THE DIELECTRIC PROPERTIES OF POLYSALT FILMS

by

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Professor Philip Franklin
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Cambridge 39, Massachusetts

Dear Professor Franklin:


Respectfully submitted,

Gary L. Falkenstein
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content of the polyion complex. The films were cast on platinum slides in
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dried, and dielectrically tested at constant temperature and a series of
relative humidities. The dielectric tests covered the frequency range from
100 to 100,000 cps. In addition, the water contents of some of the films
were determined as a function of relative humidity.

The polysalt films were found to be capable of dissolving fairly large
amounts of water, 6.7 equivalents per polysalt equivalents per polysalt
equivalent for a salt-free film at 92.5% relative humidity and 24.5°C. The
water content increased as the salt content increased, so that a film
composed of 0.46 equivalents of salt per polysalt equivalent also contained
19 equivalents of water per polysalt equivalent.

The measured dielectric constants of the films increased as the sodium
bromide content increased and reached very large values. The dielectric
constants at a frequency of 100 cps and 51% relative humidity at 27.5°C
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approximately 0.46 equivalents of salt per polysalt equivalent. Since the
mean relaxation time for the observed dispersion lay below the frequency
range studied, the static dielectric constants were much larger than the
values measured. A decrease in the water content of a film at constant tem-
perature decreased the magnitude of the observed dispersion.

The magnitudes of the measured dielectric constants decreased with time
(at constant moisture content) to new steady-state values when the films were
held at relative humidities above 75%. This change affected the dielectric
constants measured at lower relative humidities.

The dielectric behavior of an unsymmetrical polysalt film (composed of
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similar to that of a neutral polysalt film containing approximately the same
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The complex dielectric behavior of the neutral polysalt films contain-
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of small regions within the polysalt which contained free microions and/or
microions associated with unreacted polyion groups. Movement of these microions is restricted to within the particular region by the homopolar and fully reacted polyion material bordering each region. Movement of the microions within each region in response to an applied electric field can create a net polarization in each region. Changes in the dielectric constant with water content is ascribed to changes in microion mobility and in the volume fraction of polarizable regions. The decrease in dielectric constant with time when the films were held at high relative humidities is thought to be due to the consolidation of some of the small polarizable regions.
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I. SUMMARY

A. Background and Objectives

Recent research has demonstrated that synthetic, linear polyelectrolytes of opposite polyion charge can be crosslinked in aqueous solution to yield ionically cross-linked structures or "polysalts," which possess unusual structural, physicochemical and electrical properties. These polysalts resemble proteins and other biocolloids in many respects. A particularly striking similarity between the synthetic polysalts and biological tissues is to be found in their dielectric behavior, where both materials exhibit anomalously high dielectric constants and marked dielectric dispersion (frequency dependence). The objective of this investigation was to study the dielectric properties of a well-characterized polysalt (poly (vinylbenzyl-trimethyl ammonium)- poly (styrene sulfonate) or VBTA-SS) as a function of moisture and microion content, and to attempt to elucidate the microstructure of the complex through an analysis of the electrical measurements.

B. Properties of Polyion Complexes

Prior work on synthetic polyion complexes has been focused upon methods of preparation, and determination of composition, structure and physicochemical properties. Miekka (25) and Mir (27) have shown that VBTA and SS polyions coreact in a very specific fashion to yield a neutral, stoichiometric polysalt virtually free of microions. This complex is insoluble in water or organic solvents, but is capable of absorbing water and selectively sorbing electrolytes from aqueous solution. The complex swells markedly in concentrated salt solutions, and can be
dissolved in a ternary solvent of water, salt, and a water-miscible organic liquid. Using these ternary "shielding" solvents, it is possible to prepare polyion complexes which contain non-stoichiometric proportions of the component polyions; such materials behave as anion or cation exchange resins, depending upon which polyion is present in excess.

In a cursory study, Miekkä (25) measured the dielectric properties of both neutral polysalt and non-stoichiometric polyion complexes in the partially hydrated state. At 51% relative humidity and 20-25°C, he found the neutral polysalt to possess a dielectric constant of 14 at a frequency of $10^3$ cps, decreasing to 11 at $10^6$ cps. Non-stoichiometric complexes under the same conditions, however, displayed dielectric constants in the thousands at low frequencies, and exhibited a very rapid decrease in dielectric constant with increasing frequency.

These observations pointed to the need for a very careful study of the dielectric properties of these complexes, and their dependence upon water- and microin-content, not only as a means for clarifying the structure of the complexes, but also to assess their potential utility in electrical or electronic devices.

Dielectric properties of neutral polysalt were therefore measured at various relative humidities, using complexes which contained variable concentrations of sodium bromide. Water-sorption isotherms of these salt-containing complexes were also determined to permit estimation of water content as a function of relative humidity. Dielectric constants, loss factors and loss tangents were measured in the frequency range from $10^2$ to $10^5$ cps, at a temperature of 27.7°C. A polyanion (SS)-rich complex
was also examined in a similar fashion, in order to establish whether complexes containing bound microions differ significantly in electrical characteristics from neutral polysalt containing extraneous simple electrolyte.

C. Experimental Procedure

The major portion of the experimental work was concerned with the determination of the dielectric properties of the neutral polysalt films. Neutral polysalt gel was cast on platinum slides from water-acetone-sodium bromide solutions similar to those used by Miekka (25). The films were washed with distilled water and then equilibrated in distilled water or in a sodium bromide solution of normality ranging from 0.06 to 0.25. The gelled films were dried in air at 51\% relative humidity and temperatures from 21 to 28°C to clear films. The films were equilibrated at the desired relative humidity in the test apparatus for one day prior to starting the dielectric tests.

A column of mercury, butted against the exposed face of the film, and the platinum slide served as the two electrodes during the electrical tests. The capacitance and resistance of the film were determined by matching the films' impedance and phase angle with a variable standard resistor and capacitor in parallel. This was accomplished using a General Radio Company Type 1605A Impedance Comparator, which applies a 0.3 volt test signal to both the unknown and the standards. The frequency of this signal was successively set at $10^5$, $10^4$, $10^3$, and $10^2$ cps during each measurement. Several measurements were made at each condition and a representative one selected for calculation. (In general, the values varied by
% due to differing contact areas.) The relative humidity during the testing was varied from 92.5 to 33% at a temperature of 27.7 ±0.3°C.

After testing was complete, the films were fragmented by drying over P₂O₅ and the average thickness over the test area determined microscopically. The films containing the two largest quantities of sodium bromide were analyzed for their sodium content by flame photometry.

One film was also cast from water-acetone-sodium bromide solution which contained approximately 1.3 equivalents of NaSS per equivalent of VBTA-SS. The slide was washed with a dilute sodium bromide solution, approximately 0.01N, before being dried and tested at 51% relative humidity and 27.8°C. (Distilled water could not be used for the final wash because the large amount of swelling disrupted the film structure.) The dielectric tests and geometrical measurements were made as with the neutral polyelectrolyte films.

The water absorption of four neutral polyelectrolyte films similar to those dielectrically tested was determined as a function of relative humidity at 24.5°C, using a quartz helix balance; isotherms were determined over the relative humidity interval of 11-92.5%.
D. Discussion and Interpretation of Results

1. Polysalt sorption of sodium bromide from aqueous solutions

The sodium bromide contents of three neutral polysalt films, two of which were equilibrated in 0.25N sodium bromide and the other, in 0.075N sodium bromide, are shown in Table IV. The salt contents of the films containing smaller amounts of salt could not be measured because of the limited quantity of polysalt available from each film. The sorption of sodium bromide by the neutral complex at a given external salt concentration was larger than that observed by Miekka (25) in an earlier study. The differences are believed to arise from the fact that Miekka's measurements were performed with initially dried and consolidated polysalt, while those obtained in this work were performed with expanded, highly hydrated gel. However, the decrease in sorption selectivity with an increase in the sodium bromide concentration of the equilibration solution (the salt content of the polysalt doubles for a threefold increase in solution concentration) agrees with the trend found by Miekka.

2. Water sorption isotherms

Water sorption isotherms for four neutral polysalt samples containing controlled amounts of sodium bromide were determined at 24.5°C; the results are shown in Figure 11. The water sorption of the salt-free complex, listed in Table V on an equivalence basis, is calculated to be at most about 7 water molecules per polyon pair, suggesting that the water is almost completely associated with the ionic portions of the polysalt. As the sodium bromide content of the complex was
increased, the amount of water absorbed by the polysalt (at constant relative humidity) also increased. This increase is believed to originate from two sources: hydration of the added microions, and increased swelling of the polysalt network consequent to reduced cross-linkage. The latter is probably the cause of the increase, with salt content, in the ratios of "excess" water content (i.e., water sorbed in excess of that observed with salt-free polysalt), to salt content, shown in Table VI. The convergence of the isotherms for the microion-free complex and the polysalt equilibrated in the 0.020M sodium bromide solution at 92.5% relative humidity may possibly result from the presence of small microvoids in the microion-free complex; the microvoids might fill with water under these conditions. Polysalts which contain appreciable amounts of sodium bromide probably do not contain these microvoids due to a more complete consolidation of the complex during the drying of the gel. Miekka (25) previously found that complete consolidation of bulk complex could only be achieved in the presence of simple salts.

3. Dielectric behavior
   a. Theory of complex dielectrics

   Since the remainder of this section will discuss the dielectric behavior of the polysalt complexes, the theory of complex dielectrics will be briefly reviewed as an introduction to the subject. The complex dielectric constant, \( \varepsilon^* \), of a dielectric material consists of two terms; a real term reflecting the capacity of the material to store electric energy via polarization, and an imaginary part reflecting the energy dissipated as heat during a change in the magnitude of the polarization. These two terms, where \( \varepsilon^* = \varepsilon' - i \varepsilon'' \), are called the dielectric
constant, $\varepsilon'$, and the loss factor, $\varepsilon''$. The ratio of the two terms, $\varepsilon'/\varepsilon''$, is called the loss tangent.

If the polarization of a material involves a single physical process (e.g., orientation of a dipolar gas), then the rate at which this process responds to an impressed electric field will normally decay exponentially with time. This response is characterized by a time constant, $\tau$, which is called the relaxation time. When this type of material is subjected to a field which is alternating sinusoidally, the dielectric constant, loss factor and loss tangent become

$$
\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + \omega^2 \tau^2)
$$
$$
\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)/(1 + \omega^2 \tau^2)
$$
$$
\varepsilon''/\varepsilon' = (\varepsilon_0 - \varepsilon_\infty) \omega \tau / (\varepsilon_0 + \varepsilon_\infty) \omega \tau^2
$$

where $\omega$ is the frequency of the field and $\varepsilon_0$ and $\varepsilon_\infty$ are the low and high frequency asymptotic values of the dielectric constant. The difference between the latter two values, $(\varepsilon_0 - \varepsilon_\infty)$, is called the dielectric increment. The loss factor and loss tangent both go through a maximum with frequency, the former at $\omega_{\text{max.}} = 1/\tau$ and the latter at $\omega_{\text{max.}} = (\varepsilon_0/\varepsilon_\infty)^{1/2}/\tau$. The frequency range over which the major change in dielectric constant occurs, called the dispersion region, covers about two decades.

If a distribution of relaxation times exists instead of a single relaxation time, the dispersion region will extend over more than two orders of magnitudes in frequency. Both the loss factor and dielectric constant are now the result of the addition of a series of individual curves, each characterized by a dielectric increment and relaxation time.
in the distribution. The shape of the dielectric constant and loss factor curves are determined by the shape of the relaxation time distribution, with a broad distribution giving a large dispersion region. The loss tangent maximum will again occur at a higher frequency than that of the loss factor, but the ratio of the two frequencies will be less than \((\varepsilon_0/\varepsilon_\infty)^{1/4}\).

Hence, a material which behaves as a complex dielectric will exhibit an a.c. dielectric constant which undergoes a decrease in magnitude with increasing frequency, a loss-factor (related to the resistive impedance) which first increases and then decreases with increasing frequency, and a loss tangent which similarly passes through a maximum with increasing frequency. Independant examination of (a) the absolute change-in-magnitude of the dielectric constant over the frequency spectrum, (b) the range of frequencies over which such changes occur, and (c) their rate-of-change with frequency, provide a means for establishing the nature of the polarization processes occurring in the material, and rates at which such processes can take place. In many respects, therefore, dielectric measurements resemble non-destructive dynamic stress-strain measurements, in that both examine microscopic relaxation phenomena taking place within the test specimen.

b. Dielectric behavior of salt-free polysalt

The dielectric properties of salt-free polysalt, determined at 27.5°C and 51% relative humidity, are shown in Figure 12. The dielectric constant increased from 11 to 27 as the frequency was decreased from 100,000 to 100 cps. These values are in agreement with those determined
by Miekka (25) for bulk neutral polysalt. Since both the loss factor maximum and the inflection point in the dielectric constant curve occur at frequencies below 100 cps, the dielectric constant should continue to rise with decreasing frequency before finally approaching an asymptotic value much larger than 27. An increase in the relative humidity to 92.5 increased the dielectric constant by approximately a factor of 20 at 100 cps and of 2 at 100,000 cps, as shown in Figure 38. (The time-dependent change in dielectric constant at 92.5% relative humidity as shown in the figure, was not investigated in detail for this salt-free polysalt. However, the change is discussed below for salt-containing polysalt.)

c. The effect of sodium bromide content

The dielectric properties of a series of neutral polysalts containing differing amounts of sodium bromide were determined at 27.5°C and 51% relative humidity. Table VIII lists the approximate sodium bromide and water contents of the polysalts under the test conditions. The sodium bromide contents of three of the polysalts could not be measured directly, but instead were estimated from the dielectric constants. These estimates are discussed below.

The dielectric properties are shown in Figures 13, 14, and 15. The dielectric constants increased with increasing salt content and decreasing frequency. The maximum measured value (at 100 cps) of 76,000 is relative to conventional dielectrics, enormous. Moreover, in no case has the loss factor reached a maximum with decreasing frequency, nor have any of the dielectric constant curves gone through an inflection point. Since the frequency at which these occur, corresponding to the mean relaxation time,
lies below 100 cps, the dielectric constants would have continued to increase with decreasing frequency before finally approaching asymptotic values much larger than the values measured at 100 cps. Because only a fraction of the total dispersion occurred over this frequency range of four orders of magnitude, a wide distribution of relaxation times must exist. The measured dispersion only shows the effects of polarization associated with relaxation times smaller than the mean.

The a.c. conductivity of all of the polysalt complexes dropped steadily with decreasing frequency. This indicates that the direct-current conductivity (or true conductivity) of the material is very low indeed. This leads to the very important deduction that salt-containing polyion complexes, despite their high microion content, do not behave as simple ionic conductors; to the contrary, the microions evidently possess very low macroscopic mobility in an electric potential gradient.

Four polysalt films, equilibrated in the 0.011N salt solution, but of differing thickness were examined to establish whether electrode-polarization might be responsible for the anomalous dielectric behavior. The dielectric properties of three of these films and of the polysalt in the previous series were compared to those of the fourth film. The resulting conductance, capacitance, and loss tangent ratios are shown in Table VII. In each of three of the sets of ratios, the conductance and capacitance ratios are nearly equal and constant with frequency, and the loss tangent ratios are near unity. This agreement over a fivefold change in thickness provides strong support for the argument that the dielectric measurements reflect bulk properties of the polysalt, and
not extraneous electrode polarization processes.

The increase in the magnitude of the dielectric constant with salt-content might be caused by a shift in the dielectric constant-frequency curve along the frequency axis (a change in relaxation times) or by an increase in the magnitude of the dielectric constant due to the development of new polarizable regions created by the presence of the sodium bromide. The first alternative can be tested by attempting to superpose the dielectric constant curves by shifts along the frequency axis. The curves do not superpose well. In addition, the relaxation time would have to decrease by a factor of $10^7$. (This was obtained by superposing the ends of the curves for the complexes equilibrated in the 0.25N and 0.011N salt solutions and that equilibrated with distilled water.) It is much more likely that the major effect was the creation of new polarizable elements by the sodium bromide.

Figure 16 shows the dielectric constant dependence on salt content at each of four frequencies. The three polysalt complexes used for this correlation were the microion-free polysalt and the two for which sodium bromide contents were quantitatively measured. This correlation was used to estimate the sodium bromide contents of the other three polysalts studied. Table IX shows the results for each film at each of the frequencies. These estimates are in good agreement with the values expected from extrapolation of the sodium bromide sorption data obtained spectrophotometrically on the higher-salt-content complexes. The extreme sensitivity of the dielectric constant of polysalt to the presence of single electrolyte suggests that dielectric measurements might serve
(with proper calibration) as an excellent means of monitoring salt content.

d. The effect of water content

The dielectric properties of two neutral polysalts containing different concentrations of sodium bromide were measured at 27.8°C as a function of relative humidity to determine the effect of water content. The polysalt films were dried in air at 51% relative humidity and then equilibrated and tested at 92.5% relative humidity. The testing was repeated at successively lower relative humidities. The results are shown in Figures 17-19 and 22-24. The dielectric constants and loss factors of the polysalt complexes dropped slowly with time at 75% and 92.5% relative humidity to the steady-state values shown in the figures. However, during this same time period (about a week), the loss tangent maximum remained at approximately the same frequency.

Below 75% relative humidity, where the dielectric constants did not change with time, the dielectric constants decreased with a decrease in water content. The frequency of the loss tangent also decreased. The dielectric constant curves can not be superposed by a shift along the frequency axis, nor does it appear as if they are only decreased in magnitude. So, a combination of both an increase in relaxation time and a decrease in polarization appears most likely.

Four polysalt samples containing differing amounts of sodium bromide were exposed to relative humidities of 75% and 92.5%, and the dielectrically tested at 51% relative humidity. Figures 30-33 show the results. The dielectric constants (or capacitance in Figure 33) dropped during this
sequence, with the magnitude of the change increasing with increasing sodium bromide content. The loss tangent maxima, not shown in the figures, again remained at approximately the same frequency.

The initial dielectric constants of these polysalt complexes were larger than those of similar complexes tested in the first series to determine the effect of salt content. This was probably caused by casting the initial gel from a more dilute solution of polysalt in the ternary solvent (5% instead of 15%). This more open gel structure probably retained more of the salt solution from the equilibration, which resulted in a higher salt content after the gel was partially dried.

Water absorption equilibrations, carried out over several weeks under conditions corresponding to those described above, revealed no detectable changes in water content at constant relative humidity, and no sorption hysteresis during humidity-cycling. Hence, the observed time-dependent changes in dielectric properties appear to be a consequence of structural rearrangements in the polysalt complexes, and not of changes in water content.

The observed time-dependent changes in dielectric constant probably reflect a shift of a portion of the polarization to higher relaxation times. Since the relaxation times observed were much smaller than the mean values, substantial changes in the polarization characterized by these and even larger relaxation times could occur without appreciably changing the mean relaxation time or the total dielectric increment. These latter two values either remained constant or increased proportionally, since no detectable changes in the frequency of the loss tangent
maxima were observed.

e. Dielectric behavior of an unsymmetrical polysalt complex

The dielectric properties of the polysalt complex containing 1.3 equivalents of NaSS per equivalent of VBTA-SS (0.4 equivalents of microion per polysalt equivalent) were determined at 51% relative humidity and 27.8°C. These properties, shown in Figures 35-37, resemble those of the neutral polysalt equilibrated in the 0.25N salt solution, and tested in the last series of four films. The dielectric constants at 51% relative humidity again decreased when the polysalt was held at a high relative humidity (92.5% for 2.5 days). This behavior confirms the belief that the presence of microions in the complex is primarily responsible for the observed dispersion, and shows that either a mixture oppositely charged microions (from the addition of a simple salt) or of microions associated with excess polyon can cause the dispersion.

4. Interpretation of the dielectric behavior

Orientation of dipolar side groups, a common cause of polarization in amorphous polymeric materials (e.g., polyvinyl chloride and polyvinyl alcohol), is characterized by relaxation times larger than $10^{-14}$ seconds (corresponding to a frequency near 1000 cps). In these polymers, the polarization process involves the restricted rotation of permanent dipoles under the influence of the electric field. With microion-free polysalt, whose dielectric properties are not unlike those of dipole-containing polymers (although the dielectric constants are higher), the polarization process may simply involve minor displacements
of polion pairs. The increase in the dielectric constant and loss factor with increasing water content at low frequency indicates either increased number-concentration of mobile ion-pairs, increased specific ion-pair polarizability, or increased ion mobility - all of which might be expected to occur on ion hydration. On the other hand, in view of the marked dependence of the dielectric constant on salt content, it is also possible that this dispersion results from a minute, residual quantity of microion that was not washed from the complex. (The microion could either be associated with a slight excess of one of the polions or free salt that was not removed). Unfortunately, it is not possible to distinguish between these alternative possibilities from the dielectric properties. However, the similarity of the time-dependent change in dielectric constant at 92.5% relative humidity to that of the salt-containing polysalt suggests the latter is the more likely.

The anomalous and striking dielectric properties of the microion-containing polion complexes cannot be resolved in terms of a homogeneous dielectric medium. Instead, one must treat the system as a heterogeneous dielectric, and attempt to develop a microscopic model of the structure which satisfactorily predicts its macroscopic properties.

One such model of a heterogeneous material, which predicts elevated dielectric constants and dielectric dispersion via the process of "inter-facial polarization" was developed by Maxwell (24) and Wagner (42). This type of polarization occurs when the effective conductivity differs between the phases of the system causing a buildup or discharge of charge at the interphase boundaries. Fricke (15) extended the treatment to dilute
suspensions of ellipsoidal particles in a continuous second phase.

By assuming that the microion-containing polysalt consisted of a matrix of low-conductivity polymer in which was embedded discrete elements of concentrated salt solution, and making what appeared to be reasonable approximations as to the dielectric constant and conductivity of each phase, an effort was made to apply the Maxwell-Wagner-Fricke analysis to this system.

The results of the calculations were far out-of-line with experiment: the predicted dispersion-region was far above that found experimentally (in frequency), and the dielectric constants far smaller than those observed.

A more promising approach to the problem is to be found in the recent analysis of Schwartz (36), which has evolved from a study of the dielectric dispersion of polystyrene lattices (35). The crux of this analysis is the introduction of the concept of polarization of the electrical double-layer at the interface between a suspended particle and an ambient aqueous solution. Because of the nature of the electric field which causes the double-layer formation, ion mobility is much higher in the plane of the double-layer than perpendicular to it. This restriction on ion mobility causes the double-layer to act as a separate phase. The continuous phase in this system, the dilute salt solution, was most conductive. Under these conditions, the establishment of a potential difference across the suspension produces a significant potential gradient across each suspended particle, which in turn drives ion movement in the double-layer, inducing an opposing concentration gradient. The low
frequency interaction of this latter gradient with the alternating electric gradient introduces an oscillation in the ion density at each point in the double-layer. This results in a slight excess and depletion of ions at directly opposing points on the sphere surface, which in turn creates a net electric moment across the sphere. The dielectric increment produced by this dispersion is proportional to the sphere radius and the mean ion density in the double-layer (a measure of the polarizability of the double-layer) as well as the volume fraction of the suspended particles. The relaxation time is proportional to a characteristic diffusion time of an ion around the sphere (proportional to the radius squared divided by the ion mobility).

While they are not immediately apparent, there are some striking similarities between Schwartz's polystyrene suspensions and microion-containing polysalt. The latter may be envisioned as a continuous, weakly conductive matrix of nearly microion free, hydrous polysalt, in which are distributed isolated regions or domains comprising hydrated, mobile microions coulombically associated with essentially immobile, hydrated polyon. These domains possess the structure and properties of the electrical double-layers surrounding Schwartz's polystyrene spheres, while the matrix material resembles a dilute salt solution. Much as in Schwartz's model, microion movement in these regions (which will be referred to as polarizable elements) will be driven by an imposed electric field. The microion movement is restricted at the boundaries of these elements by the surrounding homopolar and fully reacted polysalt regions where microion mobility should be low. The result will be the induction of opposing
concentration fields and a net dipole moment over each polarizable element. The relaxation of the polarization will again be microion-diffusion controlled, with the relaxation time dependent on an effective path length for microion diffusion divided by a mean microion mobility. The polarizability of each element should be roughly proportional to the end-to-end length of the polarizable element times a mean ion density in the element. The total dielectric increment of the film should be proportional to the volume fraction of the these polarizable elements.

The increase in dielectric constant with salt content can thus be explained by an increase in the total volume fraction of polarizable elements, and possibly also by an increase in the mean size of the elements. The observed broad relaxation time distribution probably results from a wide distribution in the sizes of the polarizable elements. (If the mean size of the elements increases with salt content, then the mean relaxation time will also increase.) The observed decrease in dielectric constant and loss factor with water content of the system is thus a consequence of a decrease in the microion mobility (which shifts the dispersion to lower frequencies) and/or a decrease in the volume fraction of the polarizable elements (which would decrease the total increment).

Since the mean relaxation times for all the dispersion measured were greater than $1.5 \times 10^{-3}$ seconds (corresponding to a frequency of 100 cps), the portion of the dispersion directly observed was associated with relaxation times which were smaller than the mean relaxation time. Since this dispersion should be caused by the elements which are smaller than the mean size, the time-dependent changes must be due to a reduction
in the volume fraction of these small elements. This reduction is probably caused by a consolidation of these small elements with other polarizable elements in the polyanion - that is, a clustering of microions into larger domains. An increase in the volume fraction of small elements with increased salt content is probably the primary cause of the increase in the magnitude of the time-dependent changes. In addition, high concentrations of salt tend to plasticize the polyanion complex, thereby allowing the necessary microion-clustering to occur more rapidly.

