Charge injection and transport in high voltage water/glycol capacitors

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A water/ethylene glycol mixture to be operated at temperatures below 0 °C is being investigated for use as the high permittivity, low loss dielectric in pulse forming lines for pulsed power applications. High voltage open circuit decay curves show a dielectric relaxation time that decreases with initial voltage at room temperature, while at −10 °C, the open circuit decay has a negative second derivative with time in contrast to the expected exponential decay which always has a positive second derivative. It is hypothesized that this anomalous behavior is due to space-charge injection which increases the ohmic conductivity $\sigma$ to $\sigma + q \mu$, where $q$ is the time and space dependent net charge density with mobility $\mu$. A drift dominated conduction model is used to solve for the electric field and charge density distributions and the terminal voltage-current behavior of a lossy capacitor where one electrode injects charge proportional to the instantaneous local electric field. The specific case studied is of a parallel plate capacitor rapidly charged to an initial voltage and quickly open circuited. The calculated open circuit voltage decay curves show good agreement with measurements and yield experimental values for the charge injection parameter and the high field mobility of the injected charge. The value of mobility for the best fit of experimental data to the theory agrees with the value for the hydronium ion. Preliminary Kerr electro-optic field mapping measurements in highly purified water without glycol, confirm positive charge injection.

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I. INTRODUCTION

A. Background

In order to determine the suitability of highly purified ethylene glycol/water mixtures as the dielectric in the pulse forming lines of pulse power machines, measurements of the electrical properties of the mixtures as a function of mixture ratio and temperature have been made. The results of these measurements are reported in an earlier paper. During the course of this work it was found that at high electrical stress (> 5 MV/m), the open circuit voltage on parallel plate electrodes immersed in the liquid, decayed more quickly than would be indicated from low voltage measurements of the dielectric time constant. More rapid decay at high fields in itself is not too surprising as one might expect carrier mobilities to show field dependence. However, it soon became apparent that this simple picture could not explain the observed voltage decay waveforms at low temperatures. These waveforms display a change in the sign of the second derivative. Further, it was discovered that the decay was dependent on the plate separation. To explain the experimental observations, the hypothesis is made that net charge is injected into the liquid to increase its conductivity from $\sigma$ to $\sigma + q \mu$, where $q$ is the time and space dependent injected charge density with mobility $\mu$.

Charge injection for time varying and steady state excitations has been studied extensively. The transient case, which deals with the initial transport of charge through the medium, is the appropriate model for the conditions of the experiment. This paper presents a detailed study of the charge injection model and compares the results with experimentally observed high voltage waveforms. Preliminary Kerr electro-optic field mapping measurements confirm positive charge injection in pure water without glycol.

B. High voltage impulse circuit

Various water/glycol mixtures were used as the dielectric between round parallel plate bead blasted stainless steel electrodes of area 81 cm$^2$. The electrode gap spacing varied between 4–8 mm. This liquid filled capacitor is part of the high voltage impulse circuit shown in Fig. 1. When the Marx spark gap switch fires, the diode initially conducts, thereby charging the test capacitor.

During this charging interval, the response of the circuit is found by using Kirchhoff’s voltage law around the loop shown in Fig. 1. In Laplace transform notation:

$$
I \left( \frac{R_m}{R_mC_m s + 1} + R_s + \frac{R_w}{R_w C_w s + 1} \right) = 0.
$$

Solving the resulting quadratic equation for $s$ yields

$$
s_{\pm} = -\frac{a}{2} \pm \sqrt{\left(\frac{a}{2}\right)^2 - b},
$$

where

$$
a = \frac{1}{R_s} \left( \frac{R_m + R_s}{R_mC_m} + \frac{R_s + R_w}{R_w C_w} \right);
$$

$$
b = \frac{R_m + R_s + R_w}{R_m R_s R_w C_m C_w}.
$$
The test cell charging voltage has form

\[ v(t) = V_+ e^{t/\tau} + V_- e^{-t/\tau}. \]  

These solutions are valid until \( t \) becomes zero at time \( t \approx 19 \mu\text{sec}, \) when \( v(t) = v_m(t) \). At this time the diode stops conducting since thereafter \( v(t) \) is always larger than \( v_m(t) \) because the Marx decay time \( R_w C_w \) is less than the test cell decay time \( R_w C_m \). Both capacitors then decay exponentially with their respective time constants:

\[ v(t) = v(t_s) e^{-(t-t_s)/R_w C_w}, \]

\[ v_m(t) = v_m(t_s) e^{-(t-t_s)/R_w C_m}. \]

