THE DIELECTRIC PROPERTIES OF NON-STOICHIOMETRIC POLYELECTROLYTE COMPLEXES

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ABSTRACT

THE DIELECTRIC PROPERTIES OF NON-STOICHIOMETRIC POLYELECTROLYTE COMPLEXES

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David Austin Opp

Submitted to the Department of Chemical Engineering on May 16, 1965 in partial fulfillment of the requirements for the degree of Materials Engineer.

This study focused on the dielectric characteristics of non-stoichiometric complexes formed by co-reacting poly (vinylbenzyltrimethyl ammonium) with excess amounts of poly (styrene sulfonate). Cast films (using ternary solvent solutions of the complexes) were prepared containing three levels of sulfonate excess. These films were subsequently treated in dilute electrolyte solutions to prepare films with H⁺, Na⁺, or Ca⁡⁺⁺ counterions attached to the pendant sulfonate groups. The dielectric behavior was then investigated as a function of frequency, moisture content, counter-ion type, and sulfonate excess. The frequency range utilized in the study (10² - 10¹⁰ c/s) was chosen to allow a better interpretation of the dispersion phenomena.

The non-stoichiometric materials exhibited high dielectric constants and loss factors as well as broad dispersion which was very similar to that observed by Falkenstein for neutral materials containing sorbed NaBr electrolyte and/or moisture. The dielectric constants, ε', and loss factors ε'' ranged from ( > 10⁶ ) at 10² c/s to ( < 5) at 10¹⁰ c/s. The values of ε' and ε'' increased with increased residual ion content (related to sulfonate excess), increased moisture content, increased aqueous ion mobility (H⁺ > Na⁺ > Ca⁡⁺⁺), and decreased frequency.

The discrete domain concept (based on the Schwarz model) utilized by Falkenstein applies equally well to the data developed in this study. However, careful analysis revealed that at least two polarization mechanisms may have been operating simultaneously - electrode polarization and heterogeneous polarization. At the moisture contents achieved in this study (at 33 and 65% R.H.) evidence suggests that electrode polarization is the dominant mechanism below 100 KC. This view was supported by a voltage gradient analysis.

Thesis Supervisor: Alan S. Michaels
Title: Professor of Chemical Engineering

Thesis Supervisor: Harris J. Bixler
Title: Formerly Assistant Professor of Chemical Engineering
Dear Professor Greene:

The attached thesis entitled, "The Dielectric Properties of Non-Stoichiometric Polyelectrolyte Complexes", is hereby submitted in partial fulfillment of the requirements for the degree of Materials Engineer.

Respectfully submitted,

David A. Opp
Acknowledgements

The author sincerely appreciates the advice and assistance offered by his advisor Dr. H. Bixler during all stages of the thesis. The assistance of Professor A. Michaels and Dr. N. Schneider in the formulation of the thesis topic and during the early stages of the thesis development is also gratefully acknowledged.

Special thanks and acknowledgements are due Mr. William Westphal of the Laboratory for Insulation Research, M.I.T. The technical advice and assistance which he provided in all areas related to the measurement and interpretation of the electrical parameters investigated in this study enabled the author to significantly advance his understanding of these topics.

The author wishes to acknowledge the financial support provided by the International Business Machines Corporation thru its Resident Graduate Study Program which made this year of graduate study possible.

The non-stoichiometric polycrystalline materials used in this study were provided by the Amicon Corporation, Cambridge.

In the development of this thesis there were many more forms of assistance not the least of which was the patience and understanding provided by my wife and children.
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I. Summary

A. Background and Objectives

Previous investigators (7, 22) concerned with the dielectric characteristics of the complexes formed by the co-reaction of poly (styrene sulfonate) and poly (vinyl benzyl trimethyl ammonium) observed that anomalously high dielectric constant values ($\geq 10^3$) could be achieved at laboratory ambient conditions. These high dielectric constants were observed for both non-stoichiometric reaction products and for stoichiometric complexes containing electrolytes such as NaBr. The materials under these testing conditions exhibited consistently decreasing dielectric constant values throughout the frequency testing range of $10^2$-$10^5$ c/s. The dielectric constants of the stoichiometric samples containing electrolyte (NaBr) were observed to rise with increasing electrolyte concentrations at a given humidity level and with moisture content at a given electrolyte concentration.

Dielectric behavior similar in character to that determined for the polyelectrolyte complexes had previously been observed for biocolloid systems such as muscle tissue. From the many molecular models and theories proposed to explain biocolloid dielectric response, Falkenstein concluded that the recently developed Schwarz model seemed to yield qualitative agreement with the polyelectrolyte complex behavior. In the Schwarz model the tendency of the field to form the double layer ions (on the surface of a sphere) into a dipole is opposed by a diffusive flux which tends to re-establish a random configuration. The dielectric constant of the system is shown to depend on the size of the sphere and the ion mobility.

In this study it was planned to analyze the dielectric behavior of non-stoichiometric complexes of poly (styrene sulfonate) and poly (vinylbenzyl trimethyl ammonium) containing an excess amount of sulfonate and its associated counter-ion, as a function of relative humidity and frequency. The exchange of the counter-ion associated with the sulfonate group was contemplated since this would enable investigation of the influence of counter-ion mobility and therefore provide a link to the Schwarz model and previous studies. In addition
several improvements in experimental techniques including extension of the frequency testing range were planned. This latter feature was included to enable a more complete analysis of dielectric dispersion. The ultimate goal of the study was to broaden our understanding of the molecular structure of the polyelectrolyte reaction product.

B. Experimental Procedures

Using non-stoichiometric polysalt (dry powder) as supplied by the Amicon Corporation, Cambridge, Mass., casting solutions were prepared with an HCl-Dioxane-H₂O ternary solvent system. Films were subsequently formed by casting the solution on glass and evaporating the solvents. The as-cast films were placed in dilute HCl to insure that the film contained H⁺ as the counter-ion associated with the excess sulfonate groups. Representative samples from each of three series of films with different polyelectrolyte equivalence ratios were then placed in HCl, NaCl and CaCl₂ solutions. This procedure produced a set of samples containing either H⁺, Na⁺, or Ca⁺⁺ as the counter-ion associated with the sulfonate group for three levels of sulfonate excess (three degrees of stoichiometry). After suitable controlled humidity conditioning procedures the appropriate samples for dielectric tests were cut from the film samples.

Due to the fragility of the thin (approximately 5 mil) specimens, separate specimens were utilized for the moisture content studies and for dielectric tests. This pair of specimens was subjected to exactly the same environmental conditions throughout the investigation. For measurements in the frequency range 10²-10⁷ cps the dielectric specimens were mounted in cells of the type shown in Figure 3. In this frequency range capacitance measurements were made using a Schering type bridge with basically a resistance-capacitance substitution technique. At 8520 MC measurements were made using specimens mounted in a wave guide with a transverse electromagnetic standing wave and traveling wave detector technique. The dielectric measurements were performed initially with specimens conditioned at 65% R.H. and then repeated after re-conditioning the specimen at 33% R.H. Three representative samples were subsequently re-conditioned to 65% and remeasured.
Moisture contents were obtained from the film weights at 33% R.H. and 65% R.H. and the dry film weights established after drying the film under vacuum in a vacuum dessicator over P₂O₅. Residual ion contents were obtained using flame photometry techniques.

C. Discussion and Interpretation of the Results

(1) Moisture Content:

The apparent moisture contents of the non-stoichiometric materials increased with increasing relative humidity and with increasing sulfonate excess in the as-cast films. It was possible to extrapolate the moisture content data for the non-stoichiometric films containing the H⁺ counter-ion in a reasonable manner to the values determined by Falkenstein (7) for neutral samples.

A compilation of all available moisture sorption data for the polysalt systems revealed that the apparent moisture contents for neutral polysalt (Falkenstein) or non-stoichiometric polysalt (this study) were lower for a given humidity level than the values established by Gray (15) using neutral polysalt. The technique utilized by Falkenstein to establish his dry film weights required extrapolation of the observed linear moisture content vs relative humidity relationship to 0% humidity. Due to the fact that a sharp break exists in this relationship as shown by Gray and investigations on sulfonated ion exchange resins, this approach fails to account for approximately .15 gm H₂O/gm polysalt. The moisture contents noted in this study when plotted versus relative humidity exhibited similar slopes in the linear region as the neutral film samples.

By comparison to studies on sulfonated ion exchange resins the data observed for the non-stoichiometric materials are also felt to be in error by about .15 gm H₂O/gm polysalt. The error is attributed to the formation of a "skin" at the air-polymer interface due to the collapse of the network which traps moisture in the bulk of the sample. Correction of the data yields the expected result that the moisture sorption of the non-stoichiometric materials is greater at a given humidity then the stoichiometric materials.
Due to the fact that the non-stoichiometric samples exhibit an apparent linear sorption behavior in the region of 33-65% R.H., it is believed that the water is being added as "free" water rather than being incorporated into any ion hydration shell. Ion hydration data (17) supports this belief.

(2) Residual Ion Content

Correlation of the residual ion content in millequivalents/gram dry polysalt with the millequivalents of excess sulfonate/gram dry polysalt indicates that the exchange of counter-ion was approximately complete in every case. The agreement was well within experimental accuracy. The data support the belief that in the exchange process the Ca++ ion replaces two H+ ions and thereby associates with two pendant anionic groups (sulfonate) whereas the Na+ ion associates only with one group. The Ca++ ion as a result forms a "ionic" crosslink.

(3) Dielectric Behavior

The dielectric properties of the non-stoichiometric films were quite sensitive to ion content, ion type and moisture content. The specimens behaved in a manner quite similar to the neutral films with sorbed electrolytes studied by Falkenstein. As a result the data could be analyzed using the concept of "discrete domains" as utilized by Falkenstein. In this approach it is believed that a domain exists (on a microscale basis) where a pendant sulfonate group is associated with a hydrated counter-ion. Each distinct domain is thought to act as a separate polarizable element. The effects of ion content, moisture content and frequency seem to be reasonably explained by consideration of their influence on the number, size and polarity of the discrete domains.

Unfortunately the observed results can be shown to be partially the result of a simultaneous electrode polarization mechanism. Those factors which serve to increase heterogeneous polarization also act to increase electrode polarization. Techniques by which this polarization component can be minimized will be discussed in a later section.

(a) As a function of water content

The dielectric constant, $\varepsilon'$, at constant frequency is noted to rise with increasing moisture content. When this data is considered for a series of compositions of a given ion type it is observed that a
family of curves exist for the various ion types which tend to intersect at a common moisture content and high dielectric constant value. Increasing the frequency shifts the family of curves laterally to higher moisture contents.

The mutual intersection point is believed to represent that point where the domain structure has collapsed and the dielectric behavior is predominantly due to electrode polarization. Two factors serve to modify the effective domain size—the ion mobility and the imposed voltage frequency. Increasing the frequency (for a given ion type and moisture content) will act to reduce the effective path length (domain size) of the charge carrier while an increase in ion mobility will increase the effective path length. Increase of the domain size is thought to introduce greater polarization for that element. The addition of water to the matrix is thought to counter balance the decreased "effective" domain size due to increased frequency as a result of its action to increase the "effective" path length of the charge carrier. Therefore the intersection point of the family of curves for various ions shifts to higher moisture contents with increasing frequency while remaining at approximately the same high value of \( \varepsilon' \).

(b) As related to residual ion type and content

In general, the effect of changing ion type was to shift the \( \varepsilon' \) vs. frequency curve along the frequency axes. The shift is exactly related to the aqueous ionic mobility of the ions. \( H^+ > Na^+ > Ca^{++} \). This relation was very pronounced at low humidities. At high humidity (65% RH) the monovalent ion films seemed to act in a virtually identical manner. (This is undoubtedly the result of electrode polarization effects.) The shift of the curves to higher frequencies indicates a trend toward shorter relaxation times. This result is in agreement with the Schwarz model and the domain concept. As was noted in Falkenstein's studies with NaBr, the dielectric constant values increased with an increase in residual ion content.

