THE DIELECTRIC SPECTRA OF
ETHANOL-WATER MIXTURES IN THE MICROWAVE REGION

by

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Submitted to the Department of Chemistry on March 23, 1965, in partial
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ABSTRACT

The dielectric constant and loss have been measured at 8.5,
3.0, 1.0 and 0.3 kMc/sec for solutions of ethanol and water as a
function of concentration and temperature. The mixtures exhibit a
distribution of relaxation times as opposed to single time constants
for the pure components.

The distribution of time constants has been resolved as
the superposition of two dispersions, each having a single time con-
stant. The intensity and time constant of the two dispersions have
been found as a function of temperature and concentration, and
explained in terms of a mechanism in which hydrogen bonds are broken
and allowed to reorient.

In addition, the dielectric constant and loss were
measured for water from 5° to -5°C, and no abnormal behavior was
noted at 4°C or in the supercooled state.

Thesis Supervisor: Arthur R. von Hippel
Title: Institute Professor
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INTRODUCTION

Macroscopic Representation of Relaxation Spectra

The spectrum for water\(^1\) and ethanol\(^2\) in the microwave region, shown for room temperature in Fig. 1, obeys a simple relaxation equation as first used for polar molecules by Debye: \(^3\)

\[
\begin{align*}
\kappa^* - \kappa_\infty &= \frac{\kappa'_B - \kappa_\infty}{1 + j \frac{\nu}{\nu_c}}; \\
\kappa' - \kappa_\infty &= \frac{\kappa'_B - \kappa_\infty}{1 + \left(\frac{\nu}{\nu_c}\right)^2}; \\
\kappa'' &= \frac{\kappa'_B - \kappa_\infty}{1 + \left(\frac{\nu}{\nu_c}\right)^2} \left(\frac{\nu}{\nu_c}\right).
\end{align*}
\]

(1)

The dielectric constant \(\kappa'\), which is the real part of the complex permittivity \(\kappa^*\), represents the polarization component in phase with the applied electric field; the out-of-phase component \(\kappa''\) (the loss factor) is responsible for energy absorption in the sample. At the critical frequency \(\nu_c\), the loss reaches its maximum and \(\kappa'\) has fallen to half the difference between the static and optical dielectric constant, \((\kappa'_B - \kappa_\infty)\). For water at \(20^\circ\text{C}\), \(\kappa'_B = 80.36\), \(\kappa_\infty = 5.5\), and \(\nu_c = 16.7 \times 10^9 \text{ sec}^{-1}\); for ethanol at \(20^\circ\text{C}\), \(\kappa'_B = 25.0\), \(\kappa_\infty = 4.4\), \(\nu_c = 0.935 \times 10^9 \text{ sec}^{-1}\).

A useful alternative representation for relaxation spectra is the circular arc plot of Cole and Cole.\(^6\) Here \(\kappa^* - \kappa_\infty\) is shown in the complex plane with \(\kappa'\) along the horizontal and \(\kappa''\) along the vertical axis (Fig. 2). For a simple relaxation spectrum, described by one time constant \((\tau = 1/\nu_c)\), the data fall on a semicircle with its center on the \(\kappa'\) axis and a diameter of \((\kappa'_B - \kappa_\infty)\).
Fig. 1a. Dielectric constant ($\kappa'$) and loss factor ($\kappa''$) for water at 20°C. Key: ○ Collie, Hasstead and Ritson; □ Grant, Buchan, and Cook; Δ Rempola, Miller, and Smyth; ▲ Lane and Saxton; ○ Saxton.

Fig. 1b. Dielectric constant ($\kappa'$) and loss factor ($\kappa''$) for ethanol at 20°C. Key: Δ Lane and Saxton; □ Saxton, Bond, Coats, and Dickenson; ▲ Pol; ○ Slevogt; ▲ Mungall and Hart; ◆ Sagal.
Fig. 2a. Cole-Cole diagram for water at 50°C.
Key - see Fig. 1a.

Fig. 2b. Cole-Cole diagram for ethanol at 20°C.
Key - see Fig. 1b.
Often the frequency dependence of $\kappa'$ and $\kappa''$ is more involved. The spectrum may have a distribution of critical frequencies or time constants about some center frequency $\nu_c$. Then,

$$\kappa^* - \kappa_\infty = \frac{\kappa'_B - \kappa_\infty}{1 + j \left( \frac{\nu}{\nu_c} \right)^{1-\alpha}}. \quad (2)$$

Shown in the complex plane, the semicircle is maintained, but its center is depressed by an angle ($\pi \alpha / 2$) below the $\kappa'$ axis at the $\kappa$ intercept ($\kappa$) (see Fig. 3). If a nonsymmetrical distribution of critical frequencies is observed, the dielectric constant may be represented as

$$\kappa^* - \kappa_\infty = \frac{\kappa'_B - \kappa_\infty}{(1 + j \left( \frac{\nu}{\nu_c} \right)^\beta)} \quad (3)$$

Then the arc is no longer semicircular, but skewed (see Fig. 4).

The $\alpha$ and $\beta$ exponents of Eqs. 2 and 3 are related to the critical frequency distributions, shown in Figs. 3 and 4. In the limit of sufficiently narrow distributions $\alpha \rightarrow 0$, $\beta \rightarrow 1$, and we return to Eq. 1.

Models for the Dielectric Constant of Water

The relaxation spectra of ethanol and water are caused by the ability of polar molecules to respond to an electric field by preferential alignment. The polarization

$$P = \epsilon_0 \chi E' = N (\alpha_e + \alpha_a + \alpha_d) E', \quad (4)$$
Fig. 3a. Cole-Cole diagram for n-octyl bromide at 25°C. 
\( \alpha = 0.226 \).

Fig. 3b. Distribution of relaxation times, Cole-Cole equation, 
\( \alpha = 0.226 \). Distribution function \( F(s) \) \( (s = \ln \tau / \tau_0) \) versus \( \tau / \tau_0 \).

Fig. 4a. Cole-Davidson diagram for glycerol at -50°C, 
\( \beta = 0.603 \).

Fig. 4b. Distribution of relaxation times, Cole-Davidson equation, \( \beta = 0.603 \). Distribution function \( F(s) \) \( (s = \ln \tau / \tau_0) \) vs. \( \tau / \tau_0 \).
the dipole moment per unit volume, can be visualized as stemming from the action of \( N \) molecules per unit volume which contribute to such a moment by electronic (\( \alpha_e \)), atomic (\( \alpha_a \)), and dipolar (\( \alpha_d \)) polarizabilities in a local field \( E' \). \( \chi \) is the macroscopic electric susceptibility of the substance,

\[
\chi = \kappa' - 1. \tag{5}
\]

Debye's model\(^3\) of non-interacting spherical dipolar molecules in a homogeneous electric field and a medium of viscosity \( \eta \) led to a relaxation time

\[
\tau = \frac{4\pi a^3}{kT} \eta. \tag{6}
\]

By assuming as the local field \( E' \) the Lorentz expression\(^9\)

\[
E' = \frac{E}{\frac{3}{2} (\kappa' + 2)}, \tag{7}
\]

he obtained the critical frequency

\[
\nu_c = \frac{1}{\tau} \frac{\kappa' + 2}{\kappa + 2}. \tag{8}
\]

The use of the Lorentz field results in feedback which leads to a Curie-Weiss law, that is, water should become ferroelectric below 1550°K.\(^{10}\) Onsager\(^{11}\) escaped this catastrophic consequence by assuming as a model a dipole in a real cavity of molecular size. The molecule induces a dipolar field in the surroundings which polarizes the molecule but does not contribute to the orienting torque. The calculation, carried through for static fields leads to the expression
\[ \kappa'_{\text{S}} - \kappa'_{\text{o}} = \frac{N\mu_{\text{o}}^2}{kT} \left( \frac{\kappa_{\text{oo}}}{18\epsilon_{\text{o}}} + \frac{\kappa'_{\text{oo}}}{\kappa_{\text{S}}} \right) \]  

and gives for water a room-temperature dielectric constant \( \kappa'_{\text{S}} = 31 \).

Both the Debye and Onsager models have assumed for the liquid outside a reference cavity a continuum structure, to which the macroscopic dielectric constant applies\textsuperscript{12,13} as shown in Fig. 5.

\[ \]  

Clausius–Mosotti  

Onsager

Fig. 5. Comparison of cavities for Debye (Clausius-Mosotti cavity) and Onsager theories.