Also shown in Fig. 1 are the circuits of the voltage monitoring probes. The CuSO₄ resistive divider, on the Marx side of the diode, is very fast and used to record peak voltage on the test capacitor (the diode drop is negligible). The resistive probe impedance is \( \approx 100 \Omega \) and much higher than \( R_w \). Since the decay of the test cell voltage is so slow, it is necessary to use a capacitive divider probe on the test cell side of the diode in order to avoid degrading the test cell time constant \( R_w C_w \). The net probe capacitance is much less than the test cell capacitance. The capacitive divider probe circuit for excitations \( e^t \) has transfer function:

\[ V_{2}(s) = \frac{R_s C_s}{R_1 R_2 C_2 (C_0 + C_1) s^2 + s[(R_1 + R_2)(C_1 + C_0) + R_2 C_2] + 1}. \]
For time scales such that
\[
\frac{1}{(R_1 + R_2)(C_0 + C_1) + R_2 C_2} \ll |s| \ll \frac{1}{R_1 (C_0 + C_1)}
\]
\[+ \frac{1}{C_2} (1/R_1 + 1/R_2),
\]
14.3|s| \ll 5.9 \times 10^5 \text{ sec},
\]
this transfer function is constant:
\[
\frac{V_s(s)}{V(s)} \approx \frac{R_2 C_0}{(R_1 + R_2)(C_0 + C_1) + R_2 C_2}
\]
\[\approx 1.43 \times 10^{-3}.
\]

C. Open circuit high voltage decay

If the test cell is a lossy capacitor as modeled in Fig. 1 and describable by capacitance \( C_w \) and resistance \( R_w \), or equivalently by permittivity \( \varepsilon \) and resistivity \( \rho \), then after the diode opens at time \( t_o \), the test cell voltage for \( t > t_o \) decays exponentially as given in Eq. (8) with time constant \( \tau_w = R_w C_w = \varepsilon \rho \). Representative measurements of the charging \( t < t_o \) and the initial decay \( t > t_o \) of the high voltage are shown in Fig. 2. Note that the Marx capacitor voltage as shown by the CuSO_4 resistive divider decays much faster than the test cell voltage shown by the capacitive divider because \( R_w C_w \ll R_m C_m \), thus keeping the diode reverse biased. Figure 3 shows traces at longer time scales for high and low values of \( v(t_o) \). These traces are actually overlays of 10 separate tests to demonstrate waveform repeatability. The jagged part of the CuSO_4 traces at long times is due to the erratic shutoff time of the Marx trigger gaps. These tests used 80% glycol by weight at temperature of 25°C. At this temperature, \( \varepsilon = 51 \varepsilon_0 \) and \( \tau_w = 1.4 \text{ msec} \), measured at a low voltage. In all tests, \( \tau_w \) is always \( > t_o \). If the dielectric were linear [field independent values of \( \varepsilon \) and \( \rho \)] a plot of \( v(t) / v(t_o) \) vs \( (t - t_o) / \tau_w \) would be the same exponential decay for all values of \( v(t_o) \). Figure 4 compares the observed decay and shows that the initially higher voltage decays more rapidly.

![Figure 2](image2.png)

**FIG. 2.** Voltage waveforms. Bottom trace is the CuSO_4 probe which monitors the Marx voltage \( V_m(t) \) and gives accurate measure of peak voltage on the test cell (500 mV/div, 60.6 kV/V). Note the action of blocking diode at \( t \approx 19 \mu\text{s} \). Top trace is the slower responding capacitive probe which monitors the test cell voltage \( v(t) \) (200 mV/div, 70 kV/V). Note the different zero volt levels and voltage scales for each divider. Time scale is 20 \mu s/div.

![Figure 3](image3.png)

**FIG. 3.** Voltage decay at room temperature with 80% by weight glycol at 25°C. \( \tau_w = 1.4 \text{ msec} \), gap spacing = 5.1 mm. \( a \) \( v(t_o) = 99.3 \text{ kV} \), \( b \) \( v(t_o) = 64.7 \text{ kV} \). Note that \( b \) requires \( > 370 \mu\text{s} \) to decay from 4 to 3 scale divisions, while \( a \) requires only \( > 270 \mu\text{s} \) to decay through same voltage range. If the enhanced decay was simply due to field dependent mobility, curve \( a \) should decay in same time as \( b \) once it has dropped to corresponding voltage. Lower CuSO_4 trace has voltage scale 500 mV/div, while the upper capacitive probe has voltage scale 200 mV/div. Time scale is 100 \mu s/div.

The situation becomes more complex when the temperature of the liquid is lowered to \( \approx 10^° \text{C} \). At this temperature, the dielectric constant is increased to \( 61 \varepsilon_0 \) and the intrinsically different time constant \( \tau_w \) is increased fifteenfold to \( \approx 25 \text{ msec} \). The decay at low temperature is displayed in Fig. 5. These waveforms display an initial downward curvature (negative second derivative with time) in contrast to the usual exponential decay which always has upwards curvature (positive second derivative). To explain such behavior with only an enhanced mobility model, it would be necessary for the mobility to be a doubled valued function of the electric field (initially increasing with field, then decreasing). Another explanation is that net charge is injected from one electrode into the liquid and then under the action of the field, transported to the other electrode. The theory of such charge injection and transport is developed in the next section.

