The dc conductivities of seven concentrated aqueous acids, and the electrical relaxation properties of four of these, are reported. At the glass transition temperature $T_g$, as determined by differential thermal analysis, the dc conductivities increase with $T_g$ for the individual acids, according to an Arrhenius function with an activation energy (at constant structure) of $8.6 \pm 0.3$ kcal mole$^{-1}$. A similar activation energy is approached for the conductance of individual acid glasses at temperatures low enough for the structure to be completely “frozen,” suggesting all systems conduct by the same mechanism. It is believed this is a proton transfer (Grotthuss-type) mechanism. Under conditions where the structure can change with temperature, the apparent activation energy for conduction is higher, $\sim 35$ kcal mole$^{-1}$. Electrical relaxation in these media, both supercooled liquid and glass, is found to be characterized by nonexponential response functions. Data have been analyzed using an electrical modulus formalism. The Davidson–Cole distribution function gives an excellent description of the imaginary part of the modulus. The Davidson–Cole parameters remain constant for a given glass once the structure becomes frozen. It is further demonstrated that the electrical relaxation behavior of these acids is very similar to that characterizing other amorphous ionic conductors, both liquid and glassy. The generally good description of conductivity relaxation afforded by the Davidson–Cole function is discussed in terms of an ionic diffusion mechanism, similar to that described by the Glarum model for cooperative dielectric relaxation.

Electrical relaxation in amorphous protonic conductors

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The dc conductivities of seven concentrated aqueous acids, and the electrical relaxation properties of four of these, are reported. At the glass transition temperature $T_g$, as determined by differential thermal analysis, the dc conductivities increase with $T_g$ for the individual acids, according to an Arrhenius function with an activation energy (at constant structure) of $8.6 \pm 0.3$ kcal mole$^{-1}$. A similar activation energy is approached for the conductance of individual acid glasses at temperatures low enough for the structure to be completely “frozen,” suggesting all systems conduct by the same mechanism. It is believed this is a proton transfer (Grotthuss-type) mechanism. Under conditions where the structure can change with temperature, the apparent activation energy for conduction is higher, $\sim 35$ kcal mole$^{-1}$. Electrical relaxation in these media, both supercooled liquid and glass, is found to be characterized by nonexponential response functions. Data have been analyzed using an electrical modulus formalism. The Davidson–Cole distribution function gives an excellent description of the imaginary part of the modulus. The Davidson–Cole parameters remain constant for a given glass once the structure becomes frozen. It is further demonstrated that the electrical relaxation behavior of these acids is very similar to that characterizing other amorphous ionic conductors, both liquid and glassy. The generally good description of conductivity relaxation afforded by the Davidson–Cole function is discussed in terms of an ionic diffusion mechanism, similar to that described by the Glarum model for cooperative dielectric relaxation.

INTRODUCTION

It has recently been reported by Angell, Bressel, and Gammell$^1$ that the dc conductivity of a concentrated dichromic acid solution $H_2Cr_2O_7 \cdot 7.16H_2O$, at its glass transition temperature is four orders of magnitude higher than that of salt solutions of comparable concentration and the same high viscosity. The excess conductivity of the acid was attributed to the high mobility of the protons, which were presumed to diffuse by the “Grotthus” mechanism, and it was suggested that glasses of such concentrated acids may constitute a novel class of amorphous protonic semiconducting materials. Such substances are of interest both for the comparison with amorphous electronic semiconductors which they may provide, and for the selective membrane materials for fuel cells and hydrogen generators which they may lead to. The protonic mechanism for the excess conductance has since been strongly supported by ion substitution experiments described elsewhere.$^2$

In this paper we describe investigations into the factors which determine the type of materials which exhibit high protonic conductivities, and the mechanism by which conduction occurs. For this purpose the strong protonic acids obtained from aqueous solutions of HCl and ZnCl$_2$ have proved useful because their glass transition temperatures change rapidly with changing ZnCl$_2$ content, thus making it possible to separate the effects of temperature and structural relaxation on the proton mobility. Accordingly, we have studied the “dc” (low frequency limit) conductivities at the glass transition temperature for several mixtures in the HCl–ZnCl$_2$–H$_2$O system. As far as possible the water to proton ratio has been kept constant at 4.00, although in some cases solutions of this concentration could not be quenched to glasses in large enough quantities, and excess water had to be added.

The dc conductivity accurately reflects the proton mobility in these media, but it only gives information on the zero frequency component of the response of the substance to electrical field perturbations from the equilibrium state. Thus, in principle, dc conductivity studies can provide only limited information about the details of the charge migration mechanism. In an attempt to obtain a more detailed insight, and to facilitate comparison with the mechanism of conduction in the high conducting alkali metal silicate and aluminosilicate glasses, we have also studied the frequency dependence of the electrical conductivity and dielectric constant for several solutions in the HCl–ZnCl$_2$–H$_2$O system, both above and below their glass transition temperatures. Since such electrical relaxation studies have only recently been exploited in the study of supercooled and vitreous solutions, we review briefly the important elements of the data analysis.

ELECTRICAL RELAXATION

Dielectric relaxation phenomena are usually described in terms of the complex relative permittivity $\varepsilon^*$:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon' - j(\sigma - \sigma_0)/\omega\varepsilon_0,$$

where $\omega$ is the angular frequency, $\varepsilon'$ the dielectric constant, $\varepsilon''$ the dielectric loss, $\sigma$ the specific conductivity, $\sigma_0$ the dc conductivity and $\varepsilon_0$ the permittivity of free space ($8.854 \times 10^{-14}$ F cm$^{-1}$). The quantities $\varepsilon'$ and $\sigma$ are obtained directly from the experimentally measured parallel resistance $R$ and capacitance $C$:

$$\varepsilon' = C/C_0, \quad \sigma = \varepsilon_0/R C_0 = k/R,$$

where $C_0$ is the vacuum capacitance of the conductance cell with cell constant $k$. Note that if the material has a nonzero dc conductivity $\sigma_0$, this is subtracted from the measured conductivity $\sigma$, and $\varepsilon''$ calculated from $\sigma - \sigma_0$ rather than $\sigma$. This form of analysis can therefore be usefully employed only when $\sigma_0$ is accurately known, and is appropriate only if the process leading to the dc conductivity is unrelated to the dipole reorientation process of interest.