For non-associated polar liquids this is a reasonable assumption.\textsuperscript{14} However, when association of molecules is present, by hydrogen bonding, for example, at least a short-range order is imposed on the liquid and the possible axes of rotation are restricted.\textsuperscript{15} By taking into account the average structure of an associated liquid about an arbitrary reference molecule, Kirkwood\textsuperscript{16} rewrote the dipolar polarization,
\[ P_d = N \frac{\mu^2}{3kT} E'. \]  

(10)

Here \( \mu \) is the dipole moment of a molecule in an Onsager cavity and \( \bar{\mu} \) the total moment at the center of the cavity, composed of \( \mu \) and contributions of the ordered surroundings. \( \mu \) may be expressed as

\[ \bar{\mu} = \mu g = \mu (1 + Z \overline{\cos \gamma}), \]  

(11)

where \( Z \) is the number of neighbors considered and \( \overline{\cos \gamma} \) is the average of all angles made by the dipole of the reference molecule and those of its neighbors. If the molecules in the liquid are allowed free rotation, that is, if the ordered surroundings are dissolved, \( \bar{\mu} \rightarrow \mu \) and Onsager's case results. The additional term, \( \mu Z \overline{\cos \gamma} \) reflects the structure of the liquid.

Oster and Kirkwood,\(^{17}\) using the X-ray diffraction data of Morgan and Warren\(^{18}\) and the tetrahedral water structure of Bernal and Fowler,\(^{19}\) calculated for water with one shell of neighbors a dielectric constant of about 72 at 25°C. The temperature dependence of \( k_b' \) from this model is shown in Fig. 6. The water model used to calculate \( \overline{\cos \gamma} \) (Fig. 7) assumes the free rotation of the four nearest neighbor water molecules about their hydrogen bonds. The calculation uses, however, \( Z = 4.4 \), following the results of Morgan and Warren.

Pople\(^{20}\) extended Kirkwood's model for water by including the second and third shell of neighbors. The increase in nearest neighbor density to the value \( Z = 4.4 \) is a result of the bending of the hydrogen bonds. By selecting proper force constants for the bond
Fig. 6. Static dielectric constant, $\kappa_s'$, for various models.

- $\triangle$ Haggis, Hasted, and Buchanan; $\circ$ Oster and Kirkwood; $\square$ Pople; $\bigcirc$ experimental: Malmberg and Maryott.

Fig. 7. Molecular model for restricted orientation in water, Oster and Kirkwood calculation.
bending, Pople calculates, by statistical mechanics, a distribution function agreeing with that of Morgan and Warren. With this distribution function, \( \cos \gamma \) is re-calculated. At 25\(^\circ\)C, \( \kappa' = 63.8 \) results: the relative contributions of the first, second, and third shells are 1.20:0.33:0.07. The over-all temperature dependence of Pople's calculated \( \kappa' \) is improved, but the values are low (cf. Fig. 6).

A bond-breaking model was proposed by Haggis, Hastead and Buchanan.\(^{21}\) Calculations of Pauling\(^{22}\) from thermal data show that 9% of the maximum number of hydrogen bonds possible in water are broken at 0\(^\circ\)C and 26% at 100\(^\circ\)C. From that information, Haggis et al. estimate the fraction of molecules of the liquid water existing in five possible states (from zero to four hydrogen bonds); the variation in the concentrations of the various states with temperature is shown in Table 1.

Table 1. Relative concentration of the five possible hydrogen-bonded states in water.\(^{21}\)

<table>
<thead>
<tr>
<th>( T^\circ C )</th>
<th>( P )</th>
<th>( n_4 )</th>
<th>( n_3 )</th>
<th>( n_2 )</th>
<th>( n_1 )</th>
<th>( n_0 )</th>
</tr>
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<tr>
<td>0</td>
<td>9.0</td>
<td>72.0</td>
<td>20.0</td>
<td>6.0</td>
<td>1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>25</td>
<td>11.3</td>
<td>67.0</td>
<td>23.2</td>
<td>7.6</td>
<td>2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>100</td>
<td>20.2</td>
<td>49.8</td>
<td>28.3</td>
<td>15.0</td>
<td>6.0</td>
<td>1.15</td>
</tr>
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\( P \) is percent hydrogen bonds broken; \( n_1 \) is percent of water molecules having 1 bonds.
Using these values, Haggis et al. calculate $g$ of Kirkwood's equation and obtain static dielectric constants which agree well in magnitude and temperature dependence with experimental results shown in Fig. 6.

The models mentioned, with the exception of that of Debye, refer only to the static dielectric constant. Haggis et al. imply that the formation and dissolution of three bonded water molecules is responsible for the relaxation spectrum in the microwave region, but do not formally describe the process.

**Experimental Structural Information on Water and Ice**

X-ray diffraction of liquid water\(^{18,23}\) shows the number of nearest neighbors to be 4.4 at 15°C. The intermolecular distance is 2.90 Å, compared to 2.76 Å of ice at 0°C.\(^{24}\) A tetrahedral coordination throughout the liquid, as first proposed by Bernal and Fowler,\(^{19}\) would place the nearest neighbors at an average distance of 4.5 Å. Experimentally, a broad maximum is seen at about 4.5 Å, becoming less pronounced above 30°C.

In ice at 0°C, the fundamental infrared O-H stretching mode is at 3256 cm\(^{-1}\),\(^{25,26}\) while in water at 0°C it is found at 3330 cm\(^{-1}\). Lord and Marrifield\(^ {27}\) showed that a reduction of the intermolecular O-O distance along a hydrogen bond stretches the chemical O-H bond and reduces the frequency of the stretching vibration. Upon melting, the intermolecular distance along the hydrogen bonds has increased and the predominant tetrahedral
structure is maintained, although the highly ordered tridymite structure of ice(I) (shown in Fig. 8) has collapsed.

Frank and Wen\(^{28,29}\) have proposed the formal charge model for hydrogen bonding in water shown in Fig. 9, in which the formation of a first bond (dimerization) makes that of more hydrogen bonds likely due to the change in charge distribution of the molecules. The first bond causes a negative charge drift from molecule A to molecule B; the negative charge on molecule B allows its electrons to form another hydrogen bond more readily; the positive charge on molecule A allows its protons to enter into further hydrogen bonding. The effect, according to the model, can cascade, giving a momentary structure of several water molecules bonded into a cluster, thermal fluctuations causing continual changes in the size of the clusters.

Nemethy and Scheraga\(^{30}\) starting from this model, have calculated a radial distribution function for water, agreeing with that obtained experimentally by X-ray diffraction.\(^{18,23}\) They obtain an average cluster size of 57 at 20°C.

The question of the correct form of the water structure remains. The model of Bernal and Fowler\(^{19}\) assumes, near 0°C, a two-phase system containing a tridymite (ice) and a more dense quartz structure. Nemethy and Scheraga\(^{30}\) also propose a two-phase system containing the hydrogen-bonded clusters, of unspecified form, and a surrounding of nonbonded molecules. Both models are
Fig. 8. Structure of ice(I) at 0°C.
Fig. 8. Structure of ice(I) at $0^\circ$C.
Fig. 9. Polarizing effect of hydrogen bond formation, Frank and Wen.\textsuperscript{29} (a) Non-hydrogen bonded water molecules; (b) hydrogen bond induced charge shift; (c) hydrogen bonded molecules with polarizing charge separation.

There are probably clusters of hydrogen-bonded molecules in the liquid, suggesting to some extent ice-like and quartz-like structures. Tetrahedral coordination in the clusters is most probable, but the detailed linkage of the tetrahedra is in doubt.

Structure Information of Alcohols

X-ray diffraction of solid normal alcohols\textsuperscript{31,32} shows a rhombohedral crystal structure: The alcohol molecules are linked by hydrogen bonds with the oxygen atoms lying nearly in a plane and the aliphatic groups oriented perpendicular to the plane and parallel to one another; this structure is shown in Fig. 10.