II. DRIFT DOMINATED CONDUCTION MODEL
A. Governing equations

We suspect that the anomalous voltage decay characteristics are due to injected space charge so that the simple resistive-capacitive equivalent circuit for the test capacitor
in Fig. 1 is no longer valid. To model this space-charge injection case, we consider parallel plate electrodes located at \( x = 0 \) and \( x = l \), where the \( x = 0 \) electrode is assumed to be a source of positive ions with constant mobility \( \mu \) as shown in Fig. 6. The dielectric has constant permittivity \( \varepsilon \) and intrinsic ohmic conductivity \( \sigma \). Neglecting edge effects, the electric field and conduction current are \( x \) directed and all quantities only depend on the \( x \) coordinate. The governing equations are then\(^2\text{--}^4\):

**Irrotational Electric Field:**

\[
\nabla \times \mathbf{JE} = 0 \rightarrow \int_0^l \mathbf{Edx} = \mathbf{v}.
\]

(12)

**Gauss's Law:**

\[
\nabla \cdot (\varepsilon \mathbf{E}) = q \rightarrow \frac{\partial \mathbf{E}}{\partial x} = \frac{q}{\varepsilon}.
\]

(13)

**Conservation of Charge:**

\[
\nabla \cdot \mathbf{J} + \frac{\partial q}{\partial t} = 0 \rightarrow \frac{\partial}{\partial x} \left( \mathbf{J} + \varepsilon \frac{\partial \mathbf{E}}{\partial x} \right) = 0.
\]

(14)

**Conduction Constitutive Law:**

\[
\mathbf{J} = \sigma \mathbf{E} + q \mu \mathbf{E}.
\]

(15)

Integrating Eq. (14) and using Eq. (13) with Eq. (15) relates the conduction current and displacement current to \( \mathbf{J}(\mathbf{t}) \), the total terminal current per unit electrode area \( \mathbf{S} \)

\[
\varepsilon \frac{\partial \mathbf{E}}{\partial t} + \sigma \mathbf{E} + \varepsilon \mu \mathbf{E} \frac{\partial \mathbf{E}}{\partial x} = \mathbf{J}(\mathbf{t}).
\]

(16)

It is convenient to nondimensionalize the governing equations by normalizing all variables to the electrode spacing \( l \), the initial voltage \( V_0 \), and nominal injected charge transit time \( l^2/(\mu V_0) \):

\[
\tilde{x} = x/l; \quad \tilde{v} = v/V_0; \quad \tilde{E} = EL/V_0; \quad \tilde{q} = ql^2/\varepsilon V_0; \quad \tilde{J} = Jl/(\mu V_0); \quad \tilde{t} = \frac{t}{l^2}; \quad \tilde{\tau} = \frac{\varepsilon}{\sigma} \mu V_0 l^2.
\]

(17)

Then Eq. (16) reduces to

\[
\frac{\partial \tilde{E}}{\partial \tilde{t}} + \frac{\tilde{E}}{\tilde{\tau}} + \tilde{E} \frac{\partial \tilde{E}}{\partial \tilde{x}} = \tilde{J}(\tilde{t}).
\]

(18)

By taking the spatial derivative of Eq. (18), the normalized charge density \( \tilde{q} \), related from Eq. (13) to the electric field as

\[
\tilde{q} = \frac{\partial \tilde{E}}{\partial \tilde{x}}.
\]

(19)

obeys the differential equation

\[
\frac{\partial \tilde{q}}{\partial \tilde{t}} + \frac{\tilde{q}}{\tilde{\tau}} + \tilde{E} \frac{\partial \tilde{q}}{\partial \tilde{x}} + \tilde{q}^2 = 0.
\]

(20)

The terminal voltage-current relation is found by integrating Eq. (18) between electrodes and using Eq. (12):

\[
\frac{d\tilde{v}}{dt} + \frac{\tilde{v}}{\tilde{\tau}} + \frac{1}{2} \left[ \tilde{E}^2(\tilde{x} = 1, \tilde{t}) - \tilde{E}^2(\tilde{x} = 0, \tilde{t}) \right] = \tilde{J}(\tilde{t}).
\]

(21)

**B. Method of characteristics**

The partial differential equations of Eqs. (18) and (20) can be converted to ordinary differential equations by jump-
where the right-hand sides are obtained using Eq. (22) in Eqs. (18) and (20). The charge density in Eq. (24) can be directly integrated

$$\tilde{q}(t) = \frac{\tilde{q}_o(t_0)}{\left(1 + \frac{\tilde{q}_o(t_0)}{\tilde{r}}\right) e^{-t/\tau} - \frac{\tilde{q}_o(t_0)}{\tilde{r}}}$$  \hspace{1cm} (25)

where $\tilde{q}_o(t_0)$ is the charge density injected into the system at time $t_0$. Thus the charge density is known as a function of time but we do not know its position $\tilde{x}$ until we integrate Eq. (22). We cannot integrate Eq. (22) until we know $\tilde{E}$ from Eq. (23), which requires knowledge of $\tilde{J}(t)$ which can be found from Eq. (21) if we know the voltage and the electric fields at both electrodes. In general, simultaneous solution of Eqs. (21)–(23) requires a numerical method. Fortunately, the experimental conditions allow a simple approximation, which will allow analytical solution.