Electrical relaxation, which occurs by the field-
biased diffusion of ions rather than the rotation of dipoles, has been termed "conductivity relaxation." It proves advantageous, for both practical and conceptual reasons, to analyze conductivity relaxation in terms of the "electric modulus" formalism, rather than the usual permittivity formalism. The electric modulus $M^*$ is the inverse of the complex permittivity,

$$M^* = \frac{1}{\varepsilon} = M' + jM'' = \frac{\varepsilon'}{\varepsilon + \varepsilon''} + j\frac{\varepsilon''}{\varepsilon + \varepsilon''},$$

where $\varepsilon''$ now includes the contribution from $\sigma_0$. Conductivity relaxation in amorphous materials is often analyzed in terms of a distribution of conductivity relaxation times, $g(\tau)$, and the generalized expressions for $M'$ and $M''$ are

$$M' = \left(\frac{\omega \tau}{1+\omega^2 \tau^2}\right),$$

$$M'' = \left(\frac{\omega \tau}{1+\omega^2 \tau^2}\right),$$

where the notation $g(\tau) = \int_0^\infty x g(x) dx \tau$. The magnitude of the dispersion in $\sigma$ and $\varepsilon'$ is determined by $g(\tau)$, and the low and high frequency limits of the specific conductivity, $\sigma_0$ and $\sigma_\infty$, are given by

$$\sigma_0 = \varepsilon_0 \varepsilon_\infty / (\tau_\infty)$$

and

$$\sigma_\infty = \varepsilon_\infty / (1/\tau_\infty),$$

where $\varepsilon_\infty$ is the high frequency limit of $\varepsilon'$ for the conductivity relaxation. The low frequency limit of $\varepsilon'$, $\varepsilon_0$, is given by

$$\varepsilon_0 = (\varepsilon_\infty (\tau_\infty)) \varepsilon_\infty.$$

For a single relaxation time, it is clear from Eqs. (6)–(8) that $\varepsilon_0 = \varepsilon_\infty$ and $\sigma_0 = \sigma_\infty$. Thus a dispersion in conductance can only occur in systems characterized by a "distribution of relaxation times," i.e., systems for which the electric field response function is nonexponential. In this respect conductivity relaxation is qualitatively distinguished from dielectric relaxation, in which the magnitude of the dispersion in $\sigma$ and $\varepsilon'$ is determined by thermodynamic, rather than kinetic, properties of the system.

In recent years electrical relaxation in ionically conducting materials has been extensively studied and analyzed in terms of the modulus formalism. The alkali silicate glasses have been studied by Macedo, Moynihan, and co-workers, and a fused anhydrous nitrate mixture has been studied by Howell et al., a study of several molten calcium nitrate hydrates has been reported by Ambrose et al., and concentrated aqueous solutions of lithium chloride have been studied by Moynihan et al. In all of these systems the modulus is characterized by a broadly asymmetric distribution of relaxation times. In several cases the empirical relaxation function of Williams and Watts has been shown to give a good fit to these modulus data, particularly at low frequencies (see later). Hakim and Uhlmann found that the empirical DavidsonCole function best fitted their permittivity data for Cs$_2$O–SiO$_2$ and Na$_2$O–SiO$_2$ glasses, but this does not necessarily indicate a different mechanism for these materials since the distribution functions for $\varepsilon^*$ and $M^*$ are different. (They can be related by an expression suggested by Gross for the mechanical analogue.) An adequate theoretical basis for the treatment of these empirical findings remains to be developed.

**EXPERIMENTAL**

All solutions were made up with distilled, deionized water ($\sigma_0 = 10^{-6}\Omega^{-1} m^{-1}$ at 25 °C) and reagent grade salts and acids. The solutions of HCl were prepared by adding water to reagent grade concentrated hydrochloric acid, and the concentration checked by titration against freshly prepared standard sodium hydroxide.

The glass transition temperatures $T_e$ were measured by differential thermal analysis, using a technique similar to that described by Angell and Sare. Calibrated chromel/alumel thermocouples were protected from corrosion by a glass sheath, which was collapsed onto the junction to ensure a good thermal contact. The same thermocouple was used to monitor the temperature in the conductivity experiments.

The limiting low frequency (hereafter referred to as dc) conductivities were obtained with a two terminal cell described elsewhere, and the frequency dependence data with an all-metal three terminal cell also described elsewhere. For $f \leq 500$ Hz a modified Berberian–Cole bridge constructed in this laboratory was used. For 1 KHz $\leq f \leq 20$ KHz a Wayne–Kerr B221 bridge was used in conjunction with a GR1309–A oscillator and GR1232–A tuned amplifier and detector. For 50 KHz $\leq f \leq 2$ MHz a Wayne–Kerr 601 bridge was used in conjunction with a Wayne–Kerr SR268 source and detector unit. Resistance and capacitance data are precise to $\pm 1\%$, though the accuracy and reproducibility of the low conductance values being measured under our very low temperature, corrosive, and frequently non-equilibrium (vitreous) conditions, is much poorer in most cases.

For the initial dc measurements the conductance cell was placed in a large styrofoam insulated aluminum block which was immersed in liquid nitrogen contained in a large dewar. Temperature control to $\pm 0.1$ °C was achieved by dripping liquid nitrogen on the block from time to time. Data were taken over a small interval of temperature about $T_e$ sufficient to permit approximate determination of conductance activation energies.