The preceding analysis, which appears satisfactorily to account for the dielectric properties of microion-containing synthetic polyelectrolyte complexes, has interesting implications with respect to the electrical behavior of biological materials. Many explanations have, over the years, been offered to account for the high dielectric constants and low frequency dispersion of tissues, proteins, nucleic acids, and the like. All of these materials are, of course, hydrous macromolecular complexes containing variable amounts and types of microions associated with the matrix polymers. That these microions may be localized within domains in the structure, separated from one another by nearly microion-free material, seems entirely plausible. If this is the case, then the electrical characteristics of these biological substances can be explained by precisely the same phenomena which occur in synthetic polyanion complexes. Such an explanation does not invoke any special biochemical or biophysical concepts, nor does it rely upon any highly organized biological structures, to account for the observations, and for this reason may offer advantages over more complicated hypotheses.
The extremely high, low-frequency dielectric constants of the polysalt complexes coupled with their seemingly low, direct-current conductivity suggests that they might be useful in electrical energy storage devices. For instance, a material with a dielectric constant of 100,000 subjected to an imposed field of 10 k volts per cm. in a capacitive device stores approximately $10^{-4}$ watt hours per cc. However, the feasibility of this application cannot be evaluated until the d.c. conductivities of the polysalt complexes have been determined. Since the polysalt dielectric constant increases with decreasing frequency over a wide frequency range, the capacitive impedance remains relatively constant over a relatively large portion of the audio-frequency range. A polysalt device might be useful as a broad band-pass filter at these frequencies. One special application might be as a single-component filter for use in microcircuits.

E. Conclusions

1. Polysalt complexes containing sodium bromide and equi-equivalent amounts of VBTA and SS are capable of absorbing appreciable quantities of water. The sorption isotherms are convex towards the relative humidity axis. Water sorption increases as the sodium bromide content of the polysalt increases.

2. Neutral polysalt complexes containing sodium bromide show dielectric dispersion in the frequency range from 100,000 to 100 cps when equilibrated at 51% relative humidity and 27.5°C. The dielectric constant increases with sodium bromide content, rising from 27 for a microion-free complex to about 100,000 for one containing approximately 0.46 equivalents of salt per polysalt equivalent, at a frequency of 100 cps. The mean
relaxation times of the broad relaxation time distributions observed correspond to frequencies below 100 cps, so the static dielectric constants are even larger than those measured. Polarization processes associated with the presence of the sodium and bromide ions in the complex are believed to be the major cause of the dispersion in the salt-containing neutral complexes. A decrease in the water content of the complexes, caused by a reduction in the equilibrium relative humidity, decreases the measured dielectric constants at a given frequency. Similar behavior has been found with a polyion complex free of single electrolyte, but containing excess polyanion with its associated microion (Na⁺). It is thus deduced that the anomalous dielectric behavior exhibited by these systems is a consequence of the presence of microions, irrespective of their mode of introduction into the complex.

3. After consideration of a number of possible models for dielectric dispersion in heterogeneous materials, a structural picture of the microion-containing polysalt was developed for which the predicted dielectric behavior is consistent with the experimental results. In this model, the polysalt is envisioned as containing small domains, high in microion content, dispersed in a reacted-polyion matrix of low microion content. The high d.c. polarization of the material could result from the movement of microions within each domain in response to an applied electric field. Furthermore, predictions of the changes in dielectric properties with sodium bromide and water contents agree with the observed behavior. The utility of this model in describing dielectric dispersion in synthetic polysalts suggests that it may also be applicable in similar biological
materials, such as tissues, proteins and the like.

F. Recommendations

This investigation should be extended to include a thorough study of the unsymmetrical polysalt complexes. The effects of both the equivalence ratio of the two polyions and the kind of microion present in the complex should be examined. An investigation of this type should go far toward confirming the basic polarization mechanisms.

In addition to the alternating current studies, an investigation of the direct current charge and discharge characteristics of the complexes would be valuable for evaluating the total energy storage capabilities of the polysalt and for determining the effect of the rate of polarization or depolarization on these capabilities.

New fabrication techniques can produce relatively thick (1 mm), unsupported films. Use of standard dielectric test holders with these films would allow a much more efficient experimental procedure.
II. INTRODUCTION

A. Objectives of this Investigation

The dielectric behavior of synthetic polysalt materials has not previously been studied in detail. In a cursory study Miekka (25) found that fully reacted polysalt of poly (vinylbenzyl-trimethyl ammonium)-poly (styrene sulfonate) had dielectric constants of $11$ to $14$ at frequencies from $10^6$ to $10^3$ cycles per second and at 50% relative humidity. However, the dielectric constants of polysalt containing more of one polyelectrolyte than the other were much larger with maximum values in the thousands.

The dielectric properties of many kinds of biological tissues, which are polysalt materials with very complicated structures, have been experimentally determined. The dielectric constants of some of these materials are larger than a million at low frequencies. Because of the uniqueness of this behavior and the complicated structure of these materials, the phenomena responsible are not well understood at present.

This investigation was undertaken with two principle objectives; to determine experimentally the dielectric behavior of a series of polysalt films and then to use this information to obtain a better understanding of the polysalt microstructure and of polyelectrolyte interactions. In addition, similarities of this behavior with that of biological tissues might lead to a better understanding of the phenomena occurring in those more complicated materials.

Polysalt films were studied rather than bulk material for two reasons. Relatively thin films will equilibrate with imposed external conditions much more rapidly than will bulk material. Use of the films was thus expected to reduce the time necessary for each test by an appreciable amount. In
addition, anticipated large, low frequency dielectric constants held the
possibility that the material might be useful as films in dielectric devices.
Properties measured for a film would be desirable in evaluating this ap-
plication.

The next section of the Introduction contains a review of the basic
dielectric phenomena and terminology followed by a brief development of
the existing models for dielectric dispersion in heterogeneous materials. A
brief description of the polyelectrolytes used in this study and a cursory
review of some of their solution behavior serves as an introduction to this
subject. This is followed by a detailed review of the investigations of
polyelectrolyte reactions and of polysalt properties which preceded the
present investigation. The Introduction concludes with a short outline of
the experimental and data analysis procedures used.

B. Dielectric Behavior of Heterogeneous Systems
   1. Homogeneous Dielectrics
      a. Dielectric constant and complex conductivity

      Consider a perfect insulator forming an infinite sheet of
constant thickness. If this sheet is suspended normal to a uniform ex-
ternal electric field \( \vec{E} \), the field within the sheet will be of a greater magni-
tude than \( \vec{E} \). The difference between this second field, called the dis-
placement field \( \vec{D} \), and the imposed field \( \vec{E} \) is produced by the storage of
energy in the insulating material. This storage of energy is called
polarization of the insulator. A polarization field is defined as
\( \vec{P} = \frac{\vec{D} - \vec{E}}{4\pi} \),
so that it equals the net electric moment per unit volume of material pro-
duced by the storage of the energy. The ratio of the magnitude of the
displacement field to that of the electric field is called the dielectric
constant, \( \frac{D}{E} = \varepsilon^* = 1 + 4\pi \frac{P}{E} \).
If the electric field $\mathbf{E}$ is produced by two parallel infinite plates held at differing potentials, the quantity of charge stored on the plates per unit area is $Q = CE$ where $E$ is the magnitude of the imposed field (the ratio of the difference in potential between the plates to the plate separation) and $C$ is called the capacitance per unit plate area. (Since all fields are normal to the plates, the vector notation will be dropped.) If a vacuum exists between the plates the charge will be $Q_o = C_o E$.

The quantity of charge which is stored on the plates is proportional to the field generated between the plates. In general, this field will be larger in magnitude than the electric field $E$ and in fact equals the displacement field $D$. Since the displacement field and the electric field are equal with a vacuum between the plates, the quantity of charge on the plates in general will be $Q = Q_o \left( \frac{D}{E} \right)$. Substituting into the previous equations to find the capacitance gives $C = \varepsilon^* C_o$. Therefore, the capacitance per unit plate area is proportional to the dielectric constant of the material between the plates.

If the potential difference between the plates is varied sinusoidally, the electric field becomes $E_o e^{i\omega t}$, where $i$ is the imaginary operator, $\omega$ is the frequency at which the potential is varied, $E_o$ is the maximum field strength, and $t$ is time. The displacement field will, in general, lag behind the electric field because the molecular or atomic processes causing polarization cannot occur instantaneously. The displacement field can be represented by $D = D_o e^{i(\omega t - \phi)}$, where $\phi$ is the difference in time between the displacement and electric field maximum values. The complex dielectric constant now becomes $\varepsilon^* = \frac{D_o}{E_o} (\cos \phi - i \sin \phi) = \varepsilon' - i \varepsilon''$. The real part, $\varepsilon'$, is called the dielectric constant or real dielectric constant and the imaginary part, $\varepsilon''$, the loss factor. The ratio of the imaginary to the real
part $\varepsilon''/\varepsilon'$, equal to $\tan \phi$, is called the loss tangent and is a measure of the amount of energy dissipated as heat to that stored and recovered.

The charge on the plates at any time will be $Q = CE = C_0 \varepsilon^* E e^{i\omega t}$. The current entering the plates at that time becomes $I = \frac{dq}{dt} = i\omega C_0 \varepsilon^* E$. The current is also related to the electric field as $E = iZ$, where $Z$ is the impedance of the material between the plates. Rearranging, $\frac{i}{\varepsilon^*} = \frac{I}{E} = i\omega C_0 \varepsilon^*$. Reducing this to a bulk property of the insulating material gives the complex conductivity; $k = \frac{C_0}{\varepsilon^*} = i\omega \varepsilon^* \varepsilon v = \omega (\varepsilon'' + i \varepsilon') \varepsilon v$ in cgs units (ohm$^{-1}$ cm$^{-1}$), where $\varepsilon v$ is the absolute dielectric constant of vacuum in cgs units. The real term, $\omega \varepsilon'' \varepsilon v$, is often written as $\sigma$, the conductivity. For materials which are not insulators, the measured conductivity will be the sum of the direct current conductivity and the term $\omega \varepsilon'' \varepsilon v$. The above development does not consider this case, and so must be modified if the direct current conductivity is appreciable.

b. Polarization in dipolar gases

When a dipolar gas is placed in an electric field $\vec{E}$ which is changing with time at a slower rate than molecular and electronic motion, a polarization field results from two processes; a perturbation of electron clouds around atoms thereby inducing dipole moments in the molecules, and a redistribution of the initially random orientation of the molecules giving rise to an effective average moment per molecule. Polarization of this gas will be treated in detail both as an example of this kind of development and because the description of the field acting on each gas molecule will be useful later.

The field acting on a single gas molecule can be represented by the sum of three individual fields, $\vec{F} = \vec{F}_1 + \vec{F}_2 + \vec{F}_3$. $\vec{F}_1$ represents the field due to charge storage at the boundaries of the gas and so is identical with
the displacement field \( \vec{D} \). However, the field acting on the molecule will be reduced by the presence of other polarized molecules surrounding the molecule under consideration. \( \vec{F}_2 \), the field which corrects for this effect, has been found to be \( \vec{F}_2 = -\frac{8\pi}{3}\vec{F} \). (6)

The third component \( \vec{F}_3 \) represents the field produced by molecules very close to the molecule under consideration. In a gas, molecules are not normally close enough together for this type of interaction to be important and so, this component is assumed negligible. The effective field becomes \( \vec{F} = \vec{D} - \frac{8\pi}{3}\vec{F} = \vec{E} + \frac{4\pi}{3}\vec{F} \).

This field induces a dipole moment \( \vec{m}_1 \) in the molecule by perturbation of the electron clouds in the molecule. This moment is assumed linear with the field, \( \vec{m}_1 = \kappa_0 \vec{F} \), where \( \kappa_0 \) is called the molecular polarizability. If \( \kappa_0 \) is a function of molecular orientation, a mean value based on the average orientation can be used.

Due to the presence of a permanent dipole moment, \( \vec{\mu}_0 \), in each molecule, the field will also perturb the random orientation of the gas molecules to produce an average moment per molecule parallel to the field. The potential energy of the interaction of the field with a molecule which has a permanent moment \( \vec{\mu}_0 \) is \( U = \vec{\mu}_0 \cdot \vec{F} = \mu F \cos \Theta \), where \( \mu \) and \( F \) are the magnitudes of the two interacting vector quantities and \( \Theta \) is the angle between them. Boltzmann's law states that the number of molecules distributed with their dipoles pointing within a solid angle \( d\Omega \) is \( B e^{-\mu F \cos \Theta / kT} d\Omega \). Since the total number of molecules oriented over all directions is \( 4\pi \int B e^{\mu F \cos \Theta / kT} d\Omega \), the average moment of the molecules in the direction of the field is

\[
\vec{m}_2 = \frac{\int_0^{2\pi} \int_0^{\pi} e^{\mu F \cos \Theta / kT} \cos \Theta \sin \Theta d\Theta d\phi}{\int_0^{2\pi} \int_0^{\pi} e^{\mu F \cos \Theta / kT} d\Theta d\phi}
\]

Integration of this expression gives

\[
\frac{m_2}{\mu} = \coth X - \frac{1}{X} = L(X), \text{ where } X = \frac{\mu F}{kT}.
\]
For small $X$, $L (X)$ can be expanded in the series

$$L (X) = \frac{X}{3} - \frac{X^3}{15} + \ldots .$$

Under most conditions $X$ is sufficiently small that $L (X) = \frac{X}{3}$, so

$$\frac{m_2}{\mu} = \frac{\mu F}{3kT}.$$  Thus, the net moment is again proportional to the field acting on the molecules. However, for large values of $X$, this is not the case. Instead, $\frac{m_2}{\mu}$ will approach unity; essentially all the molecules are aligned with the field, so an increase in field strength has little effect on the average moment.

The total moment per molecule becomes

$$\vec{m} = \vec{m}_1 + \vec{m}_2 = \left(\xi_0 + \frac{\mu^2}{3kT}\right) \vec{F}.$$  

The polarization field was defined to equal the electric moment per unit volume or $\vec{F} = \frac{n}{R} \vec{m}$, where $n$ is the number of molecules per unit volume. Using these two equations and the value of the effective field, $\vec{F} = \vec{E} + \frac{4\pi}{3} \vec{p}$, gives the net moment in terms of the electric field.

$$\vec{m} = \left\{\frac{\xi_0 + \frac{\mu^2}{3kT}}{1 - \frac{4\pi n\xi_0}{3} + \frac{\mu^2}{3kT}} \right\} \vec{E}.$$  

c. Dielectric dispersion: relaxation times and dielectric increments

Consider the same dipolar gas between two parallel infinite plates maintained at a given potential difference. This potential difference will cause an external field $E (0)$ to act on the gas. If at time zero the plates are shorted together and, therefore, the field $E (0)$ is removed, the polarization field in the gas will start to decay to zero. This decay will not happen instantaneously, however. Since the polarization field was established by electron cloud induction and a redistribution of molecular orientation, molecular and electronic motion will control the relaxation of this field. A similar phenomenon will occur if the frequency of an
alternating field is increased from zero. As the rate of change of the field is increased beyond the rate characteristic of molecular motion, the contribution of dipolar orientation to the polarization field will vanish. The real dielectric constant will decrease from a low frequency value, $\varepsilon_0$, to a new high frequency value, $\varepsilon_\infty$. This difference, $\varepsilon_0 - \varepsilon_\infty$, represents the contribution to the dielectric constant of the dipole orientation process and is called the dielectric increment of the process*.

An example which could be applied in the above situation will now be developed to derive the frequency dependence of the dielectric properties. Consider a single polarization process subject to the following considerations:

1. the relaxation of the polarization field with time depends only on the polarization field and not on the field acting on the individual molecules.

2. the decay of the polarization field is exponential with time and can be characterized by a single time constant, called the relaxation time $\tau$; the decay takes the form $-t/\tau$.

The real and imaginary parts of the complex dielectric constant are found to be 

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + \omega^2 \tau^2}$$

and

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + \omega^2 \tau^2},$$

where $\omega$ is the frequency of the sinusoidal applied field in radians per second. (See Symth (38) for the mathematical development of these equations.)

* Confusion in nomenclature can arise when using $\varepsilon$ and $\varepsilon_\infty$ as defined above. At still higher frequencies a similar effect will occur with respect to electron cloud induction and the real dielectric constant will again drop by an amount designated as $(\varepsilon_0 - \varepsilon_\infty)$. The above definition is, however, standard when considering only one of the possible polarization processes. So, it must be kept in mind that $\varepsilon$ and $\varepsilon_\infty$ are defined for a change in dielectric constant associated with a particular physical process or set of processes.
Figure 1 shows the graphical behavior of the real dielectric constant, $\varepsilon'$, and the loss factor, $\varepsilon''$. The dispersion region is the frequency range over which the dielectric constant $\varepsilon'$ essentially changes from $\varepsilon_0$ to $\varepsilon_\infty$ and covers a range from $\pi/10$ to $10/\tau$ radians per second or two cycles in logarithmic time. The maximum value of the loss factor, equal to $(\varepsilon_0 - \varepsilon_\infty)/2$, occurs at $\omega = 1/\tau$. At this same frequency the real part is midway in value between $\varepsilon_0$ and $\varepsilon_\infty$.

The loss tangent, the ratio of the loss factor to the dielectric constant, written as a function of frequency becomes $\tan \phi = \frac{(\varepsilon_0 - \varepsilon_\infty)}{\varepsilon_0 + \varepsilon_\infty \omega^2 \tau^2}$.
The curve of tan \( \phi \) versus frequency resembles the loss factor curve in form, but differs in one important respect. The frequency at which the curve goes through a maximum, \( \frac{1}{T} \left( \frac{\varepsilon_0}{\varepsilon_\infty} \right)^{\frac{1}{2}} \), is higher than the corresponding frequency of the loss factor maximum by a factor of \( \left( \frac{\varepsilon_0}{\varepsilon_\infty} \right)^{\frac{1}{2}} \). The maximum magnitude of the loss tangent is \( \frac{\varepsilon_0 - \varepsilon_\infty}{\left( \frac{\varepsilon_0}{\varepsilon_\infty} \right)^{\frac{1}{2}}} \).

The addition of a second independent dispersion process characterized by a different relaxation time changes the equations to

\[
\varepsilon' = \frac{\varepsilon_0 - \varepsilon_1}{1 + \omega^2 \tau_1^2} + \frac{\varepsilon_1 - \varepsilon_\infty}{1 + \omega^2 \tau_2^2} \quad \text{and} \quad \varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_1) \omega \tau_1}{1 + \omega^2 \tau_1^2} + \frac{(\varepsilon_1 - \varepsilon_\infty) \omega \tau_2}{1 + \omega^2 \tau_2^2},
\]

where \((\varepsilon_1 - \varepsilon_\infty)\) is the dielectric increment produced by a dispersion process characterized by a relaxation time \(\tau_2\) and \((\varepsilon_0 - \varepsilon_1)\) is associated with a larger relaxation time \(\tau_1\). The total dielectric increment under consideration is the sum of these two increments and is again denoted by \((\varepsilon_0 - \varepsilon_\infty)\).

The loss tangent now becomes

\[
\tan \phi = \frac{(\varepsilon_0 - \varepsilon_1)}{1 + \omega^2 \tau_1^2} + \frac{(\varepsilon_1 - \varepsilon_\infty)}{1 + \omega^2 \tau_2^2} + \frac{(\varepsilon_0 - \varepsilon_1)}{1 + \omega^2 \tau_1^2} + \frac{(\varepsilon_1 - \varepsilon_\infty)}{1 + \omega^2 \tau_2^2} \cdot \frac{(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + \omega^2 \tau_1^2} + \frac{(\varepsilon_1 - \varepsilon_\infty)}{1 + \omega^2 \tau_2^2})}.
\]

If the two relaxation times are sufficiently separated in value, the dielectric constant will show two normal dispersion regions as shown in Figure 2.
Figure 2

Dielectric Constant and Loss Factor for Two Widely Separated Relaxation Times

If the two dielectric increments are of the same relative magnitudes, the loss factor will also show two normal peaks.

The curves will change shape, however, if the relaxation times are close in value. Figure 3 shows one possible situation
Dielectric Constant and Loss Factor for Two Close Relaxation Times

in which $\tau_1 = 10\tau_2$ and $(\varepsilon_\infty - \varepsilon_1) = (\varepsilon_1 - \varepsilon_\infty)$. The dielectric constant and loss factor curves are similar in shape to the curves for a single relaxation time. However, the dispersion region for this case extends over a longer range of frequency. Also, the maximum value of the loss factor is less than $\frac{1}{2} (\varepsilon_\infty - \varepsilon_\infty)$. The "mean relaxation time", corresponding to the loss factor peak, now almost lies midway between $1/\tau_1$ and $1/\tau_2$. If the dielectric increments were not equal, the mean relaxation time would lie closer to the inverse of the relaxation time associated with the larger increment.

The loss tangent curve will be determined by the relative values of $(\varepsilon_0/\varepsilon_1)^{1/\tau_1}$ and $(\varepsilon_1/\varepsilon_\infty)^{1/\tau_2}$ as well as the three dielectric constants, $\varepsilon_0$, $\varepsilon_1$ and $\varepsilon_\infty$. If $(\varepsilon_0/\varepsilon_1)^{1/\tau_1}$ and $(\varepsilon_1/\varepsilon_\infty)^{1/\tau_2}$ are sufficiently different, a peak will occur at each of these two frequencies. If this is not the case, a single peak will occur at $\omega = \beta(\varepsilon_0, \varepsilon_1, \varepsilon_\infty, \tau_1, \tau_2)/\tau_m$, where $\tau_m$ is...
the mean relaxation time corresponding to the loss factor peak. The factor in the numerator approaches \( \frac{\varepsilon_0}{\varepsilon_\infty} \) as the two relaxation times approach each other. As the two relaxation times move apart in value, the factor will decrease and the curve will broaden.

A distribution of relaxation times will cause dispersion occurring over more than two cycles of logarithmic frequency. This can be demonstrated in the following manner.(38) If \( y(\gamma) \, d\gamma \) is the dielectric increment due to a group of dipoles which have relaxation times between \( \gamma - \frac{d\gamma}{2} \) and \( \gamma + \frac{d\gamma}{2} \), the total dielectric increment will be \( \varepsilon_0 - \varepsilon_\infty = \int_0^\infty y(\gamma) \, d\gamma \).

The equations for the real and imaginary parts of the complex dielectric constant become \( \varepsilon' = \varepsilon_\infty + \int_0^\infty \frac{y(\gamma) \, d\gamma}{1 + \omega^2 \gamma^2} \) and \( \varepsilon'' = \int_0^\infty \frac{y(\gamma) \omega \gamma \, d\gamma}{1 + \omega^2 \gamma^2} \). The loss factor is now the result of the addition of an infinite number of individual loss factor curves. The addition is similar in principle to that considered for the two discrete relaxation times. The loss factor curve obtained will be broader than that for a single relaxation time and in addition, will have a maximum value of less than \( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \).

The real dielectric constant is obtained in a similar manner. The shape of the distribution function will determine the size of the dispersion region. A broad distribution function will give a large dispersion region. The loss tangent maximum will again occur at a higher frequency than that of the loss factor maximum by a factor corresponding to \( \left( \frac{\varepsilon_0}{\varepsilon_\infty} \right)^{\frac{1}{2}} \) for a single relaxation time. This factor for a distribution of relaxation times should be less than \( \left( \frac{\varepsilon_0}{\varepsilon_\infty} \right)^{\frac{1}{2}} \), but of the same magnitude. The exact value will again depend on the shape of the distribution function.
2. Heterogeneous Materials
   a. Maxwell-Wagner dispersion

   The dielectric properties of both the synthetic polynitrate materials studied by Miekka (25) and biological muscle tissues (34) have been ascribed to their heterogeneous nature. Unfortunately, the microstructure of the general heterogeneous material is too complicated to treat mathematically. Both the synthetic polynitrate and biological tissue fall in this category. However, the exact development for idealized systems can give insight into the dielectric behavior of the more complicated materials. Since a few such systems have been treated theoretically, the rest of this section on dielectric behavior will be a review of the treatment of these systems.

   The first treatment of heterogeneous materials was by Maxwell (24) and Wagner (41) for the transient behavior of two uniform layers of differing electrical properties aligned normal to an external electric field. The current densities in each layer (equal to \( \sigma \mathbf{E} = \varepsilon \mathbf{D} \)) will be equal during the transient states only when the \( \sigma / \varepsilon' \) ratios are equal. In general, there will be a current discontinuity at the interphase boundary. This will in turn cause a charge buildup or discharge at the interface. This storage of charge at the interface increases the apparent dielectric constant of the two layer material. Since this internal polarization can only relax by electron movement, the process will be characterized by a finite relaxation time. In the mathematical development of this model, each phase is treated independently except for the coupling produced by the boundary condition on the current densities at the interface. The relaxation time
for the two layer combination was found to be

\[ \tau = \varepsilon_v \left\{ \frac{\varepsilon_1 \varepsilon_2' + \varepsilon_2 \varepsilon_1'}{\varepsilon_1 \varepsilon_2' + \varepsilon_2 \varepsilon_1'} \right\}, \]

where \( \varepsilon \) is the thickness of layer \( i \) and \( \varepsilon_v \) is the absolute dielectric constant of vacuum.

The dielectric and conductivity increments associated with this polarization are directly proportional to the difference between the two \( \left( \frac{\varepsilon}{\varepsilon_v} \right) \) ratios. It must be stressed that the \( \left( \frac{\varepsilon}{\varepsilon_v} \right) \) ratios are assumed constant with frequency in the frequency range of interest and that the dispersion process occurs because of interactions between phases and not because of polarization occurring within a single phase. This type of polarization is commonly referred to as "interfacial polarization" or "Maxwell-Wagner dispersion."

A larger number of adjacent layers can be treated similarly. Each layer is coupled with adjacent layers by the interface boundary condition.

b. Suspensions of ellipsoidal particles

Interfacial polarization similar to that discussed above will also cause dispersion in a suspension of ellipsoidal particles. The chief difficulty in the development of this model is describing the field acting on each particle. This description was not difficult in the development for layered materials because the phase boundaries are assumed normal to the field and so, do not alter the direction of the field. However, a dilute suspension of ellipsoidal particles resembles a dipolar gas. In each, the polarizable elements are separated by a continuum with constant properties, a vacuum in the case of the dipolar gas and the continuous phase for the suspension. The gas molecule was assumed to be a point. Then
the field was evaluated at that point in the absence of the polarizable molecule. This field was then equated to the field acting on the dipolar molecule. The effective field was found to be the sum of the displacement field and a partially opposing field generated by the presence of other polarizable elements surrounding the molecule. The effects of close neighbors were neglected. (See Section B-1-b. of the Introduction for the details of this development.)