In the liquid phase, some of the structure remains, just as in the case of water. X-ray diffraction of liquid normal alcohols\textsuperscript{33,34} reveals the chain structure, where each molecule has a coordination number two. In liquid ethanol,\textsuperscript{35} each oxygen
has two oxygen neighbors at a distance of 2.9 Å, the spacing given by hydrogen bonds. The length of the chain is not determined, but in the higher normal alcohols improbability of packing the long aliphatic chains into such a structure precludes crystallinity. NMR and infrared data on liquid ethanol\textsuperscript{26} indicate that the percentage of free chain end groups is quite small, less than 2%. Oster and Kirkwood,\textsuperscript{17} in computing $\kappa'_s$ of ethanol, assume infinitely long chains, coiled into balls with no cross linking. A value of $\kappa'_s$ results which is within 15% of that measured. The picture is then one of long chains of ethanol molecules, connected by two hydrogen bonds each and with little or no cross linking; the water-soluble hydroxyl groups are sandwiched between the aliphatic groups (cf. Fig. 10).
Fig. 10. Linear segment of the chain structure of an alcohol.

has two oxygen neighbors at a distance of 2.9 Å, the spacing given by hydrogen bonds. The length of the chain is not determined, but in the higher normal alcohols improbability of packing the long aliphatic chains into such a structure precludes crystallinity. NMR and infrared data on liquid ethanol\(^ {36} \) indicate that the percentage of free chain end groups is quite small, less than 2%. Oster and Kirkwood\(^ {17} \) in computing \( \kappa^s \) of ethanol, assume infinitely long chains, coiled into balls with no cross linking. A value of \( \kappa^s \) results which is within 15% of that measured. The picture is then one of long chains of ethanol molecules, connected by two hydrogen bonds each and with little or no cross linking; the watersoluble hydroxyl groups are sandwiched between the aliphatic groups (cf. Fig. 10).
Fig. 11. Hydrogen bond switching. (a) Primary ethanol dispersion, $\tau \approx 1 \times 10^{-9}$ sec; (b) secondary ethanol dispersion, $\tau \approx 0.01 \times 10^{-9}$.

The relaxation spectrum of ethanol consists of two Debye type curves centered at 1 and 100 kHz/sec respectively as seen in Fig. 1b. The shorter relaxation time is caused by re-orienting the O-R moment\textsuperscript{37,38} by switching of a hydrogen bond from one pair of nonbonded orbitals to the other on the re-orienting molecule (cf. Fig. 11). Measurements in this laboratory\textsuperscript{39} have shown that the centimeter dispersion is due to the re-orienting of the O-H moment by the switching of its hydrogen bond ($\tau = \tau_0 e^{\Delta E/RT}$, with $\tau_0 = 2.56 \times 10^{-13}$ sec and $\Delta E = 4.95$ Kcal/mol.) (cf. Fig. 11).

**Dielectric Polarization of Water and the Problem of this Thesis**

The dielectric properties of water, as shown in Fig. 1, can be fitted to a Debye type curve and to a semi-circular plot.\textsuperscript{4,5}
An analysis of the low-frequency loss measurements by Grant, Buchanan and Cook,\textsuperscript{40} however, implies that the dispersion is characterized by a Cole-Cole equation (Eq. 2) with $\alpha = 0.02$ and $\kappa_\infty = 4.5$. Measurements by Rampolla, Miller and Smyth\textsuperscript{41} on water at 100 kMc/sec, in the region of maximum difference between the curves of Grant et al. and the commonly accepted curves of Fig. 2 are compatible with a single relaxation time, with $\kappa_\infty = 6.0$, well within the limits established by Collie, Hastead and Ritson,\textsuperscript{4} $\kappa_\infty = 5.5 \pm 1$. The accepted interpretation is a dispersion characterized, within experimental error, by a single relaxation time and a high-frequency dielectric constant of about 5.5. The square of the index of refraction of water at 313$\mu$ is 4.0,\textsuperscript{42} indicating the possible existence of a further dispersion region in the submillimeter region. The bond-breaking theory of Haggis, Hastead and Buchanan\textsuperscript{21} assumes this to be due to a hindered rotation of unsymmetrically two bonded molecules.\textsuperscript{43} The existence of such a spectrum is not yet confirmed.

The Debye theory assumes proportionality between relaxation time and the macroscopic viscosity. Sagal\textsuperscript{39} showed that the relaxation time is not necessarily proportional to viscosity. For ethanol diluted with cyclohexane, the viscosity decreases while the relaxation time increases. The relaxation time was found to increase because the availability of new hydrogen bonding sites decreased.
The bond-breaking model for the dielectric relaxation in ethanol (Fig. 11) might also well be applied to water. The problem of this thesis was, therefore, to study the mechanism of the dielectric relaxation of water in all dilutions with ethanol, whose dielectric properties have previously been related to its structure.\textsuperscript{14,44} The systematic destruction of the three-dimensional network of water by linear alcohol structure was to be followed by measuring the dielectric constant and loss as a function of temperature for the pure substances and for a wide range of concentrations of their solutions. In addition, pure water was to be measured from 5\degree C to -5\degree C so that any abnormal ordering effects near 4\degree C and in the supercooled state might be observed.

**EXPERIMENTAL TECHNIQUES**

**Sample Preparation**

**Water.** Distilled water was de-ionized, after which it had the resistivity of $1.48 \times 10^5$ ohm cm at 100 kc/sec. This compares to $1 \times 10^6$ ohm cm obtained by Malmberg and Maryott.\textsuperscript{45} The purity of the water affected only the ease of the low-frequency measurements, giving the same dielectric constant in both distilled water and distilled, de-ionized water. At higher frequencies, there was no noticeable effect when only distilled water was used.

**Ethanol.** "Absolute Alcohol" prepared by the U.S. Industrial Chemicals Co. was used as obtained. The dielectric constant, a very good test for the presence of water, was in agreement with
with previously reported results.\textsuperscript{39}

**Water-Ethanol Mixtures.** The solutions were weighed on an analytical balance and stored in tight glass stoppered flasks. The solutions were accurate to within 0.1 mole percent.

**Apparatus and Techniques**

**100 kc/sec.** The "static" dielectric constant was measured at 100 kc/sec to eliminate the effects of ionic conductivity. A General Radio Co. 716C capacitance bridge was used.

**0.3 kMc/sec.** The coaxial slotted waveguide and associated generating and detecting equipment were built in this laboratory.\textsuperscript{46} The frequency is established by a crystal controlled oscillator.

**8.5, 3.0, 1.0 kMc/sec.** Measurements were taken with a Microwave Dielectrometer, Model 1, of the Central Research Laboratories. This device contains the signal generator, waveguide and detector in one unit.

**Sample Holders**

**100 kc/sec.** This sample holder has monel electrodes, Teflon insulation, and the sample space is surrounded by a water jacket for temperature control.\textsuperscript{39} Because of the large volume of the sample space (approximately 15 cm\textsuperscript{3}) provisions are made for the sample to be stirred by a Teflon stirring rod.

**0.3, 1.0, 3.0 kMc/sec.** These sample holders, previously described,\textsuperscript{39} consist of a sample space placed one quarter wave-
with previously reported results.\textsuperscript{39}

**Water-Ethanol Mixtures**. The solutions were weighed on an analytical balance and stored in tight glass stoppered flasks. The solutions were accurate to within 0.1 mole percent.

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**Sample Holders**

**100 kc/sec.** This sample holder has monel electrodes, Teflon insulation, and the sample space is surrounded by a water jacket for temperature control.\textsuperscript{39} Because of the large volume of the sample space (approximately 15 cm\textsuperscript{3}) provisions are made for the sample to be stirred by a Teflon stirring rod.

**0.3, 1.0, 3.0 kMc/sec.** These sample holders, previously described,\textsuperscript{39} consist of a sample space placed one quarter wave-
length from the end of a closed waveguide. The sample space is
confined by alumina disks and is filled from two tubes fitted into
the wall of the waveguide. For measurements at 0.3, 1.0, and
3.0 kHz/sec, a coaxial line is used, and the central conductor is
fitted to allow a forced flow of thermostating liquid through it.
The holder for 8.5 kHz/sec is a circular waveguide. The holders
are made to be fixed to the ends of waveguides of the dielectric
measuring apparatus.

**Temperature Control.** Temperature is measured by thermo-
couples fixed to the surface of the sample holder. With liquid in
the holder, the variation of sample temperature from that of the
sample holder was less than 0.1°C.