In terms of the domain concept, the increased ion content leads to a greater number of polarizable elements and hence an increase in \( \varepsilon' \) at a given frequency.
(c) As a function of frequency

Every specimen investigated in this study exhibited a decreasing dielectric constant $\varepsilon'$ and loss factor $\varepsilon''$ with increasing frequency. In this respect the materials were analogous to those studied by Falkenstein. The incremental change in both $\varepsilon'$ and $\varepsilon''$ over the frequency range $10^2$ to $10^{10}$ c/s was approximately the same for the monovalent ($H^+$, $Na^+$) counter-ion samples while that for the divalent ($Ca^{++}$) sample was substantially lower. Furthermore the incremental change in $\varepsilon'$ and $\varepsilon''$ decreased with decreasing sulfonate excess in the films. A major cause of the pronounced decrease in $\varepsilon'$ and $\varepsilon''$ (approximately 4-6 decades) at a given moisture content is attributed to reduced electrode polarization.

(d) As related to degree of non-stoichiometry

The general trend observed at constant frequency was an increase in $\varepsilon'$ with increasing sulfonate excess in the original as-cast films. The increased sulfonate content is directly linked to an increased density of polarizable elements and hence increased $\varepsilon'$ values as pointed out earlier.

(5) Comments on the Anomalous Dielectric Behavior

Prior to any attempt to develop a model for the internal structure of the polysalt from the dielectric data it is necessary to consider the various mechanisms by which the observed high dielectric constants and losses, large phase shifts and broad dispersion regions occur. Reference to values of dielectric constants and characteristic dispersion zone sizes for systems which exhibit homogeneous or heterogeneous polarization indicates that these mechanisms can not be the total answer. Another mechanism that can not yet be ruled out is electrode polarization. This mechanism has been shown to have a considerable effect on the measured values of biological materials and electrolytic solutions especially at frequencies below $10^5$ c/s. As will be pointed out in the following paragraphs, it is concluded that the data developed in this and previous studies on the polysalt complexes contain at least two polarization mechanisms (heterogeneous and electrode) acting simultaneously at frequencies below about $10^5$ c/s.
(a) Electrode polarization

During the course of this study several observations were made that seemed to indicate the possibility of electrode polarization. The rapid drift noted when attempts were made to establish a balance in the bridge circuit at low frequencies \(10^2\) c/s with the \(H^+\) type samples pointed toward an appreciable conductivity that increased with time. D.C. conductivity measurements at current densities well within the limits of ohmic behavior confirmed this. The existence of a non-linear voltage gradient across the film under D.C. conditions was further proof of an electrode polarization mechanism.

A review of the circuitry and procedures used by Falkenstein to establish the fact that his films were not exhibiting electrode polarization revealed that the technique was insensitive to any electrode polarization mechanism providing that the material in the electrodes can be modeled as two impedances in series. The use of such a model is well supported by measurements on systems purposely designed to exhibit electrode polarization.

Of the experimental techniques available to minimize the influence of electrode polarization on the measured capacitance, the Shaw method appears most suitable for these materials. This technique requires measurements at a pair of electrode spacings. Since the polarization capacitance effect is linked to only the electrode region, and since it is supposedly independent of electrode spacings, \(\frac{u}{\pi}\) of the two readings allows the electrode effect to be factored out. With solid materials such as the polysalt materials, it remains to be established whether the electrode polarization is truly independent of electrode spacing, since the boundary layer thickness should be dependent to some extent on the number of charge carriers present.

A careful re-evaluation of the dielectric behavior of these materials using a correction procedure such as the Shaw method is required before any attempt to model the structure of the polysalt system can be made.

(2) Voltage Gradient Analysis

To firmly establish that electrode polarization was present and contributing to the overall capacitance, a voltage gradient analysis was performed at both 10KC and 100 KC by Mr. William Westphal of the Laboratory for Insulation Research, M.I.T. A traveling field
detector (probe) was caused to traverse the gap between the two pair of electrodes containing the film sample. The sample, maintained at laboratory ambient conditions, was subjected to the alternating voltage as in a normal dielectric test. Virtually all of the voltage drop across the film was shown to occur within a millimeter or so of the electrodes. This result confirms the suspicion that electrode polarization is a dominate effect in the observed dielectric behavior particularly at frequencies below 100 KC.

D. Conclusions

(1) The observed dielectric data while in agreement with trends predicted by the discrete domain hypothesis used in the analysis of salt laden films by Falkenstein are concluded to arise primarily from electrode polarization effects. A review of the experimental procedure used to determine the existence of electrode polarization by Falkenstein revealed that the method was not sensitive to the presence of electrode polarization. Voltage gradient analysis confirmed several qualitative observations, which pointed to a dominate electrode polarization mechanism at frequencies below approximately $10^5$ c/s.

(2) The simultaneous presence of at least two polarization mechanisms, electrode polarization and heterogeneous polarization, prevents any interpretation of the available data in terms of a molecular model. The trends noted with ion content (increased $\epsilon'$, $\epsilon''$ with ion content), moisture content (increased $\epsilon'$, $\epsilon''$ with moisture content), ion type (increased $\epsilon'$, $\epsilon''$ with increased ion mobility) and with frequency (decreased $\epsilon'$, $\epsilon''$ with increased frequency) could be interpreted with equal success by either mechanism. Additional studies in this area will be required to separate and determine the magnitude of the two effects.

(3) The water content of the non-stoichiometric films at a given humidity level increased with increasing sulfonate excess in the as-cast film. This data extrapolates in a reasonable manner to the data developed by Falkenstein for neutral polysalt. The water content appeared to increase in a linear fashion for the humidity range 33-65% RH in agreement with similar observations for neutral polysalt.
In this region the incremental water content above the 33 % RH level appears to be present at "free" water, that is, water not associated with an ion hydration shell by analogy to ion exchange studies.

(4) Excellent agreement was noted between the residual ion content and the excess sulfonate content in the as-cast films. The Ca$$^{++}$$ ion is thought to associate with two pendant anion groups based on the data. This "crosslinking" mechanism is believed to be responsible in part for the decreased dielectric response of the Ca$$^{++}$$ films and for the pronounced shrinkage during drying.

E. Recommendations

Due to the presence of electrode polarization effects the data developed by Falkenstein (7), Miekka (22) and this study need to be re-evaluated using a correction procedure such as the Shaw method. In addition careful attention should be given to minimizing stray field errors by utilizing procedures such as given by Schwann. In this future study attention should be given to the electrode polarization boundary layer dependence on electrode spacing problem so as to guarantee that the Shaw method is truly applicable to solid systems with appreciable conductivity.

From dielectric data as a function of moisture content (corrected to exclude polarization effects), it should be possible to generate a better understanding of the role of water in the matrices. A knowledge of the disposition of water, "free" or in ion hydration shells, should aid in development of a refined model for the polycrystal systems.
II Introduction

A. Objectives

An important means of linking significant molecular quantities (which are, at least in principle, calculable from molecular theories) to measurable physical effects has been shown to be the application of dielectric behavior studies. The goal of this particular study was the development of an understanding of the structure of polysalt systems through the analysis of dielectric behavior and related measurements.

In an initial survey, Miekka (22) found that the neutral (i.e. stoichiometric) polysalt of poly-(vinylbenzyltrimethyl ammonium)-poly (styrene sulfonate) exhibited dielectric constants ranging from 11-14 at 50% RH (ambient temperature) in the frequency range 10^3-10^6 c/s. A complex composed of a non-stoichiometric balance of the two polyelectrolytes (with accompanying counter-ions) under equivalent environmental conditions exhibited dielectric constants of several thousand at low frequencies which decreased rapidly with increasing frequency.

Falkenstein (7) recently conducted an investigation to examine the dielectric properties of these polyon complexes in detail in an effort to interpret the behavior in terms of both polysalt structure and composition. In his study Falkenstein worked principally with neutral films which he subsequently equilibrated with aqueous solutions of sodium bromide. By minor modifications of the approach used by Falkenstein, production of neutral or non-neutral polysalt films was possible. These films could be designed to contain varying concentrations of counterions or sorbed electrolyte.

The observed anomalous dielectric behavior, high dielectric constants at low frequencies (A.C.) coupled with extremely broad dielectric dispersion, is markedly similar to the behavior of biocolloids. Several theoretical models have been developed over the years to explain the dielectric behavior of biocolloid systems. Schwarz (36) recently has related the anomalous behavior to ionic polarization processes in the electrical double layers associated with cell membranes. Falkenstein, (7) found that the behavior of his polysalt systems could be, to some degree, explained by this model.
The principal objective of the present work was to extend the dielectric studies of polysalts to include non-stoichiometric polysalt complexes with varying polyelectrolyte equivalence ratios and counter-ion type, in an attempt to gain further knowledge of the basic polarization mechanism. In the pursuit of this objective it was also desired that the frequency range be extended beyond that used by Falkenstein \(10^2-10^5 \text{ c/s}\) so as to enable a more complete study of polysalt relaxation characteristics. Finally from the dielectric behavior it was hoped that more insight could be gained as to the polysalt microstructure.

B. A Review of Dielectric Theory—Homogeneous Systems

In order to present in detail the current dielectric theories being utilized to explain the observed behavior of these polysalt systems, a short review of dielectric phenomena follows:

In general, materials can be classified into one of two classes, conductors, or insulators. Under the influence of an imposed voltage field, conduction (electron flow) occurs in conductors whereas, in insulators, sometimes referred to as dielectrics, these fields act to displace the electrons only slightly from their equilibrium positions. This effect of relative displacement of positive and negative charges in the material is referred to as polarization.

The total polarization, \(P_t\), in any material is made up of various components, according to the nature of the charges involved. The electronic polarization component, \(P_e\), is due to the relative displacement of the electrons and nuclei of atoms. The atomic polarization, \(P_a\), is due to the relative displacement of the atoms in a molecule, involving the stretching, twisting, or bending of chemical bonds. Orientation polarization (or dipole polarization) \(P_d\), occurs in polar materials. In this case the dipole moments experience a torque in an applied field that tends to rotate them into a position more favorable to the electric field. Interfacial or Maxwell-Wagner type polarization \(P_i\), occurs in heterogeneous dielectrics when one component has a higher electrical conductivity than the others. *

* This treatment of polarization and the mechanisms that give rise to the effects are explained in detail by von Hippel (43).
If we now consider any one of these types of polarization under the influence of an applied alternating electrical field it is found that at very low frequencies the polarization will also alternate. However, as the frequency increases eventually the polarization has difficulty in following the field and as a result does not have time to attain its full value before the field reverses.

This lag in the attainment of equilibrium between the dielectric response of the material and the externally applied alternating field is commonly referred to as relaxation. Dielectric relaxation is the exponential decay with time of polarization when an externally applied field is removed. Dielectric relaxation is the cause of anomalous dispersion in which the dielectric constant decreases with increasing frequency.

The development of many of the formalized relations between dielectric constant, loss, frequency, dipole moment, molecular size, etc. is due to Debye (5). The following development of the subject parallels that of Smyth (41).

In discussing the properties of a dielectric it is convenient to imagine the material situated between the electrodes of a capacitor. Consider a perfect loss-free capacitor (e.g. two plane parallel plates in a vacuum), of capacity $C$, having an applied alternating electric potential defined by the equation: $E = E_0 \cos \omega t$ where $E$ is the potential at time $t$, $E_0$ is the maximum value of the potential, $\omega$ is the frequency in radians per second, and $t$ is the time. The displacement current vector is 90 degrees out of phase with the potential, as illustrated in Figure 1a. Thus there is zero component of the current in phase with the potential, and no electrical energy is lost by conversion to heat.

If a polar dielectric of dielectric constant $\varepsilon'$ and dielectric loss factor $\varepsilon''$ is now placed in the capacitor the displacement current vector will be slightly less than 90 degrees ahead of the potential, as shown in Figure 1b. There will now be a small component $E \omega \varepsilon'' C$ of the current in phase with the potential, giving rise to dielectric heating. The capacitative component $E \omega \varepsilon' C$ which is 90 degrees out of phase with the potential, is called the "charging current".
(a) Potential and Current Vectors - 90° out of phase- Loss free capacitor in an alternating field

(b) Potential and Current Vectors (Less than 90° out of phase) in capacitor with loss.