The same general procedure is used for ellipsoidal particles suspended in a continuous medium. In this case, however, the particle cannot be directly treated as a point. Instead the mean effective field is assumed equal to the field at the center of the particle. This field is in turn calculated by assuming it equals the field occurring at that same point in space in the absence of the particle. Any changes in the field due to the presence of this particle of finite size is assumed to be negligible or of secondary importance. Since the effect of very close neighbors cannot be evaluated in general, it is ignored and the treatment restricted to systems where the volume fraction of the suspended phase is small. With these assumptions the effective field is reduced to one identical with that found in treating a dipolar gas; the effective field equals \( E + \frac{4\pi}{3} \vec{P} \).

The analytical development of this model has been treated by Wagner (42) for spheres, Fricke (12,15) and Velick and Gorin (40) for solutions of biological ellipsoidal particles (the continuous phase is considered conductive), and Bottcher (2), Ponder and van Santeen (33), and Altschuller (1) for ellipsoidal particles in powders (a non-conductive continuous phase) and voids in sintered metals (non-conductive particles). The results presented here are in the form developed by Fricke (15) for
ellipsoids of revolution. His general conductivity equation is

\[
k = k_2 + \frac{\left( k_1 - k_2 \right) \left( 1 - p \right)}{1 + 3 \sum_{a,b,c} \frac{\left( k_1 - k_2 \right)}{k_2 + 2k_1}} \]

where the complex conductivity \( k \) equals \( \sigma + i \omega \epsilon' \epsilon_v \), \( p \) is the volume fraction of particles, \( \psi_\infty \) is a shape factor, and the subscripts 1 and 2 refer to the continuous and suspended phase, respectively. Each term in the summation corresponds to an orientation of one of the three particle axes, \( a \), \( b \) or \( c \), parallel to the field. The shape factors for each orientation differ unless two axes are the same size; then the two associated shape factors are equal. Each shape factor is independent of the absolute size of the particle, but depends only on the relative magnitude of the axis oriented with the field to the other two axes. The shape factor for the largest axis becomes larger the more anisometric the particle becomes, approaching \( \left( \frac{a}{b} \right) \frac{\left( \frac{a}{c} \right)}{\ln \left( \frac{a}{c} \right) - 1} \) for a needle-like particle where \( a \), \( b \), and \( c \) are the sizes of the long, medium, and short axes, respectively. The dielectric properties, therefore, are independent of the absolute size of the suspended particles, but depend only on the shape of these particles.

All three shape factors equal 2 for spherical particles. For this case the general conductivity equation can be rearranged to give

\[
\left\{ \frac{k_1 - k_1}{k + 2k_1} \right\} = p \left\{ \frac{k_1 - k_1}{k_2 + 2k_1} \right\},
\]

where \( k = \sigma + i \omega \epsilon' \epsilon_v \).

If \( \frac{p}{3} \sum_{a,b,c} \left\{ \frac{k_1 - k_2}{k_2 + 2k_1} \right\} \) is much smaller than unity, the denominator of the general conductivity equation can be expanded in a Taylor
series and the equation written as

\[ k = k_1 + \frac{p}{3} \sum_{\alpha, \beta, \gamma} \left\{ \frac{(k_2 - k_1)(\chi_\alpha + 1)}{(\chi_\alpha + k_2/k_1)} \right\} \]

with higher terms of the expansion neglected. Three dispersion regions, each corresponding to one term of the series, are predicted. The complex dielectric constant increase corresponding to each orientation becomes

\[ \Delta \varepsilon_\alpha^* = \frac{p}{3} \frac{(1 + \chi_\alpha)(\varepsilon_2^* - \varepsilon_1^*)}{(\chi_\alpha + \varepsilon_2^*/\varepsilon_1^*)} \]

The relaxation time for each of these dispersion regions is

\[ \tau_\alpha = \frac{1}{4\pi} \left( \frac{\varepsilon_2 + \varepsilon_1}{\sigma_2 + \chi_\alpha \sigma_1} \right) \]

The expanded equation will hold only for dilute suspensions and small dielectric increments because of two approximations:

1. the initial approximation of the effective field
2. the expansion of the denominator of the general conductivity equation.

Altschuller (1) claims that the initial approximation of the effective field is more severe than the second one and use of the general equation is not justified except when the second approximation can be made. However, the general equation should remain useful for semi-quantitative analysis outside this limited range.

c. Suspensions of ellipsoidal particles with a thin surface layer

The above treatment has been extended to include a thin,
uniform surface shell on the suspended ellipsoidal particles. Cole (3),
Danzer (5) and Fricke (13,14) treated suspended spheres with a thin non-
conducting shell as a model for red blood cells. Pauly and Schwan (32)
and Miles and Robertson (26) also considered spheres, while O'Konski (30)
treated surface conducting ellipsoids. In all of this work the usual as-
sumptions regarding the interval field were again necessary.

Miles and Robertson (26) also assumed the complex conductivity of the
inner sphere was small compared with the shell, so that any term contain-
ing the product of this complex conductivity ratio times the ratio of shell
thickness to sphere radius could be neglected as a second order effect.

With this assumption the relaxation time becomes

$$\tau = \frac{(\varepsilon_v)}{4\pi} \frac{\varepsilon_m' + \frac{2d}{R} \varepsilon_3'}{\sigma_m + 2d \sigma_3'}$$

where $\varepsilon_m$ and $\sigma_m$ refer to the properties of a pseudo-sphere dielectrically
equivalent to the sphere plus shell combination. (This is equivalent to
Fricke's equation for a sphere with all shape factors equal to 2.) The
complex conductivity of the pseudo-sphere is $k_m = k_3 + \frac{2d}{R} k_s$, where $\frac{d}{R}$ is
the ratio of the shell thickness to sphere radius and 3 and S refer to the
particle and shell, respectively. The conductivity and dielectric constant
of the pseudo-sphere are then $\sigma_m = \sigma_3 + \frac{2d}{R} \sigma_s$ and $\varepsilon_m' = \varepsilon_3' + \frac{2d}{R} \varepsilon_s'$. Miles and Robertson further reduced the relaxation time expression by as-
suming $2\varepsilon_1'$ and $\varepsilon_3' \gg \frac{2d}{R} \varepsilon_s$ and $\frac{2d}{R} \sigma_s' \gg \sigma_3' + 2d \sigma_s'$. The relaxation time be-
came

$$\tau = \frac{(\varepsilon_v)}{4\pi} \frac{R (\varepsilon_3' + \varepsilon_1')}{2d \sigma_s}.$$
O'Konski has extended this treatment to ellipsoidal particles with a slight change in the model. Instead of considering a thin shell, O'Konski introduces a surface conductivity which is equivalent to $d\psi_s$ in the Miles and Robertson model. Since O'Konski was considering surface rather than volume properties, the complex conductivity of the shell was assumed to contain only a real term. This is equivalent to assuming that $\frac{2d}{R} \varepsilon_s \approx \varepsilon_p$ as did Miles and Robertson. O'Konski found the conductivity of a pseudo-particle to be $\sigma_m = \sigma_p + k\lambda = \sigma_p + \frac{2\lambda}{R}$ for spherical particles. This is identical to the results of Miles and Robertson. When considering ellipsoids, the surface contribution was more difficult to obtain exactly. In general, the net surface conductivity, $k\lambda$, along an axis $x$ is \( \frac{C(y,z)\lambda}{\pi y z} \), where $C(y,z)$ is the circumference of an ellipse normal to the $x$ axis at a particular point on that axis and $y$ and $z$ are the magnitudes of the other two axes at that point. Since the circumference will vary along the particle, the surface contribution will also vary. O'Konski then considered the limiting cases of rods and discs, where $y = z$. The surface contribution, $k_s$, for the $x$ axis direction becomes $2\lambda/y$ for both rods and discs. The surface contribution in the $y$ and $z$ directions becomes $\lambda/y$ for rods and $\lambda/x$ for discs. Since the surface contributions for rods differ only by a factor of two along the different axes, orientation is not too important. For discs, however, the contribution along the $y$ and $z$ axes is much larger than along the $x$ axis, so orientation becomes important. O'Konski used Fricke's expanded conductivity equation to calculate the dielectric and conductivity increments and the relaxation times associated with each increment. The relaxation time with the $x$ axis parallel to the field
becomes

\[ T_\infty = \left( \frac{\varepsilon_r}{4\pi} \right) \left\{ \frac{\varepsilon'_p}{\sigma_p} + \frac{x_\alpha \varepsilon_1}{k_\alpha + x_\sigma \sigma_1} \right\} , \]

where \( k_\alpha \) depends on the shape and the absolute size of the particles. So, in this case the relaxation time depends on the size of the particles as well as their shape.

d. Frequency-dependent surface complex conductivity

The dielectric constant and conductivity of each phase has been assumed constant with frequency in all of the previous derivations. What is commonly called interfacial polarization was caused by the build- ings and discharge of charge at the interphase boundaries. Experimentally, the equations developed for this type of polarization work quite well for systems like powders and sintered metals, but for a number of other systems this is not the case. Systems such as aqueous colloidal suspensions, aqueous emulsions, damp soil, and damp cellulosic materials have low frequency dielectric dispersion with high dielectric increments and large relaxation times not predicted by the interfacial polarization model.

These latter types of systems are characterized by aqueous, ionic layers at bulk phase boundaries. An ionic double-layer forms a shell around the discontinuous phase in suspensions and emulsions. Damp soils and cellulosic materials contain free hydrated ions on the surfaces of the discontinuous phase.

Miles and Robertson (26) incorporated a surface shell on suspended el- lipsoidal particles in an effort to model the double-layer. However, they assumed the dielectric constant of the layer to be negligible and the conductivity to be independent of frequency. They neglected the possibility that ion concentration gradients in the double-layer could cause volume
polarization in this region.

Murphy and Lowry (29) had earlier suggested that ions adsorbed on surfaces might be the cause of low-frequency dispersion in cellulosic materials. For illustration, they used a sphere with adsorbed negative and positive ions interspersed on the sphere surface. The ions are restricted to motion on the surface. When an external field is applied these ions will migrate to form an induced dipole the size of the sphere. Figure 4 shows a cross-sectional cut through the center of the sphere. Presumably, steady-state

Figure 4

Surface Dipole by Murphy and Lowry

\[ E \]

\( E \) - electric Field  
\( + \) - positive ions  
\( \mu \) - dipole moment  
\( - \) - negative ions

will occur when the imposed electric field is balanced by an induced concentration field on the sphere surface. It is important to note that this type of polarization is not an interfacial phenomenon, but that the polarization extends uniformly through the surface region.

Fricke and Curtis (16) obtained low frequency dielectric data for
suspensions of glass beads, natural creams, and damp soils. The existence of a complex admittance at the interphase boundaries was suggested and a simplified analysis presented.

Schwan, Schwartz, Maczuk, and Pauly (35) studied the low frequency dielectric behavior of suspensions of uniform polystyrene spheres in dilute salt (KCl) solutions. The suspensions were stabilized with a surface coating on the spheres. This also created an ionic double-layer around each sphere. The sphere diameters ranged from 0.088 to 1.17 microns, the salt solution conductivities were approximately $10^{-3}$ mho cm.$^{-1}$, and the polystyrene volume fractions ran up to 0.30. The very large total dielectric increments* which resulted from the low frequency dispersion ranged from several hundred to about sixty thousand. These total dielectric increments increased with particle diameter and sphere volume concentration and decreased with solution conductivity. The relaxation times varied linearly with the square of the sphere radius. Figures 5 and 6 show these results. The physical properties of both the polystyrene and the bulk solution were well characterized, so comparisons with existing theoretical models were possible. Neither the interfacial polarization nor the frequency independent surface conductance models predicted dispersion in the frequency range where the phenomenon occurred. The authors ascribed the behavior to a complex conductance of the double-layer around the spheres.

Schwartz (36) then proposed a simplified model of the double layer to

* The total dielectric increment is the increase in dielectric constant caused by the dispersion under consideration. See Section B-1.C. for a more detailed discussion.
Figure 5.

The Dielectric Increment of a Colloidal Suspension of Polystyrene Beads

Temperature: 25°C
Solution Conductivity: 0.7 millimho cm⁻¹
Sphere Diameter:
○ 1.17 μ
□ 0.557 μ

Dielectric increment vs. volume concentration in per cent
Figure 6.
The Effect of Bead Diameter on Mean Relaxation Frequency

\[
\frac{1}{2\pi f} \quad \text{(cps)}
\]

mean relaxation frequency

particle diameter in microns
represent the above experimental facts. The double-layer was assumed to be infinitely thin and to contain no net charge. Two fields were treated as significant in the double-layer; the electric field normally considered, and a concentration field opposing the disturbance of a random counterion distribution in the double-layer. To simplify the derivation, the ion energy gain due to the imposed field was assumed small compared to the thermal energy of the ions, and the local ion density fluctuations small compared with the mean ion density. For an electric field varying sinusoidally, the complex double-layer conductivity was found to be

\[ k_\omega = \frac{i\omega \lambda_0}{1 + i\omega \tau} = \frac{\omega^2 \lambda_0 + i\omega \lambda_0}{1 + \omega^2 \gamma^2} \quad \text{with} \quad \tau = \frac{R^2}{2\nu kT} \quad \text{and} \quad \lambda_0 = e_0 \sigma \cdot u \]

\[ \text{the counterion mobility,} \quad \sigma \text{ is the mean ion density in the double-layer,} \]
\[ kT \text{ is the absolute temperature times the Boltzmann constant, and} \quad e_0 \text{ is the charge of an electron.} \lambda_0 \text{ corresponds to the constant surface conductance used by O'Konski. The addition of the concentration field causes the conductivity to become frequency dependent at low frequencies (} \omega < \frac{1}{\tau} \text{).} \]

At these frequencies the opposing concentration field exactly balances the imposed electric field. Current (or ion movement) in the double-layer only occurs as a result of a change in the imposed electric field. The existence of concentration gradients in the double-layer implies the separation of charge suggested by Murphy and Lowry. A net excess and depletion of mobile counterion at opposing points on a sphere surface will cause a dipole moment running through the sphere. The net moment across the sphere is the vector integration of all the moments through the sphere.

The sphere and double-layer can be combined to form a pseudo-sphere by the same procedure used by Miles and Robertson. The complex conductivity
of the pseudo-sphere becomes \( k_m = k_p + \frac{2}{R} k_\lambda \)

with \( \sigma_m = \sigma_p + \frac{2 \omega^2 \gamma^2 \lambda_0}{R(1 + \omega^2 \gamma^2)} \)

\( \epsilon'_m = \epsilon'_p + \frac{2 \lambda_0 \tau}{R(1 + \omega^2 \gamma^2)} \)

using the general conductivity equation for suspensions of spheres when \( |k_m| \ll |k_1| \) (the salt solution was the most conductive in the experiment work), Schwartz obtained

\[
k = \left(\frac{\epsilon_0 - \epsilon'_p}{1 + \omega^2 \gamma^2}\right) + \frac{2 \rho_p k_m}{4(1 + \rho/2^2)}
\]

\( k_m \) is identical with \( k_2 \) in the general conductivity equation.) Substituting for \( k_m \) gives

\[
k - k_h = \frac{2 \rho_p \epsilon'_p k_\lambda}{2R(1 + \rho/2^2)^2}
\]

where \( k_h \) is the dielectric constant due to the normal two phase Maxwell-Wagner effect in the absence of the surface conductivity. After the complex conductivities were split into real and imaginary parts, Schwartz obtained

\[
\sigma = \omega \epsilon'' \epsilon_v = \frac{\epsilon_v \left( \epsilon'_o - \epsilon'_h \right)^2}{1 + \omega^2 \gamma^2}
\]

and \( \epsilon' = \frac{(\epsilon'_o - \epsilon'_h)}{1 + \omega^2 \gamma^2} \)

where the total dielectric increment, \( \epsilon'_o - \epsilon'_h = \frac{2 \rho \epsilon_p^2 \sigma_0 R}{\epsilon_v \omega^2 \gamma} \) and \( \gamma = \frac{\sigma_0}{\epsilon_v \omega^2 \gamma} \). This simplified model of the double-layer correctly predicted for the experimental system studied:

1. the approximate values of the relaxation times
2. the dependence of the relaxation time on sphere radius
3. the approximate dependence of the static dielectric
constant increment on sphere radius (included is the assumption that the mean ion density remains constant)

(4) the static dielectric constant increment dependence on particle volume fraction for low volume fractions
(again the assumption that mean ion density remains constant is included).

The theory predicted a single relaxation time, but a small relaxation time distribution was experimentally observed. Schwartz suggested that a more rigorous theoretical treatment might result in a predicted relaxation time distribution.

The low frequency dielectric dispersion predicted by the Schwartz model is caused by the induction of an ionic concentration field in the double-layer by the electric field. When developing the model for the colloidal system, Schwartz assumed the absolute magnitude of the continuous phase conductivity was large compared to that of the suspended sphere plus double-layer. In this case, the electric field driving ion motion in the double-layer is mainly determined by the continuous phase and is approximately equal to the imposed electric field. A more general analysis (see Appendix A) shows that for this case only the following need be true:

(1) the continuous phase conductivity is larger the frequency times the dielectric constants of the sphere plus double-layer and the continuous phase ($\sigma_1 \gg \varepsilon_0$ and $\varepsilon_m$)

(2) the conductivity of the continuous phase is large compared to the double-layer conductivity

$$(\sigma_1 \gg \frac{2\omega^2\tau^2\lambda_0}{R(1 + \omega)^2\eta^2})$$

(3) the continuous phase conductivity is larger than the sphere conductivity ($\sigma_1 > \sigma_3$)
These requirements insure that the electric field driving the ion movement is at a maximum value which provides for the maximum possible polarization of the double-layer. Conversely, if the double-layer or the sphere were the most highly conducting phase, the double-layer would be at an essentially uniform potential. Most of the potential drop in the film would occur in the less conductive continuous phase. As a result, the electric field and, therefore, the concentration field, in the double-layer would be small. Thus, the absence of a strong electric field driving ion movement in the double-layer results in a weak polarization of the double-layer. Some polarization does occur, but the magnitude is reduced by roughly a factor of the ratio of the continuous phase conductivity to that of the sphere plus double-layer.

Generalizing this phenomenon one step further, dielectric dispersion can be caused by polarization of any free ion region in which the ions are relatively mobile, but cannot migrate across the region boundaries. The magnitude of this effect will be dependent on the strength of the electric field driving ion movement. The maximum polarization will occur when the continuous phase conductivity is large compared to the free ion region. However, some polarization will occur if the conductivity of the continuous phase is finite.

C. Formation and Properties of Polysalts

1. Solution behavior of the individual polyelectrolytes

The polyelectrolytes used in this investigation were linear
polystyrene derivatives; the cationic polyion* was poly-
(vinylbenzyltrimethyl ammonium) and the anionic one was poly-(styrene
sulfonate). (These names will be abbreviated VBTA and SS, respectively.)
The mer units of the two polyions are:

\[
\begin{align*}
\text{SS} & : \quad (-\text{CH-CH}_2\text{)}_n \quad \text{and} \quad (-\text{CH-CH}_2\text{)}_n \\
\text{VBTA} & : \quad \text{SO}_3^- \\
\text{H}_2 & \quad \quad \text{N}/(\text{CH}_3)_3
\end{align*}
\]

The presence of the ionized groups has an important effect on the con-
formation of an individual polyion in aqueous solution. Repulsive forces
between adjacent ionic groups of these strong** polyions make the polymer
conformation in water solutions more extended than that of a random coil.
In fact, these two strong polyelectrolytes should assume a nearly rod-like
conformation in a water solution. For instance, the intrinsic viscosities
of a number of similar, strong polyelectrolytes in dilute salt solutions
possess an intrinsic viscosity proportional to the square of polymer
molecular weight (10, 19, 20). This is expected for a rigid rod
molecule (11).

* The polyion is defined as the dissolved polyelectrolyte minus the
ionized microions which are called counterions. These particular
polyions have about one ionizable group per mer unit (or have a high
charge density).

** A polyelectrolyte which ionizes almost completely is termed a
strong polyelectrolyte. Since a weak polyelectrolyte ionizes to only
a small extent, the effect of the ionic groups on polyion conformation
is much smaller.
In solution these polyions will be surrounded by a diffuse layer of counterions held in place by electrostatic attraction. If the microion concentration is increased by the addition of simple salts, the microions will approach closer to the polyion ionic groups and partially screen the groups from each other. This reduction in the repulsive forces between adjacent polyion ionic groups will cause a reduction in the polyion extension. This in turn will reduce the viscosity of the solution, since the viscosity is approximately proportional to the volume enclosed by the polymer. This decrease in viscosity and therefore, in approximate polymer volume, may be as much as two orders of magnitude (23).

2. Previous studies of polyelectrolyte interactions

The first polyelectrolyte interaction study of necessity used naturally occurring polyelectrolytes. In 1896 Kossel (21) precipitated egg albumin with protamine.* Bungenberg de Jung and his associates (22) have since made extensive studies of the gelatin (protein) - gum arabic (polycarboxylic acid) - water system. At a pH below the isoelectric point of the gelatin, these two rather weak polyelectrolytes interact to form a second concervate phase. The addition of salt was found to decrease this interaction with multivalent microions being more effective than singly valent ones. The study of this system or immunological systems (8, 19, 31, 39) suffers the disadvantage that the exact structure of the polyions is not known. More recent work has used synthetic polyelectrolytes

* The interaction in this case was sufficiently strong so that it might more exactly be called a reaction. The product of this strong interaction or reaction will be called a polysalt.
whose structures are more simple, more easily characterized, and controllable.

Morawetz and Gobran (28) studied the interaction between two weak polyelectrolytes, one a copolymer of methyl methacrylate and methacrylic acid (4.9 mole per cent) and the other a copolymer of methyl methacrylate and dimethyl aminoethyl methacrylate (5.8 mole per cent). The equivalence point interaction, where an equal number of ionic equivalents of each polymer are present (at concentrations between 0.002 and 0.01 gms. per cc.), was strong enough to lower the osmotic pressure to one third of that expected for no interaction.

Deuel, Solms and Dengler (9) precipitated pectic acid with polyethylene imine and found this occurred in only a narrow range of relative concentrations for these two weakly ionized polyelectrolytes. At the equivalence point, all of the polyion was reacted (the supernatent was clear and had the viscosity of pure water). The affinity of the polyethylene imine for pectic acid was found to be much greater than for the pectic acid monomer, galacturonic acid.

Fuoss and Sadek (18) followed the reaction of $2.5 \times 10^{-6}$ N polyvinyl-$^\text{N}$ butylpyridinium bromide (PVBuPyBr) with $10^{-3}$ N sodium polyacrylate (NaPA) by measuring solution turbidity while titrating the NaPA into the PVBuPyBr. The turbidity went to a maximum (the associated polyions were no longer stabilized by free ionic groups) shortly beyond the equivalence point indicating an incomplete reaction. They also studied the reaction of 0.018 N PVBuPyBr and approximately 0.005 N sodium polystyrene sulfonate. This reaction was also incomplete; the stoichiometry depended on the relative amounts of the two polymers and the order of addition.

Two thermodynamic driving forces for interpolymer reaction are
probably significant in these systems. There is an electrostatic free energy decrease obtained by the mutual annihilation of the polyion electrostatic fields. Secondly, the entropy of the system is increased, and the free energy decreased, by the release of bound counterions to the bulk solution. Both of these effects are due in part to the polymeric nature of the reacting species, since both the microion binding and the electrostatic fields depend in part upon the relatively fixed array of polymer ionic groups. This is reflected in the experimental result that the corresponding monomeric units or even one polyion and the oppositely charged monomer do not react as completely as the two polyions. Because of the nature of the interaction, it is to be expected that both the degree of ionization and the charge density* of the polyelectrolyte will be important in determining the nature of the interaction product. Weakly ionized polyelectrolyte of low charge density might be expected to only interact weakly, while stronger polyelectrolytes of higher change density should associate more strongly.

3. Studies of VBTA-SS reactions

Miekka (25) and Mir (27) studied the interactions of VBTA and SS, poly-(vinylbenzyltrimethyl ammonium) and poly-(styrene sulfonate), respectively. Miekka studied the dilute solution reactions of the chloride and sodium forms of these two strong polyelectrolytes. As one of the polyelectrolytes was titrated into the other, the solutions gradually became more cloudy until the equivalence point was almost reached; then gross flocculation occurred. The specific viscosity and ionic composition of the supernatant liquid was equal to that of a sodium

* Charge density is the fraction of the polymer mer units containing ionizable groups.
chloride solution corresponding in concentration to complete release of all the microions. These results indicated the reaction was at least 95 per cent complete.

When the solutions contained more than 0.1 moles of sodium bromide per liter in addition to the polyelectrolytes, flocculation occurred well before the equivalence point. This incomplete reaction occurred with both orders of addition of the two polyelectrolyte solutions. If the polymer concentrations (in the absence of salt) were greater than approximately 0.6 per cent, intimate mixing of the two solutions was not possible. Instead, a thin continuous film formed at the interface between the solutions, stopping further reaction.

The most striking feature of these results is the completeness of the dilute solution reactions in the absence of added salt. Since the ionic spacing on each of the polymers is the same and the molecules will probably be in a highly elongated configuration under these solution conditions, the most plausible explanation was that sections of the two reacting polions lined up with the oppositely charged groups paired off on a one to one basis.

The presence of sodium bromide in the second group of experiments can affect the reaction to two ways. The microion concentration will cause a reduction in the polyon elongation. This will reduce the fraction of the charged polyon groups initially exposed for reaction. In addition, the higher microion concentration may reduce the driving force for reaction by decreasing the possible entropy gain from counterion release. Under these conditions the molecules evidently do not pair off as neatly as in the previous case.

At high polyelectrolyte concentrations, a three dimensional
structure is quickly formed in the interfacial region between solutions. This structure is strong enough to stop further penetration of the polyelectrolytes.