For the frequency dependence studies the cell was immersed in an ethanol–methanol bath which was cooled with a flow of cold nitrogen gas through a copper tube heat exchanger. Temperature control in this case was generally to within $\pm 0.2$ °C over the duration of a run (30 min), though in some cases larger drifts were tolerated. The total drifts over the frequency range in which most of the relaxation occurred ($\pm 3$ decades) are recorded in Table II. In order to minimize time, hence temperature drifts, data were obtained at only 4 frequencies/decade, namely at 1, 2, 5, and 10 Hz.
TABLE I. dc conductivities, and derived quantities, for acid and salt solutions at their glass transition temperatures $T_g$.

<table>
<thead>
<tr>
<th>System</th>
<th>$T_e$ (°K)</th>
<th>$\sigma_0$ $\Omega^{-1}$ cm$^{-1}$</th>
<th>$E_{401}(T_e)$ observed kcal mol$^{-1}$</th>
<th>$\epsilon'(T_e)$</th>
<th>$\langle \tau_p \rangle$ (sec)</th>
<th>Mobility cm$^2$ sec$^{-1}$ V$^{-1}$</th>
<th>$D$ cm$^2$ sec$^{-1}$</th>
<th>$R_{rms}$ displacement (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{Cr}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$</td>
<td>161.9</td>
<td>4.0 x 10$^{-9}$</td>
<td>31</td>
<td>6.0</td>
<td>1.3 x 10$^{-4}$</td>
<td>4.0 x 10$^{-12}$</td>
<td>5.6 x 10$^{-14}$</td>
<td>0.66</td>
</tr>
<tr>
<td>$\text{HZnCl}_2 \cdot 4\text{H}_2\text{O}$</td>
<td>185.6</td>
<td>8.9 x 10$^{-9}$</td>
<td>34</td>
<td>10.0</td>
<td>9.9 x 10$^{-5}$</td>
<td>1.8 x 10$^{-11}$</td>
<td>2.9 x 10$^{-13}$</td>
<td>1.31</td>
</tr>
<tr>
<td>$\text{HZnCl}_3 \cdot 4\text{H}_2\text{O}$</td>
<td>169.5</td>
<td>7.7 x 10$^{-9}$</td>
<td>34</td>
<td>9.6</td>
<td>1.1 x 10$^{-4}$</td>
<td>1.1 x 10$^{-11}$</td>
<td>1.7 x 10$^{-13}$</td>
<td>1.06</td>
</tr>
<tr>
<td>$\text{H}_2\text{ZnCl}_4 \cdot 12\text{H}_2\text{O}$</td>
<td>164.3</td>
<td>4.4 x 10$^{-9}$</td>
<td>28</td>
<td>8.9</td>
<td>1.8 x 10$^{-4}$</td>
<td>5.1 x 10$^{-12}$</td>
<td>9.1 x 10$^{-14}$</td>
<td>0.93</td>
</tr>
<tr>
<td>$\text{HZnCl}_4 \cdot 10\text{H}_2\text{O}$</td>
<td>152.0</td>
<td>3.5 x 10$^{-10}$</td>
<td>24</td>
<td>7.7</td>
<td>1.9 x 10$^{-3}$</td>
<td>4.9 x 10$^{-12}$</td>
<td>6.4 x 10$^{-15}$</td>
<td>0.85</td>
</tr>
<tr>
<td>$\text{H}_2\text{ZnCl}_4 \cdot 12\text{H}_2\text{O}$</td>
<td>147.1</td>
<td>2.7 x 10$^{-10}$</td>
<td>36</td>
<td>7.3</td>
<td>2.4 x 10$^{-3}$</td>
<td>4.2 x 10$^{-12}$</td>
<td>5.3 x 10$^{-15}$</td>
<td>0.87</td>
</tr>
<tr>
<td>$\text{HCl} \cdot 6\text{H}_2\text{O}$</td>
<td>128.2</td>
<td>2.0 x 10$^{-12}$</td>
<td>...</td>
<td>6.0</td>
<td>2.6 x 10$^{-1}$</td>
<td>2.7 x 10$^{-12}$</td>
<td>3.0 x 10$^{-15}$</td>
<td>0.68</td>
</tr>
<tr>
<td>$\text{Li}_2\text{ZnCl}_7 \cdot 12\text{H}_2\text{O}$</td>
<td>163.9</td>
<td>5.5 x 10$^{-12}$</td>
<td>42</td>
<td>6.0</td>
<td>9.6 x 10$^{-2}$</td>
<td>6.8 x 10$^{-15}$</td>
<td>1.1 x 10$^{-16}$</td>
<td>0.73</td>
</tr>
</tbody>
</table>

DATA ANALYSIS

The quantities $\sigma$, $\epsilon'$, $\epsilon''$, $M'$, and $M''$ were calculated from the experimentally determined quantities $1/R$, $R$, $C$, and $C_0$ using Eqs. (1)-(3). dc conductances from the three terminal cell measurements were determined from the frequency-independent conductance values or from short extrapolations of the low frequency data down to $10^{-1}$ Hz.

The Davidson–Cole relaxation function [Eqs. (9)]

$$M'' = M_s \sin(\gamma \phi)(\cos \phi') \tag{9a}$$

$$M' = M_s [1 - \cos (\gamma \phi)(\cos \phi')] \tag{9b}$$

$\phi = \arctan(\omega \tau_0)$.

The parameter $\gamma$ was determined from the halfwidth of the peak, with an estimated maximum uncertainty of $\pm 0.01$. The parameters $M_s$ and $\tau_0$ were then determined from the peak height, $M''_{max}$, and the frequency at which this maximum occurred, $f_{max}$ using the relations

$$M_s = M''_{max} / [\sin(\gamma \phi_{max})(\cos \phi_{max})] \tag{10}$$

and

$$\tau_0 = (2\pi_{max})^{-1} \tan(\phi_{max}) \tag{11}$$

where $\phi_{max} = (\pi/2)[1/(1 + \gamma)]$. For this procedure, the estimated uncertainties in $M_s$ and $\tau_0$ are about 5%.