### III. CASE STUDY

#### A. Model of experiment

In the experimental high voltage impulse circuit of Fig. 1, the test capacitor is charged in less than 19 $\mu$sec and decays thereafter in millisecond time scales. A representative charge transport time $t_r$ is estimated using representative values of $V_o = 100$ kV, $l = 5$ mm, and $\mu = 2 \times 10^{-7}$ m$^2$/Vsec:

$$t_r = l^2/\mu V_o \sim 1 \text{ msec.}$$  \hspace{1cm} (26)

Because the charging time $t_r \approx 19 \mu$sec is much shorter than either the charge transport time $t_r$, or the dielectric relaxation time $\tau_w$, we will assume that the test cell is instantaneously charged to an initial voltage $V_o$ at time $t = 0$ and open circuited for $t > 0$.

#### B. Charge injection

The problem is not completely specified until we define a relationship between the injected charge density and the electric field at the injection boundary. In general, we expect that the injected charge density increases with electrode electric field. Although numerical analysis can treat any injection law, we consider a very simple law which allows analytic solution:

$$q_o(x = 0, t) = AE(x = 0, t) = AE_0,$$  \hspace{1cm} (27)

or in terms of nondimensional variables,

$$\tilde{q}_o = \tilde{A} \tilde{E}_0; \quad \tilde{A} = \frac{A}{l/e}.$$  \hspace{1cm} (28)

$A$ is an injection level parameter indicating the constant instantaneous relationship between $q_o$ and $E_o$ at the charge injecting surface ($x = 0$). Because the surface charge density on the charge injecting electrode is itself proportional to the electrode electric field, $q_e = eE_0$, the injection law states that the injected volume charge density is some fraction of the surface charge density.

Several mechanisms can be postulated to support this simple injection law. If the injected charge were due to contact charging of small spherical conducting particulates ("microparticles") of radius $R$ and number density $N$, each sphere would pick up total charge

$$Q = \frac{2\pi R^3}{3} \epsilon R^2 E_0,$$  \hspace{1cm} (29)

where $\epsilon$ is the permittivity of the medium.
so the injected charge density is

\[ q_0 = NQ = \left( \frac{2}{3} \pi^2 e R^2 N \right) E_0. \] (30)

Then the injection level parameter \( A \) is

\[ A = \frac{2 \pi^3}{3} e R^2 N, \quad \tilde{A} = \frac{2 \pi^3}{3} R^2 N l. \] (31)

Considering microparticles of radius \( R = 1 \mu \) and number density \( N = 10^{13} / \text{m}^3 \) with \( l = 5 \text{ mm} \), we estimate \( \tilde{A} \sim 1 \).

Another charge injection mechanism is electron tunneling from the cathode. This type of field emission is described by the Fowler–Nordheim equation \(^{24,25}\)

\[ J_{\text{injected}} = B_1 E_0^2 e^{-\frac{B_2}{E_0}}, \] (32)

where

\[ B_1 = \frac{e^2}{8 \pi h \phi} \approx \frac{1.54 \times 10^{-6}}{\phi}, \] (33)

\[ B_2 = \frac{8 \pi \sqrt{2m_e} \phi^{3/2}}{3 h} = 6.83 \times 10^5 \phi^{3/2}, \]

and \( e = 1.6 \times 10^{-19} \text{ C}, \ h = 6.625 \times 10^{-34} \text{ J s}, \ m = 9.1 \times 10^{-31} \text{ kg}, \) and \( \phi \) is the electrode work function in electron volts (\( \sim 4 \text{ eV} \)). In the high field limit, \( E_0 \gg B_2 \), and once injected, the charge transport is governed by the mobility so that

\[ J_{\text{injected}} = q_0 / \mu E_0 = B_1 E_0^2. \] (34)

Thus in the high field limit this mechanism also produces an injection law of form (27) with \( A = B_1 / \mu \). Though the mechanism seems to require fields of order 100 times greater than the fields in our experiment, field enhancement due to the presence of surface irregularities and contaminants has been shown to produce substantial emission at 10 MV/m.\(^{12}\) Assuming that a field enhancement factor of 100 exists at the injecting surface, for the same conditions as the previous example, the injection parameter is estimated as

\[ \tilde{A} = \frac{1.54 \times 10^{-6}}{400} \frac{l}{\mu e} \sim 1.4 \times 10^8. \] (35)

The injection parameter in this case is characterized by large values of \( \tilde{A} \). The often assumed space-charge limiting case is \( \tilde{A} = \infty \) for then \( \tilde{E}_0 = 0 \). Another mechanism similar to Fowler–Nordheim emission is the tunneling of a bound state electron in the dielectric into the anode.\(^ {13}\)