Mir (27) extended this work using solution electrical conductivity to measure the extent of microion release. The conductivity of the reaction mixtures were compared with standard solutions corresponding in salt and excess polyelectrolyte concentration to complete release of the excess polyelectrolyte and the microions of the reacted polyions. Equal conductivity should signify complete reaction. This occurred with the sodium, calcium, chloride, and sulfate forms of the polyions at polyion concentrations of less than 0.01N and added sodium chloride concentrations of less than 0.01N. However, this was not the case when 0.005 moles per liter of an extraneous salt containing a divalent ion was added to 0.01N polyion solutions prior to reaction. After the solutions were mixed, approximately 8 per cent of the polyion opposite in charge to that of the divalent ion remained unreacted at the equivalence point irrespective of the order of addition. This was thought to be due to the greater polyion coiling caused by the divalent ion.

The hydrogen and hydroxide forms of the two polyelectrolytes (at a 0.01 normality) were also incompletely reacted at the equivalence point. Mir postulated that the absence of free microions in this latter case (since H\(^+\) and OH\(^-\) will react to form water) prevents complete reaction of the polyions; and that in reactions of the salt forms of the polyelectrolytes, the newly released counterions in the immediate vicinity of the

\* For the sodium and chloride forms, this was true for polyion concentrations up to 0.02N. The calcium and sulfate forms were not tried simultaneously, however.
polyions, by reducing the electrostatic interaction between the polyions, act as "lubricating agents" allowing polyion rearrangement to a completely reacted state. These postulates could explain how the polyions are able to form a completely reacted product, for it seems unlikely that the molecules would initially fit together so neatly.

4. Previous studies of solid polysalt properties

Miekka (25) found that the reacted VBTA-SS polysalt would completely dissolve in a ternary solvent of approximately 60-20-20 weight per cent water - acetone-sodium bromide. By carefully changing solvent composition while removing it, he formed a clear, solid material which will be called solid polysalt. Miekka was able to determine that this material was almost completely reacted; less than one per cent of the polyion groups were associated with sodium or chloride microions after a thorough water wash.

The solid polysalt absorbed 0.38 grams of water per gram of dry polysalt (8.9 equivalents of water per polysalt equivalent) when placed in distilled water. The addition of sodium bromide to the water increased the amount of solution absorbed by the polysalt; twice as much solvent was absorbed with a 10 weight per cent sodium bromide solution as with distilled water. The interval salt concentration was approximately three times the external concentration (based only on water) for a low (~2 wt.%) external salt concentration. This ratio decreased as the external salt concentration increased. The increased water absorption in the presence of sodium bromide was attributed to the breakage of some polyion-polyion bonds which allows the polysalt to assume a more expanded structure than in the salt-free case. This will both increase the water absorption and allow the internal salt concentration to be
larger than that of the external solution. The extra amount of salt associated with the unreacted polymer ionic groups becomes overshadowed at high external salt concentrations by the large total amounts absorbed.

The absorption of solvent is increased by the addition of small quantities of acetone. This is probably due to enhanced solvent affinity for nonionic portions of the polyions which decreased the homopolar associations in the polysalt allowing further expansion of the polysalt structure and to increased salt activity in the external solution.

Similar materials containing an excess of one of the polyions were also made by Miekka. None of the counterions originally associated with the polyion present in the smaller amount could be detected after a thorough water wash (to within one per cent). A solid polysalt containing two equivalents of poly-(sodium styrene sulfonate) per equivalent of poly-(vinylbenzyltrimethyl ammonium chloride) absorbed 6.0 grams of water per gram of dry polysalt when placed in distilled water. The absorption was greatly reduced by the addition of small amounts of sodium bromide to the external solution because of ion exclusion effects. At higher salt concentrations the swelling was increased by the presence of the salt due to the disappearance of the ion exclusion effect when the external ion concentration becomes comparable to that in the polyion matrix. At these conditions the breakage of polyion-polyion bonds should again allow the expansion of the polysalt matrix. Acetone addition greatly increases the swelling; this is again probably due to the increased solvent affinity for the polymer homopolar regions and increased salt activity.

These results show that the individual polyions have a much higher
mobility in the polysalt matrix than might be expected. The expansion of the matrix during swelling must require fairly large configurational changes in these polyions. This swelling and its attendant changes in the matrix structure is especially surprising in view of the almost complete inter-reaction of a salt-free matrix.

Miekka also measured the a.c. dielectric properties of these solid polysalts at frequencies from 100 to 100,000 cycles per second. The materials tested were first washed with water and then equilibrated at 50 per cent relative humidity and over dry P₂O₅. The results of the dielectric tests are shown in Table 1. The high dielectric constants of the polysalts containing an excess of one of the polyions was attributed to interfacial polarization, as generally defined in Section B-2 of the Introduction. This polarization was thought to be the result of a heterogeneous mixture of completely reacted polyion regions and other regions containing the excess unreacted polyion. Since the neutral polysalt exhibited relatively low dielectric constants, it was thought to be dielectrically homogeneous.

These high dielectric constants also occur in biological materials at low frequencies. These latter materials resemble the synthetic polysalt in two other ways; both are organo-ionic in nature and microion-polyion and polyion-polyion interactions are important in determining the structure and properties of each. Schwan in a recent review (34) presented the dielectric properties of frog thigh tissue as shown in Figure 7. Three possible explanations for the dielectric dispersion which caused the dielectric constant to increase to more than 2 x 10⁶ were listed:
TABLE 1

Dielectric constants and loss factors of polysalt equilibrated at 50
relative humidity and room temperature (22-27°C) and 0% relative humidity
(25)

<table>
<thead>
<tr>
<th>Composition:</th>
<th>2/1</th>
<th>1/1</th>
<th>1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>equiv. VBTACl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equiv. NaSS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture Content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 50 relative</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>humidity-wt.%H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%RH</td>
<td>ε'</td>
<td>ε''</td>
<td>ε'</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>10³</td>
<td>50</td>
<td>2580</td>
<td>1820</td>
</tr>
<tr>
<td>10⁴</td>
<td>50</td>
<td>1120</td>
<td>890</td>
</tr>
<tr>
<td>10⁵</td>
<td>50</td>
<td>314</td>
<td>355</td>
</tr>
<tr>
<td>10⁶</td>
<td>50</td>
<td>102</td>
<td>116</td>
</tr>
<tr>
<td>10⁷</td>
<td>50</td>
<td>41</td>
<td>33</td>
</tr>
<tr>
<td>10²</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10³</td>
<td>0</td>
<td>73</td>
<td>61</td>
</tr>
<tr>
<td>10⁴</td>
<td>0</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>10⁵</td>
<td>0</td>
<td>14</td>
<td>7.1</td>
</tr>
<tr>
<td>10⁶</td>
<td>0</td>
<td>8.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Figure 7.
The Dielectric Constant of Frog Thigh Tissue

Temperature: 25°C
○—Experimental values
Solid line assumes one relaxation time

\[10^{-6} \varepsilon'\]

frequency (cps)
(1) A gating mechanism in the cell membrane controls exchange through the membrane. An applied potential stimulates the gate which acts after a short delay in time.

(2) The inherent structure of the cell membrane is responsible.

(3) Surface conductance due to the ionic atmospheres surrounding the cells causes the dispersion.

The last was thought most likely, since experimental work had shown that the ionic double-layer in suspensions of surfactant coated polystyrene spheres in dilute salt solutions will cause low frequency dispersion with large dielectric increments.

D. This Investigation

This investigation continued the study of the solid VBTA-SS polysalt. The dielectric behavior of polysalt films, prepared from the water-acetone-sodium bromide solutions used by Miekka (25), were determined as a function of sodium bromide content and relative humidity. It was hoped that the dielectric behavior would give further insight into the microstructure of the solid VBTA-SS polysalt. In addition, the behavior of this much simpler synthetic material might lead to a better understanding of the more complicated biological materials.

The dielectric properties of neutral polysalt films containing differing amounts of sodium bromide were measured at several relative humidities. The measurements were made at four frequencies, $10^2$, $10^3$, $10^4$ and $10^5$ cycles per second. In addition, the water contents of similar films were obtained over a relative humidity range from 11 to 92.5%.
The dielectric properties of one film composed of 1.3 equivalents of NaSS per equivalent of VBTA-SS was also measured at 51% relative humidity for comparison with a neutral film containing an equivalent amount of free microion.

The tests were arranged so as to directly obtain the effects of sodium bromide content and relative humidity on dielectric properties. Initially, a series of films containing differing amounts of sodium bromide was tested at 51% per cent relative humidity. This directly gave the effect of sodium bromide content. The effect of relative humidity was determined by measuring the dielectric properties of two films as the relative humidity was progressively decreased. Four films were then studied to clarify a dielectric constant decrease with time which occurred at the high relative humidities. Finally, the dielectric properties of an unsymmetrical polysalt film were determined for comparison with those of a neutral film containing an equivalent amount of free microions. Possible models of the measured dielectric dispersion were then compared with the experimental results to see which were applicable.
III. EXPERIMENTAL PROCEDURE

A. General Procedure

The bulk of the experimental work was concerned with the measurement of the dielectric properties of the polysalt films. Neutral polysalt gel (equi-equivalent amounts of VBEA and SS) was cast on platinum slides from water-acetone-sodium bromide solutions similar to those used by Miekka (25). The films were washed with distilled water for 1 to 14 days and then equilibrated in distilled water or sodium bromide solutions of normality ranging from 0.006 to 0.25 for 1 to 8 days*. The gel films were then dried in air above a saturated calcium nitrate solution (51% relative humidity) at room temperature (21-25°C) or at 27.8°C and tested. The relative humidity during testing was varied from 92.5 to 33 per cent and the temperature was held at either 27.5 or 27.8 ± 0.2°C. After testing was complete, the films were fragmented and their thickness determined microscopically. In addition, several of the films were analyzed for sodium content.

One film containing approximately 1.3 equivalent of NaSS per equivalent of VBEA-SS was also cast on a platinum slide from a ternary solution. The slide was washed with a dilute sodium bromide solution, approximately 0.01N, before it was dried and tested. (Distilled water could not be used because the large amount of swelling disrupted the film structure.) The film thickness was again determined by fragmenting the film and examining

* A majority of the films were washed and equilibrated in the sodium bromide solutions for 3 to 6 days and 2 to 4 days, respectively. However, several films were washed and equilibrated in the 0.01N sodium bromide solution for different lengths of time. One of these films was washed and equilibrated in the sodium bromide solution each for a single day. The essentially identical properties of these films show equilibrium was reached in less than a day.
the fragments microscopically.

The water content of the neutral polysalt films was determined using films cast on platinum foil by procedures identical with those outlined above. The gel film on the foil was placed on a quartz helix balance, dried to 51 per cent relative humidity at 24.5°C, and the water content determined as a function of relative humidity at 24.5°C.

B. Specific Procedures

1. Preparation of the Neutral Polysalt Solutions

The polysalts were received from the Dow Chemical Company as dry powders containing polyelectrolyte, salt, and some unidentified solid particles. Purification of the polyelectrolytes was performed by first dissolving the individual powders in distilled water to form a solution containing approximately 4% polyelectrolyte by weight. These solutions were passed through polyethylene tubes packed with Rexyn-Analytical Grade mixed ion exchange resin (H-OH form). This step removed the simple salts and any low molecular weight polyion that could penetrate into the ion exchange beads. The basic and acidic effluents (the SS effluent was acidic, VETA basic) were then neutralized with sodium hydroxide or hydrochloric acid to a pH of 7. The resulting solutions were diluted by a factor of 1000 to 5000 to reduce the polyion concentration to less than 0.04 grams per 100 grams of solution. Aliquots of these solutions were titrated against each other and the end point determined conductimetrically. (A break occurs in the resistance curve at the end point.) The two solutions were then mixed in the ratio determined by the titration and the product allowed to settle. By further settling and centrifuging, part of the reacted neutral polysalt was isolated in precipitate form.
The precipitate was dried and added to a water-acetone-sodium bromide ternary solvent to form an equi-equivalent solution of polysalt. Four such solutions were used to cast the neutral polysalt films. (See Appendix D for the detailed compositions of these solutions.)

2. Preparation of the unsymmetrical polysalt solution

The second samples of poly-(sodium styrene sulfonate) and poly-(vinylbenzyltrimethyl ammonium chloride) used for the unsymmetrical polysalt film were received as a dry powder and as a 30% water solution, respectively. A given weight of the dried powder was dissolved in water. Aliquots of this solution and of the VBTACL solution were diluted and tetrated against each other. The endpoint was again determined by monitoring the solution resistance.

The dry NaSS powder and the VBTACL solution were mixed in a ratio of 2.3 equivalents of NaSS per equivalent of VBTACL. Water, acetone, and sodium bromide were then added to dissolve the mixture. The solution composition is shown in Appendix D.

3. Film Preparation and Treatment

a. Neutral polysalt

The films were cast on platinum slides by the following procedure. A platinum slide, approximately 3 cm. by 1.5 cm. and 0.0125 inches thick, was first flamed to remove contaminants and allowed to cool for two minutes. It was then dipped into the ternary solvent solution of polysalt and the liquid allowed to drain. This left a thin liquid layer on the surface of the slide. When the slide was exposed to the air, water and acetone evaporated from this layer causing the polysalt to gel. Excess gel was stripped from the rest of the slide leaving a band approximately 1.5 cm. by 1.5 cm. with a fairly uniform thickness. The slide was then washed with distilled water for at least
a day to remove the sodium bromide and any acetone that had not evaporated. The slides were transformed to one of the treatment solutions and equilibrated for at least one day. Table II lists the normality of these sodium bromide solutions. The normalities were obtained by titrating an aliquot of the solution with silver nitrate using Mohr's Method. (43) Potassium chromate is added as an indicator; sodium bicarbonate is used to maintain the pH near 7. A precipitate of red silver chromate forms at the endpoint, changing the solution color from yellow. Table II also lists the film designations of the films according to the treatment solution in which the film was equilibrated. A letter added following the hyphen distinguishes between films equilibrated in the same treatment solution. Thus, Film 11-A and Film 11-B are the first two films equilibrated in the 0.011N sodium bromide solution.

Films for use in the water absorption tests were similarly prepared except 0.0005 inch thick platinum foil was substituted for the thicker
platinum slides.

b. Unsymmetrical polysalt film

The unsymmetrical polysalt film was cast from the ternary solvent on a platinum slide similar to that used for the neutral polysalt films. The gelled film was first soaked in distilled water and then in a dilute salt solution, 0.01N sodium bromide. Distilled water was tried for the second washing, but the film expanded to such an extent that the film structure was destroyed. The addition of the small amount of sodium bromide to the external solution considerably reduced this swelling, so that the film structure remained intact.

4. Dielectric Tests

The films were removed from the treatment solutions and the film surfaces blotted free of liquid prior to placing the slides in the test apparatus. At this point the polysalt was still an opaque gel. All but two films in the first series were then dried to 51% RH in a desiccat placed in the room (21-25°C) before they were transferred to the test apparatus.

These two films and all of the later ones were placed directly in the test apparatus and equilibrated at 51% RH and 27.8°C. This relatively rapid drying caused the gel structure to collapse, forming a clear continuous film which adhered to the platinum slide.

The electrode apparatus used in measuring the film dielectric properties is shown in Figure 8. One end of the platinum slide was clamped against a lucite block with a copper plate. The film was held directly above and quite close to the short end of a bent glass tube (10 mm o.d. pyrex) holding a column of mercury. One of the leads to a measuring circuit was soldered to the copper plate; the other lead was dipped into the mercury.
Figure 8.
The Dielectric Test Apparatus

A - mercury column
B - glass tube
C - platinum slide
D - polysalt film
E - copper plate
F - lucite block
G - glass rod holding F
H - external electrical leads
I - desiccator
This apparatus was assembled within a desiccator with only the long end of
the glass tube extending through the desiccator cover. The desiccator was
in turn placed in a box in which the temperature was maintained to within
\( \pm 0.2^\circ\text{C} \).

The relative humidity in the desiccator was regulated by placing a
polyethylene dish containing a humidity control solution directly below
the platinum slide. The relative humidity was changed by lifting the
desiccator cover a short distance and quickly substituting a different
polyethylene dish containing the desired humidity control solution.

Before each dielectric test, mercury was added to the open end of the
glass tube. This raised the mercury level in the tube forcing mercury
against the film. The platinum-polysalt-mercury sandwich insures good
electrical contact. Since the mercury contact area varies slightly with
the head of mercury in the open tube, an effort was made to keep this head
relatively constant a series of tests. The contact was broken after the
completion of each test by removing mercury from the glass tube.

The film resistance and capacitance were measured using a General
Radio Co. Type 1605A Impedance Comparator. The comparator is basically a
bridge circuit with an impedance standard and the unknown forming two arms
of the bridge. The halves of a center tapped transformer serve as the other
two arms. An internal R. C. oscillator drives the transformer primary
winding at frequencies of 0.1, 1, 10 and 100 kilocycles per second. This
applies an 0.3 volt sinusoidal signal to the standard and the unknown. A
bridge unbalance voltage resulting from an impedance difference between
the standard and unknown arms is separated into in-phase and out-of-phase
components and displayed on meters as a phase angle and an impedance magni-
tude difference, respectively. It is possible to measure differences as
small as 0.01% in impedance, although in general, the circuit was only balanced to within \( \pm 0.2\% \).

The impedance standard was composed of a variable resistor and a variable capacitor in parallel. These were adjusted so that their joint phase angle and impedance magnitude matched that of the film. This occurs only when their net resistance and capacitance are equal to those of the film. The variable standard resistor was two General Radio Co. standard resistors in series; one a Type 1432 having six decades in series with steps of 0.1, 1.0, 10, 100, 1000 and 10,000 ohms and the other a single decade Type 510G with steps of 100,000 ohms. The accuracy of these resistors is 0.05%. Three General Radio Co. capacitors were used in parallel as the capacitor standard; Types 1422, 1419 and 1424-A. With these the capacitance could be varied from \( 0.15 \times 10^{-10} \) to \( 10^{-5} \) farads. The terminals of the resistors and capacitors had a residual capacitance experimentally determined as \( 0.053 \times 10^{-9} \) farads. This was added to the standard capacitor setting to obtain the net standard capacitance.

5. Water Absorption Measurements

The water absorption measurements were made using polysalt films cast on platinum foil. After the foil was removed from the treatment solution, the film surface was blotted free of liquid. The foil was then bent double and placed on the pan of a "Misco" quartz helix balance with an extension of approximately 1.02 millimeters per milligram (Serial Number 893 from Microchemical Specialties, Berkeley, California). The balance, shown in Figure 9, was installed in a constant temperature room held at 24.5°C \( \pm 0.4\° \)C. The relative humidity inside the balance case was lowered to 51% by placing a polyethylene boat containing the 51% RH humidity control
Figure 9.
Photograph of the Quartz Helix Balance
solution in the side arm of the balance case and the film allowed to
equilibrate. The relative humidity was then raised to 92.5% by removing
the end of the side arm and changing the solution in the polyethylene boat.
The position of the quartz helix was noted at equilibrium using the mi-
crometer eyepiece in a "Misco" Optical Reader. #184. The relative humidity
was then lowered in steps to 11.1% with the helix extension measured after
each step change*. The helix extensions at 51, 33 and 11.1% relative humidity
formed a straight line which was used to find the weight of foil plus dry
film by extrapolating to dryness. The foil was subsequently flamed to burn
off the film. The foil was then reweighed and the loss of weight used to
calculate the weight of dry film.

6. Film Thickness Determinations

The average thickness of the film used to calculate the dielectric
constants and loss factors was determined by the following technique. After
the testing was completed, the film was fragmented by drying over P₂O₅. A
number of fragments were taken from the contact area. Each fragment was
measured in a number of places by examining the fragment cross-section
microscopically through a filar micrometer eyepiece. At a magnification of
600X, the measurement could be made to within ±0.7 microns with the chief
limitation being the interference of the light at the edges of the film.
From these determinations an average fragment thickness was obtained. These

* Since the transfer of water between the control solution and the film
was diffusion controlled, the length of the period before equilibrium was
achieved was almost directly proportional to the amount of water trans-
ferred. Experimentally, this period ranged from 6 hours to 2 days.
fragment thicknesses were used to calculate an average film thickness.

7. Sodium Bromide Analyses

The salt contents of three films cast on platinum slides and dielectrically tested were experimentally determined. Film fragments obtained during the film thickness determination procedure were weighed at 11.1% RH and then ignited by standard techniques. The ash was dissolved in distilled water and the sodium content of the solution analyzed by flame spectrophotometry. A Beckman Model B Flame Spectrophotometer was used to compare the sodium emission of the unknown solutions with that of a series of sodium chloride standard solutions.

8. Relative Humidity Control

Both the desicicators held in the constant temperature box and the balance were maintained at a constant relative humidity using the solutions shown in Table III.

TABLE III

Humidity Control Solutions

<table>
<thead>
<tr>
<th>Solution</th>
<th>per cent relative humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1% caustic (by weight)</td>
<td>91.5% at 27-28°C</td>
</tr>
<tr>
<td>Saturated KNO₃</td>
<td>92.5% at 25°C</td>
</tr>
<tr>
<td>saturated NaCl</td>
<td>75.3% at 25°C</td>
</tr>
<tr>
<td>saturated NaNO₂</td>
<td>75.1% at 27.5°C</td>
</tr>
<tr>
<td>28.3% caustic</td>
<td>64.4% at 25°C</td>
</tr>
<tr>
<td>saturated Ca(NO₃)₂·4H₂O</td>
<td>63.5% at 28°C</td>
</tr>
<tr>
<td>saturated MgCl</td>
<td>51.3% at 27-28°C</td>
</tr>
<tr>
<td>saturated LiCl H₂O</td>
<td>51% at 24.5°C</td>
</tr>
<tr>
<td>saturated MgCl</td>
<td>33% at 25°C</td>
</tr>
<tr>
<td>saturated LiCl H₂O</td>
<td>11.1% at 25°C</td>
</tr>
</tbody>
</table>
The saturated salt solutions were used in all of the water content determinations and all but the initial dielectric measurements. When the caustic solutions were used, a large quantity was placed in the polyethylene dish so the amount of water vaporized or condensed would not appreciably change the solution concentration.
IV RESULTS
<table>
<thead>
<tr>
<th>Film Tested</th>
<th>Normality of NaBr Equilibration Solution</th>
<th>NaBr Content of Film in Equivalents Per Polysalt Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film 250-A</td>
<td>0.250 N</td>
<td>.49</td>
</tr>
<tr>
<td>Film 250-B</td>
<td>0.250 N</td>
<td>.42</td>
</tr>
<tr>
<td>Film 75-A</td>
<td>0.075 N</td>
<td>.23</td>
</tr>
</tbody>
</table>

**TABLE IV**

*The Sodium Bromide Content of the Polysalt Films*
Figure 10.
Water Absorption of Salt-free Polysalt

Temperature: 24.5°C
○ — polysalt film
□ — bulk polysalt by Miekka

Water content in gms per gm dry film

Per cent relative humidity
TABLE V

The Water Content of Salt-free Polysalt: Equivalence Basis

Temperature: 24.5°C

<table>
<thead>
<tr>
<th>Per Cent Relative Humidity</th>
<th>Equivalents Water Per Equivalent of Polysalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.1</td>
<td>0.67</td>
</tr>
<tr>
<td>33</td>
<td>1.9</td>
</tr>
<tr>
<td>51</td>
<td>3.0</td>
</tr>
<tr>
<td>64.4</td>
<td>3.9</td>
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<tr>
<td>75.3</td>
<td>4.9</td>
</tr>
<tr>
<td>92.5</td>
<td>6.7</td>
</tr>
<tr>
<td>100*</td>
<td>8.9</td>
</tr>
</tbody>
</table>

*From Miekka (25) at room temperature (22-25°C)
Figure II.
Water Absorption of Polysalt Containing Sodium Bromide

Temperature: 24.5°C
- O - equilibrated in 0.25N NaBr soln
- △ - equilibrated in 0.075N NaBr soln
- □ - equilibrated in 0.020N NaBr soln
dotted line – salt free polysalt

water content

per cent relative humidity
TABLE VI

Excess Water Content Associated with the Sodium Bromide

<table>
<thead>
<tr>
<th>Per Cent Relative Humidity</th>
<th>Film Equilibrated in 0.075 N NaBr</th>
<th>Film Equilibrated in 0.25 N NaBr</th>
<th>Equilibrium Solution of NaBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.1</td>
<td>0.5</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>33</td>
<td>1.8</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>51</td>
<td>2.2</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>64.4</td>
<td>2.6</td>
<td>5.1</td>
<td>7.0</td>
</tr>
<tr>
<td>75.3</td>
<td>3.7</td>
<td>7.3</td>
<td>9.7</td>
</tr>
<tr>
<td>92.5</td>
<td>11.7</td>
<td>31</td>
<td>27.2</td>
</tr>
<tr>
<td>Frequency in Cycles Per Second</td>
<td>Capacitance Ratio ( C/C_{11-A} )</td>
<td>Conductance Ratio ( G/G_{11-A} )</td>
<td>Loss Tangent Ratio ( \tan \delta/\tan \delta_{11-A} )</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>( 10^2 )</td>
<td>1.92</td>
<td>1.88</td>
<td>0.97</td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>1.72</td>
<td>1.89</td>
<td>1.08</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>1.79</td>
<td>2.10</td>
<td>1.18</td>
</tr>
<tr>
<td>( 10^5 )</td>
<td>1.89</td>
<td>2.04</td>
<td>1.08</td>
</tr>
<tr>
<td>Film 11-C</td>
<td>0.95</td>
<td>1.02</td>
<td>1.07</td>
</tr>
<tr>
<td>( 10^2 )</td>
<td>1.16</td>
<td>1.03</td>
<td>0.89</td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>1.19</td>
<td>1.06</td>
<td>0.89</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>1.25</td>
<td>1.09</td>
<td>0.87</td>
</tr>
<tr>
<td>Film 11-D</td>
<td>4.13</td>
<td>2.86</td>
<td>0.69</td>
</tr>
<tr>
<td>( 10^2 )</td>
<td>3.98</td>
<td>3.06</td>
<td>0.79</td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>4.01</td>
<td>3.30</td>
<td>0.83</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>4.65</td>
<td>3.50</td>
<td>0.75</td>
</tr>
<tr>
<td>Film 11-E</td>
<td>5.0</td>
<td>4.42</td>
<td>0.88</td>
</tr>
<tr>
<td>( 10^2 )</td>
<td>4.33</td>
<td>4.50</td>
<td>1.04</td>
</tr>
<tr>
<td>( 10^3 )</td>
<td>4.16</td>
<td>4.50</td>
<td>1.09</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>4.55</td>
<td>4.46</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*Thicknesses obtained by measuring Film 11-E and rationing the capacitance to find relative thickness.
Figure 12.
The Dielectric Properties of a Salt-free Polysalt Film

FILM O-A
Relative Humidity: 51 %
Temperature: 27.5 °C
Water Content: 0.14 gms. per gm. dry film
○ - Dielectric Constant
□ - Loss Factor
△ - Loss Tangent
TABLE VIII

The Composition of the Films Used for Dielectric Tests

<table>
<thead>
<tr>
<th>Film Number</th>
<th>Salt Content in Equiv. per Polysalt Equiv.</th>
<th>Water Content in gms per gm of Salt Plus Polysalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-A</td>
<td>.46</td>
<td>.185</td>
</tr>
<tr>
<td>75-A</td>
<td>.23</td>
<td>.150</td>
</tr>
<tr>
<td>20-A</td>
<td>.12*</td>
<td>.150</td>
</tr>
<tr>
<td>11-E</td>
<td>.08*</td>
<td>-</td>
</tr>
<tr>
<td>6-A</td>
<td>.025*</td>
<td>-</td>
</tr>
<tr>
<td>0-A</td>
<td>0.0</td>
<td>.135</td>
</tr>
</tbody>
</table>

* obtained from Table IX
Figure 13.
The Dielectric Constants of Polysalt Films Containing Sodium Bromide

Temperature: 27.5 °C
Relative Humidity: 51%

Symbols:
- • - film 250-A
- x - film 75-A
- O - film 20-A
- △ - film 11-E
- □ - film 6-A

dotted line - salt free polysalt

Dielectric constant $\varepsilon'$ vs. log$_{10}$ frequency (cps)
Figure 14.
The Loss Factors of Polysalt Films Containing Sodium Bromide

Temperature: 27.5°C
Relative Humidity: 51%

- Film 250-A
- Film 75-A
- Film 20-A
- Film 11-E
- Film 6-A

Dotted line - salt free polysalt
Figure 15.