Potential and Current Relationship

Figure 1
Figure 1b also shows the loss angle $\delta$ which is the lag in the displacement current vector due to the presence of the dielectric. The relationship between these different parameters is:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} (1)

The parameters $\varepsilon'$ and $\varepsilon''$ are frequently lumped together as a complex dielectric constant,

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$  \hspace{1cm} (2)

The relation of the apparent conductivity of the sample to dielectric constant and loss factor has been given by Murphy and Morgan (25). For our purpose the following adaptation of the presentation given by Smyth (41) should suffice. For conductors, the conductivity $\kappa$ is

$$\kappa = \frac{Z}{\varepsilon} = \omega / \varepsilon^*$$  \hspace{1cm} (3)

where $I$ is the current density, $E$, the voltage gradient and $W$, the heat developed per second in a unit cube of the material.

In a dielectric material, the current-heat proportionality does not hold since the ratio of heat to current flow varies with the material. In real dielectrics, Joule heat may be produced due to electron or ion drift in the applied field. The total heat developed, therefore, is the sum of the dielectric loss plus any additional Joule heat. Thus the dielectric loss is proportional to the total measured a.c. conductivity minus the d.c. conductivity.

In the case of the sample of dielectric material situated between the electrodes of the capacitor, assume the separation of the plates is $d$ cm. while the surface area of each plate is equal to $A$ cm$^2$. When the potential difference $V$ is established between the plates, a current flow will be established equal to $A \frac{dq}{dt}$ where $q$ is the charge per unit area on each plate. If we assume $\frac{dq}{dt}$ and that conductivity due to free ions is negligible, the conductivity is

$$\kappa = \left(\frac{\varepsilon}{\varepsilon^*}\right) \frac{dq}{dt}$$  \hspace{1cm} (4)

Since we are dealing with an alternating potential, $V$ may be expressed as the real part of $V = V_0 e^{j\omega t}$. The current density in the sample can be shown to be equal to

$$\frac{dq}{dt} = j \omega \left(\varepsilon' - j \varepsilon''\right) \frac{V_0 e^{j\omega t}}{4\pi d}$$  \hspace{1cm} (5)

which reduces to the complex conductivity

$$\kappa^* = \kappa' + \kappa''$$  \hspace{1cm} (6)

where $\kappa' = \frac{\varepsilon' \omega}{4\pi}$ and $\kappa'' = \frac{\varepsilon'' \omega}{4\pi}$

Schwan (32) has presented an excellent review of the general dielectric relaxation theory. The following represents a summary of the more pertinent aspects of the subject as applied to this study.
As pointed out earlier, the term "relaxation" as applied to dielectrics refers to the rate at which a system subjected to changing external fields approaches its new state of equilibrium. Ordinarily this is expressed in terms of the imposed field $E$ and its relation with the dielectric displacement $D$ (this latter term is related by definition to the surface charge density). In the simplest case, the alternating voltage applied to the specimen can be regarded as a step potential. The resulting dielectric displacement $D$ is found to be a function of time. The usual behavior is an initial rapid rise after applying a constant field at $t=0$ followed by a slower approach to a larger limiting value.

The rapid initial response for this hypothetical ideal step function is usually attributable to induced electronic or nuclear displacements and is partially due to internal molecular structure as well as a molecular interactions and energy transfer. The slower response (times longer than $10^{-12}$ second) is the one usually considered to be in the domain of dielectric relaxation. For times in the range $10^{-4}$ to $10^{-11}$ seconds the steady state response to a sinusoidal field variation is more easily studied experimentally than the transient effect for an instantaneous field. However, both types are consequences of the same molecular behavior, and the connection between them can be formulated in terms of Laplace or Fourier transform theory providing that the principle of superposition holds, namely that the total response to a series of stimuli is the sum of the separate responses at and after the time of these stimuli.
As mentioned before, with a stepwise application of $E$ at time $t=0$, the simplest form of relaxation effect and the one found quite often experimentally, is an exponential rise of $D$ expressed by

$$D(t) = \varepsilon_\infty E + (\varepsilon_0 - \varepsilon_\infty) \left[ 1 - e^{-\frac{t}{\tau}} \right]$$

**(7)**

where $\varepsilon_\infty$ is the instantaneous or high frequency dielectric constant and $\varepsilon_0$ is the static or equilibrium value. $\tau$ is defined as the macroscopic relaxation time. For a sinusoidal field, the corresponding dielectric constant is given by

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

**(8)**

In his derivation of the conductivity term $k$, Schwan includes a component $k_0$ which summarizes any additional conductance terms that may develop (e.g., ionic conductance). Thus

$$k = k_0 + \frac{(k_0 - k_\infty)(\omega \tau)^2}{1 + (\omega \tau)^2}$$

**(9)**

The positive term $\varepsilon_0 - \varepsilon_\infty$ corresponds to a non-instantaneous part of the total polarization which is due to charges moving with the field. If $\varepsilon_0 < \varepsilon_\infty$ charges would have had to move against the field which is impossible unless the applied step potential is assumed to release additional emf of opposite charge within the material.

Further examination of equation **8** shows that $\varepsilon''$ approaches zero for both small and large values of $\omega \tau$ while it is a maximum for $\omega \tau = 1$.

Normally dispersion occurs over a wider frequency range and with a maximum value of $\varepsilon''$ lower than that predicted by the Debye equation.

The effect has been attributed to a distribution of relaxation times.

If the transient behavior cannot be represented by an exponential curve, it may be thought of as a series of exponential curves, each characterized by a different time constant $\tau$. The resulting complex dielectric constant is

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

**(10)**

where the function $F(\tau)$ characterizes the distribution of time constants in a plot of the number of time constants per element $d\tau$ versus $\tau$.

If we consider the case of dielectric absorption it is frequently found that the behavior of solids with a range of relaxation times can be represented by Fuoss and Kirkwood’s (1933) empirical equation.

$$\varepsilon'' = \varepsilon''_{\text{max.}} \tan \left( \frac{\tau}{\tau_{\text{max.}}} \right)$$

**(11)**

where $f$ is the frequency in cycles per second and $f_{\text{max.}}$ is the frequency of maximum absorption. The value of $\alpha$ varies between unity for a single relaxation time and zero for an infinite range.
C. Heterogeneous Dielectrics

Observation by Falkenstein of a broad dispersion range and anomalously high dielectric constants \((10^4 \text{ to } 10^6)\) for the treated polysalt cast considerable doubt on the validity of the homogeneous dielectrics model for explaining the noted behavior. Most homogeneous dielectrics exhibit dispersion over only a narrow range (approximately 2 decades) of frequency and rarely possess dielectric constants in excess of \(10^3\). As an alternative Falkenstein found that the data could be reasonably explained by the heterogeneous dielectric model originally developed by Schwarz (36) for suspensions of colloidal particles in aqueous electrolyte solutions.

The Schwarz model represents only one of several models that have been adopted to allow mathematical analysis of the non-homogeneous case. A review of the more noteworthy models that have been subjected to analysis will follow to develop this facet of dielectric behavior.

The earliest theoretical treatment of a heterogeneous dielectric system was generated by Maxwell (21) when he analyzed the case of a material composed of layers of homogeneous dielectrics with non-equal dielectric constants and conductivities. Consider the situation shown below where the dielectric consists of two parallel sheets of materials (1) and (2) possessing dielectric constants \((\varepsilon_1', \varepsilon_2')\) conductivities \((k_1, k_2)\) and thicknesses \((d_1, d_2)\). The equivalent electrical circuit for this model is also shown in the same figure.

(a) Dielectric Sample

(b) Equivalent Circuit
Upon application of a d-c field the instantaneous field distribution obeys the electrostatic requirement of constant flux density, however the ultimate field distribution is governed by current continuity conditions. Analysis of the transient behavior for this model reveals that the two layer condenser gives a relaxation spectrum indistinguishable from simple orientation polarization of homogeneous dielectric theory. Due to the variation in current densities in the transient state charges pile up at the interface between materials (1) and (2). This buildup of charge at the interface increases the apparent capacitance and hence the dielectric constant of the combination.

Relaxation of this form of polarization occurs by the flow of excess interfacial charge away from the interface. A step by step review of the mathematical aspects of this model has been given by von Hippel [43].

Wagner (46, 47), using a distribution law for time constants proposed by von Schweidler (45), extended Maxwell's theory by considering a medium composed of spheroidal particles randomly distributed in a non-conducting matrix. The spheroids, present in low concentration, had a dielectric constant \( \epsilon_L \) and conductivity \( k_2 \), while the matrix had dielectric constant \( \epsilon_I \) and conductivity \( k_1 \). Mathematical analysis of this model produced the following relationships where \( \epsilon' = \) apparent dielectric constant,

\[
\epsilon' = \epsilon_\infty \left( 1 + \frac{k}{1 + (\omega \tau)^2} \right)
\]  \hspace{1cm} (12)

and

\[
\epsilon_\infty = \epsilon_I' \left[ 1 + \frac{3 q (\epsilon_L' - \epsilon_I')}{2 \epsilon_L' + \epsilon_I'} \right]
\]  \hspace{1cm} (13)

where \( k = \frac{q b \epsilon_I'}{2 \epsilon_L' + \epsilon_I'} \) and \( \tau = \frac{2 \epsilon_I' + \epsilon_L'}{1.13 \times 10^{13} k_2} \).
$k_2$ is expressed in ohm$^{-1}$ cm$^{-1}$, $q$ is the volume fraction of phase 2. From this one arrives at a

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

(14)

and a loss tangent

$$
\tan \delta = \frac{\kappa \omega \tau}{1 + \kappa + (\omega \tau)^\kappa}
$$

(15)

Inherent in the analysis by Wagner was the assumption that the concentration of spheres was so dilute that interactions between spheres could be neglected. With this simplification the distortion of the field distribution around a suspended particle is only influenced by the particle's shape and orientation relative to the applied field. The apparent dielectric constant can be varied by a change in shape or orientation of the suspended particles as was pointed out in studies by Sillars (39) for suspensions of ellipsoids and rods. A distribution of relaxation times may be produced simply by varying the orientation of ellipsoidal particles and similar non-spherical particles. The absolute size of the particles does not influence the calculation of apparent dielectric constants and relaxation times, however, the mass ratio of the components is required.

The theories developed on the basis of suspended spheroidal and ellipsoidal particles were extended to include the refinement that the particles had a thin surface shell. Investigators such as Cole (3), Danzer (4) and Fricke (9, 10) utilized a spheroidal particle with a non-conducting shell as a model for red blood cells.

Fricke (9, 10, 11) in conjunction with conductivity studies on suspension of particles such as cream and blood developed expressions for the dielectric behavior of membrane covered ellipsoidal particles. Several other investigators including Velick and Gorin (42) (solutions of biological ellipsoidal particles) and Altschuller (1) (particle shape studies) have also dealt with this model.
In the Frick model high dielectric constants are shown to arise for conducting particles dispersed in a conducting medium with thin insulating membranes at their interfaces. The system acts then as a parallel and series combination of high capacitance condensors. To treat this model mathematically it was necessary to assume that the interior of the particle is at a constant potential and further that the field distribution in the external medium around the particle is the same as if the whole particle were a perfect insulator. The derived mathematical expressions for the conductance and capacitance of the systems include shape factors to account for the orientation of the axes of the particle with the field. The simplified expressions for a spheroidal particle predict three dispersion regions in each of which the complex dielectric constant increase becomes

\[ \Delta \varepsilon^* = \frac{p}{\varepsilon} \left( \frac{(1 + \chi_m)(\varepsilon_\omega^* - \varepsilon_r^*)}{\chi_\omega + \varepsilon_\omega^*/\varepsilon_r} \right) \]  

(16)

where \( p = \) volume fraction of particles
\( \chi_m = \) shape factor

and subscripts refer to suspended phase (2) and continuous phase (1) respectively. The relaxation time for each dispersion region is

\[ \tau_m = \left( \frac{\varepsilon_v}{4\pi} \right) \frac{\varepsilon_l + \varepsilon_i}{\sigma_l + \chi_\omega \sigma_i} \]  

(17)

where \( \varepsilon_v = \) absolute dielectric constant vacuum
\( \sigma_i = \) conductivity

In 1934 Murphy and Lowry observed that the available evidence suggested that the direct-current conductivity of most solid dielectrics occurred along sub-microscopic paths of higher conductivity than the bulk of the dielectric. They reasoned that the surface area of these sub-microscopic paths should be large in comparison to their volume and hence any adsorbed ions at this interface between the conducting path and the insulating medium should have important effects on the electrical characteristics of the body. They proceeded to propose a mechanism to account for the influence of frequency, voltage and temperature on dielectric loss. Their model was developed from these assumptions:

(a) The materials under consideration contained insulating particles on which were adsorbed ions of both charges.