C. Open circuit decay

The solution to Eqs. (22) and (23) with \( \tilde{J} = 0 \) for open circuit conditions breaks up into regions separated by a single demarcation curve emanating from the origin as shown in Fig. 7 for various values of \( \tau \).

\[ \frac{d\tilde{E}}{d\tilde{t}} = -\tilde{E} \tilde{\tau} e^{-\tilde{t} / \tilde{\tau}}, \] (36)

\[ \frac{d\tilde{x}}{d\tilde{t}} = \tilde{E} e^{-\tilde{t} / \tilde{\tau}} \rightarrow \tilde{x}(\tilde{t}) = \tilde{E}_0 [1 - e^{-\tilde{t} / \tilde{\tau}}] + \tilde{x}_0, \] (37)

where \( \tilde{t}_0 \) is the time and \( \tilde{x}_0 \) is the position where the trajectory first begins. Note that \( \tilde{x}_0 = 0 \) for \( \tilde{t}_0 > 0 \) and that for \( \tilde{t}_0 = 0, \ 0 < \tilde{x}_0 < 1 \).

1. Region I

Because the dielectric was initially uncharged at \( \tilde{t} = 0 \), all trajectories emanating from the \( \tilde{J} = 0 \) boundary from all positions \( \tilde{x}_0 \) where \( 0 < \tilde{x}_0 < 1 \) have \( \tilde{q}_0 \) \( (\tilde{t} = 0) = 0 \) so that this region is everywhere uncharged. The electric field distribution is thus uniform in space above the demarcation curve and is equal to the electric field \( \tilde{E}_d \) along the demarcation trajectory.

Because \( \tilde{E}(\tilde{x}, \tilde{t} = 0) = 1 \) the electric field time dependence in this region is

\[ \tilde{E}(\tilde{x} > \tilde{x}_d, \tilde{t}) = \tilde{E}_d = e^{-\tilde{t} / \tilde{\tau}}. \] (38)

The demarcation trajectory is then

\[ \frac{d\tilde{x}_d}{d\tilde{t}} = \tilde{E}_d = e^{-\tilde{t} / \tilde{\tau}} \rightarrow \tilde{x}_d = \tilde{\tau} (1 - e^{-\tilde{t} / \tilde{\tau}}). \] (39)

Note that the maximum value of \( \tilde{x}_d \) is

\[ \lim_{\tilde{t} \to \infty} \tilde{x}_d = \frac{\tilde{\tau}}{1}, \quad \tilde{\tau} < 1. \] (40)

![FIG. 7. Charge transport trajectories for an initially charged but open circuited lossy capacitor where the lower \( \tilde{x} = 0 \) electrode injects charge proportional to the instantaneous local electric field. The demarcation curves \( \tilde{x}_d \) emanating from the origin shown for various values of dielectric relaxation times \( \tilde{\tau} \) separate the initial value problem with \( \tilde{q}(\tilde{x}, \tilde{t} = 0) = 0 \), \( \tilde{E}(\tilde{x}, \tilde{t} = 0) = 1 \) from the subsequent charge injection problem.](image)
If $\tau > 1$, the charge transport time $\tilde{t}_d$ when the demarcation curve reaches the opposite electrode at $\tilde{x} = 1$ is
\[ \tilde{x}_d = 1 = \tilde{\tau}(1 - e^{-i/\tilde{\tau}}) = \tilde{\tau} \ln[\tilde{\tau}/(\tilde{\tau} - 1)]. \quad (41) \]

If $\tilde{\tau} = 1$, $\tilde{t}_d$ is infinite while if $\tilde{\tau} < 1$ injected charge never reaches the opposite electrode as the voltage and electric field decay due to dielectric relaxation faster than the charge can migrate.

From Eq. (17), we see that this will be the case for low initial voltages or with high conductivity such as with pure water, with no ethylene glycol.

2. Region II

Trajectories emanate from the $\tilde{x}_0 = 0$ boundary at time $\tilde{t}_0$. The injected charge density is given by Eq. (28) so that Eq. (18) evaluated at the $\tilde{x} = 0$ electrode is
\[ \frac{d\tilde{E}_0}{dt} + \frac{\tilde{E}_0}{\tilde{\tau}} + \tilde{q}_0 \tilde{E}_0 = \frac{d\tilde{E}_0}{dt} + \frac{\tilde{E}_0}{\tilde{\tau}} + \tilde{A} \tilde{E}_0^2 = 0 \quad (42) \]
with solution
\[ \tilde{E}_0(\tilde{t}) = \frac{1}{\tilde{\tau}([\tilde{\tau} + 1/\tilde{\tau}] e^{i/\tilde{\tau}} - \tilde{A})}, \quad (43) \]
where we used the initial condition $\tilde{E}_0(\tilde{t} = 0) = 1$.