The Loss Tangents of Polysalt Films Containing Sodium Bromide

Temperature: 27.5°C
Relative Humidity: 51%

- film 250-A
- film 75-A
- film 20-A
- film 11-E
- film 6-A

dotted line — salt free polysalt
Figure 16.
The Effect of Sodium Bromide Content on the Dielectric Constant

Temperature: 27.5°C
Relative Humidity: 51%
Frequency:
- □ - 100 cps
- ○ - 1000 cps
- △ - 10,000 cps
- × - 100,000 cps

sodium bromide content - equiv per equiv polysalt

dielectric constant - ε'
TABLE IX

Sodium Bromide Contents Based on the Dielectric Constants

Sodium Bromide Content
in Equiv. per Polysalt Equiv.

<table>
<thead>
<tr>
<th>Frequency in cps</th>
<th>Film 20-A</th>
<th>Film 11-E</th>
<th>Film 6-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2$</td>
<td>.10</td>
<td>.07</td>
<td>.025</td>
</tr>
<tr>
<td>$10^3$</td>
<td>.11</td>
<td>.07</td>
<td>.025</td>
</tr>
<tr>
<td>$10^4$</td>
<td>.13</td>
<td>.09</td>
<td>.03</td>
</tr>
<tr>
<td>$10^5$</td>
<td>.14</td>
<td>.08</td>
<td>.02</td>
</tr>
<tr>
<td>average value</td>
<td>.12</td>
<td>.08</td>
<td>.025</td>
</tr>
</tbody>
</table>
Figure 17.
Steady-state Dielectric Constants: Film 250-C

Dielectric Constant - $\varepsilon'$

FILM 250-C
Sodium Bromide Content: 0.46 equiv per equiv of polysalt
Temperature: 27.8 °C

- 92.5 % RH
- 75 % RH
- 64.4 % RH
- 51 % RH
- 33 % RH

0.33 gms $H_2O / gm$ film
0.25
0.18
0.11

$\log_{10}$ frequency (cps)
Figure 18.
Steady-state Loss
Factors: Film 250-C

FILM 250-C
Sodium Bromide Content:
0.46 equiv per equiv of polysalt
Temperature: 27.8°C

- 92.5% RH
- 75% RH
- 64.4% RH
- 51% RH
- 33% RH

0.84 gms H₂O/gm film
Figure 19.
Steady-state Loss
Tangents: Film 250-C

FILM 250-C
Sodium Bromide Content:
0.46 equiv per equiv polysalt
Temperature: 27.8 °C
⊗ - 92.5 % RH
○ - 75 % RH
△ - 64.4 % RH
□ - 51 % RH
☒ - 33 % RH

\[ \frac{\varepsilon''}{\varepsilon'} \]

loss tangent

frequency (cps)
Figure 20.
Transient Dielectric Constants: Film 250-C

FILM 250-C
Sodium Bromide Content: 0.46 equiv per equiv polysalt
Temperature: 27.8 °C
Relative Humidity: 75%
- \(\triangle\) - initial value; after 2 days
- \(\bigcirc\) - after 3 days
- \(\square\) - after 4 days
- \(\bullet\) - final value; after 9 days

\[ \text{log}_{10} \text{ frequency (cps)} \]
Figure 21.
Transient Loss Tangents: Film 250-C

FILM 250-C
Sodium Bromide Content: 0.46 equiv per equiv polysalt
Temperature: 27.8 °C
Relative Humidity: 75%

- Initial value; after 2 days
- after 3 days
- after 4 days
- final value; after 9 days
Figure 22.
Steady-state Dielectric
Constants: Film 75-B

FILM 75-B
Sodium Bromide
Content: 0.23
equiv per equiv
polysalt
Temperature: 27.8°C
- 92.5% RH
- 75% RH
- 64.4% RH

log₁₀ frequency (cps)
Figure 23.
Steady-state Loss Factors: Film 75-B

FILM 75-B
Sodium Bromide Content:
0.23 equiv per equiv polysalt
Temperature: 27.8°C
⊗ — 92.5% Relative Humidity
○ — 75% RH
△ — 64.4% RH
□ — 51% RH
⊗ — 33% RH

$10^3$ $10^4$ $10^5$ $10^6$ $10^7$ $10^8$ $10^9$

$\epsilon''$

$\log_{10}$ frequency (cps)

0.40
0.19
0.14
0.10

0.24 gms H$_2$O/gm film
Figure 24.
Steady-state Loss Tangents: Film 75-B

FILM 75-B
Sodium Bromide Content:
0.23 equiv per equiv polysalt
Temperature: 27.8 °C
⊗ - 92.5 % RH
○ - 75 % RH
△ - 64.4 % RH
□ - 51 % RH
⊗ - 33 % RH

10^2  10^3  10^4  10^5
frequency (cps)

$\varepsilon'' / \varepsilon'$
Figure 25.
Transient Dielectric Constants: Film 75-B

FILM 75-B
Sodium Bromide Content:
0.23 equiv per equiv polysalt
Temperature: 27.8 °C

○ - initial 92.5%, after 1 day
△ - after 5 days at 92.5% RH
□ - initial 75% RH, after 2 days
● - after 5 days at 75% RH

$\varepsilon'$

log$_{10}$ frequency (cps)
Figure 26.
Transient Loss Tangents: Film 75-B

FILM 75-B
Sodium Bromide Content: 0.23 equiv per equiv polysalt
Temperature: 27.8°C
○ - initial 92.5% RH, after 1 day
△ - after 5 days at 92.5%
□ - initial 75% RH, after 2 days
● - after 5 days at 75% RH

loss tangent $\frac{\varepsilon''}{\varepsilon'}$

frequency (cps)
Figure 27.
The Effect of Water Content on the Dielectric Constant: Film 250°C

Sodium Bromide Content: 0.46 equiv per equiv polyanion
Temperature: 27.8 °C
Frequency:
- O - 100 cps
- X - 1000 cps
- △ - 10,000 cps
- □ - 100,000 cps

grams water per gram dry film
Figure 28.
The Effect of Water Content on the Dielectric Constant: Film 75-B

Dielectric constant $\varepsilon'$

grams water per gram of dry film

Temperature: 27.8°C

Sodium Bromide
Content of Film: 0.23 equiv per equiv polysalt

Frequency:
- $100$ cps
- $1000$ cps
- $10000$ cps
- $100000$ cps
Figure 29.
The Effect of Exposure to High Relative Humidity on Water Content

\[ \sim 0.15 \text{ gms water per gm polysalt} \]

Temperature: 24.5°C
Film initially equilibrated in 0.25 N NaBr

at 51% RH
at 75% RH
at 51% RH

balance reading

days since start of test
Figure 30.
Transient Dielectric Constant Behavior: Film 0-B

Dielectric constant vs. days held at 75 percent relative humidity

Temperature: 27.8°C
Relative Humidity of Test: 51%

Frequency:
- 100 cps
- 1000 cps
- 10,000 cps
- 100,000 cps

Film 0-B
Figure 31.
Transient Dielectric Constant Behavior: Film 20-B

FILM 20-B
Temperature: 27.8°C
Relative Humidity of Test: 51%
Frequency: ○ - 100 cps
        ⊗ - 1,000 cps
        △ - 10,000 cps
        □ - 100,000 cps

days held at 75 percent relative humidity
Figure 32.
Transient Dielectric Constant Behavior: Film 75-C

FILM 75-C
Temperature: 27.8°C
Relative Humidity of Test: 51%
Frequency:
- ○ - 100 cps
- ★ - 1000 cps
- △ - 10,000 cps
- □ - 100,000 cps

days held at 75 percent relative humidity
Figure 33.
Transient Dielectric Constant Behavior: Film 250-D

FILM 250-D
Temperature: 27.8 °C
Relative Humidity of Test: 51%
Frequency:
- ○ - 100 cps
- ⊙ - 1000 cps
- △ - 10,000 cps
- □ - 100,000 cps

at 75% RH
at 92.5% RH

days exposed to 92.5% RH
FILM 250-D
Temperature: 27.8°C
Relative Humidity: 51 %
○ — initial capacitance
□ — initial loss
△ — capacitance after 2.5 days at 92.5 % RH
Figure 35
The Dielectric Constant of an Unsymmetrical Polysalt Film

Temperature: 27.8°C
Relative Humidity: 51%

- initial values
- after standing at 92.5% RH for 2.5 days

Dielectric constant $\varepsilon'$ vs. $\log_{10}$ frequency (cps)
Figure 36. The Loss Factor of an Unsymmetrical Polysalt Film

Temperature: 27.8°C
Relative Humidity: 51%

- Initial values
- after standing at 92.5% RH for 2.5 days

Loss factor on the logarithmic scale against frequency (cps).
Figure 37.
The Loss Tangent of an Unsymmetrical Polysalt Film

Temperature: 27.8 °C
Relative Humidity: 51%

- □ - initial values
- ◇ - after standing at 92.5% RH for 2.5 days

![Graph showing the loss tangent ratio (ε''/ε') against frequency (cps).]
V. DISCUSSION OF RESULTS

A. The Polyelectrolyte Materials

The solid polyanion studied in this investigation was composed of two polyions; the anionic polyion was poly-(styrene sulfonate) and the cationic, poly-(vinylbenzyltrimethyl ammonium). (These will be abbreviated SS and VETA, respectively.) The bulk of the experimental work used neutral polyanion containing equi-equivalent amounts of the two polyions. The particular polyelectrolytes used for the neutral polyanion were identical with those studied by Mir (27). The degree of polymerization of the VETA and SS polyions were approximately 1200 and 3200, respectively. Mir (27) determined the equivalent weight of the sodium and chloride forms of these two polyions by evaporating a solution of known normality to dryness. The results are shown in Table X. The measured equivalent weights are about 10% higher than

<table>
<thead>
<tr>
<th>TABLE X</th>
</tr>
</thead>
</table>

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VETA Cl</td>
<td>equivalent weight</td>
<td>NaSS equivalent weight</td>
</tr>
<tr>
<td></td>
<td>experimental value</td>
<td>theoretical value*</td>
</tr>
<tr>
<td>231 ± 5</td>
<td>211.7</td>
<td>227 ± 5</td>
</tr>
</tbody>
</table>

* based on one charge unit per mer unit of polyion

the values based on one charge unit per mer unit of polyion, showing that about one mer unit in ten does not contain an ionic group. However it
is also possible that each of the mer units has a strongly attached water of hydration which cannot be removed by normal drying techniques. The addition of 18 to the theoretical value brings it within the accuracy of the experimental determinations. In the absence of experimental evidence to support either of these explanations, this report will use the experimental equivalent weights. This makes the neutral polysalt equivalent weight equal to 399 grams (the sum of the individual polyelectrolyte equivalent weights minus that of sodium chloride).

A second molecular weight sample of each polyelectrolyte was used in a film containing approximately 1.3 equivalents of NaSS per equivalent of VBTA-SS. (This film is later referred to as the unsymmetric polysalt film.) These samples of NaSS and VBTACl had average degrees of polymerization of about 2000 and 200, respectively, and equivalent weights comparable to the other samples.

B. Polysalt Film Microstructure

The clear, polysalt films are produced by partially drying an opaque gel containing water and sodium bromide in addition to the polysalt. The weight ratio of water to polysalt in this gel depended on the sodium bromide content of the equilibration solution, varying from about 3 with the 0.25N sodium bromide solution to about 7 with distilled water. As the water is removed during drying, the gel structure collapses and, in the films containing sodium bromide, the aqueous phase becomes more concentrated in sodium bromide. This will drive an increasing fraction of the sodium bromide from the aqueous phase into the polysalt phase where it can serve two functions. By reducing the electrostatic interaction energy between reacted polyions, the sodium bromide can serve as a
"lubricant" for changes in polyanion configuration which help relieve stresses introduced by the collapse of the gel structure. In addition, the dissociated microions can act as ion sinks allowing the breakage of the highly stressed polyanion-polyion bonds. As a result, the films which contain salt should have a more consolidated structure than those equilibrated in distilled water.

When the film has been dried to 51% relative humidity, it will contain two distinctly different types of regions; the homopolar portions of the polyanions, which may be associated to some extent, and a more highly ionic hydrophilic region. The latter contains reacted polyanion, microions associated with unreacted polyanion groups, water, and free sodium bromide. The distribution and state of these elements should have an important effect on the polyanion properties.

In salt-free polyanion the hydrophilic regions should be composed of reacted polyanion-polyion groups and water in addition to an extremely small quantity of residual microions. However, the water content of this region may not be uniform since the absence of sodium bromide or other microion species during the drying process may prevent complete consolidation of the polyanion. Consequently, the resulting microstructure may contain microvoids which, if the surrounding material is hydrophilic, can fill with water.

The presence of the sodium bromide in the hydrophilic region of the films containing salt increases the complexity of the film microstructure. A considerable fraction of these microions should be directly associated with unreacted polyanion groups. These microion-polyion associations should
result during the initial drying from a combination of high local microion concentrations and of stresses induced by the collapse of the gel structure. The remaining sodium bromide will probably be localized in small regions within the hydrophilic portion of the film. These small regions will be bounded by reacted polysalt and the homopolar portions of the polynomials.

Both the homopolar and hydrophilic portions of the polysalt undoubtedly run continuously through the film. In the salt-free films the hydrophilic portion, composed almost entirely of reacted polion groups and water, probably resembles to some extent a number of twisting and intersecting ribbons. The presence of sodium bromide should introduce small, discontinuous regions in the hydrophilic portions of the film. These small regions will contain the associated microions and polion groups or these species plus the free sodium bromide.

C. Sodium Bromide Content

The sodium bromide contents of three films, Film 250-A, Film 250-B and Film 75-A, are shown in Table IV. The determinations were made by weighing a number of film fragments on the quartz helix balance, igniting these fragments, and dissolving the ash in distilled water. Flame photometry was then used to find the sodium bromide content of the resulting solution. Because of the small amount of polysalt available from each film, only the two largest salt contents could be measured. The two films equilibrated in 0.25N sodium bromide solution contained an average of 0.46 equivalents of sodium bromide per equivalent of polysalt; the film equilibrated in the 0.075N solution contained 0.23 equivalents per
equivalent. Films equilibrated in the solutions of lower sodium bromide normality, the 0.020N, 0.011N and 0.006N solutions, should show a steadily decreasing salt content. It is impossible, however, to extrapolate from the two measured values to lower equilibration solution normalities because the shape of the curve is unknown.

D. Film Water Content

1. Salt-free polysalt

The water content of a film originally equilibrated in distilled water was determined as a function of relative humidity at 24.5°C. The film was rapidly dried from the gel state to 51 per cent relative humidity (%RH) while on the balance. The relative humidity was then raised to 92.5% and an equilibrium reading obtained. This was repeated at successively lower relative humidities. The readings at 33 and 51%RH were extrapolated to dryness to find the dry weight of film.* Figure 10 shows the results of this test in grams of water per 100 grams of dry film as a function of relative humidity. The chief uncertainty in these results lies in the weight of dry film obtained from the extrapolation of the balance readings to dryness. However, the accuracy in the extrapolation should be sufficient to give the results to within 2.0%.

---

* A reading could not be obtained at 11.1%RH because the film fragmented and some of the fragments could be seen at the bottom of the balance case. However, films containing sodium bromide did not fragment at this low humidity. The 11.1, 33, and 51%RH balance readings for each of the two films next highest in salt content formed a straight line when plotted against relative humidity. These lines were extrapolated to dryness to obtain the dry film weight. Therefore, the same procedure was utilized for the salt-free film using only the 33 and 51%RH readings.
Bulk polysalt water absorption in distilled water as obtained by Miekka (25) is also shown in Figure 10. The dashed line extending the relative humidity data to the 100% RH point (or liquid water point) fits quite well with the trend in the rest of the data.

The absolute amount of water absorbed per equivalent of polysalt is quite large reaching 6.7 equivalents per equivalent at 92.5% RH. Table V shows these values for six relative humidities and for liquid water. (These values are based on a polysalt equivalent weight of 399. There is a possibility that this includes two additional equivalents of water which are not removed by normal drying techniques. See Section A.)
2. Polysalt films containing sodium bromide

Water absorption isotherms of three additional films, those equilibrated in the 0.020N, 0.075N and 0.25N sodium bromide solutions, were also determined at 24.5°C. These absorption isotherms as well as that of the salt-free polysalt are shown in Figure 11. The procedure used in making these measurements was the same as that used for the salt-free polysalt. The equilibration period ran as long as twenty hours, due mainly to the slow diffusive transfer of water in the balance.

As the sodium bromide content increased, the amount of water absorbed by the polysalt at constant relative humidity increased with one exception. At low relative humidities, the films equilibrated in the 0.020N sodium bromide solutions contained essentially equal amounts of water in contrast to high relative humidities where the water content of the films diverged sharply. This low humidity behavior is probably due to the uncertainties in obtaining the dry weight of the films. Movement of the curve for each film by less than 2% would separate the curves and give the expected increase in water content with increased salt content.

This increased water absorption with salt-content is probably caused by both an increase in the ionic character of the polysalt and by an expansion of the polysalt structure at high sodium bromide contents. The latter probably causes the increase, with salt content, in ratio of excess water absorption to salt content. These ratios, shown in Table VI along with an equilibrium sodium bromide solution for comparison, were calculated by subtracting the amount of polysalt associated water (obtained from the
salt-free polysalt isotherm) from the total absorbed water and then dividing by the salt content. The accuracy of the ratios is probably no better than ± 25% because of the uncertainty in the film water content. However, the polysalt equilibrated in the 0.075N sodium bromide solution had significantly smaller ratios than the one equilibrated in the 0.25N solution.

The absorption isotherm for the polysalt equilibrated in the 0.020N sodium bromide solution converges with that for the salt-free polysalt at 92.5% relative humidity. This should not be due to experimental error, since the shape of the two curves is significantly different. The behavior may instead result from the presence of small microvoids in the salt-free polysalt. The microvoids will fill with water at high relative humidities if the walls are hydrophilic. Miekka (25) previously found that complete consolidation of bulk polysalt could only be achieved in the presence of simple salts. Hence, the collapse of the salt-free polysalt gel during drying may leave microvoids in the film because of the inability of the polysalt to completely consolidate.

Since the water content determinations were made at 24.5°C and the dielectric tests carried out of 27.5 and 27.8°C, there will be a small difference in water content at the dielectric test conditions due to chemical potential changes with temperature. However, the three degree temperature change at constant relative humidity should change the water content by only a small amount. For instance, concentrated ionic solutions such as aqueous sodium bromide and sodium chloride change water content by less than one per cent under the same circumstances. The behavior of the
polysalt and the concentrated salt solutions should be somewhat comparable due to the strong electrostatic forces acting on the water in both cases. For this report, therefore, the film water content at the dielectric test conditions will be assumed equal to that at 24.5°C and the same relative humidity.
E. Measurement of Dielectric Properties

1. Geometrical measurements

The film thickness and the contact area must be used to reduce the measured resistance and capacitance to specific properties of the polysalt. The average mercury contact area was obtained by examining a number of films after the testing was completed. A circular area on the film surfaces at the point of contact was slightly discolored by the presence of some mercury residue. The diameter of this area, about 0.7 centimeters, was less than the 0.8 centimeter diameter glass tube holding the mercury column. This difference agrees well with the appearance of the contact when viewed from the side. The area of the 0.7 centimeter circle, 0.38 square centimeters, was used as the average contact area.

The dielectric measurements at each test condition were repeated a number of times. The contact area variations, as shown by variations in capacitance and resistance, was usually below ± 8%. When occasionally a single value would deviate by as much at 25% from the mean, visual observation of the contact after the measurement indicated an abnormal contact area. For each condition an intermediate value of the capacitance and resistance were selected as representative.

The film thickness was determined by averaging the thicknesses of a number of film fragments taken from the test contact area. Each fragment was measured in a number of places to determine an average value. The variation of values obtained from the different fragments was less than ± 12%; and in the majority of cases, the variation was less. An average for all of the fragments was used as the film thickness. Since
the variations in thickness were small, the use of an average geometric thickness in calculating the dielectric constant introduces negligible error.

The film thickness was measured at room conditions, about 20-40% relative humidity and 21-25°C. These levels of temperature and relative humidity are both lower in magnitude than the dielectric test conditions. At these lower humidities the film should have undergone shrinkage due to water loss and therefore, should possess a smaller thickness than during the dielectric testing. However, since the thickness change with water content is not known, the measured thickness was used in all calculations. The largest error using this procedure would occur under the high humidity test conditions with the film equilibrated in the 0.25N sodium bromide solution. As a result, the true dielectric constant will always be somewhat larger than the one calculated and the changes in dielectric constant with water content, larger than those presented.

2. Tests for specific dielectric properties

A primary initial question is whether specific dielectric properties of the polyanion are measured by the experimental technique used. In fact, two related questions exist:

1. Is electrode polarization, similar to that found when studying aqueous solutions, causing the high dielectric constants?

2. Are the measurements greatly affected by the interfacial potential between the platinum and mercury electrodes?

Five films of differing thickness were equilibrated in the 0.011N sodium
bromide solution prior to drying in a room desiccator. The films were transferred to the dielectric test apparatus and the resistance and capacitance measured at 51% RH. The thickness of only one of the films, Film 11-A, was directly measured. Approximate thicknesses of the remaining films were obtained from the equality \( t_x = \frac{C}{C_{11-A}} t_{11-A} \), assuming the contact areas are equal. \( C \) is the capacitance at a frequency of \( 10^5 \) cps, \( t \) is the film thickness, and 11-A refers to Film 11-A.

The capacitance, conductance, and loss tangent of four films were ratioed with the equivalent quantities of the fifth film, Film 11-A. Table VII shows these ratios and, in addition, the approximate film thickness. The conductance and capacitance ratios for each film should be equal and remain constant with frequency if

a. surface effects are small compared to volume polarization

and

b. the two films, 11-A and the one under comparison possess identical volume properties.

The latter implicitly assumes the dielectric properties to be independent of field strength and, therefore, of film thickness for this constant r. m. s. voltage system. The loss tangent ratios should always be unity under these same conditions.

The ratios for Film 11-D were the only ones which did not conform closely to this behavior. This difference in behavior was probably caused by a smaller sodium bromide content for Film 11-D. This could have been due to excessive blotting of the surface of the gelled film prior to drying. A portion of the salt solution within the gel may have been
removed. A second possible cause may have been holding the film in a room desiccator at 51% RH for nine days as opposed to a one to four day period for the other films. A widely fluctuating room temperature could cause transient relative humidities greater than 51% RH. The exposure to relative humidities greater than 51% will later be shown to have a significant effect on dielectric properties. However, the consistency of the results for the other three films shows that indeed specific properties of the polysalt were being measured over this five-fold range in thickness.

The mercury-platinum electrode arrangement was used to insure good electrical contact with the film. Good contact would have been extremely hard to obtain using two solid plates. Silver painting one electrode on a cast film could not be attempted because of the possible effect of the solvent on the film. However, casting the film on a platinum slide and butting a column of mercury against the film did insure good contact. The possible effects of the interfacial potential between the two metals was deemed to be of secondary importance for three reasons:

1. the mercury contact was made only during testing
2. the interfacial potential should be less than 0.2 volts (estimated by adding a series of potentials obtained from "The Handbook of Physics and Chemistry") which is less than the 0.3 rms test potential
3. both of these potentials are less than the oxidation-reduction potentials of sodium bromide.
F. Dielectric Behavior of a Salt-free Polysalt Film

1. Experimental Results

The dielectric properties of Film O-A, a film equilibrated in distilled water, are shown in Figure 12. After the film was cast and equilibrated in distilled water, the platinum slide was placed in the test desiccator and the film gel dried at 51% to a clear, continuous film. Following an equilibration period of one day, the capacitance and resistance of the film were measured. The dielectric constant increased from 11 to 27 and the loss factor from 0.34 to 13 as the frequency was decreased from 100,000 to 100 cps. (The conductivity decreased with frequency over this frequency range which shows the direct current conductivity was still much lower than the measured conductivity. Therefore, the rising loss factor was not caused by a constant d.c. conductivity.) Both the maximum in the loss factor curve and the inflection point in the dielectric constant curve occur at a frequency below 100 cps. Therefore, the mean relaxation time for the polarization causing the increase in dielectric constant must be greater than 1.5 x 10^{-3} seconds (corresponding to a frequency of less than 100 cps). The maximum in the loss tangent curve, shown in Figure 12, also occurs below 100 cps. Since this maximum will occur at a higher frequency than that of the loss factor peak (See Section B-1 of the Introduction.), the mean relaxation time is probably much larger than the above lower limit of 1.5 x 10^{-3} seconds. Therefore, the low frequency, asymptotic dielectric constant should be much larger than 27.
2. Summary of the dielectric behavior of the salt-free polysalt film

The salt-free polysalt film at 51% relative humidity and 27.5°C showed dielectric dispersion in the frequency range from 100,000 to 100 cps with the dielectric constant rising from 11 to 27 as the frequency was decreased. However, the mean relaxation time of this polarization is much larger than $1.5 \times 10^{-3}$ seconds, so the dielectric constant would have continued to increase with decreasing frequency below 100 cps.