(b) Under the influence of a field an ion could move freely over the surface,
(c) The ion could not leave the surface until a critical voltage was attained, and

(d) The concentrations of ions decreased at increasing distance from the interface.

Murphy and Lowry (25) considered that the particle alone is electrically equivalent to pure capacitance and that the ions beyond the interface are equivalent to parallel capacitances with series resistance of different values, and therefore with different relaxation times. They then set up expressions for the capacitance and power factor of such a system of condensers, but did not evaluate the various constants involved.

The Murphy Lowry model therefore can be represented by a sphere with adsorbed negative and positive ions on the surface. Application of an external field causes the ions to shift on this surface so as to form in effect, an induced dipole. Removal of the field allows the ions to return to their normal distribution. By proposing that it is possible to have layers of adsorbed ions each of which possess a different relaxation time it was possible to show evidence for a distribution of relaxation times.

Miles and Robertson (23), using a model somewhat similar to that of Murphy and Lowry (25), were able to mathematically express the relationships between particle size, dielectric constant and dielectric loss. The dielectric in this analysis was assumed to consist of poorly conducting particles of varying size surrounded by ionic atmospheres and imbedded in a non-conducting medium. The analysis assumed that the particles were spheres surrounded by concentric shells of a certain conductivity in rough analogy to the accepted picture of colloidal particles possessing an electric double-layer.

Using the assumption that the conducting shell is thin compared to the radius of the sphere, that the complex conductivity of the shell is large compared with that of the particle and following Wagner, that the dielectric constant of the sphere and the surrounding medium are equal, they developed an expression for the relaxation time of the system

\[ \tau = \frac{3 \varepsilon \varepsilon' \alpha}{8 \pi \varepsilon' \lambda L d} \]  

(18)
\( \varepsilon_i' = \text{dielectric constant of particle} = \text{medium dielectric constant} \)

\( \alpha = \text{radius of particle and shell} \)

\( \lambda_k = \text{conductivity of shell} \)

\( d = \text{thickness of shell} \)

\( c = \text{ratio of cmu to esu} \)

Note that in this derivation the relaxation time is related to particle size (radius) whereas in Wagner's treatment the radii of the spheres were not involved in the final expression. As a consequence of this fact a distribution of relaxation times can be expected for a system with particle size variations.

Through the use of a surface conductivity mechanism, O'Konski (27) extended the treatment of Miles and Robertson (using ellipsoids) to explain the frequency dependent dielectric properties of polyelectrolytes and colloidal electrolytes. The concept of surface conductivity was generalized to include contributions from all species in the ion atmosphere, and other charge carriers, such as protons, electrons or holes, which are confined to a thin region on or near the surface of the particle. Equations were then obtained for the dielectric constant and conductivity of dilute systems of variously shaped particles of arbitrary dielectric constant, volume and surface conductivity, random or oriented arrangement in a solvent of arbitrary dielectric constant and conductivity, at an arbitrary frequency.

Using an expression developed by Polder and von Santeen (29) relating a system dielectric constant to the volume fraction and dielectric constants of two phases, O'Konski found that the expression for dielectric constant increment \( \Delta \varepsilon = \varepsilon_i' - \varepsilon_i' \) for a suspension of spheres was

\[
\left( \frac{\Delta \varepsilon}{\bar{\delta}_s} \right)_{\delta_s \to 0} = \frac{3 \varepsilon_i' X + 3 \varepsilon'' Y}{Z}
\]

(19)

\( \varepsilon_i' = \text{apparent dielectric constant} \)

\( \bar{\delta}_s = \text{volume fraction spheres} \)

\( \varepsilon_i' = \text{dielectric constant medium} \)

\( \varepsilon_i'' = \text{dielectric constant of spheres} \)

\( \varepsilon_i'' = \text{dielectric constant of equivalent sphere with surface conductivity} \)

\[
X = (\varepsilon_i')^2 + \varepsilon_i' \varepsilon_i'' - 2 (\varepsilon_i')^2 + (\varepsilon_i'')^2 + \varepsilon_i' \varepsilon_i'' - 2 (\varepsilon_i'')^2
\]

\[
Y = \varepsilon_i' \varepsilon_i'' - \varepsilon_i' \varepsilon_i''
\]

\[
Z = (\varepsilon_i + 2 \varepsilon_i')^2 + (\varepsilon_i'' + 2 \varepsilon_i'')^2
\]
He shows that in the limit of very low frequencies, where ionic conduction dominates the electrical field distribution that

\[
\left( \frac{\Delta \varepsilon}{\delta \varepsilon} \right)_{\omega \rightarrow 0} = 3 \left[ \frac{(r^2 - 2r - 2) \varepsilon_i + 3 \varepsilon_L}{(r^2 + 2)^2} \right]
\]

(20)

where

\[
r = \frac{k_s}{k_l}
\]

\(k_s\) = effective volume conductivity of electrically equivalent sphere

(includes contributions of sphere surface and bulk conductivity)

\(k_l\) = conductivity of medium

Thus the low frequency dielectric increment is strongly dependent upon the conductivity ratio, which involves both the bulk conductivities and the surface conductivity.

At frequencies well above dispersion regions, where dielectric constants largely determine the field distributions,

\[
\left( \frac{\Delta \varepsilon}{\varepsilon_i \delta \varepsilon_L} \right)_{\omega \rightarrow 0} = 3 \left( \frac{\varepsilon^2_i + \varepsilon_i \varepsilon_L - 2 \varepsilon^2_L}{(\varepsilon_L + 2 \varepsilon_i)^2} \right)
\]

(21)

similar expressions can be developed in each case for the conductivity increment.

Thus the dielectric increment is independent of conductivities where frequency is so high that ionic currents are negligible compared to the displacement currents.

Recently Schwan, Schwarz, Maczuk and Pauly (33) found in an investigation of the dielectric behavior of well characterized polystyrene suspensions, that the observed low frequency behavior could not be explained by Maxwell-Wagner models or later models using a frequency independent surface conductivity. Schwarz (36) proposed that the behavior could be explained by diffuse double layer model with the following properties.

A suspended sphere is electrically charged by fixed or adsorbed ions, and surrounded by counterions, which can move along the surface but not perpendicular to it. The double layer is assumed to be infinitely thin compared to the sphere radius and to possess a total net charge equal to zero. With the application of an external field, the random
distribution of counterions is modified by a shift of counterions along the surface. This surface flux of counterions is opposed by a diffusion flux which tends to re-establish the random distribution.

Mathematical treatment of this situation shows that the counterion density changes only slightly from the random distribution if the assumption is made that the electric field along the surface is of the same order of magnitude or smaller than the external field. Further development of the continuity equations for surface charge produces an expression for the relaxation time

$$\tau = \frac{R^2}{2 \mu \kappa T}$$  \hspace{1cm} (22)

where

- $R$ = radius of sphere
- $\mu$ = counterion surface mobility
- $k$ = Boltzmann constant, ergs/°K
- $T$ = temperature, °K

Thus the relaxation time $\tau$ is determined by the rate of diffusion of counterions along the particle.

Using a surface dielectric constant as opposed to a surface conductivity such as proposed by O'Konski, Schwarz develops the following equation for the dielectric behavior of a suspension of spheres with counterion layers:

complex dielectric increment

$$\varepsilon^* - \varepsilon_\infty = \Delta \varepsilon^* = \frac{\Delta \varepsilon_0}{1 + j \omega \tau}$$ \hspace{1cm} (23)

with the static dielectric increment

$$\Delta \varepsilon_0 = \frac{3}{4} \varepsilon_0 \varepsilon_\infty \frac{9 \varepsilon_\infty R \sigma_0}{(1 + \varepsilon_\infty)^2}$$ \hspace{1cm} (24)

$p$ = volume concentration of spheres

$\varepsilon_0$ = electric charge

$\varepsilon_\infty$ = absolute dielectric constant of free space

$\sigma_0$ = counterion density

where $\Delta \varepsilon^*$ displays a simple Debye-type dispersion with a characteristic frequency

$$\frac{\omega}{\tau} = \frac{kT}{\mu R^2}$$ \hspace{1cm} (25)
Analysis of the Schwarz model reveals that three requirements must be met before a dielectric could be classified as a Schwarz-type dielectric. These are the existence in the matrix of mobile ions associated with immobile counterions, discrete domains where the mobile ions are isolated from other similar regions and finally the existence in the domain of a potential gradient of sufficient magnitude that significant ion-displacement occurs.

Falkenstein (7) observed that the polycrystal matrix could be interpreted as meeting these restrictions. The dielectric data for the neutral polycrystal with various moisture contents and NaBr contents was then observed to behave in a predictable manner according to such a model. An order of magnitude calculation of the characteristic relaxation time for a polycrystal matrix containing NaBr electrolyte was presented based on the assumption of a simple relaxation mechanism that was in agreement with observed results. Several assumptions of questionable validity were required to make this calculation however.

The Schwarz model has recently been shown to contain an objectionable boundary condition assumption in an analysis by Schurr (31). In his analysis Schurr develops arguments which indicate that the analysis by O'Konski (27) may be more correct.
D. Formation and Properties of Polysalt Materials

The material used in this study was the precipitate product formed by co-reacting two oppositely charged linear synthetic polyelectrolytes. The polyelectrolytes used were linear polystyrene derivatives; the anionic polyion* was poly-(styrene sulfonate) while the cationic polyion was poly-(vinyl benzyl trimethyl ammonium). In conformance with previous studies these names will be abbreviated SS and VBTA respectively. The mer units of the two polyions are:

\[
\begin{align*}
\text{poly-(styrene sulfonate)} & & \text{poly-(vinyl benzyltrimethyl ammonium)} \\
\end{align*}
\]

\[
\begin{align*}
\text{poly-(styrene sulfonate)} & & \text{poly-(vinyl benzyltrimethyl ammonium)} \\
\end{align*}
\]

The properties of such products are of interest because of their similarities to biological systems (6, 32), ion exclusion resins (16) as well as ion exchange resins and membranes. In fact, several studies are currently being made on the possible application of such films in desalination systems.

Dilute solution interactions between oppositely-charged polyelectrolytes have been studied by several investigators (14, 22, 24). A review of much of the previous literature was presented by Deuel (6).

Prior studies have shown that the presence of ionized groups has an important effect on the conformation of these polyions in aqueous solution. The repulsive forces between adjacent ionic groups make the polymer configuration more extended than that of a neutral random coil.

* The polyion is defined as the dissolved polyelectrolyte minus the ionized microions which are designated counterions. These polyions have about one ionizable group per mer unit.
Miekka (22) studied the interaction characteristics of poly-
(sodium styrene sulfonate) and poly-(vinylbenzyl trimethyl ammonium
chloride). These polyelectrolytes were polymerized by a free radical
mechanism from aqueous solutions of the corresponding para-substituted
atactic polymers. His work showed that polysalts with distinctly different
properties could be formed depending on the reaction scheme. With dilute
(<0.2 gram/dl) aqueous solutions of the polymers, white hydrous partic-
ulate polysalt was formed. Co-reaction of solutions with concentration
greater than 0.6 gram/dl caused the formation of a thin film at the
solution interfaces which hindered further reaction. Dissolving the two
polymers into a (NaBr-acetone-water) ternary solvent allowed the for-
mation of polysalts containing widely varying relative amounts of the two
polymers by precipitation.