Charge trajectories that enter the system from the $\tilde{x} = 0$ electrode at time $\tilde{t}_0$ are given by Eq. (37) with $\tilde{x}_0 = 0$ and using Eq. (43) evaluated at time $\tilde{t}_0$:
\[ \tilde{x}(\tilde{t}) = \frac{[1 - e^{-i/\tilde{\tau}}]}{[\tilde{\tau} + 1/\tilde{\tau}] e^{i/\tilde{\tau}} - \tilde{A}}. \quad (44) \]

For a particular value of $\tilde{x}$ and $\tilde{t}$ we can find the time $\tilde{t}_0$ when the trajectory began by solving Eq. (44) for $e^{i/\tilde{\tau}}$,
\[ e^{i/\tilde{\tau}} = \frac{1 + \tilde{A} \tilde{x}}{[\tilde{x} + 1/\tilde{\tau}] + e^{-i/\tilde{\tau}}}, \quad (45) \]
so that the electric field distribution of Eq. (36) is linear with position and the charge density distribution of Eq. (25) is uniform:
\[ \tilde{E}(\tilde{x}, \tilde{t}) = \frac{(1 + \tilde{A} \tilde{x})}{\tilde{\tau}([\tilde{\tau} + 1/\tilde{\tau}] e^{i/\tilde{\tau}} - \tilde{A})}, \quad (46) \]
\[ \tilde{q}(\tilde{x}, \tilde{t}) = \frac{\partial \tilde{E}}{\partial \tilde{x}} = \frac{\tilde{A}}{\tilde{\tau}([\tilde{\tau} + 1/\tilde{\tau}] e^{i/\tilde{\tau}} - \tilde{A})}. \quad (47) \]

In Fig. 8 we plot the time dependence of the uniform charge density which also equals the slope of the electric field and in Fig. 9 we plot the spatial dependence of the electric field distribution at various times for $\tilde{\tau} = 1$ and $\tilde{\tau} = \infty$ with $\tilde{A} = \infty$ (space-charge limited condition) and $\tilde{A} = 1$.

3. Terminal voltage

Although the open circuit terminal voltage can be found by solving Eq. (21) with $J = 0$, once we know the electric field distribution it is easier to use the normalized form of Eq. (12):


\[ \ddot{\hat{v}}(t) = \int \dot{\hat{E}}(\hat{x}, t) d\hat{x} = \begin{cases} \int_{x_0}^{x_i} \dot{\hat{E}}(\hat{x}, t) d\hat{x}, & 0 < \hat{x} < \hat{t}_d, \\ \int_{x_i}^{\hat{t}_d} \dot{\hat{E}}(\hat{x}, t) d\hat{x}, & \hat{t} > \hat{t}_d, \end{cases} \]

\[ = \begin{cases} e^{\frac{-\hat{t}}{\tau}} - \frac{\hat{A} \tau [1 - e^{\frac{-\hat{t}}{\tau}}]}{2[A + \frac{1}{\tau} e^{\frac{-\hat{t}}{\tau}} - \hat{A}]}, & 0 < \hat{t} < \hat{t}_d, \\ \frac{\hat{A} \tau [1 - e^{\frac{-\hat{t}}{\tau}}]}{1 + \hat{A} / 2}, & \hat{t} > \hat{t}_d \end{cases} \]

(48)

The open circuit voltage for representative values of \( \hat{A} \) and \( \tau \) is plotted in Fig. 10.

We find conditions where the second derivative of the voltage is negative by twice differentiating Eq. (48) and evaluate at \( \hat{t} = 0 \) to obtain

\[ \frac{d^2 \hat{v}}{dt^2} \bigg|_{\hat{t} = 0} = \frac{1}{\tau^2} - \hat{A} \rightarrow \hat{A} > 1 \text{ for } \frac{d^2 \hat{v}}{dt^2} \bigg|_{\hat{t} = 0} < 0. \] (49)

Thus, if \( \hat{A} > 1 \), the initial curvature is negative. For \( \hat{t} > \hat{t}_d \), the second derivative of the voltage is always positive. The time \( \hat{t}_2 \) when the second derivative of the voltage is zero occurs for \( 0 < \hat{t} < \hat{t}_d \) when the inequality of Eq. (49) is obeyed. Figure 11 plots the time \( \hat{t}_2 \) vs \( \hat{A} \). For a given value of \( \tau \), as \( \hat{A} \) is increased from \( 1 / \tau^2 \), the time \( \hat{t}_2 \) increases until a maximum value of \( \hat{t}_2 \) is reached. Then larger values of \( \hat{A} \) tend to decrease \( \hat{t}_2 \). For large values of \( \tau \), Eq. (48) reduces to

\[ \lim_{\tau \to \text{large}} \hat{v}(\hat{t}) = \begin{cases} \frac{1 - \hat{A} \hat{t}^2}{2(1 + \hat{A} t)}, & 0 < \hat{t} < \hat{t}_d, \\ \frac{1 + \hat{A} / 2}{(1 + \hat{A} t)}, & \hat{t} > \hat{t}_d. \end{cases} \] (50)

