt.* New York, Plenum Press, p. 430–42.)

Gränicher, H. 1969. Evaluation of dielectric dispersion data. (*In* Riehl, N., *and others*, ed. *Physics of ice: proceedings of the international symposium on physics of ice, Munich, Germany, September 9–14, 1968. Edited by N. Riehl, B. Bullemer, H. Engelhardt.* New York, Plenum Press, p. 527–33.)

Grant, F. A. 1958. Use of complex conductivity in the representation of dielectric phenomena. *Journal of Applied Physics*, Vol. 29, No. 1, p. 76–80.

Gross, G. W. 1962. Four-electrode method for measuring the direct-current resistivity of ice. *Science*, Vol. 138, No. 3539, p. 520–21.

Gross, G. W. 1965. Ion incorporation and activation energies of conduction in ice. *Annals of the New York Academy of Sciences*, Vol. 125, Art. 2, p. 380–89.

Gross, G. W. 1968. Some effects of trace inorganics on the ice/water system. *Advances of Chemistry Series* (Washington, D.C., American Chemical Society), Vol. 73, p. 27–97.

Gross, G. W. 1975. Dielectric relaxation spectrum and conductivity of ice crystals doped with ionic impurities. *Annual Report. Conference on Electrical Insulation and Dielectric Phenomena, 1974* (National Academy of Sciences, Washington, D.C.), p. 347–58.

Gross, G. W., *and others.* 1975[a]. Concentration dependent solute redistribution at the ice/water phase boundary. I. Analysis, [by] G. W. Gross, C. McKee and Chen-ho Wu. *Journal of Chemical Physics*, Vol. 62, No. 8, p. 3080–84.

Gross, G. W., *and others.* 1975[b]. Concentration dependent solute redistribution at the ice/water phase boundary. II. Experimental investigation, [by] G. W. Gross, Chen-ho Wu, L. Bryant and C. McKee. *Journal of Chemical Physics*, Vol. 62, No. 8, p. 3085–92.

Gross, G. W., *and others.* 1977. Concentration dependent solute redistribution at the ice/water phase boundary. III. Spontaneous convection. Chloride solutions, [by] G. W. Gross, Pui Mun Wong and K. Humes. *Journal of Chemical Physics*, Vol. 67, No. 11, p. 5264–74.

Hobbs, P. V. 1974. *Ice physics.* Oxford, Clarendon Press.

Jaccard, C. 1959. Étude théorique et expérimentale des propriétés électriques de la glace. *Helvetica Physica Acta*, Vol. 32, Fasc. 2, p. 89–128.

Kelly, D. J., *and* Salomon, R. E. 1969. Dielectric behavior of NaOH-doped ice. *Journal of Chemical Physics*, Vol. 50, No. 1, p. 75–79.

Levi, L., *and* Lubart, L. 1968. On the electric properties of ice doped with NH_4F. *Physik der kondensierten Materie*, Bd. 7, Ht. 5, p. 368–71.

Maeno, N. 1973. Single crystals of ice grown from KCl solution and their dielectric properties. *Canadian Journal of Physics*, Vol. 51, No. 10, p. 1045–52.

Maidique, M. A., *and others.* 1971. Transfer of protons through "pure" ice I_h single crystals. III. Extrinsic versus intrinsic polarization; surface versus volume conduction, [by] M. A. Maidique, A. [R.] Von Hippel and W. B. Westphal. *Journal of Chemical Physics*, Vol. 54, No. 1, p. 150–60.

Mounier, S., *and* Sixou, P. 1969. A contribution to the study of conductivity and dipolar relaxation in doped ice crystals. (*In* Riehl, N., *and others*, ed. *Physics of ice: proceedings of the international symposium on physics of ice,*

Munich, Germany, September 9–14, 1968. Edited by N. Riehl, B. Bullemer, H. Engelhardt. New York, Plenum Press, p. 562–70.)

Noll, G., and Käss, M. 1969. Untersuchung zur Segregation von Ammonium-fluorid bei Eis-Einkristallen. Physik der kondensierten Materie, Bd. 8, Ht. 4, p. 312–22.

Seidensticker, R. G. 1972. Partitioning of HCl in the water–ice system. Journal of Chemical Physics, Vol. 56, No. 6, p. 2853–57.

Steinemann, A. 1957. Dielektrische Eigenschaften von Eiskristallen. II. Dielektrische Untersuchungen an Eiskristallen mit eingelagerten Fremdatomen. Helvetica Physica Acta, Bd. 30, Fasc. 7, p. 581–610.

Von Hippel, A. R. 1971. Transfer of protons through pure ice I_h single crystals. II. Molecular models for polarization and conduction. Journal of Chemical Physics, Vol. 54, No. 1, p. 145–49.

Von Hippel, A. R., and others. 1971. Transfer of protons through "pure" ice I_h single crystals. I. Polarization spectra of ice I_h, [by] A. [R.] Von Hippel, D. B. Knoll and W. B. Westphal. Journal of Chemical Physics, Vol. 54, No. 1, p. 134–44.