RESULTS

Two terminal cell measurements

Two terminal cell dc conductivities at $T_e$ were obtained for acid solutions of the following stoichiometries: $\text{HZnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{HZnCl}_3 \cdot 4\text{H}_2\text{O}$, $\text{H}_2\text{ZnCl}_4 \cdot 12\text{H}_2\text{O}$, $\text{H}_2\text{ZnCl}_4 \cdot 10\text{H}_2\text{O}$, and $\text{H}_2\text{Cr}_2\text{O}_7 \cdot 12\text{H}_2\text{O}$, also for $\text{Li}_2\text{ZnCl}_7 \cdot 12\text{H}_2\text{O}$. The values obtained are collected in Table I, together with several derived quantities, calculated as follows:

1. The average relaxation times for charge migration, $\langle \tau_p \rangle$, were calculated from Eq. (6) using $\epsilon'$ values estimated from the high frequency measurements described below.

2. The mobilities were obtained by equating the densities at $T_e$ to those measured at room temperature (estimated error ~ 1%), and assuming that all of the acid protons contributed equally to the conductivity:

$$\mu = \sigma_0 M/FN\rho$$

where $F$ is the Faraday constant, $M$ the formula weight, $\rho$ the density, and $N$ the number of protons per formula unit.

3. The diffusion coefficients $D$ of the charge-transporting species were calculated from the Nernst–Einstein equation:

$$D = k_B T \mu/e$$

where $k_B$, $T$, and $e$ have their usual meaning.

4. The root mean square jump distances $\bar{r}$ were obtained by equating $\langle \tau_p \rangle$ to the waiting time between jumps for an isotropic random walk process:

$$\bar{r}^2 = 6D \langle \tau_p \rangle \tag{14}$$

A plot of $\ln g_{\tau} (T_e)$, versus $1/T_e$ is given in Fig. 1. This plot suggests that $\sigma_0$ at $T_e$ is a common function of $T_e$ for all acids except $\text{HZnCl}_2 \cdot 4\text{H}_2\text{O}$, the anion of which is, presumably, extensively polymerized. The

FIG. 1. Limiting low frequency conductivity at the glass transition temperature, $\sigma_0(T_e)$, versus $1/T_e$ for the indicated acids.
which was never resolved. The upper temperature limit for relaxation measurements in these cases was 10 °C. The lower temperature limit was usually that at which the inverse relaxation time was less than the lower frequency bridge limit. The strongest acids, which are better defined in the following measurement, were all similar at about 30–34 kcal/mole. When the data are analyzed using the electrical modulus formalism $M''(f)$, this is primarily because the frequency dependence of $M''$ is independent of polarization processes, provided these are characterized by capacitances which are much larger than the bulk capacitance. As a result, the fitting of theoretical loss functions to the experimental curves is weighted minimally by spurious effects acting at low frequencies.

Figure 3 shows the frequency dependences of $M''(f)$ for all of the acids studied. The solid lines are the best fit Davidson–Cole functions. The latter are seen to give a good fit to the data, with large deviations occurring only at frequencies more than ~2 decades above the peak maximum. The parameters of the best fit Davidson–Cole functions are listed in Table II, which serves as a summary of the relaxation data.

The average relaxation time for charge migration, $\langle \tau_\phi \rangle$, is given by the product of the Davidson–Cole parameters $\gamma$ and $\tau_0$. It is shown (log scale) as a function of inverse temperature in Fig. 4 for the acid HZnCl$_4$·4H$_2$O. According to Eq. (6), $\langle \tau_\phi \rangle$ should have essentially the same temperature dependence as $\sigma_0$ since $M_0 (= 1/\epsilon_0)$ is a very weak function of temperature. To show this, and other features of the migration kinetics to be dealt with in the discussion section, the $\sigma_0$ values obtained both by (1) extrapolation of the low frequency conductances as in Fig. 2 (to exclude the polarization effects) and (2) calculation from Eq. (16) using $\langle \tau_\phi \rangle = \gamma \tau_0$ are plotted in the Arrhenius form in Fig. 4. For the remaining acids, only the calculated and observed $\sigma_0$ values are plotted in order to avoid congestion.