The voltage second derivative then is negative over the entire interval \( 0 < \hat{t} < \hat{t}_d \), and positive for \( \hat{t} > \hat{t}_d \), abruptly switching signs at \( \hat{t} = \hat{t}_d \):

\[ \lim_{\tau \to \text{large}} \frac{d^2 \hat{v}}{dt^2} = \begin{cases} -\frac{\hat{A}}{(1 + \hat{A} t)^3}, & 0 < \hat{t} < \hat{t}_d, \\ \frac{2 \hat{A}^2 (1 + \hat{A} / 2)}{(1 + \hat{A} t)^3}, & \hat{t} > \hat{t}_d. \end{cases} \] (51)

For large but finite \( \tau \), there is an intermediate range of \( \hat{A} \) where \( d^2 \hat{v}/dt^2 < 0 \) but where there is no value of \( \hat{t}_2 \) to make \( d^3 \hat{v}/dt^3 = 0 \) in the interval \( 0 < \hat{t} < \hat{t}_d \). The second derivative thus changes signs at \( \hat{t}_d \). This is shown in Fig. 11 by the straight lines \( \hat{t}_2 = \hat{t}_d \) for \( \hat{t} > 6 \).

IV. COMPARISON OF THEORY AND EXPERIMENT

The theory is characterized by two parameters: \( \hat{A} \), the injection parameter, and \( \tau \), the charge relaxation and transport parameter. These are related to the physical quantities by Eqs. (17) and (28):

\[ \tau = \tau_0 V_0 \mu / I^2, \quad \hat{A} = A \mu / \epsilon. \] (52)

Comparison of the experimentally observed voltage waveforms with the theoretical equation of (48) will yield values for the mobility of the injected species and the injection constant. This is done in the following way.

Best-fit values for the parameters \( \hat{A} \) and \( \tau \) may be found by computer minimization of the sum of squares error (SSE) between the experimental data and Eq. (48):

\[ \text{SSE} = \sum_{i=1}^{n} [\hat{v}_{\text{theor}}(t_i, \hat{A}, \tau) - \hat{v}_{\text{Exp}}(t_i)]^2. \] (53)

The goodness of fit is estimated by the standard deviation error (SDE):

\[ \text{SDE} = \sqrt{\frac{\text{SSE}}{n - 1}}. \] (54)

Figure 12 shows low temperature open circuit voltage

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**FIG. 10.** Open circuit voltage decay vs time for various values of \( \hat{A} \) with \( \tau = \infty \) (solid lines) and \( \tau = 1 \) (dashed lines).
decay curves differing only in the gap spacing of the electrodes. Note the apparent difference in the time scale of the decays as the smaller gap system decays approximately twice as fast. Figure 13 shows families of voltage decay curves differing only by initial voltage. These and the other experimental curves given in the paper were hand digitized ($n = 10$), and the least squares approach used to calculate optimum values of $A$ and $\tau$ for each curve. The results of this procedure are summarized in Table I. SDE in all cases is very small, of order 0.05 oscillograph scale division, and it was found that computer generated curves based on the optimum values of $A$ and $\tau$ would overlay the experimental waveforms to the resolution of the hand assessment ($\approx 0.1$ oscillograph scale division). The result for the low voltage, high temperature case [Fig. 3(a)] is not reliable since the curve only deviated very slightly from the normal dielectric decay. It was evaluated mainly to determine the sensitivity of the method.

The most striking result is the consistent value of the mobility of the injected species, confirming the scaling of $\mu$ with $V_{dc}/l^2$. From equivalent conductance data\textsuperscript{4} the mobility of the hydronium ion (H$_3$O$^+$) in water is

$$\mu_{H_3O^+} = 2.5 \times 10^{-7} (1 + 3.3 \times 10^{-2} T) \text{ m}^2/\text{V sec},$$

with $T$ in Celsius. This ion has a uniquely high mobility in aqueous solution. The hydronium mobility is 2.5 times high-

![Figure 11](image1.png)

**FIG. 11.** Time $i_2$ when the second derivative of the open circuit voltage is zero as a function of injection level parameter $A$ for various values of $\tau$. Note that $i_2 = i_4$ for $\tau > 6$ over a range of $A$.

![Figure 12](image2.png)

**FIG. 12.** Voltage decay at different gap spacings with same initial voltage of $\pm 68$ kV with 80% glycol at $-10^\circ$ C. $\tau_0 = 25$ msec. (a) $l = 5.1$ mm, (b) $l = 7.3$ mm. Note approximate factor of 2 difference of time scale of decays, indicating $\tau$ parameter scaling with square of gap spacing. See Table I. All traces have voltage scales of 200 mV/div and time scale of 500 $\mu$sec/div.