The sample holder is immersed in a temperature regulating
bath. Liquid taken from the bath at the level of the sample space
is forced through the central conductor. The bath is cooled by a
copper coil, through which is pumped a glycol-water solution cooled
in a separate dry ice-acetone bath. Temperature is maintained to
within 0.025°C by an electric heater controlled by a temperature-
sensitive switch in the bath. For measurements at 100 kc/sec
coolant was pumped from the bath into the water jacket of the sample
holder.

**Measurements.** The standing-wave method of Roberts and von
Hippel is used. The sample is located one quarter wavelength
from the closed end of the waveguide in the region of maximum field
Fig. 12. Standing-wave technique.

(see Fig. 12). The impedance at the rear face of the sample, $Z_T$, is infinite. The reflection of radiation at this boundary sets up a standing wave in the waveguide. The impedance at the front of the sample space, $Z_B$, is a function of the geometry of the sample space and of the dielectric constant of the sample. The movable probe, running in a slot in the side of the waveguide, establishes the distance of the node from the boundary having $Z_B$. This distance, $X_0$, and the width of the node, $\Delta X$ (the distance between points where the power is twice that of the node) allow calculation of $Z_B$. Knowing $Z_B$ for the sample space full and empty allows calculation of the dielectric constant and loss.

To insure that the sample space is full, with no bubbles, two readings are taken. Between readings, the sample space is dried with pre-purified dry nitrogen. The sample is fed from a syringe into the sample holder, through the sample space and into
another syringe. Bubbles can be washed out by pumping the syringe, and the sample contacts only dry nitrogen.

**Supercooled Water.** Routine supercooling of water to \(-20^\circ C\) has been reported.\(^4^9\) Preliminary investigation showed that water could be supercooled to at least \(-15^\circ C\) in a test tube, but repeatedly froze at \(0^\circ C\) in a copper cup. To allow supercooling of water in a copper waveguide, the sample space was coated with a thin film of polyethylene. The sample space of a warm \(70^\circ C\) sample holder was filled with a \(70^\circ C\), 15% solution of polyethylene in xylene. After the solution had been removed, the holder was put into an oven to dry at \(70^\circ C\). The higher temperature drying avoids the deposition of a two-phase liquid on the walls and the resulting lumpy film.\(^5^0\)

**EXPERIMENTAL RESULTS**

The static dielectric constants of water, alcohol and their solutions are given in Appendix A and are represented graphically for the temperature interval \(5^\circ C\) to \(50^\circ C\) in Fig. 13. The \(\kappa'\) and \(\kappa''\) measured at 8.5, 3.0, 1.0, and 0.3 kMc/sec for the same solutions and temperature range are given in Appendix B.

Plotting \(\kappa'\) and \(\kappa''\) in the complex plane shows that solutions of water and ethanol are not described by a single relaxation time, as are the pure components. Figure 14 shows the complex plane plot for a 50 mole percent ethanol-water solution at \(5^\circ C\). The semi-
Fig. 13. Static dielectric constant, $\kappa_s'$, for ethanol-water solution.
Fig. 14. Complex plane representation of 50 mole percent ethanol in water at 50°C.

circular arc of Eq. 2 and the skewed arc of Eq. 3 cannot be fitted to the measured \( \kappa' \) and \( \kappa'' \), a skew in the curves eliminating Eq. 2 and the angle at which the high frequency side of the curve approaches the \( \kappa' \) axis eliminating Eq. 3. Further, the flat side of the curve shifts to the low-frequency side with increasing water concentration.

It has been shown$^{51}$ that some relaxation systems apparently represented by Eq. 3 can be described by a superposition of two Debye type dispersion regions, each having a distinct relaxation time,

\[
\kappa^* - \kappa_\infty = \frac{\kappa'_1 - \kappa_\infty}{1 + j\nu \tau_1} + \frac{\kappa'_2 - \kappa_\infty}{1 + j\nu \tau_2} .
\]  

(12)

Equation 12 can explain the shift in the skewed side of the complex plane curve by the change in the values of the intensities \( \Delta \kappa_1 = (\kappa'_1 - \kappa'_\infty) \) and \( \Delta \kappa_2 = (\kappa'_2 - \kappa'_\infty) \) with concentration.
If a dispersion can be described by Eq. 12, there is a unique set of parameters, $\Delta \kappa_1$, $\Delta \kappa_2$, $\tau_1$ and $\tau_2$ which describe it (shown in Appendix D) and the problem is then one of determining the four parameters $\Delta \kappa_1$, $\Delta \kappa_2$, $\tau_1$ and $\tau_2$. This has been done and the results are given in Table 2 and shown graphically in Fig. 15. Using the values in Table 2 and Eq. 12, the dielectric constant calculated agrees within experimental error (±2%) with those measured. The limits of error in the given values of $\tau_1$ and $\tau_2$ are 3% at temperatures below 50°C, and 5% at 50°C. For $\Delta \kappa_1$ and $\Delta \kappa_2$, the limits of error are 5% of $\kappa'_0 - \kappa_\infty$. Figure 15 shows clearly that an increase in the concentration of water or ethanol shifts the values of $\Delta \kappa_1$ and $\tau_1$ or $\Delta \kappa_2$ and $\tau_2$, respectively, toward the pure component values of water or ethanol. At any temperature and concentration, $\tau_1$ is less than $\tau_2$, and, as $\tau_1$ and $\tau_2$ are associated unambiguously with $\Delta \kappa_1$ and $\Delta \kappa_2$, there is an identification of the dispersion region characterized by $\Delta \kappa_1$ and $\tau_1$ with water, and that by $\Delta \kappa_2$ and $\tau_2$ with ethanol.

A plot of $\log \tau$ versus $1/T$ (Fig. 16) for both $\tau_1$ and $\tau_2$ over the entire concentration range gives the values of $\tau_0$ and $\Delta E$ shown in Table 3.

The electric polarization, $P$ (Eq. 4), can be described as macroscopic dipole moment per unit volume induced by an applied field, $E$. The difference in the static and high-frequency dielectric constants, $\Delta \kappa$, represents the polarization due to dipoles and may
Fig. 15. $\Delta k_1, \Delta k_2$ versus $\tau_c$ at the various temperatures and concentrations of ethanol-water solutions.
Fig. 16a. $\tau_1$ versus $1/T$ for various ethanol-water solutions.

Fig. 16b. $\tau_2$ versus $1/T$ for various ethanol-water solutions.
Table 2. Dispersion parameters for the ethanol-water dispersion.

\[ \begin{align*}
\kappa_1 &= \kappa_{B1} - \kappa_{\infty 1}; \quad \tau_1 = 1/\nu c_1; \\
\kappa_2 &= \kappa_{B2} - \kappa_{\infty 2}; \quad \tau_2 = 1/\nu c_2.
\end{align*} \]

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<thead>
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<th>Mole fraction ethanol</th>
<th>( \Delta \kappa_1 )</th>
<th>( \Delta \kappa_2 )</th>
<th>( \tau_1 \times 10^9 ) sec</th>
<th>( \tau_2 \times 10^9 ) sec</th>
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Table 2. (cont.)

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<th>Mole fraction ethanol</th>
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50°C

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<th>$\Delta \kappa_2$</th>
<th>$\tau_1 \times 10^9$</th>
<th>$\tau_2 \times 10^9$</th>
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be written

$$\Delta \kappa = \frac{P_d}{E E_0}$$

$\Delta \kappa_1$ and $\Delta \kappa_2$ have been normalized by dividing by the number of water and alcohol molecules present, to give the effective dipole moment per molecule, per unit electric field. The effective dipole moments, $\mu_{\text{eff}}$, are shown in Fig. 17 versus concentration in Fig. 18 versus $1/T$. 
Fig. 17a. Effective dipole moment ($\mu_{\text{eff}}$) for water molecules vs. concentration.

Fig. 17b. Effective dipole moment ($\mu_{\text{eff}}$) for ethanol molecules vs. concentration.
Fig. 13a. Effective dipole moments ($\mu_{\text{eff}}$) for water molecules versus $1/T$.

Fig. 13b. Effective dipole moments ($\mu_{\text{eff}}$) for ethanol molecules versus $1/T$. 
Table 3. Relaxation parameters of the two dispersions.