### Table II. Best fit Davidson–Cole parameters for relaxation data. Parameters determined from $M''(f)$.

<table>
<thead>
<tr>
<th>System</th>
<th>Average temperature °C</th>
<th>Drift °C</th>
<th>$\gamma$</th>
<th>$\tau_0$ (sec)</th>
<th>$\sigma_0$(calc) (Ω$^{-1}$cm$^{-1}$)</th>
<th>$\epsilon_\infty$(calc)</th>
<th>$\epsilon_\infty$(calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZnCl$_4^-$·4H$_2$O</td>
<td>-106.8</td>
<td>0.7</td>
<td>0.38</td>
<td>0.110</td>
<td>1.37x10$^{-1}$</td>
<td>1.52x10$^{-11}$</td>
<td>16.3</td>
</tr>
<tr>
<td>4H$_2$O</td>
<td>-101.0</td>
<td>0.7</td>
<td>0.38</td>
<td>0.110</td>
<td>5.28x10$^{-2}$</td>
<td>3.98x10$^{-11}$</td>
<td>16.4</td>
</tr>
<tr>
<td>$T_g$ = -87.7</td>
<td>-87.8</td>
<td>0.5</td>
<td>0.35</td>
<td>0.110</td>
<td>1.26x10$^{-2}$</td>
<td>1.80x10$^{-10}$</td>
<td>17.3</td>
</tr>
<tr>
<td>±0.5</td>
<td>-81.7</td>
<td>1.3</td>
<td>0.22</td>
<td>0.118</td>
<td>2.10x10$^{-5}$</td>
<td>8.66x10$^{-8}$</td>
<td>20.7</td>
</tr>
<tr>
<td>±0.5</td>
<td>-75.0</td>
<td>0.2</td>
<td>0.22</td>
<td>0.107</td>
<td>1.71x10$^{-6}$</td>
<td>1.62x10$^{-7}$</td>
<td>23.4</td>
</tr>
<tr>
<td>HZnCl$_2$·H$_2$O</td>
<td>-118.7</td>
<td>0.5</td>
<td>0.38</td>
<td>0.100</td>
<td>3.04x10$^{-2}$</td>
<td>7.56x10$^{-11}$</td>
<td>17.9</td>
</tr>
<tr>
<td>4H$_2$O</td>
<td>-109.0</td>
<td>0.2</td>
<td>0.36</td>
<td>0.102</td>
<td>3.60x10$^{-3}$</td>
<td>6.56x10$^{-10}$</td>
<td>18.2</td>
</tr>
<tr>
<td>$T_g$ = -103.7</td>
<td>-105.0</td>
<td>0.2</td>
<td>0.33</td>
<td>0.105</td>
<td>1.07x10$^{-3}$</td>
<td>2.37x10$^{-8}$</td>
<td>19.1</td>
</tr>
<tr>
<td>±0.5</td>
<td>-99.7</td>
<td>0.2</td>
<td>0.25</td>
<td>0.109</td>
<td>3.77x10$^{-5}$</td>
<td>8.59x10$^{-8}$</td>
<td>22.9</td>
</tr>
<tr>
<td>±0.5</td>
<td>-96.3</td>
<td>0.7</td>
<td>0.22</td>
<td>0.112</td>
<td>6.21x10$^{-6}$</td>
<td>5.77x10$^{-7}$</td>
<td>24.7</td>
</tr>
<tr>
<td>H$_2$ZnCl$_2$·12H$_2$O</td>
<td>-124.0</td>
<td>0.3</td>
<td>0.37</td>
<td>0.116</td>
<td>1.16x10$^{-1}$</td>
<td>1.75x10$^{-11}$</td>
<td>16.7</td>
</tr>
<tr>
<td>12H$_2$O</td>
<td>-115.0</td>
<td>1.0</td>
<td>0.35</td>
<td>0.112</td>
<td>9.46x10$^{-3}$</td>
<td>2.39x10$^{-10}$</td>
<td>17.2</td>
</tr>
<tr>
<td>$T_g$ = -109.3</td>
<td>-113.8</td>
<td>0.4</td>
<td>0.31</td>
<td>0.117</td>
<td>5.04x10$^{-3}$</td>
<td>4.75x10$^{-10}$</td>
<td>17.8</td>
</tr>
<tr>
<td>±0.5</td>
<td>-108.3</td>
<td>0.2</td>
<td>0.25</td>
<td>0.125</td>
<td>4.26x10$^{-4}$</td>
<td>6.47x10$^{-8}$</td>
<td>19.5</td>
</tr>
<tr>
<td>H$_2$ZnCl$_4$·10H$_2$O</td>
<td>-133.5</td>
<td>1.0</td>
<td>0.29</td>
<td>0.148</td>
<td>6.5x10$^{-1}$</td>
<td>4.6x10$^{-12}$</td>
<td>15.0</td>
</tr>
<tr>
<td>10H$_2$O</td>
<td>-129.7</td>
<td>0.3</td>
<td>0.28</td>
<td>0.147</td>
<td>1.9x10$^{-1}$</td>
<td>1.13x10$^{-11}$</td>
<td>15.5</td>
</tr>
<tr>
<td>$T_g$ = -121.7</td>
<td>-118.7</td>
<td>0.1</td>
<td>0.26</td>
<td>0.141</td>
<td>6.0x10$^{-4}$</td>
<td>4.0x10$^{-9}$</td>
<td>17.1</td>
</tr>
<tr>
<td>±114.5</td>
<td>0.05</td>
<td>0.26</td>
<td>0.128</td>
<td>2.6x10$^{-5}$</td>
<td>1.03x10$^{-7}$</td>
<td>18.8</td>
<td>7.81</td>
</tr>
</tbody>
</table>
FIG. 2. Frequency dependences of the conductivity $\sigma$ and relative permittivity $\varepsilon'$ for the acid $\text{HZnCl}_3 \cdot 4\text{H}_2\text{O}$ at the indicated temperatures. Dotted lines indicate the expected behavior in the absence of electrode polarization (see text).

Where available, values of $\sigma_0$ obtained by the two terminal cell method (near or at the DTA $10^o\text{ min}^{-1}$ $T_g$), are also included. If the phenomenon under study is a conductivity relaxation, the calculated and observed $\sigma_0$ values should be in agreement over the whole temperature range studied. Figure 4 satisfies these expectations within acceptable limits of accuracy for the conditions of experimentation.
**DISCUSSION**

**dc conductivities**

The dc conductivities of the acids studied are compared at their glass transition temperatures because the latter phenomenon, for glasses of the same thermal history (quench rate and heating rate), occurs when the average structural relaxation time of the substances have the same value. For our \( T_g \) determinations this value is estimated to be about 10 sec. The data in Table I and Fig. 1 show that the corresponding average electrical field relaxation times defined by Eq. (6) vary enormously, from values of the same order as the structural relaxation time (for HCl \( \cdot 6H_2O \)) to values four orders of magnitude smaller. For the acid solutions the factor determining the magnitude of this relaxation time disparity would appear to be the absolute temperature at which the glass transition occurs. The exception to this generalization is the acid HZnCl \( _5 \cdot 4H_2O \). However, this is not unexpected since, for this HCl : ZnCl \( _2 \) ratio, the anionic structure must be highly polymerized, and the solution structure may not even be homogeneous on the microscopic level near the glass transition temperature. In either case some disruption of the proton transfer mechanism may be anticipated, and this is consistent with the larger rms jump distance observed for this glass (Table I). The smooth increase in jump distance as the Cl/Zn ratio decreases from 4 to 2.5 is also consistent with other evidence that, in excess chloride, concentrated aqueous solutions of ZnCl \( _2 \) contain ZnCl \( _2^2- \) and \( (ZnCl_2) \_n \) species only.