The precipitate* product formed by the reaction of the dilute poly-
electrolytes was found to be composed of a stoichiometric balance of the
electrolytes irregardless of the ratios in which they are mixed. However,
when electrolyte (e.g. 1M NaBr) was present coprecipitation occurred
over a broad range of equivalence ratios which depended both on polion
concentration and order of addition. The results suggested that the reaction
might depend on the polion conformation in solution prior to precipitation.

Mir (24) extended Miekka's work to include reaction between pol-
ions containing divalent counterions in the acid or base form, both in the
absence and presence of added electrolyte. It was seen from this study
that the stoichiometric reaction required an extended conformation of
the reacting polions. Steric restrictions were present when divalent
counterions were used that blocked complete reaction. The neutralization
of the counterions in the reaction of the polyacid and polybase left the
reacting ionic functions without the necessary coulombic shielding so
that a network structure formed with isolated unreacted ionic groups.

Miekka and Falkenstein both have previously studied some aspects
of the dielectric behavior of these polysalt materials. Through the use
of a ternary solvent composed of approximately 60-20-20 weight per-
cent water-acetone sodium bromide, Miekka was able to make solutions
of the VBTA-SS polysalt. From this solution, by careful solvent composition
control, he then formed a clear solid product. The reaction was virtually

* Precipitation occurs due to the strong electrostatic attraction between
oppositely charged polymer chains which causes them to be drawn together
and react ionically, giving off their associated counterions as free salt.
complete, since less than one per cent of the polion groups were found to be associated with sodium or chloride ion after the product was thoroughly washed.

Miekka found that the solid (neutral) polysalt absorbed approximately .38 grams of water per gram of dry polysalt when placed in distilled water. Falkenstein in a later study, related the moisture content of the polysalt to relative humidity levels. The addition of salt (sodium bromide) to the solution increased the absorption of solution. The polysalt tended to remove salt from the solution, since Miekka noted that for low solution concentrations (~2% by weight) the internal salt concentration was approximately three times the external solution concentration. With a decrease of the external solution concentration this ratio decreased.

Miekka attributed the increased solution absorption in the presence of added salt to the creation of an expanded structure by the rupture of polion-polion bonds. The internal-external salt concentration ratio was also explained by this mechanism.

Further studies showed that the absorption of solvent by polysalt was increased by the addition of small quantities of acetone. This was explained by enhanced solvent affinity for non-ionic portions of the polions which decreased the homopolar associations in the polysalt-further expanding the polysalt structure.

By similar techniques to those used for the neutral polysalt, Miekka was able to form materials containing an excess of one of the two polions (non-stoichiometric polysalt). The product containing a 2:1 equivalence ratio of NaSS to VBTACl was found to absorb 6.0 grams of water per gram of dry polysalt in distilled water. Addition of salt (sodium bromide) in this case decreased the water absorption presumably due to ion-exclusion effects. When the external ion concentration became comparable to that of the polion matrix (high salt concentration) the swelling increased since the ion exclusion effect had vanished.

As shown in Table I, Miekka found the dielectric behavior to vary; the neutral films acted as if they were homogeneous systems whereas the non-stoichiometric films behaved in a manner that appeared related to interfacial polarization. Falkenstein, in an extension of Miekka's work, studied the dielectric behavior of neutral polysalt films as a function of salt (sodium bromide) content and relative humidity. In addition a test
TABLE I
Dielectric Properties of Non-Stoichiometric and Stoichiometric Polyelectrolyte Complexes *

<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>equiv. NaSS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture Content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(at 50% R.H.)</td>
<td>13</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>grams water/gram dry film</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frequency (c/s)</th>
<th>% R.H.</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3$</td>
<td>50</td>
<td>2580</td>
<td>1820</td>
<td>14</td>
<td>2.5</td>
<td>138</td>
<td>150</td>
</tr>
<tr>
<td>$10^4$</td>
<td>50</td>
<td>1120</td>
<td>890</td>
<td>12.5</td>
<td>.83</td>
<td>50</td>
<td>36</td>
</tr>
<tr>
<td>$10^5$</td>
<td>50</td>
<td>314</td>
<td>355</td>
<td>11.8</td>
<td>.95</td>
<td>25</td>
<td>11.4</td>
</tr>
<tr>
<td>$10^6$</td>
<td>50</td>
<td>102</td>
<td>116</td>
<td>11.3</td>
<td>.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^7$</td>
<td>50</td>
<td>41</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$10^2$</td>
<td>0</td>
<td></td>
<td>6.2</td>
<td>.08</td>
<td>6.7</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>$10^3$</td>
<td>0</td>
<td>73</td>
<td>61</td>
<td>5.9</td>
<td>.08</td>
<td>5.8</td>
<td>.53</td>
</tr>
<tr>
<td>$10^4$</td>
<td>0</td>
<td>30</td>
<td>20</td>
<td>5.9</td>
<td>.09</td>
<td>5.2</td>
<td>.27</td>
</tr>
<tr>
<td>$10^5$</td>
<td>0</td>
<td>14</td>
<td>7.1</td>
<td>5.7</td>
<td>.13</td>
<td>5.0</td>
<td>.14</td>
</tr>
<tr>
<td>$10^6$</td>
<td>0</td>
<td>8.9</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* per Miekka (22)
was made on one non-stoichiometric (1.3 equivalents NaSS/equivalent VBTA-SS) film at 51% RH, 27.5°C. Falkenstein's results for the neutral polysalt at 51% RH, 27.5°C were slightly higher than those of Miekka, ranging from 11 at $10^5$ c/s to 27 at $10^2$ c/s. The observation was made that the inflection point in the dielectric constant vs. frequency curve had not been reached and therefore even higher dielectric constants (below $10^2$ c/s) should be noted. The mean relaxation time for the polarization phenomena responsible for the increase in dielectric constant was calculated to be greater than 1.5 x $10^{-3}$ seconds (i.e. less than $10^2$ c/s).

Equilibration of neutral polysalt films in sodium bromide solutions of varying concentration yielded films which when tested exhibited markedly higher dielectric constants than the original film. (See Figure 2). Again in this case the dielectric constant curve did not exhibit an inflection point nor did the loss factor curve (vs. frequency) reach a maximum.

Falkenstein concluded from an analysis of the behavior of the treated films that the introduction of sodium bromide created new polarization processes which were the major cause of the observed dispersion. The increase in dielectric constant was attributed to the increased total polarization developed by these processes.

The dielectric constants of sodium bromide treated films increased with increasing water content. When the films were held at high relative humidities (92%) the dielectric constants shifted to lower values with increasing time. During this period however, the loss tangent curve remained relatively constant. Experimental results showed that below 75% relative humidity, a shift of dielectric constant did not occur. The behavior was concluded to be the result of time-dependent structural readjustments. The magnitude of change increased with the sodium bromide content of the film.

Falkenstein found in his study of a non-stoichiometric film that the material exhibited analogous behavior to sodium bromide treated neutral films.

E. This Investigation

The objective of this investigation was to develop from the observed dielectric behavior of non-stoichiometric polyelectrolyte complexes some further understanding of the microstructure of the system. The influence of counter-ion type, moisture content, and degree of non-stoichiometry on the dielectric behavior were studied to aid in this interpretation.
FIGURE 2

DIELECTRIC CONSTANT OF NEUTRAL POLYSALT AS A FUNCTION OF NaBr CONTENT

[PER FALKENSTEIN (7)]

0.46 EQUIV. NaBr PER EQUIV PS

TEMPERATURE: 27.5°C
RELATIVE HUMIDITY: 31%
III Experimental Procedure:

A. General Procedure

Using non-stoichiometric polyanion (dry powder) as supplied by Amicon Corporation; 15.2% by weight solutions were prepared with an HCl-Dioxane-H_2O ternary solvent system. Films were cast on glass from these solutions and subsequently dried at 70°C. During the initial 15 minutes of a 35 minute drying period the film was heated while covered to promote plasticization of the surface and to retard the tendency of the solution to "retreat" along its periphery. The films thus cast were immediately soaked in .2N HCl and removed from the glass substrate. Films were stored in 0.2N HCl to prevent excessive swelling.

Three film samples for each of three levels of non-stoichiometry were then placed respectively in fresh solutions of .2N HCl, .34N NaCl and .34N CaCl_2.* The films after equilibration were conditioned at 65% relative humidity and laboratory ambient temperature (24-28°C) while stretched in embroidery hoops. Finally the films were brought to 33% relative humidity at laboratory ambient temperature. At this point the appropriate samples for dielectric tests were cut from the films. The dielectric test specimen and a specimen for moisture content studies were then placed in open polyethylene vials in a dessicator at 33% relative humidity where they remained for approximately 14 hours. At this point samples were loaded into a set of specially constructed dielectric sample cells (see Figure 3) and returned to the dessicator. Measurements on the loaded and empty cells were made at 10^7 c/s by the susceptance variation method. The cells were reloaded and measurements were made over the frequency range 10^2-10^7 c/s by either a resistance capacitance substitution method or a capacitance substitution method using a

* Miekka (22) observed that swelling of non-neutral polyanion was a minimum for external solutions containing about 2% by weight of NaBr. It was desirable to use highly consolidated films in the study therefore, the rinse solutions were purposely held to concentration levels equivalent to this.
(a) assembled test cell

(b) exposed electrode arrangement (note sample of film held between clamps)

Figure 3 Dielectric Test Cell
Schering type bridge. Simultaneously measurements were made at 8520 MC using a standing wave method with traveling wave detector. (Samples at 33% RH). The procedure was repeated with the same samples conditioned at 65% RH (for 16 hours). Finally 3 specimens were returned to 33% RH for 19 hours and remeasured, from $10^2 - 10^7$ c/s.

Moisture contents were obtained by weighing the films while at 33% and 65% RH and then obtaining dry film weights by drying the film under vacuum in a vacuum dessicator over $P_2O_5$.

Residual ion contents were determined by flame photometry. Film samples were put into crucibles and ignited to remove all combustible matter. The residue was put into solution with deionized water in volumetric flasks. Absorption measurements were then made for the samples, control standards and a blank of deionized water. From a knowledge of the original sample weight, and the ion content of the resultant solution calculation of the ion content of the films was possible.

D.C. conductivity measurements were made on two films using a series circuit composed of a microammeter, a 3 volt battery and the sample. Knowledge of the film geometry, the resultant current and the imposed voltage allowed the film resistivity or conductivity to be calculated.

B. Specific Procedures

(1) Preparation of the non-stoichiometric polysalt.

The method used by Amicon personnel to prepare the non-stoichiometric polysalt powders was analogous to that used by Falkenstein, (7) Fleming (8) and Gray (15). The method will be illustrated by a review of the procedures used by the author to prepare neutral polysalt.

The (VBTACL) polyelectrolyte was received as an approximately 29.5% aqueous solution. The (Na-SS) polyelectrolyte was received as a dry powder.

Known weight portions * of the as-received materials were dissolved in distilled H₂O to form dilute ($<3 \times 10^{-4}$ gram/ml) aqueous solutions. The solutions were magnetically stirred for approximately 24 hours.

* A check on the true dry solids content of these two materials was conducted by drying the materials at approximately 80°C to constant weight on an Ohaus Moisture Balance. This check confirmed that within the limits of experimental error the reported values were correct.
A conductometric titration of the NaSS solution into VBTACL (in 200 ml H₂O) was then performed to establish the equivalence ratio. As a check on this experiment a run was also made titrating VBTACL into NaSS (in 200 ml H₂O). * Close (less than 1% difference) agreement existed between the two runs.

The next step was to form a polysalt ternary solvent solution (10% by weight level chosen in this case).