<table>
<thead>
<tr>
<th>Mole fraction ethanol</th>
<th>( \tau_0 \times 10^{14} ) sec</th>
<th>( \Delta E_1 ) kcal/mole</th>
<th>( \tau_0 \times 10^{14} ) sec</th>
<th>( \Delta E_2 ) kcal/mole</th>
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<td>7.44</td>
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<td>Water</td>
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<td>4.42</td>
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</table>

The measured \( \kappa' \) and \( \kappa'' \) for water at one degree intervals from 5°C to -5°C is given in Appendix C. Both in the supercooled state and in the region of maximum density, the dielectric constant and loss are described by a single dispersion which is an extension in \( \kappa'_e - \kappa'_{\infty} \) and \( \tau \) of that observed in the region zero to fifty degrees. The plot of log \( \tau \) versus 1/T for this region is shown in Fig. 19. The calculated \( \Delta E = 4.6 \) is that obtained from water at higher temperatures (see Table 3).
Fig. 19. $\tau$ versus $1/T$ for water near $0^\circ C$. 
DISCUSSION

According to the Debye theory of dielectric relaxation, the relaxation time is proportional to the macroscopic viscosity, \( \eta \), of the liquid. Viscosity versus \( 1/T \) is shown in Fig. 20 for ethanol-water solutions\(^{52} \) and comparison with the values of \( \tau_1 \) and \( \tau_2 \) (Fig. 16) shows that there is no overall dependence of \( \tau \) upon \( \eta \). In a hydrogen bonded system the reorienting of molecules involves the breaking and reforming of hydrogen bonds\(^{39} \) and it is

![Graph showing viscosity versus \( 1/T \) for ethanol-water solutions.](image-url)

Fig. 20. Viscosity (in centipoise) of water-ethanol solutions versus \( 1/T \).
DISCUSSION

According to the Debye theory of dielectric relaxation, the relaxation time is proportional to the macroscopic viscosity, $\eta$, of the liquid. Viscosity versus $1/T$ is shown in Fig. 20 for ethanol-water solutions and comparison with the values of $\tau_1$ and $\tau_2$ (Fig. 16) shows that there is no over-all dependence of $\tau$ upon $\eta$. In a hydrogen bonded system the reorienting of molecules involves the breaking and reforming of hydrogen bonds and it is

![Graph showing viscosity versus 1/T for ethanol-water solutions at different temperatures and mole fractions.](image)

*Fig. 20. Viscosity (in centipoise) of water-ethanol solutions versus 1/T*
more instructive to follow the behavior of the parameters $\tau_C$ and $\Delta E$ in the rate equation $1/\tau = 1/\tau_C e^{-\Delta E/kT}$. $1/\tau_C$ is proportional to the frequency with which a molecule finds itself in a configuration favorable to reorientation and the exponential term is proportional to the probability that a molecule will have the energy necessary to surmount the energy barrier $\Delta E$ between initial and final states.\(^{53}\) Factors affecting $\tau_C$ would be 1) original orientation of a molecule and orientation of its neighbors, 2) the number of new hydrogen-bonding sites available, 3) the number of hydrogen bonds already broken in the solution. $\Delta E$ would contain both the energy necessary to break the existing hydrogen bond and to turn the molecule to its new position. This is shown by the more or less regular procession of $\Delta E$'s as the aliphatic chain length increases in the series of alcohols from methanol ($\Delta E = 3.4$ kcal/mol)\(^{54}\) to n-octanol ($\Delta E = 8.9$ kcal/mole),\(^{55}\) the larger chain being more difficult to move; see Fig. 11.

From the low value for methanol, the $\Delta E$ for breaking a hydrogen bond in solution is less than the energy of the bond relative to the molecules at infinite separation, about 5 kcal/mole.\(^{56}\) This has been explained by the close approach of a third molecule approaching, bending and weakening an established hydrogen bond, as in Fig. 11.

The two dispersion regions in the alcohol-water solutions imply that there are two non- or weakly-interacting relaxation
more instructive to follow the behavior of the parameters \( \tau_0 \) and \( \Delta E \) in the rate equation \( 1/\tau = 1/\tau_0 e^{-\Delta E/kT} \). \( 1/\tau_0 \) is proportional to the frequency with which a molecule finds itself in a configuration favorable to reorientation and the exponential term is proportional to the probability that a molecule will have the energy necessary to surmount the energy barrier \( \Delta E \) between initial and final states.\(^5\) Factors affecting \( \tau_0 \) would be 1) original orientation of a molecule and orientation of its neighbors, 2) the number of new hydrogen-bonding sites available, 3) the number of hydrogen bonds already broken in the solution. \( \Delta E \) would contain both the energy necessary to break the existing hydrogen bond and to turn the molecule to its new position. This is shown by the more or less regular procession of \( \Delta E \)'s as the aliphatic chain length increases in the series of alcohols from methanol \( (\Delta E = 3.4 \text{ kcal/mol})\(^5\) to n-octanol \( (\Delta E = 8.9 \text{ kcal/mole})\),\(^5\) the larger chain being more difficult to move; see Fig. 11.

From the low value for methanol, the \( \Delta E \) for breaking a hydrogen bond in solution is less than the energy of the bond relative to the molecules at infinite separation, about 5 kcal/mole.\(^5\) This has been explained by the close approach of a third molecule approaching, bending and weakening an established hydrogen bond, as in Fig. 11.

The two dispersion regions in the alcohol-water solutions imply that there are two non- or weakly-interacting relaxation
mechanisms whose behavior depends on the concentration, and in
the limit of high concentration each dispersion region approaches
the behavior of one of the pure components. This is explained by
the presence in the solution of the possibility of two different
kinds of structure, the tetrahedral of water and the linear of
ethanol. This is not to say that only water molecules participate
in tetrahedral and only ethanol molecules in linear structures,
but rather the presence of the two kinds of molecules allows
regions, however small, in which one or the other structure pre-
dominates. Considering first the low-frequency ethanol associated
dispersion region, the intial addition of water to ethanol, 20 mole
percent water decreases $\tau_{02}$ by a factor of about $\frac{40}{4}$ and increases
$\Delta E_2$ by about one fifth. The water molecules entering the solution
have the effect of replacing aliphatic groups with O-H groups, in-
creasing the number of possible hydrogen bonding sites, and struc-
turally they are able to cause cross linking of the ethanol
chains; this the ethanol molecules cannot do because of steric
hinderance. The cross linking areas, where there will be water
molecules, are sites of tetrahedral bonding disrupting the chain
structure. Making available additional bonding sites in the middle
of what were long chains will decrease $\tau_{02}$, and the restricted
mobility of the chain after cross linking will increase the distance
to which a depolarizing nonbonded molecule can approach an existing
bond, resulting in an increase in $\Delta E_2$. 
As the solution is further diluted with water, the tetrahedral bonding areas are increased and the aliphatic portions of the ethanol molecules become regions of disrupted tetrahedral structure. Although the concentration of O-H groups has increased, the onset of tetrahedral hydrogen bonding has reduced the number of sites at which a hydrogen bond is possible but not yet formed. In diluting from 20 to 80 mole percent water, $\tau_{o2}$ increases by two orders of magnitude while $\Delta E_2$ decreases by two thirds. The large increase in $\tau_{o2}$ is due in part to the decrease in the relative availability of new hydrogen bonding sites, but such a large increase may be due to an additional configuration factor, namely that the aliphatic tail of the ethanol must be located in a tetrahedral region which is disrupted to an extent which allows motion of the aliphatic group through it. The large decrease in $\Delta E_2$ can be accounted for by the close approach of a water molecule which is loosely bound on the edge of the disturbed tetrahedral region. If $\Delta E$ were to contain a molecular friction factor, it might be expected to appear strongly at high water concentrations, as the molar volume of water is about one third that of alcohol. This is not clearly shown in the data, and it appears that any restrictions to rotation at low ethanol concentrations appear in the configurational term of $\tau_{o2}$.