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**FIG. 3.** The frequency dependences of the electric loss modulus, \( M'' \), for all of the acids studied.
The observed correlation of $\sigma_0$ at $T_f$ with the value of $T_e$, and particularly its Arrhenius form with $E_{\text{act}} = 8.6$ kcal mole$^{-1}$, can be understood in terms of a common mechanism for migration protons through the vitreous quasilattice. Such a common mechanism can be demonstrated directly for all the chlorozincate acids studied, by the common activation energy exhibited by each low temperature ($T \ll T_e$) glass. This is seen in Fig. 4, which shows clearly the decrease in dc conductivity activation energy as the solution structure finally ceases to change with decreasing temperature (i.e., becomes frozen even on the longer time scale of the conductance sample equilibrations). In this region the activation energy of these acids is seen to tend to a value close to the 8.6 kcal mole$^{-1}$ of Fig. 1.

The changes in slope in the Fig. 4 plots occur at a temperature some 10°C below the DTA-determined value of $T_e$. This results from the fact that in the DTA experiment the temperature is changing at 10° min$^{-1}$, and the system has less time to come to structural equilibrium than in the conductance cell, where some 10$^3$ sec were allowed for temperature equilibration at each chosen temperature. The structural relaxation which occurs below $T_e$ (DTA, 10° min$^{-1}$) can, under appropriate conditions, be monitored by the change in conductivity with time at constant temperature. For example, in a trial experiment a structural relaxation time of 150 sec was observed for the acid $\text{H}_2\text{Cr}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ at $-116$°C, some 5° C below $T_e$ (DTA, 10° min$^{-1}$).

The change of slope in Fig. 4 associated with structural arrest clearly shows that the conductivity of the glasses depends both on the absolute temperature and on the particular structure assumed by the glass at the temperature of measurement (see Ref. 9). In the vicinity of the DTA-determined $T_e$ each system shows an apparent conductance activation energy much greater than 8.6 kcal mole$^{-1}$ simply because the structure of the liquid is able to change in the time of the experiment, and the measured activation energy includes the activation energy for this structural rearrangement. That
this structural relaxation varies similarly with temperature for each solution is indicated by the comparable activation energies, 34 ± 2 kcal/mole for the solutions in Fig. 4 measured in the vicinity of $T_r$.

The approximate coincidence of the Fig. 1 Arrhenius plot slope with the individual solution frozen structure slopes (Fig. 4) suggests that at $T_r$ (i.e., at constant structural relaxation time) each acid solution exhibits, to the protons, the same structure (since at constant structure all that changes with temperature is the probability of crossing the fixed structure energy barrier). A common energy barrier is usually taken to imply a common migration mechanism. 22

The common element of the migration mechanism presumably lies in the dynamics of the [H$_2$O$^+$(H$_2$O)$_n$] species ($n > 1$). The activation energy may be determined by the same processes which occur in ice, and which lead to a common activation energy of 12.7 kcal/mole$^{-1}$ for both proton migration$^{21(a)}$ and dielectric relaxation in this substance.$^{22(a)}$ This activation energy corresponds to the breaking of three hydrogen bonds. The observed activation energy of 8.6 kcal/mole$^{-1}$ in the glasses is consistent with the possibility that in these materials the water molecules are arranged in two dimensional sheets between the chlorozincate anions, rather than in the three dimensional structure of ice (although it is recognized that direct comparisons with a substance as unique as ice must be made with great caution). In any event, the low activation energy observed in these materials may be taken as evidence that the conduction mechanism in the glasses studied is indeed proton hopping. It should also be noted, however, that the activation energy for molecular diffusion in ice is also of similar magnitude (15 kcal/mole$^{24}$) to those of the two processes referred to above, despite the different (interstitial$^{25}$) mechanism involved. This cautions that the possibility of H$_2$O$^+$ diffusion contributing to the conductivity of the acid glasses should not be dismissed, although the existence of channels in the glass structure large enough to permit H$_2$O$^+$ diffusivities four orders of magnitude greater than those of other cations seems rather improbable. Additional evidence for low activation energy conductance by protons through hydrated (silicate) glasses is provided by the work of Boksay et al.,$^{26}$ but the best evidence for a purely protonic mechanism in the vitreous acids is the precipitous decrease in conductivity at $T_r$ (i.e., at constant structural relaxation time) which occurs when protons are replaced by Li$^+$ ions. 2 However, the possibility that the protons migrate as mobile H$_2$O$^+$ ions cannot be excluded until $^{17}$O studies of H$_2$O diffusivity in these materials become available.

**Electrical relaxation**

The agreement of the calculated limiting low frequency conductivities, $\sigma_0$ in Table II, with the experimental values (see Fig. 4) indicates that the process under study is indeed a conductivity relaxation. Since a dispersion in $\sigma$ and $\epsilon'$ due to conductivity relaxation can only be observed if the response function is nonexponential [Eq. (8)], we see immediately that the nearly exponential responses characteristic of proton migration and dielectric relaxation in ice and pure water do not apply to the protonic media of this study. In their nonexponential responses, the present conduction processes resemble more those of ordinary ionic conductivity in glassy media. A question of interest, therefore, is whether or not the small size and mass of the mobile protons leads to response functions distinct from those describing the migration of relatively heavy ions, such as alkali cations, in other vitreous media. Before comparing our relaxation data with those for ionic conductors, however, we briefly review the relaxation functions which have been utilized for data analysis by previous authors, and the relation of these functions to the Davidson–Cole function with which we have fitted the present data.