Based on previous studies (Fleming, Gray, Falkenstein), a ternary solvent composition of 22.5% NaBr, 22.5% Acetone, and 55% water, was chosen. Starting with the aqueous solution of VBTACL, NaBr was added to promote electrostatic shielding. The required amounts of acetone and water were then added. Finally the equivalent ratio of NaSS was added. The mixture was stirred (magnetically) until a transparent (slightly amber colored) solution was established.**

Portions of the polysalt ternary solution were then added to small (approximately 200 ml) portions of distilled water in a Waring Blender at high speed. Under these conditions a fluffy white precipitate was formed.

The precipitate was collected by filtration in a Buechner funnel. After repeated washings the wet polysalt precipitate was placed in a 4 liter beaker covered with distilled water and allowed to stand over night. The filtered product was then dried at 50°C in a vacuum oven for 1 week. During the latter stages of this drying period the material was ground with a mortar and pestle to form a fine powder.

In the case of the polymers used in this study, the Amicon personnel converted the as-received NaSS polyelectrolyte to the hydrogen ion form by passing an aqueous solution of the polyelectrolyte through a mixed cation-anion exchange resin. The exact degree of non-stoichiometry achieved by reacting a known excess amount of HSS with VBTACL was determined by standard base titration.

* 200 ml H₂O was added initially in both cases to reduce the volumetric correction factor effect.

** In the preparation of a non-stoichiometric polysalt one would vary the portions of reacting species (cationic or anionic) at this point to create the desired degree of non-stoichiometry.
By correlating the achieved non-stoichiometric product $\text{H}^+$ excess with the mixing ratio (equivalents HSS/equivalents VBTACL) Amicon personnel were then able to formulate varying concentrations of $\text{H}^+$ ion excess.

The material identification given by Amicon has been used in the balance of this study. For example a sample designated 1.64 Na$^+$ refers to a film prepared from a polysalt powder that had 1.64 meq. $\text{H}^+$ excess / gram dry powder which was subsequently treated with a sodium chloride solution to exchange the $\text{H}^+$ ion for a Na$^+$ ion. Similarly 1.64 Ca$^{++}$ refers to a 1.64 meq. $\text{H}^+$ excess film treated with CaCl$_2$ solution.

(2) Preparation of Non-stoichiometric polysalt solutions

Based on the experience of other investigators, it was felt that a casting solution of approximately 15% by weight polysalt would produce acceptable quality films (particularly with regard to thickness). The ternary solvent system chosen for this investigation was composed of HCl, H$_2$O, and Dioxane in the volume ratio of 50:5:45.

The dry non-stoichiometric polysalt was dissolved first in dioxane followed by the addition of HCl and finally H$_2$O. This approach tended to minimize the formation of small globules of H$_2$O rich polysalt which dissolved slowly in the polysalt solution. The mixture thus formed was magnetically stirred for 24 hours. At this point, all the solutions were transparent with a slight amber color. Care was taken to avoid solvent loss during this period by insulating the weighing bottles in which the solutions were mixed. The bottles were then sealed with insulation tape to await the casting operation.

(3) Film Preparation

Following preparation of the mixed polysalt solutions, films were cast from these solutions within 24 hours of the conclusion of the mixing operation.

Drawing on the experience of investigators at Amicon, the required films were cast in the following manner:

Using a glass rod drawbar a wet film approximately 15 mils thick with an area 4" x 6" was drawn down on a clean glass plate. Care was taken in this operation to move the drawbar smoothly and quickly so
that no surface "skinning" effect would occur. The drawn film was inspected by reflected light to establish that no dust particles or other surface irregularities were present. The wet film was then placed under a glass cover dish in such a manner that a portion of the cover overlapped the edge of the plate. The assembly was placed on a pre-aligned flat shelf in a vacuum type oven at 70°C and atmospheric pressure. After exactly 15 minutes the cover was removed and a small amount of air was allowed to bleed through the oven. This continued for exactly 15 minutes, at which time a slight vacuum was applied (1-2 psig) for 5 minutes (oven still at 70°C). The film at this point when exposed to the atmosphere did not appear to be evaporating HCl and was fairly firm. A check was made by reflected light of the film surface to insure that it was still uniform and free of dirt, etc.

The glass plate plus film was then immersed in 2N HCl standard photographic developing tray and allowed to soak for 5-10 minutes. The film then could be removed from the glass substrate by slowly and carefully working a spatula along the interface. Care was taken not to stretch or puncture the film.

The films thus prepared were placed into their respective trays of fresh 2N HCl to await the counter-ion treatments.

(4) Film treatment

Following the preparation of the 3 types of film (varying degree of non-stoichiometry) one film of each type was placed into the following solutions, 2N HCl, 34N NaCl (2% by wt), 34N CaCl₂ (1.9% by wt).

The films were allowed to soak in the solutions for approximately 18 hours at which time the solutions were discarded and fresh stock solutions added. After another 9 hour soak period the films were removed from the solution and placed in 4" diameter embroidery hoops.

In general the films were stretched limply over the entire hoop frame. However, due to the severe shrinkage of the Ca⁺⁺ ion type in solution these films covered only about 2/3's of the hoop area. The assembled hoops were then placed into the 65% dessicator, (saturated Magnesium acetate) at room temperature (approx 24-27°C).
After approximately 16 hours in this environment the films were transferred to the 33% dessicator (saturated Magnesium chloride). The films were allowed to remain in this environment for 10 hours. At this point the films were removed from the hoops one at a time and samples cut using a surgical knife or punched with a steel die.

Two styles of specimens were needed for the dielectric tests. For the $10^2$ - $10^7$ cps frequency range a 1" x 1" sample was necessary. The $8.5 \times 10^9$ frequency test required a 1" diameter disk. Attempts were made to punch the latter specimens out of the films, however, for the more neutral film (.005 H⁺, .005 Na⁺) and all Ca⁺⁺ films it was found that the films were too brittle to allow this. Where possible these specimens were obtained by tracing the punch with the surgical knife.

The specimens once obtained were placed immediately into the 33% dessicator to await dielectric property tests.

(5) Dielectric Measurements

Through the cooperation of the personnel of the Laboratory for Insulation Research (M.I.T.), in particular, Mr. William Westphal, arrangements were made to utilize their equipment for the dielectric tests.

To cover the 8 decades of frequency, $10^2$ - $10^{10}$ c/s, use was made of two Schering style bridges as well as a Central Research Laboratories Microwave Dielectrometer and a resonant circuit device. One of the Schering bridges was a standard General Radio Model 716C while the other was a recently constructed wide-range bridge. This latter bridge is briefly described in a report by von Hippel and co-workers(44).

The measurements made by the standing wave method (Microwave Dielectrometer) required a 1" diameter sample. A detailed treatment of the technique, calculations and theory for this type of measurement has been given in several reports by personnel from the Laboratory for Insulation Research (30, 48, 49). It will not be repeated here.
The open-circuit measurement was made by placing the film between two .2500 inch thick cross-linked polystyrene spacers. This assembly was then loaded into a closed end sample holder in such a fashion that the assembly fit intimately with the walls of the guide and rested flush against the bottom of the sample holder. This unit then was attached to wave guide by a screw thread fitting.

Measurements made over the range $10^2$-$10^7$ cps were conducted with the specimen mounted in a cell of the type shown in Figure 3. The upper and lower electrodes opened to allow insertion of the sample. Then by adjusting one electrode pair tight against the film the film could be drawn taut and the remaining electrode tightened. The electrode assembly was then returned to the proper dessicator to await measurements. A sufficient number of cells (ten) were constructed so that once a sample was mounted in the cell it remained there until the conclusion of the particular test run.

Initially an attempt was made using a resonant circuit to obtain the necessary data to calculate the loss tangent and the dielectric constant by means of the susceptance variation method for the $10^2$-$10^7$ c/s frequency region. Data was taken on the equipment for the cells with and without samples, (the samples being maintained at 33% RH). For reasons discussed later, it was found necessary to make these measurements on the Schering bridges mentioned earlier.

The cells were reloaded and placed into the 33% dessicator. Then the cells were taken one at a time - as needed from the dessicator and threaded onto the glass jar as tightly as possible. Measurements were generally made from $10^2$-$10^7$ cps in steps of 1 decade. A complete run usually took less than 1/2 hour.

During a given run-depending on the particular specimen, it was usually necessary to switch from the GR 716C bridge to the "new" wide-range bridge. The exact frequency decade where the transition occurred varied with the specimen. (see data Tables XII, XIX) Furthermore it was necessary to switch from the resistance capacitance substitution method as $\tan \delta$ decreased. Where the resistance capacitance substitution method applied, one simply adjusted the level
of resistance in parallel with the sample while simultaneously adjusting capacitance until a null of the bridge was established. In the capacitance method usually it was necessary only to adjust the capacitance to a suitable null point.

The cells were measured with the samples essentially at 33% RH. The cells were immediately placed in a 65% dessicator and after approximately 16 hours, samples were withdrawn one at a time and measured.

Three specimens (0.81 H⁺, 1.64 Na⁺, 1.64 Ca++) were returned to the 33% dessicator for purposes of a re-run at that humidity level. After a period of approximately 20 hours, these samples were tested again.

The thickness of all specimens used in the dielectric tests were obtained by measurement with a metric micrometer. Five readings per specimen were used to obtain the average thickness.

As mentioned earlier, while in general the experimental plan was to work from 10²-10⁷, in certain cases it was expedient to work in a discontinuous manner due to the necessary equipment changes. The order of measurement is shown on the data sheets.

(6) Moisture Content determinations

At the time when the dielectric test specimens were placed into the 33% dessicator to await tests, one sample (usually 1" x 1") of each film and ion type was placed into an open polyethylene vial in the same dessicator.

Since a typical dielectric test run required 1/2 hr., it was decided that a more accurate representation of the moisture content would exist if all samples were weighed just prior to the dielectric test series and then reweighed immediately following completion of the run. Therefore, two measurements were made for each humidity level, one prior to and one following the dielectric tests. These weights readings were made on a Mettler balance which was carefully checked each time to insure that the zero point was accurate.

Readings were taken for the 33% RH level and then along with the dielectric test specimens, the moisture content samples were placed into the 65% RH dessicator.
Originally it had been felt that the films would have equilibrated at 33% R.H. in about 24 hours based on Falkenstein's work. However, the continued decrease of moisture content following dielectric tests at 33% R.H. suggested that the samples were not stabilized at that condition. Therefore, following the 65% R.H. tests the samples were returned to the 33% dessicator for an additional 70 hour period to enable a more accurate determination of moisture content to be made.

The data taken prior to and after the dielectric test were averaged so as to more accurately represent the moisture content of the film during dielectric tests. The same procedure was used at 65%. These results have been labeled "transient moisture contents". For purposes of comparison with prior studies the data obtained initially at 65% and that after the 70 hour 33% RH conditioning have been used since it was felt they more accurately represented the "long term" behavior at these conditions.

The dry weight of the various films was established by putting the films into small preweighed weighing bottles and mounting these bottles in a vacuum dessicator over \( \text{P}_2\text{O}_5 \). A vacuum was drawn continuously on the dessicator for approximately 100 hours. At the end of this period air was let into the dessicator slowly through a drying tube. The vials were promptly capped and weighed. A recheck made after 24 hours further conditioning verified the results.

(7) Ion Content Analytical Procedures

A determination of the residual ion content for the sodium and calcium treated films was made using flame photometry.

Samples of the films from which the test specimens were cut were placed into polyethylene vials in a 33% (magnesium chloride) dessicator at the start of the dielectric test measurements. From these samples small (0.05-0.15 gram) samples were taken and placed in pre-cleaned crucibles. The covered crucibles were then ignited using an oxidizing flame from a Meeker burner. Samples were ignited until no evidence of carbon existed at which time the residue was transferred to extensively cleaned, deionized water rinsed, 25 ml. volumetric flasks with deionized water.
The samples were then analyzed using a Beckman Model B Flame spectrophotometer. Care was taken to make this analysis quickly to avoid loss of ions due to adsorption on the glassware. An oxygen hydrogen flame was used and the wavelength dial set at 586 millimicrons for sodium or 418 millimicrons for calcium. Following the instrument manufacturers’ recommendation* the instrument was equipped with a "UV Phototube" (blue sensitive).