The behavior of $\tau_{o2}$ and $\Delta E_2$ in ethanol-water solutions compares with $\tau_0$ and $\Delta E$ of ethanol in cyclohexane, whose behavior
Table 4. $\tau_0$, $\Delta E$, ethanol in cyclohexane.\textsuperscript{39}

<table>
<thead>
<tr>
<th>Mole fraction ethanol</th>
<th>$\tau_0 \times 10^{14}$ sec</th>
<th>$\Delta E$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>25.4</td>
<td>4.95</td>
</tr>
<tr>
<td>.90</td>
<td>13.3</td>
<td>5.4</td>
</tr>
<tr>
<td>.75</td>
<td>13.3</td>
<td>5.55</td>
</tr>
<tr>
<td>.50</td>
<td>1.71</td>
<td>6.8</td>
</tr>
<tr>
<td>.25</td>
<td>1.41</td>
<td>6.7</td>
</tr>
</tbody>
</table>

is shown in Table 4. Here again is seen an increase in $\tau_0$ and decrease in $\Delta E$ as aliphatic groups in the solution are replaced by O-H groups. As cyclohexane is diluted with alcohol, more hydrogen bonding groups are added, more hydrogen bonding is introduced, and the ratio of nonbonded to bonded sites decreases with the onset of the alcohol structure. The aliphatic groups serve to protect an established hydrogen bond from depolarization by the close approach of an nonbonded molecule.

The higher frequency dispersion associated with water, and so with the tetrahedral portion of the ethanol-water solution, displays a behavior similar to that of ethanol in the transition from linear to tetrahedral structure. At low water concentrations the tetrahedral cross linking regions in the alcohol chains are small and have a high surface to volume ratio. Since the surface molecules do not participate in four hydrogen bonds, and
the breaking of some of the bonds is necessary to turn a water molecule, the high percentage of water molecules which are able to reorient is reflected in the low value of $\tau_{01}$. The tetrahedral regions are well protected by the aliphatic portion of the chains and, as in the case of the ethanol dispersion region, the close approach of an nonbonded molecule to a hydrogen bond is made more difficult, increasing $\Delta E_1$. As the water concentration increases, the tetrahedral bonding regions grow in size, reducing the surface to volume ratio and increasing $\tau_{01}$. At the same time, the chain structure is being broken up and ethanol molecules no longer protect the surface of the tetrahedral structure. This would, as in the case of the ethanol dispersion, allow closer approach of nonbonded molecules to the existing hydrogen bonds, and so reduce $\Delta E_1$.

The polarizabilities of the two regions vary greatly in concentration and temperature dependence. For both dispersions at low concentration of their identifying component, the temperature dependence of $\mu_{\text{eff}}$ is higher than in the pure substance, so that $\mu_{\text{eff}}$ is greater than in the pure compound at low temperatures and less at high temperatures (see Figs. 17 and 18). It appears that the low concentration component, residing in a region of disturbed competing structure, is able to exert a polarizing influence on molecules of the other species which is out of proportion to its concentration. At high temperature other
disturbed areas appear in the high concentration structure which are not necessarily connected with disruptions by the low concentration component and the low temperature component begins to lose its identity as a polarizing agent; it is dissolved. In the case of the tetrahedral cross-link regions at low water concentrations, at low temperatures, they bind the ethanol chains and as the temperature rises they begin to break up and water molecules enter the chain structure. At low ethanol concentrations, low temperature confines the disturbed tetrahedral areas mainly to regions near the ethanol molecules; raising the temperature expands these disturbed regions and introduces others, the ethanol molecule loses its disrupting characteristics and is more fully incorporated in the broken down water structure. The resulting values of $\tau_0$ and $\Delta E$ are determined by the actual molecular composition of the two regions.

When the dilution of ethanol with water is viewed as the replacement of aliphatic groups with O-H groups and the systematic buildup of tetrahedral water structure, the high frequency water related dispersion follows the behavior noted in a bond switching process, namely, that to reorient a molecule a hydrogen bond must be broken and a new one formed. Thus, in water, the reorientation is one of hydrogen bond switching as opposed to the rotation of a molecule in a region of macroscopic viscosity.
Conclusions

1. In solutions of ethanol and water, there are two dispersions in the centimeter wavelength region, each having a distinct relaxation time and being related to water and alcohol structures.

2. The relaxation times of both dispersions show the behavior characteristic of bond switching spectra.

3. In the rate equation, \(1/\tau = 1/\tau_0 e^{-\Delta E/kT}\), \(\tau_0\) is proportional to the probability that a new bonding site for re-orientation is available and \(\Delta E\) is the energy needed to break the existing hydrogen bond and reforming a bond on the new site. \(\Delta E\) is reduced appreciably by the close approach to the existing bond of the new bonding site.


APPENDIX A

Table AA-1. Static dielectric constants for ethanol-water solutions measured at 100 kc/sec.

<table>
<thead>
<tr>
<th>Mole fraction ethanol</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>5</td>
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<tr>
<td>1.00</td>
<td>28.0</td>
</tr>
<tr>
<td>.90</td>
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<tr>
<td>.50</td>
<td>42.1</td>
</tr>
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<td>.40</td>
<td>47.4</td>
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<td>.20</td>
<td>62.4</td>
</tr>
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<td>.10</td>
<td>74.2</td>
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<td>Water</td>
<td>86.7</td>
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</tbody>
</table>
**APPENDIX B**

**Dielectric Constant and Loss Factors for Ethanol-Water Solutions**

Table AB-1. Dielectric constant and loss factor for water.

<table>
<thead>
<tr>
<th></th>
<th>8.5 kMc</th>
<th></th>
<th>3.0 kMc</th>
<th></th>
<th>1.0 kMc</th>
<th></th>
<th>0.3 kMc</th>
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<tbody>
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<td></td>
<td>$\kappa'$</td>
<td>$\kappa''$</td>
<td>$\kappa'$</td>
<td>$\kappa''$</td>
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<td>82.90</td>
<td>5.10</td>
<td>81.65</td>
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<td>25</td>
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<td>26.93</td>
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<td>3.99</td>
<td>77.40</td>
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<td>35</td>
<td>67.96</td>
<td>22.20</td>
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<td>9.58</td>
<td>75.94</td>
<td>3.19</td>
<td>75.40</td>
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<td>66.10</td>
<td>16.08</td>
<td>69.50</td>
<td>5.87</td>
<td>68.35</td>
<td>2.04</td>
<td>68.55</td>
</tr>
</tbody>
</table>

Table AB-2. Dielectric constant and loss factor for 0.05 mole fraction ethanol in water solution.

<p>| | | | | | | | |</p>
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<th></th>
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<td>5</td>
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<td>58.50</td>
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<td>78.90</td>
<td>13.18</td>
<td>79.98</td>
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<td>34.78</td>
<td>62.75</td>
<td>16.49</td>
<td>77.30</td>
<td>8.95</td>
<td>75.94</td>
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<td>6.01</td>
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<td>59.00</td>
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<td>6.56</td>
<td>61.45</td>
<td>2.56</td>
<td>63.65</td>
</tr>
</tbody>
</table>

Table AB-3. Dielectric constant and loss factor for 0.10 mole fraction ethanol in water solution.

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<th></th>
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<td>11.18</td>
<td>69.65</td>
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<td>36.20</td>
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<td>7.26</td>
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</tr>
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<td>43.85</td>
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<td>12.08</td>
<td>64.22</td>
<td>5.38</td>
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<td>21.05</td>
<td>57.40</td>
<td>8.06</td>
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<td>3.29</td>
<td>58.20</td>
</tr>
</tbody>
</table>
Table AB-4. Dielectric constant and loss factor for 0.20 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'</td>
<td>k''</td>
<td>k'</td>
<td>k''</td>
</tr>
<tr>
<td>5</td>
<td>11.42</td>
<td>16.84</td>
<td>31.31</td>
<td>22.45</td>
</tr>
<tr>
<td>15</td>
<td>16.06</td>
<td>20.58</td>
<td>39.30</td>
<td>22.42</td>
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<td>22.78</td>
<td>23.67</td>
<td>44.95</td>
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<td>28.41</td>
<td>22.88</td>
<td>45.35</td>
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</tr>
<tr>
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<td>34.56</td>
<td>20.33</td>
<td>44.49</td>
<td>8.89</td>
</tr>
</tbody>
</table>