Von Hippel, A. R., and others. 1972. Dielectric and mechanical response of ice I_h single crystals and its interpretation, [by] A. [R.] Von Hippel, R. Mykolajewycz, A. H. Runck and W. B. Westphal. Journal of Chemical Physics, Vol. 57, No. 6, p. 2560–71.

Workman, E. J., and Reynolds, S. E. 1950. Electrical phenomena occurring during the freezing of dilute aqueous solutions and their possible relationship to thunderstorm electricity. Physical Review, Second Ser., Vol. 78, No. 3, p. 254–59.

Young, I. G., and Salomon, R. E. 1968. Dielectric behavior of ice with HCl impurity. Journal of Chemical Physics, Vol. 48, No. 4, p. 1635–44.

DISCUSSION

C. JACCARD: With blocking electrodes, dielectric parameters can be obtained from the measurements only indirectly. What are the errors on the values plotted in the figures?

G. W. GROSS: We were greatly concerned about this matter. We investigated it in two ways: (i) For pure ice samples, the apparent Debye relaxation times measured with blocking electrodes were corrected for the Maxwell–Wagner effect. These corrected values agree very closely with the values published by Auty and Cole (1952). (ii) Cycling a sample through the temperature range (that is, measuring the complete spectra at approximately the same temperatures both on cooling and heating) gave values for principal relaxation times and static conductivity that agreed within 5–10% in most cases. The weaker high-frequency ranges were less consistent. The lack of hysteresis, especially in proton-increasing solutes, is in notable contrast with results obtained with metal electrodes (even evaporated gold).

JACCARD: What do you estimate the concentration inhomogeneity of the samples to be?

GROSS: This can be estimated from the complete concentration profiles (example in our Fig. 1). Typically it would amount to at most a factor of two, and generally much less (1.1 or 1.2).

J. H. BILGRAM: Did you observe out-diffusion of Cl?

GROSS: No, we did not. Samples measured at intervals of the order of a year gave identical spectra within experimental error.

R. TAUBENBERGER: The reason for taking blocking electrodes in the case of proton-enhancing doped samples was apparently to suppress to some extent the large space-charge dispersion found with metal electrodes. How can you make sure that the $\sigma_0(1/T)$ data worked out from the former (blocking-electrodes) method are linked to proton concentrations available in the same way as are the σ_0 values you get from the latter as you do not know how the spectra look at lower frequencies in both cases?

GROSS: Another reason for using blocking electrodes was to obtain a better separation of spectral ranges, as discussed by Mounier and Sixou (1969). Admittedly, there is an ambiguity in the determination of σ_0, especially if there are no measurement points close to the abscissa intersection of the linearized plot (i.e. of ϵ' where $\omega\epsilon'' = 0$). In such cases, we used a Cole–Cole plot to find the intersection. Incidentally, the complete interpretation, not just that of σ_0, is

impossible if the abscissa intersection cannot be reliably established. We were forced to discard a considerable amount of data for this reason. In any case, you are right that there is always an ambiguity. Moreover the static conductivity is derived from a circuit analog and therefore it is an approximation. The results are, however, strikingly self-consistent and reproducible, much more so than straight d.c. measurements.

TAUBENBERGER: How is the scatter in the $\Delta\epsilon$ values for blocking-type measurements compared with that with metal electrodes? Could the scatter or significant differences be due to uncertainties or errors in reducing data with Maxwell's layer model and/or to Von Hippel's method of spectra analysis in the plot ϵ' versus $\omega\epsilon''$, beginning at the highest frequency?

GROSS: We believe that the scatter in $\Delta\epsilon$ is the result of several factors: (i) Small irregularities in the blocking electrodes vary with temperature, they affect $\Delta\epsilon$ more than they do the other parameters (σ, τ). (ii) The magnitude of $\Delta\epsilon$ and its range of variation over the temperature range is very different from those of the other parameters. (iii) The two correction procedures (Maxwell–Wagner and Von Hippel's) conspire to make the principal (or Debye) dielectric constant (ϵ_2) especially vulnerable to small errors. This becomes evident when looking at linearized graphs $(\epsilon''\omega$ versus $\epsilon')$ and the expression for extracting the corrected ice value of ϵ_2 from the layered dielectric data. (iv) The scatter also seems to be related to the degree of overlap of relaxation ranges because it was not observed in data for pure ice and ice grown from solutions of proton-depressing solutes (which show less overlap in the $\Delta\epsilon_D$ region). A detailed analysis of the model is being prepared for publication.

TAUBENBERGER: I find it very interesting that you also never reached a clear-cut cross-over in the sense of Jaccard's model. Would you take this also as a proof—or at least a hint—that charge carriers depicted by σ_0 do not interfere with the Bjerrum defects as they are thought to do in this model?

GROSS: To a large extent, the physics of the electrical properties of ice owes its development to the theoretical work by Jaccard and Gränicher. But it must be recognized that their model is built on a very narrow experimental base. I believe that the time has come for methodical and comprehensive measurements with the best available techniques. It should not come as a surprise if, after such measurements are in and the complete evidence is analysed, the models were found to require adjustment or change. In the meantime, let us not jump to conclusions. In our view the data presented in this paper *suggest* (but do not prove) that the charge carriers responsible for the static conductivity do not interfere with those that cause the dielectric conductivity.