A minimum of three measurements were made on each sample as well as a blank and a known standard. The standards employed were both 40 ppm concentration (Sodium or Calcium).

(8) D.C. Conductivity Measurements

To augment the a.c. conductivity measurements, a quick check was made of the d.c. conductivity behavior for two representative samples, 1.64 Ca⁺⁺ and 1.64 H⁺.

The equipment consisted of the sample mounted in the dielectric cell connected in series with a 3 volt "A" Battery and a Keithley Instrument Model 150A Microvolt-ammeter. The latter device was capable of reading currents to $10^{-12}$ amperes with an accuracy of 3% on all scales. The unit after 1 hour warmup exhibited drift less than $+2\times10^{-11}$ amperes/day.

The voltage of the battery was periodically checked using a Simpson Model 303 Vacuum tube voltmeter.

Using this equipment measurements were made initially on the 1.64 Ca⁺⁺ samples (@ 65% RH). The Keithley microvolt-ammeter was allowed to warm up for approximately one hour prior to use. The circuit was then interrupted and the zero suppress adjustment made to correct the zero point. The circuit was re-established and readings taken instantaneously. Readings of the current level as well as the battery voltage were taken periodically for approximately 3 hrs.

The same procedure was used to determine the response of the cell containing a 1.64 H⁺ film sample. In this case readings were taken periodically for approximately 5 1/2 hrs.

All measurements were made at room temperature (24-27°C).

*Beckman Instruction Manual 334-B Sept 1963
IV Results

In the following section the significant results of this study are summarized in graphical and tabular form.

The dielectric constants (\( \varepsilon' \)), loss factors (\( \varepsilon'' \)) and loss tangents (\( \tan\delta \)) of the 8 samples studied are shown in Figures 4-11 as a function of relative humidity and frequency. The same data is presented in tabular form in Tables II - IV. The effect of a humidity cycling operation is presented in Figures 6, 7 and 10 as well as Table V.

Figures 12 and 14 show the influence of ion type on the observed dielectric response at two levels of sulfonate excess. Figures 12 and 13 show the influence of ion type on the observed dielectric response at two levels of relative humidity.

The influence of moisture content on the observed dielectric response is summarized in Figure 15 for two levels of frequency. Table VI presents the moisture content data for 9 samples at two humidity levels.

Figures 16 and 17 present the influence of excess sulfonate content on the dielectric constant \( \varepsilon' \) at both 1 KC and 10 KC. Tables VII and VIII introduce the data developed for the residual ion content and water content / ion in the various samples.

Figure 18 presents the moisture content of the materials as a function of the relative humidity. Figure 19 shows the influence of sulfonate excess on moisture content at 33% and 65% relative humidity.

Figure 20 shows the relationship between residual ion content and the degree of stoichiometry in the as-cast film (sulfonate excess). Figures 21 and 22 present the influence of residual sodium and calcium ion content on the value of \( \varepsilon' \). The significant conductivity results are summarized in Table IX.
FIGURE 4
SAMPLE 1-64 H⁺
Figure 9

Sample: 0.005 Na⁺
FIGURE 10  SAMPLE 1.64 CA++
### TABLE II
Non-stoichiometric polycrystal Dielectric Constants ($\varepsilon$)

Temperature: 24-26°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>%R. H.</th>
<th>Frequency (c/s)</th>
<th>$10^2$</th>
<th>$10^3$</th>
<th>$10^4$</th>
<th>$10^5$</th>
<th>$10^6$</th>
<th>$10^7$</th>
<th>$10^8$</th>
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</thead>
<tbody>
<tr>
<td>1.64 H⁺</td>
<td>33</td>
<td></td>
<td>4.02x10⁵</td>
<td>4.14x10⁴</td>
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<td>65</td>
<td></td>
<td></td>
<td>1.14x10⁷</td>
<td>5.73x10⁴</td>
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<td>2.91x10³</td>
<td>7.84x10¹</td>
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<tr>
<td>1.33 H⁺</td>
<td>33</td>
<td></td>
<td>1.66x10⁶</td>
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<td>9.84x10¹</td>
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<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td>4.33x10⁶</td>
<td>6.01x10⁵</td>
<td>5.17x10⁴</td>
<td>3.02x10³</td>
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TABLE III
Non-stoichiometric Polysalt Loss Factors ($\varepsilon'$)

Temperature: 24-26°C

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### TABLE V

Humidity Variation Study

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Temperature: 24-26°C
% RELATIVE HUMIDITY: 33

LOG FREQUENCY

DIELECTRIC CONSTANT vs. COUNTER ION TYPE

FIGURE 12
FIGURE 13

% RELATIVE HUMIDITY: 65

LOG FREQUENCY
DIELECTRIC CONSTANT VS COUNTER ION TYPE
Figure 14

% Relative Humidity: 65

Log $\epsilon'$ vs. Log Frequency
Dielectric Constant vs. Counter Ion Type

0.81 H⁺
0.81 Na⁺
0.81 Ca²⁺
Figure 15
Dielectric Constants as a Function of Moisture Content
(Data Points Omitted For Purposes Of Clarity - Trend Lines Indicated)
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<th>33% R.H. Transient</th>
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<th>33% R.H. Reconditioned</th>
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* Average moisture content at the time of dielectric tests.
FIGURE 16

DIELECTRIC CONSTANT vs. EXCESS SULFONATE CONTENT AT 1 KC

FREQUENCY: 1 KC

LOG $\varepsilon'$

0.4 0.8 1.2 1.6 2.0
MEQ. SULFONATE EXCESS / GRAM DRY POLYSALT

65% R.H., $H^+$
65% R.H., $Na^+$
33% R.H., $H^+$
33% R.H., $Na^+$
65% R.H., $Ca^{++}$
FIGURE 1T

DIELECTRIC CONSTANT VS. EXCESS SULFONATE CONTENT AT 10 Kc

FREQUENCY: 10 KC %

MEQ. SULFONATE EXCESS / GRAM DRY POLYSALT
TABLE VII
Residual Ion Content

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* Weight of 399 grams has been assumed in conformance with Falkensteins studies
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<td>6.7</td>
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<td>14.0</td>
</tr>
<tr>
<td>0.005 Na⁺</td>
<td>6.3</td>
<td>10.2</td>
<td>2.4</td>
<td>2.2</td>
<td>10.8</td>
<td>9.9</td>
</tr>
<tr>
<td>1.64 Ca²⁺</td>
<td>9.5</td>
<td>14.9</td>
<td>5.6</td>
<td>6.9</td>
<td>4.6</td>
<td>5.6</td>
</tr>
<tr>
<td>0.81 Ca²⁺</td>
<td>9.5</td>
<td>14.0</td>
<td>5.6</td>
<td>6.0</td>
<td>8.9</td>
<td>9.2</td>
</tr>
<tr>
<td>0.005 Ca²⁺</td>
<td>8.7</td>
<td>13.4</td>
<td>4.8</td>
<td>5.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutral</td>
<td>3.9</td>
<td>8.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* per Falkenstein (7)
Figure 18
Moisture content as a function of relative humidity.
FIGURE 19
LONG TERM MOISTURE CONTENT vs. EXCESS SULFONATE CONTENT

GRAMS WATER / GRAM DRY FILM

LONG TERM MOISTURE CONTENT

1.33 H⁺, 65% R.H.
65% R.H., Na⁺
65% R.H., H⁺
65% R.H., Ca²⁺

1.33 H⁺, 33% R.H.
33% R.H., H⁺
33% R.H., Ca²⁺
33% R.H., Na⁺

O NEUTRAL FILM
(FALKENSTEIN)

NEQ. SULFONATE EXCESS / GRAM DRY POLYSALT
FIGURE 20

RESIDUAL ION CONTENT vs. EXCESS SULFONATE CONTENT

MEQ. SULFONATE EXCESS / GRAM DRY POLYSALT

NEQ. ON / GRAM DRY FILM

RESIDUAL ION CONTENT

Na⁺

Ca⁺⁺
FIGURE 21

RESIDUAL SODIUM ION CONTENT vs. DIELECTRIC CONSTANT

RESIDUAL ION CONTENT
(MEQ ION/GRAM DRY POLYSALT)
FIGURE 22

RESIDUAL CALCIUM ION CONTENT vs. DIELECTRIC CONSTANT

RESIDUAL ION CONTENT (MEQ. ION/GRAM DRY POLYSALT)
### TABLE IX

**D.C. Conductivity Measurements**

<table>
<thead>
<tr>
<th>Sample</th>
<th>1.64 Ca$^{++}$</th>
<th>1.64 H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t = 0$ $\rho = 1.66 \times 10^5$ ohm cm</td>
<td>$t = 0$ $\rho = 2.50 \times 10^3$ ohm cm</td>
</tr>
<tr>
<td></td>
<td>$k = 6.03 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$</td>
<td>$k = 4.0 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$t = 3$ hrs $\rho = 1.56 \times 10^5$ ohm cm</td>
<td>$t = 5$ hrs $\rho = 3.8 \times 10^3$ ohm cm</td>
</tr>
<tr>
<td></td>
<td>$k = 6.41 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$</td>
<td>$k = 2.6 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$</td>
</tr>
</tbody>
</table>

Avg. Current density = $7 \times 10^{-6}$ amperes/cm$^2$

Avg. Current density = $3.9 \times 10^{-4}$ amps/cm$^2$
V. Discussion and Interpretation of Results

A. Moisture Content

The moisture contents of the non-stoichiometric polysalt films were determined from the difference between film weights for a given relative humidity level and those weights established after 100 hours under vacuum in a desiccator (over P₂O₅). See Section III B-6). As can be seen from Figure 19 and Table VI the water content (with the exception of the 1.33 H⁺ film) increased with increasing degree of non-stoichiometry in the original film. In every case the water content increased with increased % relative humidity.

Falkenstein (7) found that the moisture content of neutral (stoichiometric) film increased with increasing % relative humidity as shown in Figure 18. In his study Falkenstein assumed that the linear weight behavior of the polysalt films and metal foil support could be extrapolated to 0% R.H. to determine the weight of the dry film and metal foil. The foil weight was established by burning off the polysalt film and reweighing the foil. Gray (15) re-investigated the moisture sorption behavior of neutral polysalt and found that the linear curve noted in the region between 30-80% RH did not extrapolate directly to zero. (See Figure 18). Extrapolation of the linear region intercepted the ordinate at approximately .15 gm H₂O/gm polysalt.

A review of the results noted in Figure 18 reveals that Falkenstein's neutral film sample apparently absorbed less moisture as a function of relative humidity than did the non-stoichiometric samples or Gray's neutral sample. Correction of Falkenstein's data to include the .15 gm H₂O/gm polysalt shifts his curve to the position shown in Figure 18. The fact that the corrected data lies somewhat above that reported by Gray fits well with the expected behavior for a less consolidated film. (Falkenstein's films were prepared by a process that produced relatively porous films). Improvements in film casting techniques have enabled the achievement of higher degrees of consolidation in the films used by Gray and in this study as well.

The non-stoichiometric films while generally exhibiting the same slopes as the neutral films tend to lie below Gray's neutral film curve. Intercept values range from .05 to .11 grams H₂O/gram dry polysalt. Note also that the deviation from the neutral film curve was greatest for those samples which were only slightly non-stoichiometric.
Hydration data for sulfonated styrene ion exchange materials (17) suggests that the non-stoichiometric samples should contain approximately 1 to 2 moles of water per ionogenic group at low relative humidities. Data shown by Helfferich (17) for moisture sorption of the H+, Na+, Ca++, and N(CH₃)₄⁺ forms of cation exchangers (Dowex 50) extrapolate to approximately 1.2 to 1.5 moles H₂O/ion equivalent at zero % R.H. (A similar analysis of the reported data for various anion exchangers Cl⁻, etc. extrapolates to less than .5 moles H₂O/ion equivalent.)