It has been found by Macedo, Moynihan, and co-workers$^{14-16}$ that conductivity relaxation due to migration of alkali cations in Na and Li/Al silicate glasses$^{4,5}$ and in K/Al nitrate glasses, 9 may be described by the response function

$$E(t) = E(0) \exp[-(t/\tau)^\beta], \quad 0 < \beta < 1,$$

where $E(t)$ is the electric field vector at time $t$. A stress decay function of this form has long been used to describe viscoelastic processes in inorganic glasses,$^{57}$ but its application to dielectric processes has been pointed out only recently, first by Williams and co-workers.$^{12,28}$ We will refer to Eq. (15) and its frequency domain equivalent as the Williams–Watts function.

The time derivative of Eq. (15) is

$$\phi(t) = \dot{E}(t) = E(0)(\beta/\tau \partial t/\partial \tau)\exp[-(t/\tau)^\beta]$$

which is to be compared with the corresponding Davidson–Cole function$^{29}$

$$\phi(t) = [E(0)/\tau_0 \Gamma(\gamma)](t/\tau_0)^{-\gamma}\exp[-t/\tau_0],$$

where $\Gamma$ is the gamma function.

For the polar liquids studied by Williams and co-workers,$^{12}$ and also for the silicate glasses,$^{4,6}$ $\beta$ has a value close to 0.5. In this case the Fourier transform of Eq. (16) yields an expression for $M^*$ which can be written in terms of commonly occurring functions$^{12}$:

$$M^* = M_s\left[1 - (\pi/2)^{1/2} \frac{1-j}{\rho} \exp(-z^2) \operatorname{erfc}(-jz)\right],$$

where $\rho = (\omega \tau_0)^{1/2}$ and $z = [(1+j)/\rho][j = (-1)^{1/2}]$. For other values of $\beta$, $M^*$ is obtained by numerical integration.$^{7,58}$

$M''$ has also been fitted, less successfully, using logarithmic Gaussian, and double logarithmic Gaussian, distributions of relaxation times, in the cases of conductance in LiCl–H$_2$O solutions$^{11}$ and in silicate glasses,$^{4,6}$ respectively.

A comparison of the Williams–Watts and Davidson–Cole functions for one of the acids studied is given in Figs. 5(a) and (b). In Fig. 5(a) is shown the fit to data for glassy HZnCl$_3$·4H$_2$O taken at $-118.7^\circ C$, some 15 °C below its $T_r$. It is seen that the low frequency fits are practically indistinguishable, but that at high frequencies the Davidson–Cole function is clearly superior.
As the temperature increases, the Williams–Watts function gives increasingly poorer fits, whereas the Davidson–Cole fit remains good over most of the temperature range. This is illustrated in Fig. 5(b), where the two functions are fitted to data for HZnCl$_3$·4H$_2$O at −99.7 °C, some 4 °C above $T_r$. A somewhat better fit at low frequencies by the Williams–Watts function could be achieved by allowing $\beta$ to assume larger values, but the high frequency fit would still remain poor.

Figures 6(a)–(c) and 8(a) demonstrate that the Davidson–Cole function also provides a reasonably satisfactory description of the modulus for several ionic glasses. The observed high frequency losses in excess of the Davidson–Cole predictions are probably due to secondary relaxations of the $\beta$ type, which are observed separated from the principle relaxation in studies of the loss dependence on temperature at constant frequency, but which merge into it in isothermal loss vs frequency experiments. The $\beta$ relaxation in these materials will be discussed in a forthcoming publication, but in general they appear to originate in a localized charge-displacing mechanism, different in character from that leading to long range ionic migration, and for this reason alone it should perhaps not be expected that any simple function will provide a good fit over the whole frequency range. Overall, the fit to the high frequency data by the Davidson–Cole function seen in these figures is clearly superior to that of the functions chosen by the respective authors, although the low frequency data are generally better described by the Williams–Watts function. The Davidson–Cole parameter $\gamma$ which determines the half-width and shape of the $M''$ peaks for these ionic conductors, has values within the range of those best fitting the protonic glass data.

It is notable also that common to both ionic and protonic systems is an increase in the shape parameter with decreasing temperature as long as the liquid structure can change, and a constant value at lower temperatures. This is illustrated in Fig. 7, where the temperature dependences of $\gamma$ for the acids are compared with the corresponding variation in the Williams–Watts $\beta$ parameters for a nitrate glass. Apart from the exceptional behavior of the acid H$_2$ZnCl$_4$·10H$_2$O, which is discussed later, the temperature dependences of the shape parameters are strikingly similar. Their constancy far below $T_r$ is demonstrated in Fig. 8(a) and (b), in which the Davidson–Cole function has been fitted to master curves for the acids and for a silicate glass. It is noteworthy that the behavior of the shape parameter for the acid H$_2$ZnCl$_4$·4H$_2$O is indistinguishable from that of the other acids, thus confirming the conclusion arrived at earlier that the conductivity mechanism for this acid is essentially the same as for the others, differing only in the average time scale of proton migration.

The temperature dependence of $\gamma$ for the acid H$_2$ZnCl$_4$·10H$_2$O, Fig. 7, is much weaker than for the other acids, and the values of $\gamma$ itself are anomalously low. The anomalies can be shown, by constant fre-
frequency loss versus temperature data on this and other acids, \( n \) to be due to overlap of a structure-related \( \beta \) relaxation with the main \( \alpha \) conductivity relaxation for this acid. The \( \text{H}_2\text{ZnCl}_4 \cdot 10\text{H}_2\text{O} \) glass is the only case affected because it is the only case in which there is close proximity of the conductivity and structural relaxation times in the glass transition region. This overlap also gives rise to the anomalously high values of \( M' \), Table II, observed for \( \text{H}_2\text{ZnCl}_4 \cdot 10\text{H}_2\text{O} \), and resolves the apparent conflict between Fig. 4 (which indicates that the conductivity activation energy is the same for this case as for the others) and Fig. 7 (which suggests that a different mechanism is operative). For the other acids the conductivity relaxation time is shorter than the dielectric relaxation time for the \( \beta \) process, so that the latter is "short circuited" and does not contribute to the observed conductivity relaxation.