Table AB-5. Dielectric constant and loss factor for 0.30 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'</td>
<td>k''</td>
<td>k'</td>
<td>k''</td>
</tr>
<tr>
<td>5</td>
<td>8.97</td>
<td>12.06</td>
<td>24.72</td>
<td>17.76</td>
</tr>
<tr>
<td>15</td>
<td>11.71</td>
<td>14.92</td>
<td>30.76</td>
<td>19.24</td>
</tr>
<tr>
<td>25</td>
<td>15.95</td>
<td>17.88</td>
<td>32.65</td>
<td>16.74</td>
</tr>
<tr>
<td>35</td>
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<td>18.00</td>
<td>35.00</td>
<td>14.14</td>
</tr>
<tr>
<td>50</td>
<td>24.81</td>
<td>18.20</td>
<td>36.20</td>
<td>9.10</td>
</tr>
</tbody>
</table>

Table AB-6. Dielectric constant and loss factor for 0.40 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'</td>
<td>k''</td>
<td>k'</td>
<td>k''</td>
</tr>
<tr>
<td>5</td>
<td>7.51</td>
<td>9.06</td>
<td>16.08</td>
<td>14.50</td>
</tr>
<tr>
<td>15</td>
<td>9.41</td>
<td>11.25</td>
<td>21.25</td>
<td>16.03</td>
</tr>
<tr>
<td>25</td>
<td>11.92</td>
<td>13.59</td>
<td>25.00</td>
<td>15.09</td>
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<td>35</td>
<td>14.71</td>
<td>14.80</td>
<td>26.05</td>
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<td>50</td>
<td>18.51</td>
<td>15.62</td>
<td>29.68</td>
<td>9.55</td>
</tr>
</tbody>
</table>
Table AB-7. Dielectric constant and loss factor for 0.50 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'</td>
<td>k''</td>
<td>k'</td>
<td>k''</td>
</tr>
<tr>
<td>5</td>
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<td>6.96</td>
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<td>15</td>
<td>8.03</td>
<td>8.41</td>
<td>15.99</td>
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<td>25</td>
<td>9.41</td>
<td>10.36</td>
<td>19.09</td>
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<td>11.27</td>
<td>11.57</td>
<td>22.31</td>
<td>11.67</td>
</tr>
<tr>
<td>50</td>
<td>13.96</td>
<td>12.44</td>
<td>24.22</td>
<td>9.45</td>
</tr>
</tbody>
</table>

Table AB-8. Dielectric constant and loss factor for 0.60 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'</td>
<td>k''</td>
<td>k'</td>
<td>k''</td>
</tr>
<tr>
<td>5</td>
<td>5.58</td>
<td>5.56</td>
<td>9.50</td>
<td>9.29</td>
</tr>
<tr>
<td>15</td>
<td>7.07</td>
<td>6.58</td>
<td>12.39</td>
<td>11.13</td>
</tr>
<tr>
<td>25</td>
<td>7.89</td>
<td>7.81</td>
<td>14.40</td>
<td>11.87</td>
</tr>
<tr>
<td>35</td>
<td>8.82</td>
<td>9.17</td>
<td>17.58</td>
<td>11.85</td>
</tr>
<tr>
<td>50</td>
<td>11.02</td>
<td>10.33</td>
<td>20.00</td>
<td>9.32</td>
</tr>
</tbody>
</table>

Table AB-9. Dielectric constant and loss factor for 0.70 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'</td>
<td>k''</td>
<td>k'</td>
<td>k''</td>
</tr>
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<td>4.12</td>
<td>7.72</td>
<td>7.24</td>
</tr>
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<td>5.85</td>
<td>5.05</td>
<td>9.41</td>
<td>8.83</td>
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<td>6.66</td>
<td>5.94</td>
<td>11.08</td>
<td>9.57</td>
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<td>7.66</td>
<td>6.89</td>
<td>13.81</td>
<td>10.73</td>
</tr>
<tr>
<td>50</td>
<td>8.72</td>
<td>8.27</td>
<td>16.29</td>
<td>9.05</td>
</tr>
</tbody>
</table>
Table AB-10. Dielectric constant and loss factor for 0.80 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>θ(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'</td>
<td>k''</td>
<td>k'</td>
<td>k''</td>
</tr>
<tr>
<td>5</td>
<td>5.20</td>
<td>3.18</td>
<td>6.46</td>
<td>5.87</td>
</tr>
<tr>
<td>15</td>
<td>5.47</td>
<td>4.13</td>
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<td>7.16</td>
</tr>
<tr>
<td>25</td>
<td>6.02</td>
<td>4.64</td>
<td>8.80</td>
<td>8.10</td>
</tr>
<tr>
<td>50</td>
<td>7.10</td>
<td>6.61</td>
<td>14.52</td>
<td>9.29</td>
</tr>
</tbody>
</table>

Table AB-11. Dielectric constant and loss factor for 0.90 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>θ(°C)</th>
<th>4.74</th>
<th>2.48</th>
<th>5.35</th>
<th>4.45</th>
<th>11.11</th>
<th>11.35</th>
<th>24.45</th>
<th>10.22</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>5.20</td>
<td>2.92</td>
<td>6.35</td>
<td>5.89</td>
<td>15.04</td>
<td>11.92</td>
<td>25.22</td>
<td>7.55</td>
</tr>
<tr>
<td>15</td>
<td>5.06</td>
<td>3.62</td>
<td>7.29</td>
<td>6.97</td>
<td>16.55</td>
<td>10.45</td>
<td>24.36</td>
<td>5.29</td>
</tr>
<tr>
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<td>5.58</td>
<td>4.32</td>
<td>8.33</td>
<td>7.40</td>
<td>18.42</td>
<td>9.16</td>
<td>23.35</td>
<td>3.66</td>
</tr>
<tr>
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<td>5.85</td>
<td>5.42</td>
<td>10.83</td>
<td>8.02</td>
<td>19.50</td>
<td>5.99</td>
<td>21.33</td>
<td>2.18</td>
</tr>
<tr>
<td>50</td>
<td>4.68</td>
<td>2.19</td>
<td>5.07</td>
<td>4.08</td>
<td>10.91</td>
<td>10.43</td>
<td>22.65</td>
<td>10.34</td>
</tr>
</tbody>
</table>

Table AB-12. Dielectric constant and loss factor for 0.95 mole fraction ethanol in water solution.

<table>
<thead>
<tr>
<th>θ(°C)</th>
<th>4.79</th>
<th>2.63</th>
<th>5.61</th>
<th>5.13</th>
<th>12.18</th>
<th>11.07</th>
<th>23.59</th>
<th>7.66</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.12</td>
<td>2.63</td>
<td>5.61</td>
<td>5.13</td>
<td>12.18</td>
<td>11.07</td>
<td>23.59</td>
<td>7.66</td>
</tr>
<tr>
<td>15</td>
<td>4.79</td>
<td>3.06</td>
<td>6.62</td>
<td>6.53</td>
<td>14.92</td>
<td>10.56</td>
<td>23.35</td>
<td>5.58</td>
</tr>
<tr>
<td>35</td>
<td>5.80</td>
<td>4.62</td>
<td>9.94</td>
<td>7.45</td>
<td>17.66</td>
<td>6.45</td>
<td>21.00</td>
<td>2.32</td>
</tr>
<tr>
<td>50</td>
<td>4.68</td>
<td>2.19</td>
<td>5.07</td>
<td>4.08</td>
<td>10.91</td>
<td>10.43</td>
<td>22.65</td>
<td>10.34</td>
</tr>
</tbody>
</table>
Table AB-13. Dielectric constant and loss factor for ethanol.