G. The Effect of Sodium Bromide Content on Dielectric Properties

1. Experimental results

The dielectric properties at 51% relative humidity and 27.5°C of a series of films containing differing amounts of sodium bromide are shown in Figures 13, 14, and 15. The behavior of the salt-free film is also shown for comparison by a dotted line in each figure. The polysalt films were equilibrated in sodium bromide solutions ranging in normality from 0.25 to 0.006 before being dried and tested. Table VIII lists the approximate water and sodium bromide contents of these films at the test conditions. The sodium bromide contents of three of the films could not be measured directly, but instead were estimated using the dielectric constants of the films. These estimations are discussed below. The water content of the films at constant temperature and relative humidity increased with increased sodium bromide content due to the relatively large quantity of water associated with the salt ions. (The water contents were obtained from Figure 11.)

The measured dielectric constants ranged up to a maximum of 76,000. However, in no case has the dielectric constant curve gone through an
inflection point, nor has the loss factor reached a maximum with decreasing frequency. (The conductivity decreased with decreasing conductivity over the frequency range studied showing that the loss factor increase was due to dispersion and not to a constant d.c. conductivity.) The frequency at which both of these occur corresponds to the mean relaxation time, \( \tau_m = \frac{1}{2\pi f_m} \). Since the mean relaxation frequency lies below 100 cps, the dielectric constants would have continued to increase with decreasing frequency before finally approaching asymptotic values much larger than those measured at 100 cps. Because only a fraction of the total dispersion has occurred over this four decade range of logarithmic frequency, a wide distribution of relaxation times must exist. Dispersion characterized by a single relaxation time will, by contrast, occur over only two decades of logarithmic frequency.

The increase in the magnitude of the dielectric constant curve with increased salt content might be caused by a shift in the dielectric constant-frequency curve along the frequency axis or by an increase in the magnitude of the dielectric constant due to new dispersive processes created by the presence of the sodium bromide. If the nomenclature of Section B-1 of the Introduction is used, the total dielectric increment, \( \varepsilon_0 - \varepsilon_\infty \), equals \( \int_0^\infty y(\tau) \, d\tau \) where \( y(\tau) \) is the relaxation time distribution. The first alternative means a shift of \( y(\tau) \) along the \( \tau \) axis to lower \( \tau \), or a shift of the increase in dielectric constant to higher frequency, without a change in the magnitude of the increment. The second alternative is an increase in the magnitude of the \( y(\tau) \) curve for
the $\tau$ range from less than $1.5 \times 10^{-6}$ seconds to much greater than $1.5 \times 10^{-3}$ seconds.

If the effect of sodium bromide addition were only a decrease in the relaxation times, it would be necessary for these relaxation times to decrease by a factor of $10^7$. (This was obtained by superimposing the ends of the dielectric constant curves for Film 250-A, Film 11-E, and Film 0-A. The complete set of curves do not superimpose.) It is much more likely that the introduction of the sodium bromide created polarizable regions which increased the magnitude of the $\gamma(\tau)$ curve in the relaxation time range of interest. Small shifts of the complete $\gamma(\tau)$ curve along the relaxation time axis may have also occurred, but it seems probable that this was not the major cause of the increased dielectric constants.

The loss tangent curves for the two films highest in salt content go through a maximum with frequency in the frequency range studied. It also appears that the maximums for the next two films lower in salt content occur at or just below 100 cps. The maximum for Film 6-A and the salt-free film lie below the frequency range studied. The occurrence of the loss tangent maximum at a higher frequency than that of the loss factor maximum is to be expected. (See Section B-1 of the Introduction.) The frequency of the loss factor maximum, $1/\tau_m$, defines $\tau_m$ as the mean relaxation time; that of the loss tangent equals $f(\varepsilon_\infty/\varepsilon)/\tau_m$, where $\varepsilon_\infty/\varepsilon_0$ is the ratio of the low to high frequency asymptotic dielectric constants. The function $f(\varepsilon_\infty/\varepsilon)$ depends on the nature of the relaxation time distribution, equaling $(\varepsilon_\infty/\varepsilon)^{1/2}$ for a single relaxation time and decreasing in value as the relaxation time distribution broadens. However,
this factor should still be of comparable magnitude for a fairly broad
distribution.

The increase in the frequency of the loss tangent maximum with in-
creased salt content may, therefore, be due to a decreased mean relaxa-
tion time or an increased film polarization. These alternatives are the
same as those discussed with reference to increased dielectric constants
with higher salt content. The most likely alternative is that the sodium
bromide creates new polarizable elements in the polysalt and that as the
salt content increases, the total polarization developed in these elements
also increases.

2. The effect of sodium bromide content on dielectric constant

The previous section presented the experimental result that the
dielectric constant at a given frequency increases with increasing sodium
bromide content of the polysalt film. Figure 16 shows this dielectric
constant dependence on sodium bromide content at each of four frequencies.
The three films used in this correlation were the salt-free polysalt film
and the two films for which sodium bromide contents could be measured
(Films 0-A, 75-A and 250-A). Using this correlation, it is possible to
estimate the sodium bromide contents of the other three films studied,
Films 20-A, 11-E and 6-A. The results will only be approximate, but should
be fairly close. Table IX shows these results for each film at each of the
four frequencies. The results for Film 20-A drifted quite badly with
frequency; the salt contents of the other two films remained fairly
constant.
3. Summary of the effect of sodium bromide on dielectric properties

The dielectric properties of a series of neutral polycrystalline films containing differing amounts of sodium bromide were determined at 27.5°C and 51% relative humidity. The water content increased slightly with sodium bromide content under these constant water activity conditions. The dielectric constants increased with salt content and decreasing frequency. The maximum measured value was 76,000 at 100 cps for a film containing approximately 0.46 equivalents of sodium bromide per polycrystalline equivalent and 0.185 grams of water per gram of dry polycrystalline and sodium bromide. A fairly wide distribution of relaxation times is associated with the polarization causing the dielectric dispersion. The mean relaxation time is greater than $1.5 \times 10^{-3}$ seconds (which corresponds to a frequency of less than 100 cps). Therefore, the dielectric constant would have been much larger if the frequency could have been decreased below 100 cps.

New polarization processes created by the presence of the sodium bromide in the polycrystalline were probably the major cause of the observed dispersion. The increase in dielectric constant with salt content was then due to an increase in the total polarization developed by these processes.

H. The Effect of Water Content on Dielectric Properties

1. Experimental results

Additional tests on two of the films discussed in the previous section, Films 0-A and 11-E, showed that the dielectric constants of the films increased when the water content of the films was increased by equilibrating the films at 92% relative humidity. Moreover, the dielectric constants at these high relative humidities did not remain at a constant
value but decreased with time to a new steady-state value. However, the loss tangent curve remained relatively constant over this transient time period, which was longer than a week. When the films were returned to 51% relative humidity and retested, the dielectric constants differed from their initial values. (See Section E of the Appendix for the details of these tests.)

Two films, Films 250-C and 75-B, were tested to study these effects on the dielectric properties more closely. Each film was dried from the gel to 51% RH in a test desiccator held at a constant temperature of 27.8°C. The relative humidity in the desiccator was then raised to 92.5%. The film capacitance and resistance were measured periodically until they remained constant with time. The relative humidity was then lowered to 75% and this procedure repeated. This was followed by a similar procedure at successively lower relative humidities of 64.4%, 51% and 33%.

The dielectric properties of Film 250-C, a film equilibrated in a 0.25N sodium bromide solution, during this sequence are shown in Figures 17 through 21. The water content of the film at each relative humidity is shown next to that relative humidity curve in grams per gram of dry film. (These were obtained from the water content data shown in Figure 11.) The measurements at 92% relative humidity could only be made at a frequency of 10,000 cps because of the high capacitances and resistances encountered. Both the dielectric and loss tangent remained essentially constant with time. Large changes in the dielectric properties did occur, however, at 75% RH. Figure 20 shows the dielectric constant decrease with time; the dielectric constant dropped by approximately a factor of fifty. However, the loss
tangent made only a slight change over the time period, as shown in Figure 21. The dielectric properties at lower humidities did not change with time. Figures 17, 18 and 19 show the steady-state values of the dielectric constant, loss factor and loss tangent at each of the relative humidities.

Figures 22 through 26 show the results for a similar sequence of relative humidities with Film 75-B, a film equilibrated in the 0.075N sodium bromide solution. The water contents of the film are again shown next to the relative humidity curves. Substantial changes in the dielectric properties occurred at 92.5% RH as shown in Figures 25 and 26. The dielectric constant curve dropped in magnitude by about 60%. The loss tangent curve retained the same shape but increased in value at the three frequencies tested. An additional small change occurred at 75% RH, where both the loss tangent at high frequencies and the dielectric constant at low frequencies dropped slightly in value. Again the dielectric properties at low relative humidities did not change with time. The steady-state values of the dielectric constant, loss factor and loss tangent are shown in Figures 22, 23 and 24.

2. The effect of water content on dielectric properties

Since the dielectric properties did not drift with time at the lower humidities, differences in these properties with relative humidity should be directly due to the effect of water content. Figures 27 and 28 show the dielectric constant as a function of water content for Film 250-C and Film 75-B, respectively. In both cases, the dielectric constant decreased with water content. In addition, the loss tangent peak
shifted to lower frequencies as the water content decreased. These changes are probably due to a combination of a decrease in the dielectric increment and an increase in relaxation times (both a decrease in the magnitude of the relaxation time distribution curve, \( y(T) \), and a shift of the curve to larger relaxation times).

If a change in relaxation times is solely responsible, it should be possible to superimpose the dielectric constant curves for the different relative humidities. The shift factor or displacement of each curve would be a measure of the changes in relaxation time. However, the curves cannot be superimposed. Nor do the curves appear as if they are only decreased in magnitude. Therefore, it appears probable that a combination of these two factors is responsible for dependence of the dielectric properties on water content.

A comparison of the 51% RH properties of Films 250-C and 75-B with Films 250-A and 75-A shows that the change in dielectric properties with time affects the magnitudes of these properties at lower relative humidities as well. A more complete investigation of the possible causes of these high humidity changes will be considered below.

3. Summary

The dielectric properties of two films of different sodium bromide content were measured at 27.8°C and a series of relative humidities. The dielectric constants and loss factors of both films at 75% and 92.5% relative humidity dropped with time to new steady-state values. However, during this same time period (which lasted on the order of a week or longer), the loss tangent maximum remained at approximately the same
frequency. This dielectric constant change with time was larger for
the film with the higher sodium bromide content.

Below 75% relative humidity where the dielectric constant did not
drift with time, the dielectric constants decreased with a decrease in
water content. The frequency of the loss tangent maximum also de-
creased. This behavior was probably due to both an increase in the re-
 laxation times of the polarization processes and a decrease in the
magnitude of the polarization developed by each process.

I. Time-dependent Changes in Dielectric Properties at High Relative
   Humidities

   1. The effect of high relative humidity on water content

   One possible explanation of the previous history effects is
that the changes in dielectric properties at high relative humidity are
caused by an internal structural change resulting in the release of an
appreciable quantity of water. The decrease in dielectric constant
might then be due to the lower water content of the film. This was
tested with the quartz helix balance using a film equilibrated in the
0.25N sodium bromide solution. The film was dried to 51%RH on the
balance. After four days the relative humidity was raised to 75% and
kept there for nine days. The film was then again dried to 51%RH. The
balance readings were recorded throughout this procedure and are shown
in Figure 29. (The balance reading decreases with increasing weight.)
The difference in weight between the two relative humidity conditions
is approximately 0.15 grams of water per gram of dry polysalt (obtained
from Figure 11). The water content at 75%RH did not change signifi-
antly with time nor was the amount absorbed at 51%RH changed by holding the
film at 75%RH. (The variations at each condition with time were mainly due to a fluctuating room temperature. The largest variation at 75%RH resulted from a small fire in the room. The doors of the room were opened to purge the smoke and fumes after the fire was extinguished.)

2. Time-dependent effects at high relative humidities

A series of four films was dielectrically tested to answer the question of whether the time-dependent changes in dielectric properties are caused by exposure to electrical stress at the high humidity conditions or just by the exposure to these conditions. These films were dried from the gel state to 51% relative humidity in the test apparatus held at a constant temperature of 27.8°C and then tested at this condition. The relative humidity was raised to 75% for 3 days and then returned to 51%. The films were again dielectrically tested. This procedure was repeated several times for three of the films, Film 0-B, Film 20-B and Film 75-C.

Figure 30 shows the results obtained for Film 0-B. The dielectric constants are plotted as a function of the number of days the film was held at 75% relative humidity. The decrease in dielectric constant may be the result of changes in the contact area rather than an actual dielectric constant change. The platinum slide was at a slight angle to the end of the glass tube containing the mercury column. This resulted in a fairly large uncertainty in the actual mercury contact area. The similarity of the fluctuations at all frequencies supports this explanation.

In addition, the dielectric constants of this film are higher than
those of a similar film, Film 0-A, shown in Figure 12. Moreover, the maximum probable error in area estimation and thickness (the film was quite thick, 6.9 microns) of approximately 25-30% can not account for the high dielectric constants at the lower frequencies. These are probably caused by a combination of an appreciable quantity of residual sodium bromide and an excess of one of the polyions present in the polysalt. This series of films was cast from different polysalt solutions than the original series investigating the effect of salt content, so it is possible that the latter could have occurred. The film properties seem midway between those of Film 11-E and Film 20-A which, as estimated in Section G-2, contained approximately 0.08 and 0.12 equivalents of sodium bromide per polysalt equivalent. Assuming that the effect of a given concentration of sodium bromide is comparable to the same concentration of counterion associated with the excess polyion, this indicates a polyion ratio between 1.12 and 1.25 in the polysalt. This seems too large to have occurred, so that it is unlikely that this is the sole cause of the increased dielectric constants. (There is a possibility that effect of the associated counterions is sufficiently different from that of the sodium bromide to cause the observed dielectric constant with a much lower polyion ratio.)

The dielectric properties of Film 20-B, shown in Figure 31, did undergo some change, most significantly at 100 cps. The initial values of the dielectric constant were within 10% of those measured for Film 20-A, which is within experimental error. Figure 36 shows the change in the dielectric constant of Film 75-C. The low frequency dielectric constants
first increased and then decreased below the initial values. The high frequency values also dropped by appreciable amounts. In this case, the initial dielectric constant curve lies above that for Film 75-A by a factor ranging from 1.6 at high frequencies to 3 at low frequencies. It appears as if the sodium bromide content of Film 75-C was appreciably higher than that of Film 75-A. This may have been due to the lower polysalt concentration of the ternary solution from which Film 75-C was cast. This could have resulted in a more open gel structure which would contain a greater quantity of the sodium bromide equilibration solution per equivalent of polysalt.

The fourth film of the series, Film 250-D, was also tested at 51% RH, held at 75% RH for 2.5 days and then re-equilibrated and tested at 51% RH. However, the relative humidity was next raised to 92.5% RH for 1.3 days instead of 75% RH. The film was then retested at 51% RH. Figure 33 shows the film capacitance during this treatment, since the film thickness could not be measured. The film would not fragment and attempts to remove pieces of the film resulted only in producing pieces too small to handle. The change in the dielectric constant due to the film being held at 75% RH is even larger than that of the films discussed above.

These tests have answered the question posed above. The change in dielectric constant with time at high relative humidity is caused by the exposure to these humidities and not by the exposure to electrical stress at these conditions. These tests also show that the time-dependent changes in dielectric constant will occur at 75% RH as well as 92.5% RH. In addition, the amount of change in the dielectric constant again
increased as the sodium bromide content increased.

The initial shape of the capacitance curve and therefore, of the
dielectric constant curve, for Film 250-D is quite different from those
obtained previously with films equilibrated in the 0.25N sodium bromide
solution. This capacitance and loss are shown as functions of frequency
in Figure 34; the latter is proportional to the loss factor. (The
constant of proportionality between the loss factor and loss is the same
as that between the dielectric constant and capacitance. Therefore, the
relative magnitudes of the dielectric constant and loss factor curves are
the same as that of the capacitance and loss curves that are shown.) In
this case, the capacitance appears to approach a constant, asymptotic
value at low frequency. However, it is possible that the capacitance
might have continued rising at lower frequencies, since the loss has not
dropped by a significant amount. The difference in behavior as compared
to Film 250-A was probably caused by a larger sodium bromide content
similar to that for Film 75-C which was discussed above.

The shape of the capacitance curve changed significantly after the
film was exposed at 75% RH for 2.5 days. This second capacitance curve
is also shown in Figure 34 for comparison. The change is evidently due
to both a shift in the relaxation time distribution to higher relaxation
times and a change in the shape of the distribution. Neither a shift in
the capacitance curve along the frequency axis nor an increase in the
magnitude of the curve will cause it to coincide with the initial curve.
This type of change in the relaxation time distribution is illustrated in
in the following sketch with the solid line serving as the original curve and the dotted line representing the new distribution. This corresponds to a change in relaxation time for some of the dispersion processes, but not a shift in the whole curve. Since the loss tangent peak in both cases occurred at a frequency above $10^5$ cps, it can not be ascertained whether this frequency remained constant. So, the shape of the two curves at high relaxation times remains speculation. However, the change in mean relaxation time is probably not as large as it appears from the dielectric constant changes, since there is probably an appreciable amount of dispersion occurring below 100 cps which is not greatly changed.

The results discussed in Section H showed that the loss tangent peak remained at the same frequency during the time-dependent changes in dielectric constant. This peak will be at a frequency equal to $\frac{\gamma (\varepsilon_\infty / \varepsilon_{\infty})}{\tilde{\tau}_m}$ in radians per second, where $\tilde{\tau}_m$ is the mean relaxation time corresponding to the loss factor peak and $\gamma (\varepsilon_\infty / \varepsilon_{\infty})$ is a function of the total dielectric increment. These last data show a movement of the
polarization to larger relaxation times, so that if any change in $\bar{\tau}_m$ occurs it should increase. If the mean relaxation time does increase, $\tau_0(\varepsilon_0/\varepsilon_\infty)$ must also increase if the loss tangent peak is to remain relatively stationary with frequency. At low salt contents the dielectric constant change is smaller and it is possible that neither $\bar{\tau}_m$ or $\tau_0(\varepsilon_0/\varepsilon_\infty)$ change, that the portion of relaxation time spectrum around the mean relaxation time is unaffected.

3. Summary

Four films containing differing amounts of sodium bromide were tested to investigate more closely the dielectric constant decrease with time when the films are held and tested at high relative humidity. The films were exposed to relative humidities of 75% and 92.5% between dielectric tests at 51% relative humidity. The tests showed that the change in dielectric constant with time at high relative humidity is caused by time-dependent structural readjustments, and not by exposure to electrical stress. In addition, these high-relative-humidity, time-dependent changes in dielectric constant occurred at 75% RH as well as 92.5% RH for all the films which showed appreciable change. The magnitude of the change in dielectric constant again increased with the sodium bromide content of the film. A time-dependent water content test showed that the water content of the films did not show a time-dependent change at these high humidities. Therefore, the changes in dielectric constant with time were not due to changes in water content.

The changes in dielectric constant with time were probably the result
of changes in the relaxation time and dielectric increment of some of the elements causing dispersion, especially those elements on the low end of the relaxation time distribution. The total dielectric increment should have either remained relatively constant or increased slightly during the time-dependent dielectric constant changes.

J. Dielectric Properties of an Unsymmetrical Polysalt Film

1. Experimental results

The dielectric properties of an unsymmetrical polysalt film were determined for comparison with the neutral polysalt films containing sodium bromide. The unsymmetrical polysalt film was cast from a ternary solvent containing 1.3 equivalents of NaSS per equivalent of neutral polysalt. The gelled film was washed in a dilute sodium bromide solution, dried at 51%RH and dielectrically tested. The relative humidity was then raised to 92.5%RH and held there for 2.5 days before being returned to 51%RH. The film was then retested at this condition. Figures 35, 36, and 37 show the results of these tests.

The unsymmetrical film contains 0.4 equivalents of microion per equivalent of polyon. Assuming the counterions in the unsymmetrical film

*When distilled water was used to wash a similar film, the very large swelling which occurred destroyed the film continuity. A small amount of sodium bromide added to the external solution reduces this swelling to a considerable extent. The amount of the sodium bromide absorbed by the gel should be quite small due to Donnan Equilibrium effects.
and the sodium bromide in the neutral polysalt film have comparable effects on the dielectric behavior, the properties of the unsymmetrical film should roughly correspond to a neutral polysalt containing approximately 0.46 equivalents of sodium bromide per equivalent of polysalt, Film 250-A or the other films equilibrated in the 0.25N sodium bromide solution.

The initial dielectric constants of the unsymmetrical polysalt film are all larger than the corresponding ones for Film 250-A (shown in Figure 13). The loss tangent peak also occurs at a higher frequency than that of Film 250-A. However, the shape of the dielectric constant curve is quite similar to that initially obtained for Film 250-D at 51%RH. In addition, the loss tangent peaks both occur above 10^5 cps.

Holding the unsymmetrical polysalt film at 92.5%RH for 2.5 days caused a drop in the magnitudes of the dielectric constants. This change resembles that of Film 250-D where the high frequency values dropped by a greater percentage than did the lower frequency ones. The change in magnitude was not as large, but this may have been due to exposing the film to 92.5%RH rather than 75%RH as was Film 250-D.

2. Summary

The dielectric properties of a polysalt film composed of 1.3 equivalents of NaSS per equivalent of VBTA-SS were determined at 51%RH and 27.8°C for comparison with the neutral polysalt films containing sodium bromide. The dielectric behavior of this film resembled that of a neutral polysalt film containing approximately 0.5 equivalents of sodium bromide per equivalent of polysalt. The unsymmetrical polysalt
film also underwent time-dependent changes in dielectric properties when exposed to high relative humidities.

K. Interpretation of the Dielectric Behavior

1. Review of the experimental results and conclusions

The dielectric behavior discussed in the previous sections has led to a number of conclusions concerning this behavior. These will be briefly reviewed before a physical interpretation is presented.

The dielectric constant of the salt-free polysalt rose from 11 to 27 as the frequency decreased from 100,000 cps to 100 cps. Since the mean relaxation time of this dispersion is greater than $1.5 \times 10^{-3}$ seconds (corresponding to a mean frequency below 100 cps), the dielectric constant would have continued to rise with decreasing frequency below 100 cps. The addition of sodium bromide to the polysalt films greatly increased the dielectric constant of the films. In fact, dielectric constants greater than 100,000 were measured. An increase in the sodium bromide content increased both the magnitude of the dielectric constant at a given frequency and the frequency at which the loss tangent goes through a maximum. The main cause of this dispersion is probably the creation of new polarizable elements by the sodium bromide rather than decreases in the relaxation times of inherent polysalt dispersion. A fairly wide distribution of relaxation times is associated with this observed dispersion.

An unsymmetrical polysalt film showed dielectric behavior quite similar to that of the neutral films that contain sodium bromide.
A decrease in the water content of the polysalt at constant temperature caused a decrease in both the frequency of the loss tangent peak and the value of the dielectric constant at a given frequency. This behavior appeared to be due to changes in both the relaxation time and the dielectric increment of each of the polarization processes.

When the polysalt films were held at a high relative humidity, the dielectric constants measured at that humidity and lower ones decreased with time to new steady-state values. However, the frequency of the loss tangent maximum remained relatively constant. These changes are caused by the movement of some of the polarization to larger relaxation times (to lower frequencies), especially the polarization associated with the lower relaxation times (that associated with the high frequency end of the dielectric constant increase). If there was change in the total dielectric increment, it probably was an increase.

2. Molecular orientation

Orientation of dipolar side groups is a common cause of low frequency polarization in amorphous polymeric materials. Polyvinylchloride plasticized with diphenyl is an example of this type of behavior (17). An 80-20 mixture of PVC and diphenyl at 40°C possesses dispersion characterized by a mean relaxation time of \(3.4 \times 10^{-3}\) seconds. This relatively long relaxation time is a result of the nature of orientation processes. The total dielectric increment for this mixture at 40°C is about 7; the dielectric constant increases from 3 to 10.

The dielectric dispersion in the salt-free film at frequencies below
100 cps might be caused by this type of polarization. Relatively small movements of the individual polion side groups could create net electric moments in the direction of the field. Because of the bulky nature of these side groups, their movement should take place very slowly or only at very low frequencies. The mean relaxation time for this dispersive process might well be much greater than $1.5 \times 10^{-3}$ seconds (occur at a frequency much less than 100 cps). The addition of sodium bromide to the polysalt might decrease this relaxation time to some extent, but should not change it by more than an order of magnitude. The mean relaxation time should certainly not change by a factor of $10^7$, as would be necessary if this were the sole effect of the sodium bromide addition. (See Section G-1 for a discussion of this shift in relaxation time.) The increased dielectric constants of the films containing sodium bromide is much more likely the result of dispersion processes directly related to the sodium bromide present in the film. This dispersion is probably superimposed on the lower frequency dispersion of the salt-free films.

However, it is also possible that the observed dielectric dispersion occurring in the salt-free polysalt is the result of a small amount of residual sodium bromide and not of the partial orientation of the polion side groups. Unfortunately, it is not possible to distinguish between these two possibilities.