It is apparent from Figs. 3, 5, 6, and 8 that the Davidson-Cole function gives a good overall fit to data for a
great many vitreous systems, and that there seems little to distinguish the conductivity relaxation in the present systems from that characterizing other vitreous ionic conductors. The high frequency tails observed for almost all amorphous materials, including the vitreous acids, are well described by the Davidson–Cole function. One explanation of the similarity could be that the vitreous acid conductivity is in fact not purely protonic in nature but instead depends on the (field biased) diffusion of hydronium ions through the vitreous structure—a possibility mentioned earlier. However, other considerations given earlier suggest that it is protons jumping from one water molecule to another which may be closely analogous to, for example, alkali ions jumping from one silicate cage to another. There is evidence that electrical conductance in silicate glasses occurs by a cooperative interstitiality mechanism, in which an alkali ion is displaced by another ion jumping into the same, or possibly an adjacent, cage. The analogy in the vitreous acid systems would be the displacement of a proton from a water molecule as a result of another proton jumping onto the same, or adjacent, molecules, i.e., the Grotthus mechanism.

Some universal features of electrical relaxation in materials containing hopping charges have been recently summarized by Jonscher. He observes that both \((\epsilon' - \epsilon_0)\) and \(\epsilon''\) have the same simple \(\omega^n\) frequency dependence at high frequencies, so that the ratio \(\epsilon''/\epsilon'\) is independent of frequency, i.e., the ratio of energy lost to energy stored per cycle is independent of frequency. This implies that \(M''\) should also have a simple \(\omega^n\) frequency dependence at high frequencies [where \(\epsilon' - \epsilon_0 \gg \epsilon''\) see Eq. (3)], and this is observed for the protonic conductors, with \(n = 0.2\). The Davidson–Cole function also predicts a simple \(\omega^n\) dependence for \(M''\) at high frequencies: \(M'' \approx M_0 \sin (\pi n / 2) \times (\omega T)^n\). The mechanism proposed by Jonscher to account for this universal feature is analogous to the Debye–Falkenhagen effect: The ionic atmosphere relaxes to neutralize the excess dipole created by a jumping ion. The detailed nature of this atmospheric relaxation does not affect the result that \(\epsilon''/\epsilon'\) is independent of frequency, but it presumably arises from ionic diffusion. The atmosphere may relax by a mechanism analogous to the Glarum model for dielectric relaxation in polar liquids, which leads to a response function very similar to the Davidson–Cole function.

The high frequency tail of the Glarum function arises from diffusion of nearest neighbor "defects" to a trapped dipole. The latter can relax with a single relaxation time, or be relaxed by the first defect to arrive at the dipole site. The single relaxation time characterizing the dipole is essential for a well-behaved low frequency response in the Glarum model, and this necessity for a relaxation mechanism distinct from the diffusional one has been criticized. A satisfactory low frequency response can be generated without invoking a second mechanism, however, if second nearest neighbor defects are considered, according to Phillips et al. The calculations cannot be done exactly but, to an approximation which overestimates the low frequency response, Phillips et al. predict a response function which is similar to the Williams–Watts function with \(\beta \approx 0.514\). As is shown in Fig. 5(a), the low frequency response for values of \(\beta < 0.6\) is similar to the Davidson–Cole function with a value of \(\gamma\) near 0.4. If the reference dipole is identified with the excess dipole of Jonscher’s mechanism, and if the "defects" are identified with a center of charge of some sort, e.g., the diffusing ions themselves, a conductivity relaxation mechanism which is consistent with the observed behavior becomes apparent. The similarity of the high frequency responses observed in vitreous media may therefore reflect the fact that the short range order in the different media gives rise to similar electrical responses.

The shape parameter of the Davidson–Cole function is, in terms of the proposed relaxation mechanism, determined by the relative probability of first and second nearest neighbor defects diffusing to the reference dipole. Thus at constant structure the shape parameter should be independent of temperature, as observed. This invariance indicates that the nonexponential response function does not arise from a distribution in activation energies, and careful measurements on glasses with different thermal histories confirm this. This is consistent with the expectation that the first and second nearest neighbor defects cross energy barriers of the same average height, i.e., that they are both characterized by the same diffusion coefficient at all temperatures well below \(T_r\). However, above \(T_r\) the long range structure is able to relax as the short range order persists, thus introducing a difference in the average diffusion activation energies and a temperature-dependent response function.

CONCLUDING REMARKS

The present measurements identify a class of vitreous systems in which electricity is conducted predominantly by protons and in which the vitreous state conductivity seems to be limited only by the loss of rigidity at the glass transition temperature. Structural modification of the acids, e.g., by utilization of rigid polymeric anions, must lead to useful materials with very high proton conductivities at room temperature. Acid resins such as the Naions represent practical examples of such materials, though it remains to be established that the proton transport mechanism in such substances is the same as in the present glasses.

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Note that the acid HZnCl$_5$ • 4H$_2$O, which does not lie on the linear section of Fig. 1, is nevertheless characterized by the common activation energy of ~8.5 kcal mole$^{-1}$ in the glassy state far below $T_g$. Also the measured activation energy at its $T_g$ is comparable with that of the other acids. These observations indicate that the polymeric anion of this acid does not affect the overall proton migration mechanism but just the average time scale of this migration. The relaxation data, discussed below, confirm this.

The heating rate is ~0.2°C sec$^{-1}$, so that at $T_g$

$$\frac{d\tau}{dt} \approx \frac{\tau E_a}{RT^2} \left(0.2, \frac{E_a}{RT}\right) \approx \frac{\tau}{13}$$

for $E$ ~20 kcal mole$^{-1}$. The latter is estimated from $[E_a$(observed) - 8.6] $\approx E_a$(structural).

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