<table>
<thead>
<tr>
<th>T°C</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k' )</td>
<td>( k'' )</td>
<td>( k' )</td>
<td>( k'' )</td>
</tr>
<tr>
<td>5</td>
<td>4.50</td>
<td>2.00</td>
<td>5.09</td>
<td>3.84</td>
</tr>
<tr>
<td>15</td>
<td>4.71</td>
<td>2.31</td>
<td>5.48</td>
<td>4.40</td>
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<tr>
<td>25</td>
<td>4.88</td>
<td>2.80</td>
<td>6.28</td>
<td>5.81</td>
</tr>
<tr>
<td>35</td>
<td>4.94</td>
<td>3.43</td>
<td>6.61</td>
<td>6.20</td>
</tr>
<tr>
<td>50</td>
<td>5.10</td>
<td>4.34</td>
<td>8.68</td>
<td>6.87</td>
</tr>
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</table>
APPENDIX C

Table AC-1. The Dielectric constant and loss factors for water near 0°C.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>8.5 kMc</th>
<th>3.0 kMc</th>
<th>1.0 kMc</th>
<th>0.3 kMc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k'&lt;</td>
<td>k''</td>
<td>k'&lt;</td>
<td>k''</td>
</tr>
<tr>
<td>5</td>
<td>53.18</td>
<td>39.53</td>
<td>81.60</td>
<td>20.95</td>
</tr>
<tr>
<td>4</td>
<td>52.00</td>
<td>40.08</td>
<td>79.20</td>
<td>21.20</td>
</tr>
<tr>
<td>3</td>
<td>50.66</td>
<td>40.20</td>
<td>79.05</td>
<td>22.32</td>
</tr>
<tr>
<td>2</td>
<td>49.31</td>
<td>40.58</td>
<td>79.26</td>
<td>22.89</td>
</tr>
<tr>
<td>1.</td>
<td>48.09</td>
<td>40.72</td>
<td>79.20</td>
<td>23.40</td>
</tr>
<tr>
<td>0°</td>
<td>46.70</td>
<td>40.71</td>
<td>77.95</td>
<td>23.93</td>
</tr>
<tr>
<td>-1</td>
<td>45.30</td>
<td>41.20</td>
<td>78.40</td>
<td>24.70</td>
</tr>
<tr>
<td>-2</td>
<td>44.15</td>
<td>40.74</td>
<td>77.42</td>
<td>25.49</td>
</tr>
<tr>
<td>-3</td>
<td>42.63</td>
<td>41.13</td>
<td>77.80</td>
<td>26.55</td>
</tr>
<tr>
<td>-4</td>
<td>41.04</td>
<td>40.75</td>
<td>75.43</td>
<td>26.70</td>
</tr>
<tr>
<td>-5</td>
<td>39.62</td>
<td>40.32</td>
<td>75.25</td>
<td>27.73</td>
</tr>
</tbody>
</table>
APPENDIX D

Evaluation of the Dispersion Parameters for Two Superposed Debye Dispersions

If one has a dispersion composed of two superposed Debye type dispersions, the vector \( \kappa^* - \kappa = R \) in the complex plane has the components

\[
R = R_x + R_y = A_x + B_x + A_y + B_y = A + B, \quad (AD.1)
\]

where \( A \) and \( B \) are the individual dispersion vectors, and \( A_x, B_x \) and \( A_y, B_y \) their real and imaginary components. From Eq. AD.1

\[
\nu = \frac{A_y}{A_x} = \frac{B_y}{B_x}, \quad (AD.2)
\]

From Fig. AD-1, one may also write

\[
A = \Delta \kappa_1 \cos \phi = \Delta \kappa_1 \left( \frac{A_y}{A} \right), \quad (AD.3)
\]

\[
B = \Delta \kappa_2 \cos \theta = \Delta \kappa_2 \left( \frac{B_y}{B} \right).
\]

Fig. AD-1. The vector superposition of two Debye spectra.
APPENDIX D

Evaluation of the Dispersion Parameters for Two
Superposed Debye Dispersions

If one has a dispersion composed of two superposed Debye type
dispersions, the vector $\mathbf{\kappa}^* - \mathbf{\kappa} = \mathbf{R}$ in the complex plane has the
components

$$\mathbf{R} = \mathbf{R}_x + \mathbf{R}_y = \mathbf{A}_x + \mathbf{B}_x + \mathbf{A}_y + \mathbf{B}_y = \mathbf{A} + \mathbf{B}, \quad (\text{AD.1})$$

where $\mathbf{A}$ and $\mathbf{B}$ are the individual dispersion vectors, and $\mathbf{A}_x, \mathbf{B}_x$ and
$\mathbf{A}_y, \mathbf{B}_y$ their real and imaginary components. From Eq. AD.1

$$\frac{\nu}{\nu_{c_1}} = \frac{\mathbf{A}_y}{\mathbf{A}_x} ; \quad \frac{\nu}{\nu_{c_2}} = \frac{\mathbf{B}_y}{\mathbf{B}_x}. \quad (\text{AD.2})$$

From Fig. AD-1, one may also write

$$\begin{align*}
\mathbf{A} &= \Delta \kappa_1 \cos \phi = \Delta \kappa_1 \left( \frac{\mathbf{A}_y}{\mathbf{A}_x} \right), \\
\mathbf{B} &= \Delta \kappa_2 \cos \theta = \Delta \kappa_2 \left( \frac{\mathbf{B}_y}{\mathbf{B}_x} \right). \quad (\text{AD.3})
\end{align*}$$

---

Fig. AD-1. The vector superposition of
two Debye spectra.
Then, from Eqs. AD.1 and AD.3

\[ \Delta \kappa = \Delta \kappa_1 + \Delta \kappa_2 = R_x + \frac{A_x^2}{B_x} + \frac{B_y^2}{C_x} \]  \hspace{1cm} (AD.4)

In Eqs. AD.1 to AD.4 there are six unknowns, \( A_x, A_y, B_x, B_y, \nu_{c_1}, \) and \( \nu_{c_2}, \) while there are five equations, Eq. AD.1 being the sum of the real and imaginary parts of \( R. \) Making measurements at two frequencies gives another set of five equations, and four more unknowns, \( \nu_{c_1} \) and \( \nu_{c_2} \) being the same in all cases. Thus, if \( \kappa'_s \) and \( \kappa'_\infty \) are known, measurements at two frequencies within the dispersion region are sufficient to solve for the parameters of the two superposed dispersions.

Adding Eqs. AD.2 and using Eq. AD.1 to rearrange gives

\[ B_y (\nu_{c_1} - \nu_{c_2}) = R_x - R_y \nu_{c_1} \]  \hspace{1cm} (AD.5)

and from Eqs. AD.4 and AD.2,

\[-B_y (\nu_{c_1} - \nu_{c_2}) = \frac{(\Delta \kappa - R_x) \nu}{c_1 c_2} - R_y \nu_{c_2} \]  \hspace{1cm} (AD.6)

Adding Eqs. AD.5 and AD.6 gives Eq. AD.7, a function only of

\[ \frac{R_x}{R_y} = -\frac{(\nu_{c_1} \nu_{c_2}) (\Delta \kappa - R_x)}{R_y} + (\nu_{c_1} + \nu_{c_2}) \]  \hspace{1cm} (AD.7)

the quantities measured, \( \Delta \kappa = \kappa'_s - \kappa'_\infty, \) \( R_x = \kappa' - \kappa'_\infty \) and \( R_y = \kappa'' \). \( R_x/R_y \) is plotted against \( \Delta \kappa - R_x/R_y \) for the several frequencies;
the slope is \((\nu_1 \times \nu_2)\) and the intercept \((\nu_1' + \nu_2')\). From this, values of \(\nu_1\) and \(\nu_2\) are computed.

Knowing \(\nu_1\) and \(\nu_2\) leaves the problem of determining \(\Delta x_1\) and \(\Delta x_2\) and assigning to them their respective \(\tau\)'s. From Eqs. AD.2:

\[
R_x = \Delta x_1 \cos^2 \theta + \Delta x_2 \cos^2 \theta, \tag{AD.8}
\]

where \(\theta = \arctan \frac{\nu}{\nu_1}\) and \(\theta = \arctan \frac{\nu}{\nu_2}\). Rearranging with the help of Eq. AD.1,

\[
\Delta x_1 = \frac{R_x - \cos^2 \theta}{\cos^2 \theta - \cos^2 \theta}; \quad \Delta x_2 = \frac{R_x - \cos^2 \theta}{\cos^2 \theta - \cos^2 \theta}. \tag{AD.9}
\]

Solving either of Eqs. AD.9 using either of the \(\nu_1\)'s, results in the proper \(\Delta x\) being calculated for both \(\tau_1\) and \(\tau_2\), leaving no ambiguity in assigning the pairs \(\Delta x_1, \tau_1\) and \(\Delta x_2, \tau_2\).
BIBLIOGRAPHY


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BIOGRAPHICAL NOTE

The author was born in Idaho Falls, Idaho, on April 26, 1936. He attended the public schools there, graduating from high school in 1954. In 1958 he graduated from The College of Idaho with a B.S. degree in chemistry. In 1958 and 1959 he was on active duty with the U.S. Air Force and in 1960 enrolled at M.I.T. He is a member of Sigma Xi.