3. Maxwell-Wagner dispersion

Maxwell-Wagner dispersion, or interfacial polarization, will also cause dielectric dispersion in heterogeneous materials. This type of dispersion occurs when the effective conductivity, the ratio of the conductivity to dielectric constant, differs between the phases of the
system. The difference in effective conductivity causes a net buildup or discharge of electrical charge at the interphase boundaries. This creates electrical moments across these boundaries resulting in a polarization field. Fricke (15) has developed theoretical equations describing this phenomenon for dilute suspensions of ellipsoidal particles in a continuous second phase. (See Section B-2 of the Introduction for a more complete description of this phenomenon and for a review of the development of Fricke's equations.) Three dispersion regions were predicted, each characterized by an orientation of one of the particle axes parallel to the field. The dispersion occurring at the lowest frequency is characterized by a relaxation time of \[ \tau = \left( \frac{\varepsilon_v}{4\pi} \right) \left( \frac{\varepsilon_2 + \varepsilon_0}{\varepsilon_2 + \varepsilon_0} \right) \], where \( \varepsilon_v \) is the absolute dielectric constant of vacuum (8.89 X 10^{-12} farads per cm.), the subscripts 1 and 2 refer to the continuous and dispersed phase, respectively, and \( \varepsilon_0 \) is the shape factor corresponding to an orientation of the long axis of the particle with the field. Visualization of the polyanion film structure in terms of this model is quite difficult. However, an order of magnitude comparison of predicted relaxation times with the experimentally determined lower limit of 1.6 X 10^{-3} seconds (corresponding to a frequency of 100 cps) should show whether this model is at all applicable.

If the dielectric increment of this dispersion region is to be large, the continuous phase must have a higher conductivity than the dispersed phase. In this case, the regions containing the salt must be considered continuous. The relaxation time is then approximately 3 X 10^{-10} seconds
\( (\xi_2 = 2.5, \xi_1 = 20, \sigma_2 = 0, \text{ and } \sigma_1 = k_9^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}) \). The hydrophilic phase conductivity, \( \sigma \), may be lower than the value used, but the predicted relaxation time will still be many orders of magnitude less than the experimental lower limit. It is, therefore, unlikely that interfacial polarization is responsible for the observed dispersion. (If the magnitude of the dielectric increment is ignored and the organic phase considered continuous, a relaxation time of \( 10^{-3} \) seconds can be obtained, but only with extremely asymmetric conducting regions. \( \sigma^{11} \text{, where } a, b \text{ and } c \text{ are the long, middle and short axes, respectively,} \))

Therefore, occurrence of Maxwell-Wagner dispersion is unlikely in and below the frequency range studied. Instead, this type of dispersion should occur at much higher frequencies, so the associated dielectric increment is a constant over the frequency range studied and is included in all the dielectric constants measured.

4. Polarization of the microion regions
   a. Review of the Schwartz model

Schwartz (36) theoretically treated the low frequency dielectric dispersion which occurs in colloidal suspensions of spherical particles in dilute salt solutions. (See Section B-2 of the Introduction for the theoretical development and a more complete description of this model.) The development was based on the Fricke model with the addition of an ionic double-layer surrounding the spheres. Because of the nature of the electric field which causes double-layer formation, ion mobility is much higher along the double-layer than perpendicular to it. This restriction on ion mobility causes the double-layer to act like a separate
phase.

The continuous phase in this system, the dilute salt solution, was the most conductive. The electric field, which is mainly determined by this phase, drives ion movement in the double-layer inducing an opposing concentration field. The low frequency interaction of this latter field with the alternating electric field introduces an oscillation in the ion density at each point in the double-layer. This results in a slight excess and depletion of ions at directly opposing points on the sphere surface. This in turn creates a net electric movement across the sphere.

In one respect this is somewhat analogous to interfacial polarization where charge builds up at the phase boundaries because of differing effective conductivity in the two phases. Ion buildup in the Schwartz model is caused by a restriction on ion movement perpendicular to the double-layer. However, the two cases differ by the introduction of the ion concentration field in the double-layer and by the consideration of the volume polarization of the double-layer region.

The magnitude of the double-layer polarization is a maximum only when the electric field acting on the double-layer is at its maximum value; this occurs only when the continuous phase has the highest conductivity. If the continuous phase conductivity were less than that of the sphere and double-layer, the electric field (or potential gradient) between particles would be larger than that in the vicinity of the particle. The induced concentration field in the double-layer would now be smaller than previously, as would the polarization of the double-layer. It is
important to note that some polarization would still result, but it would be reduced in magnitude from the case of a highly conductive continuous phase.

The additional dispersion predicted by the Schwartz model (interfacial polarization still exists) would normally occur at fairly low frequencies. The relaxation time is proportional to a characteristic diffusion time of an ion around the sphere (proportional to the radius squared divided by the ion mobility). The dielectric increment is proportional to the sphere radius and the mean ion density in the double-layer (a measure of the polarizability of the double-layer) as well as the volume fraction of the suspended particles.

b. Polarization in the polsalt films

A phenomenon similar to that found in the colloidal system discussed above seems likely in those polsalt films that contain sodium bromide. The sodium bromide in the film will exist both as relatively free salt and as microions associated with unreacted polyions. The associated microions will form a layer similar in some respects to an ionic double-layer and the free salt will probably accumulate in regions bounded by the unreacted polyions and their associated microions. If the associated or free microions are driven by an electric field, dielectric dispersion similar to that modeled by Schwartz should occur.

* The simultaneous movement of a number of adjacent microions resembles a series of singularly polarized microion-polyion pairs. However, the pairs will not be independent. The unreacted polyion side groups are so close together that interactions will occur. Microions will be able to jump from the force field of one polyion group to the field of an adjacent group. The net effect will then be larger than just a series of polarized ion pairs. In addition, the interactions will cause the relaxation to occur at a rate characteristic of the entire region and not just of an isolated pair.
Microion movement is restricted at the boundaries of these polarizable elements by the surrounding homopolar and reacted polyion regions in which microion mobility should be quite low. This will result in the induction of concentration fields opposing the electric field and the creation of a net electric moment over each element. The dielectric increment of each element should be proportional to the end-to-end length of the element times a mean ion density in the element. The total dielectric increment will result from the summation of the dielectric increment of each element times its volume fraction over all the polarizable elements. The relaxation of the polarization will be microion diffusion controlled, and the relaxation time dependent on the effective path length for diffusion divided by the microion mobility. (This mobility should be dependent on the size of the migrating species as in dilute aqueous solutions. However, it should also be dependent on the electrical interactions of the ion with the fixed polyion ionic groups. The relative magnitude of these two resistances to ion movement is not known. A study using a series of different microions might gather some valuable information on this question.)

One major cause of the increase in dielectric constant with sodium bromide content should be the increase in the volume fraction of the polarizable elements. The wide distribution of relaxation times experimentally observed is probably due to a distribution in the sizes of these polarizable elements and to a lesser extent, to differing mobilities of the free and associated microions. If different ion mobilities for the free and associated microions were the primary cause of the relaxation
time distribution, two loss tangent peaks might be expected. These were not observed. In addition, the same wide distribution of relaxation times occurred for the unsymmetrical polysalt where only associated microions are present.

A second cause of the increased dielectric constant may be an increase in the mean size of the polarizable elements with increasing salt content. This increases the mean polarizability of the elements and in addition, will increase the mean relaxation time. The experimental results of increasing dielectric constants with increases in salt content in the frequency range studied (rather low relaxation times) do not contradict this conclusion, since there should also be an increase in the quantity of the very small polarizable regions.

A decrease in the water content of the film might have two effects. Probably the most important effect will be a decrease in the microion mobility in the polarizable elements. This should increase the relaxation times of the dispersion and shift the dielectric constant increase and the loss tangent maximum to lower frequencies as was experimentally observed. The other effect should be a decrease in the volume fraction of the polarizable elements. This should decrease the total dielectric increment.

c. Time-dependent effects at high relative humidity

Since the mean relaxation times for all the dielectric dispersion encountered (with the possible exception of the initial measurements on Film 250-D and the unsymmetrical polysalt film) were greater than \(1.5 \times 10^{-3}\) seconds, the bulk of the dispersion occurred at frequencies below 100 cps. Therefore, the dispersion experimentally observed in the
frequency range from 100,000 to 100 cps was associated with relaxation times which were smaller than the mean relaxation time. Since the relaxation time spectrum is thought to be mainly caused by a distribution in the sizes of the polarizable elements, the observed dispersion should be due to the relatively small polarizable elements. The time-dependent change in dielectric constant when the films were exposed to high relative humidities was probably caused by a consolidation of these regions with each other or with larger elements. This specifically reduces the volume fraction of polarizable elements with relaxation times corresponding to the 100,000 to 100 cps range in frequency. So, the movement of the polarization to larger relaxation times probably results from the movement of the microions from the small polarizable elements to larger ones. The increase in the amount of change with salt content is partially due to the greater number of these small polarizable elements which are present.

Miekka (25) and Mir (27) have shown there is a large driving force for complete reaction between the two polyions. Presumably, this is partially caused by the possibility of the two polyions interacting over a large number of consecutive polyion ionic groups. At the conclusion of drying the films, a number of small unreacted polyion regions may have been created by stress relieving microions. The change in dielectric constant with time may be no more than the elimination of the microions from these regions by slight changes in polyion configuration. The driving force for such rearrangements would then be the same as that in the dilute solution reactions studied by Miekka and Mir.
The microions may well have a significant role during the rearrangement. Mir found that dilute solution reactions between the hydrogen and hydroxide forms of the polyions did not go to completion as did the reactions between polyions with permanent microions. He concluded that small amounts of permanent microions are necessary as "lubricants" to achieve complete reaction. The microions may perform similar duties in the dried polysalt films by reducing the energy barrier for movement of one polyion ionic group relative to the other charged polyion groups in the immediate vicinity. It may be significant that the decrease in dielectric constant with time only occurs at high relative humidities, above the relative humidity of a saturated solution of sodium bromide. Dissolution of the free salt may be a necessary requirement. (Increases in the mobility of the polyion ionic groups with increasing water content might also be an important factor.) If this is the case, it points out the importance of the microions in allowing changes in polyion configuration.
VI. CONCLUSIONS

1. Polysalt films composed of sodium bromide and equi-equivalent amounts of poly (vinylbenzyltrimethyl ammonium) and poly (styrene sulfonate), abbreviated VBTA and SS, were found to be capable of dissolving appreciable quantities of water. At 92.5% relative humidity and 24.5°C, a salt-free polysalt film contained about 6.7 equivalents of water per equivalent of polysalt. The water content at constant relative humidity and temperature increased as the sodium bromide content of the film increased. However, the amount of water directly associated with the polyions appears to decrease if an appreciable amount of sodium bromide is present. This is probably due to the formation of a more compact polysalt structure in the presence of sodium bromide.

2. Polysalt films composed of sodium bromide and equi-equivalent amounts of VBTA and SS showed a large amount of dielectric dispersion in the frequency range from 100 cps to 100,000 cps when measured at 51% relative humidity and 27.5°C. The dielectric constants of the films increased as the sodium bromide content increased, rising from 27 for a salt-free film to about 100,000 for a film containing approximately 0.46 equivalents of sodium bromide per polysalt equivalent at a frequency of 100 cps. Since the mean relaxation times in the fairly wide distributions of relaxation times were larger than 1.5 x 10⁻³ seconds (corresponding to a mean frequency below 100 cps) for all of the films, the dielectric constants at lower frequencies would have been even larger.

3. Polarization processes created by the presence of the sodium bromide in the film were the major cause of the measured dispersion for those neutral polysalt films which contained sodium bromide. Specifically,
the polarization is probably caused by the formation of small polarizable elements or regions which contain unassociated sodium bromide and/or microions associated with unreacted polion groups. Microion migration within each element due to the imposed electric field should create a net dipole moment over the element producing the observed dispersion. An increase in the sodium bromide content increases the total polarization by increasing both the volume fraction of the polarizable elements and the mean polarizability of the elements. The latter should be proportional to the end-to-end length of, and ion density in, a representative element. The relaxation time for each element should be proportional to a characteristic time for an ion to diffuse from one end of the element to the other (a path length divided by an ion mobility). The observed broad relaxation time distribution probably results chiefly from a large distribution in the sizes of the polarizable elements.

4. When the water contents of the films were decreased by lowering the relative humidity at constant temperature, the measured dielectric constants at a given frequency decreased. The chief cause was probably a lowering of the microion mobility, which should increase the relaxation time and shift the dispersion to lower frequencies. In addition, the total dielectric increment may have also decreased due to a decrease in the volume fraction of the polarizable elements.

5. When the films were first equilibrated and held at relative humidities above 75%, the magnitude of the measured dielectric constants decreased with time (at constant moisture content) to new steady-state values. When the films were subsequently returned to lower relative humidities and retested, the dielectric constants were lower than their initial values.
The magnitude of this change increased as the sodium bromide content increased. This change is believed due to the movement of sodium bromide from small polarizable elements to larger ones, thus reducing the number of the smaller elements. This reduces the polarization associated with the elements of relatively short relaxation times or of smaller size. The mean relaxation time and total dielectric increment appears to remain fairly constant or increases only slightly during these changes.

6. The dielectric behavior of a polysalt film composed of 1.3 equivalents of sodium SS per equivalent of VBTA-SS was fairly comparable to that of an equivalent neutral polysalt film containing sodium bromide, thus confirming the belief that dielectric heterogeneity may be produced by microions associated either with polyions, or with other (oppositely charged) microions.
VII. RECOMMENDATIONS

1. This investigation should be extended to include a thorough study of the unsymmetrical polysalts. The effect of the equivalence ratio of the two polyions on the dielectric properties should be studied in detail.

2. The above study should be followed by an investigation of the change in dielectric properties which may result if the kind of counterion associated with the excess polyions is changed. Substitution of a hydrogen or calcium ion for sodium ion should change the dielectric properties because of differing mobility and charge. Use of the unsymmetrical polysalt allows the study of a single microion at a time.

3. In addition to the alternating current studies listed above, direct current charge and discharge studies would be quite valuable for evaluating the total energy storage capabilities (static dielectric constant) of the films. This type of study should include measurements of the direct current resistivities of the films and the effect of temperature on these resistivities. The latter could be used to calculate an activation energy for microion diffusion through the polysalt matrix assuming microion diffusion causes the direct current conduction.

4. New fabrication techniques allow the formation of thick (0.1 mm or greater), unsupported films. Use of standard dielectric test holders when studying these films would eliminate the present uncertainties in measuring contact area and test thickness as well as eliminate the possible effects of the interfacial polarization between the mercury and platinum electrodes. The use of this system could help make a much more efficient experimental procedure.
5. An analytical model for this type of dielectric dispersion in an idealized system should be developed. Two of the more simple models would be a spherical cavity filled with a salt solution and a cylindrical cavity aligned perpendicular to the electric field and again containing a salt solution.
VIII. APPENDIX

A. General Criteria for Schwartz Model Dispersion

The general conductivity equation for a suspension of spheres in a continuous second phase is

\[
\frac{k - k_1}{k + 2k_1} = p \frac{k_2 - k_1}{k_2 + 2k_1},
\]

where \(k\) is the complex conductivity, \(p\) is the volume fraction of spheres, and the subscripts 1 and 2 refer to the continuous phase and the sphere plus double-layer combination, respectively. (See Section B-2 of the Introduction.) Solving this equation for the complex conductivity of the mixture gives

\[
k = k_1 \frac{k_2(1+2p) + 2k_1(1-p)}{k_2(1-p) + k_1(2+p)}.
\]

By separating all of the complex conductivities into real and imaginary parts, reducing the right-hand side to a real and imaginary part and then equating these latter two parts to the conductivity and dielectric constant of the mixture, the following two equations are obtained

\[
\sigma = (1-p) \sigma_1 \frac{2\sigma_1^2(2+p) + \omega^2 \xi_v^2 \left[\xi_2^2(1+2p) + 4\xi_1' \xi_2' (1-p) + 2\xi_1'^2(2+p)\right]}{\left[\sigma_2(1-p) + \sigma_1(2+p)\right]^2 + \omega^2 \xi_v^2 \left[\xi_2'(1-p) + \xi_1'(2+p)\right]^2},
\]

\[
+ \sigma_2 \frac{\sigma_1^2(4+p+4p^2) + \sigma_1 \sigma_2 (1-p)(1+2p) + \omega^2 \xi_v^2 \xi_1'^2g_p}{\left[\sigma_2(1-p) + \sigma_1(2+p)\right]^2 + \omega^2 \xi_v^2 \left[\xi_2'(1-p) + \xi_1'(2+p)\right]^2}.
\]
and $\xi' = (1-p) \xi'_1 \left\{ \frac{\sigma_2^2 (1+2p)+4\sigma_1 \sigma_2 (1-p)+2\sigma_1^2 (2+p)+\omega^2 \xi_v \xi'_1 2^2(2+p)}{\left[ \sigma_2 (1-p)+\sigma_1 (2+p) \right]^2 + \omega^2 \xi_v^2 \left[ \xi'_2 (1-p)+\xi'_1 (2+p) \right]^2} \right\}

+ \xi'_2 \left\{ \frac{9p \sigma_1^2 + 4p^2 \xi_v^2 \left[ \xi'_1 (4+p^2)+\xi'_1 \xi'_2 (1-p)(1+2p) \right]}{\left[ \sigma_2 (1-p)+\sigma_1 (2+p) \right]^2 + \omega^2 \xi_v^2 \left[ \xi'_2 (1-p)+\xi'_1 (2+p) \right]^2} \right\}

where $\sigma$ is the real part of the complex conductivity and $\xi_v, \xi'_v$ is the imaginary part. ($\xi_v$ is a conversion factor to cgs units.)

The effective dielectric constant and conductivity of the sphere plus double-layer combination are (36):

$$\xi'_2 = \xi'_3 + \frac{\Delta \xi}{1+\omega^2 \tau^2}$$

and

$$\sigma = \sigma_3 + \frac{\xi_v \Delta \xi \omega^2}{1+\omega^2 \tau^2}$$

where $\Delta \xi$ is the dielectric increment due to the double-layer, $\tau$ is the relaxation time and 3 refers to the sphere. If the apparent dielectric constant of the mixture is to be a strong function of the dielectric increment due to the double-layer, the factor multiplying $\xi'_2$ must have a value near unity or

$$\left\{ \frac{9p \sigma_1^2 + \omega^2 \xi_v^2 \left[ \xi'_1 (4+p^2)+\xi'_1 \xi'_2 (1-p)(1+2p) \right]}{\left[ \sigma_2 (1-p)+\sigma_1 (2+p) \right]^2 + \omega^2 \xi_v^2 \left[ \xi'_2 (1-p)+\xi'_1 (2+p) \right]^2} \right\} \approx 1.0$$

Schwartz assumed $|\sigma_1 + i\omega \xi_v \xi'_1| \gg |\sigma_2 + i\omega \xi_v \xi'_2|$ and $|\sigma_1| \gg |\omega \xi_v \xi'_1|$
to find the above expression as \( \frac{\sigma_p}{(2+p)^2} \approx \frac{\sigma_p}{4} \).

However, the conditions do not have to be so stringent. If \( |\sigma_1| \) and \( |\sigma_3| \gg |\omega \xi_1 \xi_0|, |\omega \xi_0 \xi_2| \) and \( |\xi_1 \Delta \xi/\tau| \), then this expression equals

\[
\frac{\sigma_p}{\left[2+p+\frac{\sigma_2}{\sigma_1}(1-p)\right]^2}.
\]

As \( \sigma_3 \) becomes large compared with \( \sigma_1 \), the expression will go to zero. At \( \sigma_3/\sigma_1 = 1 \), the expression equals \( p \) or \( 4/9 \) of the value for \( \sigma_3/\sigma_1 = 0 \). Therefore, the requirement is only that \( \sigma_3 \) be roughly the same magnitude as or less than \( \sigma_1 \).

B. Some Observations on the Mechanical Characteristics of Dried Films.

All of the films were dried during the film thickness determination procedure in order to obtain fragments for microscopic examination. The characteristics of the dried film varied considerably according to the amount of salt in the film. Films containing no sodium bromide (equilibrated in distilled water) fragmented into small pieces (~1 mm), most of which continued to adhere to the platinum slide. Observations made during the water absorption tests indicate that considerable fragmentation has occurred at 11.1% RH.
The addition of sodium bromide to the films increases the fragment size and decreases the tendency of the film to adhere to the slide after drying. In addition the time the film had to be held at 0% RH before fragmentation occurred increased with the salt content. The films containing the most salt, approximately .46 equivalents per polysalt equivalent, fragmented only with considerable difficulty. In one case, Film 250-D, the film could not be made to fragment.

These characteristics again reflect the plasticizer role that salt plays in the polysalt. The salt-free polysalt fragments due to shrinkage stresses induced by the removal of water. Addition of sodium bromide allows some relaxation of these stresses. The relaxation for the films containing the most sodium bromide becomes so significant that no fragmentation occurs.

C. Two Initial Films Tested at Relative Humidities of 51% and 0%

During the initial stages of the project two films were prepared by the standard procedure except that the polysalt gel was not thoroughly washed with distilled water or equilibrated in a sodium bromide solution. Instead, the slide was briefly dipped into the water and then dried, leaving a
considerable amount of sodium bromide in the film. The capacitance and resistance of the films was measured at 51% and 0% (over P₂O₅) at room temperature (21-25°C). The results of these tests are shown in Table XI. The 0% relative humidity tests were accomplished without film fragmentation by leaving the mercury in contact with the film forcing a very slow drying rate. Film B was dried in this way for a longer period of time than Film A; the loss tangent values and the change of capacitance with frequency for Film B during a test previous to the one reported closely resembled the reported properties for Film A. This shows that Film A was not completely dried.

The 51% relative humidity behavior of Film B closely resembles that of Film 75-A. Both the dielectric constant change with frequency and the values of the loss tangent are very similar for these two films. The sodium bromide content of Film A is less than that of Film B; the capacitance of Film A changes much less with frequency than that of Film B. In addition, the loss tangent peak occurs below 100 cps for Film A and at about 1000 cps for Film B.

The 0% relative humidity data show two interesting points. The first is the relatively small drop in dielectric constant from 51% to 0% relative humidity. Assuming the dielectric
### TABLE XI

**Dielectric Properties of Two Initial Films**

<table>
<thead>
<tr>
<th>Per Cent Relative Humidity At 21-25°C</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in m farads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>FILM A</th>
<th>Capacitance in m farads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^2</td>
<td>7.90</td>
<td>809,000</td>
<td>1.17</td>
<td></td>
<td></td>
<td>154</td>
<td>7540</td>
<td>1.37</td>
</tr>
<tr>
<td>10^4</td>
<td>5.82</td>
<td>125,500</td>
<td>0.749</td>
<td></td>
<td></td>
<td>10.0</td>
<td>3920</td>
<td>4.06</td>
</tr>
<tr>
<td>10^5</td>
<td>3.90</td>
<td>11,000</td>
<td>0.850</td>
<td></td>
<td></td>
<td>2.11</td>
<td>3120</td>
<td>2.42</td>
</tr>
<tr>
<td>10^6</td>
<td>1.69</td>
<td>1660</td>
<td>0.565</td>
<td></td>
<td></td>
<td>1.13</td>
<td>1860</td>
<td>0.758</td>
</tr>
<tr>
<td>10^7</td>
<td>0.560</td>
<td>1.2x10^8</td>
<td>0.025</td>
<td>0.2880</td>
<td>5.5x10^8</td>
<td>0.019</td>
<td>5.9x10^7</td>
<td>0.014</td>
</tr>
<tr>
<td>10^8</td>
<td>0.545</td>
<td>1.8x10^7</td>
<td>0.017</td>
<td>0.2841</td>
<td>5.9x10^7</td>
<td>0.014</td>
<td>4.2x10^6</td>
<td>0.010</td>
</tr>
<tr>
<td>10^9</td>
<td>0.532</td>
<td>1.8x10^6</td>
<td>0.017</td>
<td>0.2803</td>
<td>4.2x10^6</td>
<td>0.010</td>
<td>3x10^5</td>
<td>0.011</td>
</tr>
<tr>
<td>10^10</td>
<td>0.519</td>
<td>1.6x10^5</td>
<td>0.019</td>
<td>0.2751</td>
<td>3x10^5</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
constants are comparable with those shown in the body of the report, these values indicate that 0% RH dielectric constant is probably between 4 and 8. The differences between this value and the dielectric constant of polystyrene, approximately 2.5, is probably due to the presence of some microcrystalline sodium bromide ( \(\varepsilon' \approx 10\)) and to the effects of Maxwell-Wagner dispersion.

Secondly, there is still some low frequency polarization occurring even in this extremely dry state. This is shown by slight increases in capacitance and resistance with decreasing frequency. It is probable that equilibrium has not been attained and that a longer equilibration period would further reduce the magnitude of these changes in capacitance and resistance.
D. Summary of Data and Calculated Values


<table>
<thead>
<tr>
<th>Solution</th>
<th>Approximate Polysalt Content in % by Weight</th>
<th>Approximate Solvent Composition in wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.8</td>
<td>H₂O 57  Acetone 19  NaBr 24</td>
</tr>
<tr>
<td>2</td>
<td>18.2</td>
<td>H₂O 57  Acetone 19  NaBr 24</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>H₂O 62  Acetone 14  NaBr 24</td>
</tr>
<tr>
<td>4</td>
<td>4.2</td>
<td>H₂O 61  Acetone 14  NaBr 25</td>
</tr>
</tbody>
</table>
### 2. Polysalt Films and Dielectric Data.

**Film O - A**

**Thickness:** 8.0 microns  
**Test Temperature:** 27.5°C

Cast from ternary solution number 4.