![Figure 13](image3.png)

**FIG. 13.** Families of voltage decay curves at different initial voltages but same gap spacing of $l = 7.3$ mm. 80% glycol at $-10^\circ$ C. $\tau_0 = 25$ msec. Oscilloscope scale for family (a) set at 200 mV/div and (b) set at 250 mV/division for best resolution. Time scale is 500 $\mu$sec/div. See Table I. Above the highest voltage shown, dielectric breakdown occurs.
er than its partner hydroxyl ion (\(\text{OH}^-\)) and is 5–10 times higher than the mobility of light metal ions (e.g., \(\text{Na}^+\)). The measured values of the mobility of the injected carrier leads us to speculate that the injected carrier is, or becomes, the hydronium ion at or near the injecting surface.

The results for the injection parameter are less conclusive. The numerics of the least squares approach are relatively insensitive to changes in the values of \(A\). The physics of the injection mechanism are still unsettled. \(A\) seems to show a temperature dependence and an inverse relationship with mobility as might be expected from a mobility limited barrier tunneling process, but the magnitude of the injection current is far too small. These results might be consistent with the mechanism briefly described in Ref. 13, wherein electrons move from the liquid into the anode, leaving a positive ion behind.

V. CONCLUDING REMARKS

This work has shown that measured anomalous open circuit voltage decay curves in water/glycol capacitors can be explained by a unipolar drift dominated conduction model. Comparisons with the theory and measurements show that parameters scale as predicted with voltage and electrode spacing. Measurements currently in progress are extending these voltage-current terminal measurements to electric field mapping using the Kerr electro-optic effect.\(^{15,16}\) Water is significantly electrically birefringent when stressed by high voltage. Since this birefringence is proportional to the square of the electric field magnitude, optical and photographic measurements of light transmission maxima and minima provide good measurements of the electric field distribution in space, as a function of time, which will be compared to results of this analysis.

Preliminary Kerr electro-optic results are shown in Fig. 14 for stainless steel rod-rod electrodes of 1/2 in. diam, 16 3/8 in. length, and center-to-center spacing of 2.27 cm. These measurements were taken at 10° C with highly purified water (without glycol) of resistivity \(\approx 40 \text{ M}\Omega\) cm. The electrodes were vertically spaced and directly connected to a Marx impulse generator charged to 100 kV. This voltage then decayed as also shown in Fig. 14 with time constant \(\approx 4.5\) msec. A pulsed dye laser at free space wavelength 590 nm was deflected by the injected carrier, leaving a positive ion behind.

![Graph](image_url)
nm and 100 nsec pulse width was then triggered at various delayed times. The Kerr measurement system used aligned polarizers at 45° to the vertical instead of the usual crossed polarizers as the light transmission minima occur at lower voltages. On either side of the Kerr water cell and between the polarizers we used quarter wave plates at 0° and 90° to the vertical to remove isoclinic fringes which depend only on electric field direction and not magnitude. The relative light transmission intensity is then

$$I = \cos^2 \frac{\pi}{2} \left( \frac{E}{E_m} \right)^2,$$

where $E_m$ is here the electric field necessary for the first light transmission minima. Dark fringes occur for

$$E_n = \sqrt{2n + 1}, \quad n = 0, 1, 2, \ldots$$

In our test cell, $E_n \approx 60$ kV/cm.

In Fig. 14 the upper electrode is positive and at $t = 0$ we see two fringe lines with a symmetric pattern which agrees with the space-charge-free electric field distribution (see Ref. 8, pp. 93–103). For later times we see the fringes near the positive electrode propagating towards the negative electrode. The light transmission behind the moving fringe indicates a weaker field, thus requiring positive charge injection from the positive electrode. This is consistent with the positive ion mobility found in Eq. (55). If the voltage polarity is reversed, the fringe pattern also reverses so that the moving fringe propagates from the now positive lower electrode towards the upper negative electrode. A secondary complication at later times is the loss of sensitivity because the voltage is dropping.

Future work, to be the subject of another paper, will perform Kerr electro-optic measurements in water/glycol systems with longer electrodes, higher fields, and slower decaying voltages to increase measurement sensitivity.

Future work will also repeat the analysis in a coaxial cylindrical and concentric spherical geometry, which will be compared to terminal and Kerr electro-optic measurements. Such field mapping measurements also yield the time and space dependence of the charge density and provide information on the charge injection process by relating the charge density to the electric field through Gauss's law.

Presumably, the charge injection parameter $A$ depends on the state of the electrode surface, hence the decay should be sensitive to changes in surface preparation of the electrodes. Preliminary tests with passivated, polished stainless steel electrodes, as opposed to bead blasted electrodes used in this work, show a marked change in the decay waveform. Experiments with mixed electrodes, one bead blasted, one passivated, indicate that the anode is indeed the primary injecting surface. A detailed report on the effects of electrode surface preparation will be the subject of a future paper.

An important result necessary to have confidence in the analysis presented here is that the charge density be of one polarity. If future Kerr electro-optic measurements show bipolar injection, as has been shown in nitrobenzene, it will be necessary to extend the analysis to two charge carriers of opposite polarity. Such an extension is not difficult, but will most likely not be amenable to analytical solutions but rather require numerical integration.

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