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in myfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mymho cm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51%</td>
<td>$10^2$</td>
<td>1.140</td>
<td>1,440,000</td>
<td>0.97</td>
<td>27.0</td>
<td>26.2</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>0.705</td>
<td>621,000</td>
<td>0.36</td>
<td>16.6</td>
<td>6.03</td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>0.550</td>
<td>210,000</td>
<td>0.14</td>
<td>12.9</td>
<td>1.77</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>0.479</td>
<td>55,000</td>
<td>0.061</td>
<td>11.3</td>
<td>0.684</td>
<td>38</td>
</tr>
<tr>
<td><strong>Initial</strong></td>
<td>$10^2$</td>
<td>62.0</td>
<td>6950</td>
<td>3.75</td>
<td>1460</td>
<td>5480</td>
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Film O - B

Thickness: 6.9 microns
Test Temperature: 27.8°C

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<th>Capacitance in µfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in µmho cm</th>
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<td>280</td>
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<td>2.78</td>
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<td>7.52</td>
<td>116,000</td>
<td>1.83</td>
<td>153</td>
<td>280</td>
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<tr>
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<td>$10^3$</td>
<td>2.78</td>
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<td>0.983</td>
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<td>6,740</td>
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<td>18.2</td>
<td>4.79</td>
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**Film 6 - A**

Thickness: 13.4 microns  
Test Temperature: 27.5°C  
Cast from ternary solution number 1.

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<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mymho cm</th>
</tr>
</thead>
<tbody>
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**Film 11 - A**

Test Temperature: 27.5°C  
Cast from ternary solution number 2.

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<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
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<tbody>
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**Film 11 - B**

Test Temperature: 27.5°C  
Cast from ternary solution number 2.

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<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
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<td>Frequency in Cycles Per Second</td>
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Film 11-E

Thickness: 11.1 microns  
Test Temperature: 27.5°C  

Cast from ternary solution number 1.

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<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in μmho cm</th>
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</table>
**Film 20 - A**

Thickness: 10.0 microns  
Test Temperature: 27.5°C

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<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in μmho cm</th>
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<td>120</td>
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<tr>
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<td>$10^4$</td>
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<tr>
<td></td>
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</table>

**Film 20 - B**

Thickness: 11.1 microns  
Test Temperature: 27.8°C

<table>
<thead>
<tr>
<th>Initial</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in μmho cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2$</td>
<td></td>
<td>5.20</td>
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<td>1010</td>
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<tr>
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<td>$10^5$</td>
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<td>11,300</td>
<td>0.267</td>
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<td>5.53</td>
<td>308</td>
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<tr>
<td>51% after</td>
<td>$10^2$</td>
<td>8.29</td>
<td>45,000</td>
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<td>323</td>
<td>1230</td>
<td>68.7</td>
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<tr>
<td>2.7 days</td>
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<td>1.49</td>
<td>36,300</td>
<td>2.95</td>
<td>58.1</td>
<td>171</td>
<td>95.5</td>
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<td>at 75%</td>
<td>$10^4$</td>
<td>0.772</td>
<td>23,700</td>
<td>0.870</td>
<td>30.2</td>
<td>26.3</td>
<td>147</td>
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<tr>
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<td>0.305</td>
<td>19.9</td>
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<td>229</td>
<td>1140</td>
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<td>total at</td>
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</table>
Film 75-A

 Thickness: 20.0 microns  
 Test Temperature: 27.5°C

<table>
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<tr>
<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mho cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>51%</td>
<td>$10^2$</td>
<td>72.2</td>
<td>12,180</td>
<td>1.81</td>
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<td>7700</td>
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<tr>
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<td>3.94</td>
<td>368</td>
<td>1450</td>
<td>806</td>
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<tr>
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<td>77.5</td>
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Film 75-B

 Thickness: 7.75 microns  
 Test Temperature: 27.8°C

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<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mho cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2$</td>
<td>8890</td>
<td>19.9</td>
<td>0.90</td>
<td>203,000</td>
<td>183,000</td>
<td>102,000</td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>$10^4$</td>
<td>622</td>
<td>8.4</td>
<td>3.05</td>
<td>14,200</td>
<td>43,400</td>
<td>242,000</td>
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<tr>
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<td>6.7</td>
<td>6.7</td>
<td>810</td>
<td>5,430</td>
<td>303,000</td>
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</table>

<table>
<thead>
<tr>
<th>After 5 days at 92.5%</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mho cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2$</td>
<td>5834</td>
<td>18.9</td>
<td>1.45</td>
<td>132,000</td>
<td>192,000</td>
<td>107,000</td>
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<tr>
<td>$10^3$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^4$</td>
<td>336</td>
<td>12.0</td>
<td>3.95</td>
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<td>30,300</td>
<td>169,000</td>
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<tr>
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<td>10.0</td>
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<td>504</td>
<td>3,660</td>
<td>204,000</td>
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<table>
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<th>Initial 75% after 2 days</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mho cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^2$</td>
<td>1095</td>
<td>1170</td>
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<td>25,000</td>
<td>31,000</td>
<td>1730</td>
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<tr>
<td>$10^3$</td>
<td>131.</td>
<td>600</td>
<td>2.02</td>
<td>2990</td>
<td>6040</td>
<td>3370</td>
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</tr>
<tr>
<td>$10^4$</td>
<td>10.4</td>
<td>374</td>
<td>4.09</td>
<td>237</td>
<td>970</td>
<td>5410</td>
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</tr>
<tr>
<td>$10^5$</td>
<td>1.52</td>
<td>303</td>
<td>3.74</td>
<td>34.6</td>
<td>129</td>
<td>7200</td>
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Film 75-B (Continued)

Thickness: 7.75 microns
Test Temperature: 27.8°C

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<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in m(\mu)farads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in m(\mu)mho cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 5 days at 75%</td>
<td>(10^2)</td>
<td>888</td>
<td>1402</td>
<td>1.28</td>
<td>20,300</td>
<td>26,000</td>
<td>1450</td>
</tr>
<tr>
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<td>743</td>
<td>1.96</td>
<td>2,500</td>
<td>4,900</td>
<td>2730</td>
</tr>
<tr>
<td></td>
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<td>461</td>
<td>3.69</td>
<td>214</td>
<td>790</td>
<td>4400</td>
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<tr>
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<td>(10^5)</td>
<td>1.44</td>
<td>365</td>
<td>3.03</td>
<td>32.8</td>
<td>99.4</td>
<td>5540</td>
</tr>
<tr>
<td>At 65%</td>
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<td>4110</td>
<td>3440</td>
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<td>(10^3)</td>
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<td>2,311</td>
<td>1.61</td>
<td>978</td>
<td>1576</td>
<td>879</td>
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<td>296</td>
<td>1650</td>
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<td>903</td>
<td>1.94</td>
<td>20.7</td>
<td>40.1</td>
<td>2240</td>
</tr>
<tr>
<td>At 51%</td>
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<td>101.1</td>
<td>17,000</td>
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<td>2300</td>
<td>2130</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>(10^3)</td>
<td>16.0</td>
<td>5340</td>
<td>1.87</td>
<td>364</td>
<td>681</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td>(10^4)</td>
<td>1.64</td>
<td>3340</td>
<td>2.91</td>
<td>37.4</td>
<td>109</td>
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<td>(10^5)</td>
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<td>2280</td>
<td>1.12</td>
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<td>16.0</td>
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</tr>
<tr>
<td>At 33%</td>
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<td>565</td>
<td>961</td>
<td>53.6</td>
</tr>
<tr>
<td></td>
<td>(10^3)</td>
<td>2.27</td>
<td>22,200</td>
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<td>51.8</td>
<td>164</td>
<td>91.5</td>
</tr>
<tr>
<td></td>
<td>(10^4)</td>
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<td>15.4</td>
<td>23.2</td>
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<td></td>
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<td>0.506</td>
<td>8.85</td>
<td>4.48</td>
<td>2500</td>
</tr>
</tbody>
</table>
Film 75-C

Thickness: 8.7 microns
Test Temperature: 27.8°C

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<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in mufarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mhos cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial 51%</td>
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<td>1250</td>
<td>2.63</td>
<td>13,100</td>
<td>34,400</td>
<td>1920</td>
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<td>10^4</td>
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<td>931</td>
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<td>4,390</td>
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<tr>
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<td>10^5</td>
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<td>729</td>
<td>3.41</td>
<td>164</td>
<td>560</td>
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<td>10^6</td>
<td>2.34</td>
<td>486</td>
<td>1.40</td>
<td>59.5</td>
<td>83.3</td>
<td>4650</td>
</tr>
<tr>
<td>51% after 2.7 days at 75%</td>
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<td>19,300</td>
<td>36,100</td>
<td>2020</td>
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<td>10^4</td>
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<td>713</td>
<td>3.85</td>
<td>1490</td>
<td>5740</td>
<td>3200</td>
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<td>10^5</td>
<td>6.27</td>
<td>567</td>
<td>4.47</td>
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<td>720</td>
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<td>1.80</td>
<td>54.6</td>
<td>98.5</td>
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<td>51% after 5.7 days at 75%</td>
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<td>2.14</td>
<td>2340</td>
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<tr>
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<td>15.5</td>
<td>865</td>
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<tr>
<td>51% after 8.7 days at 75%</td>
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<td>1600</td>
<td>1280</td>
<td>71.5</td>
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<td>0.831</td>
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Film 250-A

Thickness: 11.0 microns  
Test Temperature: 27.5°C  
Cast from ternary solution number 3.

<table>
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<tr>
<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in µfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in µmho cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>51%</td>
<td>$10^2$</td>
<td>2370</td>
<td>462</td>
<td>1.46</td>
<td>76,400</td>
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</tr>
<tr>
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<td>253</td>
<td>3.89</td>
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<td>11,300</td>
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<tr>
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<td>13,800</td>
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<tr>
<td></td>
<td>$10^5$</td>
<td>3.77</td>
<td>164</td>
<td>2.57</td>
<td>122</td>
<td>314</td>
<td>17,500</td>
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</table>

Film 250-B

Thickness: 11.4 microns  
Test Temperature: 27.5°C  
Cast from ternary solution number 3.

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<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in µfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in µmho cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>51%</td>
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<td>2770</td>
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<td>0.97</td>
<td>91,100</td>
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</tr>
<tr>
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<td>$10^3$</td>
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<td>11,100</td>
<td>25,100</td>
<td>14,100</td>
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<td>125</td>
<td>440</td>
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Film 250-C

Thicknness: 10.2 microns  
Test Temperature: 27.8°C  
Cast from ternary solution number 4.

<table>
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<tr>
<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in μmhos cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>At 92.5%</td>
<td>$10^2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>7800</td>
<td>2.1</td>
<td>0.971</td>
<td>238,000</td>
<td>231,000</td>
<td>1,290,000</td>
</tr>
<tr>
<td>Initial 75%</td>
<td>$10^2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>5270</td>
<td>35.6</td>
<td>0.85</td>
<td>158,000</td>
<td>134,000</td>
<td>74,800</td>
</tr>
<tr>
<td>after 2 days</td>
<td>$10^5$</td>
<td>901</td>
<td>12.1</td>
<td>1.45</td>
<td>27,200</td>
<td>39,400</td>
<td>220,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>119</td>
<td>6.8</td>
<td>1.97</td>
<td>3560</td>
<td>7010</td>
<td>391,000</td>
</tr>
<tr>
<td>After 3 days</td>
<td>$10^2$</td>
<td>5230</td>
<td>299</td>
<td>1.02</td>
<td>157,000</td>
<td>160,000</td>
<td>8920</td>
</tr>
<tr>
<td>at 75%</td>
<td>$10^4$</td>
<td>1610</td>
<td>86.4</td>
<td>1.15</td>
<td>48,500</td>
<td>55,800</td>
<td>31,100</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>145</td>
<td>72.5</td>
<td>1.51</td>
<td>4360</td>
<td>6590</td>
<td>36,700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.3</td>
<td>45.3</td>
<td>1.65</td>
<td>640</td>
<td>1060</td>
<td>59,100</td>
</tr>
<tr>
<td>After 4 days</td>
<td>$10^2$</td>
<td>2290</td>
<td>631</td>
<td>1.10</td>
<td>68,600</td>
<td>75,500</td>
<td>4210</td>
</tr>
<tr>
<td>at 75%</td>
<td>$10^4$</td>
<td>479</td>
<td>275</td>
<td>1.21</td>
<td>14,400</td>
<td>17,400</td>
<td>9700</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>50.6</td>
<td>234</td>
<td>1.34</td>
<td>1520</td>
<td>2040</td>
<td>11,400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.9</td>
<td>101.5</td>
<td>1.76</td>
<td>267</td>
<td>470</td>
<td>26,200</td>
</tr>
</tbody>
</table>
**Film 250-C (Continued)**

Thickness: 10.2 microns  
Test Temperature: 27.8°C

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in myfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in mhos cm¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>After</strong></td>
<td>$10^2$</td>
<td>510</td>
<td>3110</td>
<td>1.00</td>
<td>15,400</td>
<td>15,400</td>
<td>860</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>132</td>
<td>1274</td>
<td>0.947</td>
<td>3960</td>
<td>3750</td>
<td>2090</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>18.6</td>
<td>676</td>
<td>1.26</td>
<td>561</td>
<td>707</td>
<td>3950</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>3.09</td>
<td>230</td>
<td>2.24</td>
<td>92.7</td>
<td>208</td>
<td>11,600</td>
</tr>
<tr>
<td><strong>At 65%</strong></td>
<td>$10^2$</td>
<td>150.6</td>
<td>9850</td>
<td>1.08</td>
<td>4500</td>
<td>4860</td>
<td>272</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>36.6</td>
<td>3370</td>
<td>1.30</td>
<td>1095</td>
<td>1420</td>
<td>792</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>10.48</td>
<td>919</td>
<td>1.65</td>
<td>318</td>
<td>525</td>
<td>2930</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>2.36</td>
<td>337</td>
<td>2.01</td>
<td>70.7</td>
<td>142</td>
<td>7920</td>
</tr>
<tr>
<td><strong>At 51%</strong></td>
<td>$10^2$</td>
<td>99.6</td>
<td>18,400</td>
<td>0.867</td>
<td>3000</td>
<td>2600</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>25.8</td>
<td>6620</td>
<td>0.933</td>
<td>775</td>
<td>723</td>
<td>403</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>5.17</td>
<td>1900</td>
<td>1.62</td>
<td>155</td>
<td>251</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>6.94</td>
<td>1000</td>
<td>2.28</td>
<td>20.8</td>
<td>47.4</td>
<td>2640</td>
</tr>
<tr>
<td><strong>At 33%</strong></td>
<td>$10^2$</td>
<td>47.1</td>
<td>40,600</td>
<td>0.829</td>
<td>1420</td>
<td>1180</td>
<td>65.8</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>10.64</td>
<td>11,000</td>
<td>1.36</td>
<td>319</td>
<td>434</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>1.185</td>
<td>5170</td>
<td>2.59</td>
<td>35.6</td>
<td>92.3</td>
<td>515</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>0.314</td>
<td>3560</td>
<td>1.42</td>
<td>9.37</td>
<td>13.3</td>
<td>742</td>
</tr>
</tbody>
</table>
Film 250-D

**Thickness:** -  
**Test Temperature:** 27.8°C  
**Cast from ternary solution number 3.**

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in m(\mu)farads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>(10^2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>51%</td>
<td>(10^4)</td>
<td>10,900</td>
<td>33.2</td>
<td>0.439</td>
</tr>
<tr>
<td></td>
<td>(10^5)</td>
<td>2090</td>
<td>4.53</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>(10^6)</td>
<td>136</td>
<td>2.8</td>
<td>4.18</td>
</tr>
</tbody>
</table>

At 51%

<table>
<thead>
<tr>
<th>after temperature fluctuations in constant temperature box *</th>
<th>(10^3)</th>
<th>9830</th>
<th>545</th>
<th>0.297</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10^4)</td>
<td>6690</td>
<td>45.1</td>
<td>0.527</td>
</tr>
<tr>
<td></td>
<td>(10^5)</td>
<td>1190</td>
<td>7.5</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>(10^6)</td>
<td>80</td>
<td>4.7</td>
<td>4.24</td>
</tr>
</tbody>
</table>

At 51%

<table>
<thead>
<tr>
<th>after 2.5 days at 75%</th>
<th>(10^3)</th>
<th>1100</th>
<th>2410</th>
<th>0.601</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 days after 75%</td>
<td>(10^4)</td>
<td>391</td>
<td>507</td>
<td>0.800</td>
</tr>
<tr>
<td></td>
<td>(10^5)</td>
<td>48.6</td>
<td>151</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>(10^6)</td>
<td>2.97</td>
<td>105</td>
<td>5.12</td>
</tr>
</tbody>
</table>

At 51% after an additional 1.5 days at 92.5%

<table>
<thead>
<tr>
<th>92.5%</th>
<th>(10^3)</th>
<th>797</th>
<th>2980</th>
<th>0.672</th>
</tr>
</thead>
<tbody>
<tr>
<td>an additional 1.5 days at 92.5%</td>
<td>(10^4)</td>
<td>221</td>
<td>747</td>
<td>0.965</td>
</tr>
<tr>
<td>92.5%</td>
<td>(10^5)</td>
<td>23.5</td>
<td>288</td>
<td>2.36</td>
</tr>
<tr>
<td>92.5%</td>
<td>(10^6)</td>
<td>1.77</td>
<td>197</td>
<td>4.56</td>
</tr>
</tbody>
</table>

At 92.5%

| \(10^2\) | - | - | - |
| \(10^3\) | - | - | - |
| \(10^4\) | - | - | - |
| \(10^5\) | - | - | - |
| \(10^6\) | - | - | - |

* Caused by burnout of heating element in box.
3. Unsymmetric Polysalt Film
   
a) Polysalt Solution Using Ternary Solvent
   
   Approximate Polysalt Content    - 25 wt%
   
   Approximate Solvent Composition - 59 wt% H₂O
                                       18 wt% Acetone
                                       23 wt% NaBr
b) Dielectric Properties

Thickness: 13.0 microns  
Test Temperature: 27.5°C

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Frequency in Cycles Per Second</th>
<th>Capacitance in μfarads</th>
<th>Resistance in ohms</th>
<th>Loss Tangent</th>
<th>Relative Dielectric Constant</th>
<th>Relative Loss Factor</th>
<th>Conductivity in μmho cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial 51%</td>
<td>$10^2$</td>
<td>9370</td>
<td>535</td>
<td>0.318</td>
<td>358,000</td>
<td>114,000</td>
<td>6340</td>
</tr>
<tr>
<td></td>
<td>$10^3$</td>
<td>6220</td>
<td>78.2</td>
<td>0.328</td>
<td>238,000</td>
<td>73,000</td>
<td>43,300</td>
</tr>
<tr>
<td></td>
<td>$10^4$</td>
<td>2920</td>
<td>8.2</td>
<td>0.664</td>
<td>112,000</td>
<td>74,300</td>
<td>413,000</td>
</tr>
<tr>
<td></td>
<td>$10^5$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>At 51% after</td>
<td>$10^2$</td>
<td>4610</td>
<td>508</td>
<td>0.681</td>
<td>176,500</td>
<td>120,000</td>
<td>6670</td>
</tr>
<tr>
<td>Standing</td>
<td>$10^3$</td>
<td>1750</td>
<td>138</td>
<td>0.658</td>
<td>67,000</td>
<td>44,700</td>
<td>24,500</td>
</tr>
<tr>
<td>2 1/2 days</td>
<td>$10^4$</td>
<td>650</td>
<td>28</td>
<td>0.876</td>
<td>24,900</td>
<td>21,800</td>
<td>121,000</td>
</tr>
<tr>
<td>at 92.5%RH</td>
<td>$10^5$</td>
<td>107</td>
<td>7.1</td>
<td>2.10</td>
<td>4100</td>
<td>8600</td>
<td>476,000</td>
</tr>
</tbody>
</table>
4. Water Absorption Tests

Temperature: 24.5°C

<table>
<thead>
<tr>
<th>Normality of NaBr solution</th>
<th>Per Cent Relative Humidity</th>
<th>Approximate Weight of dry film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film was equilibrated in</td>
<td>92.5 75.3 64.4 51.0 33.0 11.1 No Film</td>
<td></td>
</tr>
<tr>
<td>.25 balance reading*</td>
<td>.53 6.31 7.21 7.98 8.78 9.60 21.31</td>
<td>5.76 milligrams</td>
</tr>
<tr>
<td>water content in gms H₂O per 100 gms of dry film</td>
<td>84.6 33.2 25.2 18.4 11.3 4.0</td>
<td></td>
</tr>
<tr>
<td>water content in gms H₂O per 100 gms of dry film</td>
<td>39.6 24.4 19.2 14.8 9.9 3.4</td>
<td></td>
</tr>
<tr>
<td>water content in gms H₂O per 100 gms of dry film</td>
<td>31.1 23.6 19.7 15.3 10.0 3.3</td>
<td></td>
</tr>
<tr>
<td>distilled water balance reading*</td>
<td>7.875 8.67 9.11 9.525 10.00 20.71</td>
<td>4.85 milligrams</td>
</tr>
<tr>
<td>water content in gms H₂O per 100 gms of dry film</td>
<td>30.2 22.1 17.7 13.5 8.6</td>
<td></td>
</tr>
</tbody>
</table>

* balance reading decreases as weight increases
E. The Effect of Relative Humidity on Dielectric Properties: Initial Tests

The dielectric properties of two of the films discussed in Section G of the Discussion of Results, Film 0-A and Film 11-E, were also measured after equilibration at 92.5% RH to determine the effect of a change in relative humidity. The films were then held at this relative humidity for a fairly long period of time, 9 days and 1 month for Film 0-A and Film 11-E, respectively, and the dielectric properties re-determined. The relative humidity was lowered to 51% RH and the films re-tested at this condition. Figures 38, 39 and 40 show the results of these tests for Film 0-A, the salt-free film. The dielectric constant, loss factor and loss tangent at 92.5% RH were all appreciably higher than those at 51% RH, increasing by as much as a factor of 16 at 100 cps. However, the final values at 92.5% RH differed from the initial ones. Both the dielectric constant and the loss factor curves dropped in magnitude, while the loss tangent peak appears to have shifted to a slightly lower frequency. In addition, the dielectric properties did not return to their original values when the film was re-tested at 51% RH. The magnitudes of both the loss tangent and loss factor decreased. While the absolute difference between the dielectric constant curves at high frequency is within experimental error, the divergence of the curves at low frequency also indicates that a change in dielectric behavior occurred.

Figures 41 and 42 show the results for Film 11-E, a film equilibrated in the 0.011N sodium bromide solution. The dielectric constant was again much larger at 92.5% RH than at 51% RH. The dielectric constant at 92.5% RH decreased after being held at this relative humidity for a month. In addition, the dielectric constant at 51% RH loss tangent
Figure 38.
The Effect of Relative Humidity on the Dielectric Constant: Film O-A

**FILM O-A**

Temperature: 27.5 °C

- □ - initial 51% RH
- ○ - initial 92.5% RH
- × - after 9 days at 92.5% RH
- △ - at 51% RH after above sequence

Dielectric Constant $\varepsilon'$

log$_{10}$ frequency (cps)
Figure 39.
The Effect of Relative Humidity on the Loss Factor: Film 0-A

FILM 0-A
Temperature: 27.8°C
- initial 51% RH
- initial 92.5% RH
- after 9 days at 92.5% RH
- at 51% RH after above sequence

log_{10} frequency (cps)
Figure 40. The Effect of Relative Humidity on the Loss Tangent: Film O-A

FILM O-A
Temperature: 27.5°C

- □ - initial 51% RH
- ○ - initial 92.5% RH
- × - after 9 days at 92.5% RH
- ▲ - at 51% RH after above sequence
Figure 41.
The Effect of Relative Humidity on the Dielectric Constant: Film 11-E
curve remained almost the same.

These tests show first that the relative humidity at which the films are equilibrated has a large effect on their dielectric properties. Secondly, the tests show that the dielectric properties depend on the moisture content history. All of the films tested to find the effect of salt content were quickly dried from the gel state to 51% RH. Films 0-A and 6-A were placed directly in the constant temperature test desicatords. The other films were initially held for a one to seven day period in a desicatord kept in the room. It is possible, but unlikely, that the fluctuated room temperature exposed these films to relative humidities sufficiently high to allow changes in the dielectric properties similar to those observed at 92.5% RH. (This could occur if the temperature of the film followed the room temperature fluctuations more closely than did the partial pressure of water in the gas surrounding the film. However, for this effect to be appreciable, extremely rapid temperature changes of several degrees would be necessary. This does not seem likely because the tests were carried out in the late fall and early winter when room temperature was fairly constant.) After the testing at 51% RH had started, no change in dielectric properties with time was observed.
F. NOMENCLATURE

\( a, b, c \) - length of three axes of ellipsoid, cm.

\( B \) - constant of proportionality

\( C(y, z) \) - circumference normal to \( x \) axis at a given point on \( x \) axis, cm.

\( C \) - capacitance, farads

\( d \) - thickness of shell on sphere

\( D \) - displacement field, volts per cm.

\( e_0 \) - charge of an electron, statcoulomb

\( E \) - electric field, volts per cm.

\( F \) - effective electric field, volts per cm.

\( i \) - imaginary operator

\( I \) - electric current, amperes

\( k \) - Boltzmann constant, ergs per \( ^\circ \)K

\( k \) - complex conductivity, mho per cm.

\( l \) - thickness, cm.

\( m \) - average dipole moment, statcoulomb cm per molecule

\( n \) - molecular density, molecules per cc.

\( p \) - volume fraction

\( P \) - polarization field, volts per cm.

\( Q \) - charge, statcoulomb

\( R \) - radius of sphere, cm

\( t \) - time, seconds

\( T \) - temperature, \( ^\circ \)K

\( \mu \) - ion mobility
$\mathbf{u}$ - potential energy, ergs
$x, y, z$ - three axes of ellipsoid, cm
$X$ - shape factor
$y (\tau)$ - relaxation time distribution function, sec.$^{-1}$
$Z$ - impedance, ohms
$\kappa$ - polarizability
$\varepsilon^*$ - complex dielectric constant
$\varepsilon'$ - real dielectric constant
$\varepsilon''$ - loss factor
$\varepsilon_v$ - dielectric constant of vacuum, farads per cm.
$\theta$ - angle between dipole moment and electric field, radians
$\lambda$ - surface conductivity
$\mu$ - permanent dipole moment, statcoulomb cm per molecule
$\sigma$ - conductivity, mho per cm.
$\phi_0$ - ion density in the double-layer, molecules per square cm.
$\tau$ - relaxation time, seconds
$\phi$ - impedance phase angle, radians
$\omega$ - frequency, radians per second
$\Omega$ - solid angle, radians
G. Literature Citations

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H. Biographical Note

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