With these data in mind it is suspected that the location of the non-stoichiometric curves in Figure 18 is incorrect. If each curve was shifted upward by about 2 moles H₂O/mole polysalt (approximately .15 gm H₂O/gm pollysalt) a more reasonable relationship would result. It is believed that the low "apparent" moisture contents resulted from incorrect dry film weight. During the drying process the collapse of the pollysalt network occurs first at the air-polymer interface forming in effect a skin which may trap moisture in the bulk of the sample.

It was expected that the degree of consolidation of the original film might also play a part in the ability of the system to sorb water. Data currently being developed by Fleming (8) suggests that the deviation in moisture sorption for the film casting procedure described earlier is quite small (1-2%) on the basis of gm H₂O/gm pollysalt. It is therefore felt that this mechanism plays a minor role in the location of the non-stoichiometric film curves.

It is suggested that in the linear range of the moisture content versus % relative humidity curves (Figure 18), the increased moisture is "free" water. That is, water not tied up in the form of hydration shells. If these non-stoichiometric materials can be considered to be analogous to weakly cross linked ion exchange resins then previous evidence (17) suggests that the tendency to sorb free solvent is dependent on the number of counter-ions/unit volume and the valence of these counter-ions. This point will be considered later with reference to Figure 19.

In spite of their questionable accuracy the data shown in Figure 18 reveal several interesting facts. There appears to be a distinct difference in terms of the water absorption characteristics of the films between the 33% and 65% relative humidity levels. A linear relation exists at 65% R.H. between the apparent moisture content and sulfonate excess whereas at the low (33% RH) humidity the relationship is definitely non-linear.
The moisture content data obtained in this study for the 0.81 and 1.64 H+ films at 65% extrapolate exactly to the value obtained by Falkenstein for neutral film. The behavior of the 33% data also seems to indicate that the H+ film data (0.81 and 1.64) agrees with prior work.

A possible explanation for the variation in moisture sorption at 65% R. H. with degree of non-stoichiometry (as shown in Figure 19) may be the following: It is suggested that for the Na+, and H+ films at 65% the sorbed moisture has filled completely the hydration shells. Therefore "free" water exists in an amount dependent on the number of counter ions per unit volume and the strength of interactions between the hydrated ions and water molecules.

It was noted in the course of film preparation (See Section III B-4) that when the original H+ form films were placed in the final ion treatment solutions the Ca++ films tended to shrink whereas, the H+ film expanded slightly while the Na+ form remained at near its original size. The consolidated structure of the Ca++ film would retard moisture absorption whereas the expanded structure of the H+ form would favor increased absorption.

In the case of the Ca++ samples it is believed that the chain network is partially cross linked due to interaction of pendant anionic groups from neighboring chains with the divalent calcium cation. This interaction causes a decreased chain-chain spacing and a consolidation of the system generally. This structure while it would tend to hydrate would restrict diffusion of water molecules to sulfonate sites. Apparently the presence of only a few calcium ions is sufficient to substantially "freeze" the structure into a consolidated packing. Thus the moisture gain as a function of degree of non-stoichiometry is relatively constant.

After considering several possible explanations for the observed behavior at 33% RH (in Figure 19) the following theory appears most reasonable. It is suggested that the ability to remove water from the polyanion matrix decreases as the degree of non-stoichiometry increases. Data obtained by a drying operation therefore should be most accurate at low levels of non-stoichiometry. Furthermore it is suspected that most of this water involved in the transfer process is "free" water as opposed to "bound" water (water in hydration shells). The observed behavior should be therefore a linear increase in moisture with increasing degree of non-stoichiometry. The deviation from linear behavior
is a consequence of the combined skin retardation effect at the air-polymer interface and increased intermolecular binding forces due to the increased polar character of the system.

It is interesting that the H⁺ data at 33% RH also tends to extrapolate to that noted by Falkenstein for neutral film. This further serves to reinforce the suspicion that the moisture content is about 2 moles H₂O/mole polysalt low.

With the exception of the 1.33 H⁺ film, all films received exactly the same conditioning treatment. Based on Falkenstein's studies it was felt that exposure to the 33% environment for approximately 24 hours would be sufficient for the films to reach equilibrium. This was not the case since decreasing moisture contents were noted between measurements taken after 24 hours and 36 hours exposure to 33% R.H. (It should be pointed out here that the temperature variation of the dessicator did not exceed 2°C during this period and that the magnesium chloride salt solution remained saturated throughout period). The data used therefore were accumulated after 70 hours exposure to 33% R.H. The 70 hour period was chosen based on studies with neutral polysalt. It now appears from more recent investigations that an equilibrium steady state value for moisture content may be impossible to attain due to relaxation processes in the network.

The data shown for the H⁺ form in Figure 19 are irregular in that the moisture content of the 1.33 H⁺ film at 33% and 65% R.H. appears to be too high. As shown in Figure 19 the data seem to be out of 'true' position by about .03 - .04 grams water/gram dry film. The difference between the pre-test history of the 1.33 H⁺ film as compared to the balance of the test specimens is not great. Only two notable differences exist.

(a) the 1.33 H⁺ film had been allowed to soak for approximately 160 hours in .2N HCl prior to humidity conditioning whereas the other H⁺ specimens were stored for only 50 hours (average) in this environment. (All other specimens saw the .2N HCl for approximately 20 hours prior to salt solutions treatments).
(b) The 1.33 H+ film had accumulated approximately 120 hours more exposure to 33% R.H. prior to the dielectric test than any other film. From this point the 1.33 H+ sample was treated in an identical manner as the other specimens. (See Appendix Figure 23).

It is suspected that the extended 0.2N HCl soaking period allowed structural rearrangement more conducive to higher moisture absorption capacity. The shielding effect of the HCl may have expanded the matrix. If relaxation followed this it would be possible to create an effect a less dense network structure. This new structure would exhibit higher moisture absorption capacity due to the increased free volume in regions where the cations exist. In the case of samples not exposed to the prolonged soak period, the relaxation effect would not have exposed to the prolonged soak period, the relaxation effect would not have proceeded to the same extent and therefore, when placed in the drying atmospheres (65% RH followed by 33% R.H.) recovery (shrinkage) would occur to a greater degree, with a lower residual (trapped plus bound) moisture content.

Undoubtedly there are other possible explanations which can be formulated for the behavior. For example, the moisture content data was developed based on single representative film specimens. A statistical analysis of the variance existing between samples taken from the same film or films made in an identical manner was not made. The relative error in the case of the 1.33 H+ film was approximately 12%. Analysis of the experimental errors suggests that the moisture content should be accurate to within 2%. Furthermore the 1.33 H+ sample was free of voids as seen by the unaided eye.

(1) Summary

The apparent weight gain at 65 and 33% RH when plotted versus the excess sulfonate content extrapolated in a reasonable fashion to the data obtained by Falkenstein for neutral polysalt. Comparison of the moisture sorption values for various relative humidities with recent data developed by Gray for neutral polysalt suggests that the drying operation used in this study failed to remove the total moisture content. This same error has been noted in Falkenstein's data. The
formation of a collapsed network at the polymer - air interface which hinders moisture removal is thought to be the prime factor responsible for the error. At the humidity conditions used for the dielectric tests these non-stoichiometric materials seem to exhibit a linear increase in moisture content with increasing relative humidity. By analogy to ion exchange resin systems this behavior is thought to be due to the addition of "free" water to a matrix where the ions are totally hydrated.

(B) Residual Ion Content

The exchange of ions (Ca\(^{++}\), Na\(^{+}\)) with the H\(^{+}\) form of the non-stoichiometric films was made under conditions quite favorable to the total replacement of all excess H\(^{+}\) ions. In the H\(^{+}\) form the films tended to be swollen due to the high hydration tendency of H\(^{+}\), the high internal pressure which this creates and the weakly cross-linked nature of the system. Exchange of Na\(^{+}\) or Ca\(^{++}\) for H\(^{+}\) in this swollen structure is favored by additional factors such as the higher valence of Ca\(^{++}\) and the greater polarizability of both Na\(^{+}\) and Ca\(^{++}\).

As shown in Figure 20 (and in Table VII) the residual ion content (Na\(^{+}\), Ca\(^{++}\)) of the non-stoichiometric films tended to increase with increasing degree of non-stoichiometry. For a strict 1 to 1 correspondence on this plot the curves should approach a 45\(^{0}\) slope. The Na\(^{+}\) ion content seems to behave in this manner as nearly as one can tell from the available data. The variation between identical runs from the same film suggests that the accuracy of the measurements is only approximately 40\% at these levels of Na\(^{+}\) content. However, it could be also argued that the error is not one of measurement technique but actually exists. A larger number of samples would have to be run to settle this problem.

As can be seen from Figure 20, when related on an equivalent basis, the Ca\(^{++}\) data falls very closely to the 45\(^{0}\) line representing a 1 to 1 relationship between equivalents of residual ion and equivalents of H\(^{+}\) excess in the original film. If the residual ion data were converted to a mole basis the slope of the Ca\(^{++}\) vs. degree of non-stoichiometry
would be almost exactly $1/2$ that of the $\text{Na}^+$ data. Thus it would seem that there is a definite relationship between the residual ion content and the known degree of non-stoichiometry. Furthermore it is believed that in the process of swapping ions the $\text{Ca}^{++}$ ions associate with two pendant anion groups whereas the $\text{Na}^+$ or $\text{H}^+$ ions link up with only one group.

C. Dielectric Behavior

The dielectric properties of the non-stoichiometric films were quite sensitive to ion content, ion type and moisture content. The specimens behaved in a manner quite similar to the neutral films (with sorbed electrolyte) studied by Falkenstein. The concept of discrete domains which Falkenstein used for interpretation of his data seems to apply equally well to this case. The effects of ion content, moisture content and frequency seem to be reasonably explained by consideration of their influence on the number, size and polarity of the discrete domains as will be explained in the following sections.

The "discrete domain" model may be partially illustrated by the following remarks. It is believed that a domain exists (on a microscale basis) where a pendant sulfonate group is associated with a hydrated counter-ion. In view of the moisture content data (see section V-A) undoubtedly in these tests "free" water exists weakly associated with the hydrated cation. Each distinct domain is thought to act as a separate polarizable element. The total polarization as a result includes a contribution directly influenced by the number of discrete domains (i.e. degree of non-stoichiometry).

As will be pointed out later in Section D the concept of a heterogeneous structure with discrete domains and its contributions to the total observed capacitive or resistive response can not be resolved completely due to the simultaneous presence (at frequencies below approximately $10^5$ c/s) of electrode polarization effects. Those factors which serve to increase heterogeneous polarization also could be interpreted as aiding electrode polarization. In the following sections 1-5 the influence of the controlled variables in this study (relative humidity, ion type, degree stoichiometry) will be interpreted in terms of a discrete domain hypothesis primarily. The significance of electrode polarization will be reserved for analysis in Section D.
(1) As a function of water content

The variation in dielectric constant $\varepsilon'$ with transient moisture content is shown in Figure 15. In these figures, $\varepsilon'$ at constant frequency is noted to rise with increasing moisture content. Transient moisture content refers to the average weight existing at the time of the dielectric tests as established by weighings prior to and following the tests. In each case ($10^2$ c/s and $10^3$ c/s) there is the suggestion that a family of curves exist. These curves tend to intersect at a high dielectric constant value and a common moisture content. The slopes of the log $\varepsilon'$ vs $H_2O$ content curves reveal that films in the Ca$^{++}$ form exhibit greater moisture dependence than the monovalent forms.

It is believed that the intersection point represents a critical point where the domain structure has collapsed and the dielectric behavior is predominantly due to electrode polarization. Collapse of the domain structure is meant to imply that the charge carriers in the matrix move freely throughout the body. That is, the effective domain size approaches that of the specimen. Two factors serve to modify the effective domain size—the ion mobility and the imposed voltage frequency. Increasing the frequency (for a given ion type and moisture content) will act to reduce the effective path length (domain size) of the charge carrier while an increase in ion mobility (using H+ instead of Na+, for example) will increase the effective path length.

Consideration of the reported data by Miskka and Falkenstein in an analogous manner reveals that while the NaBr doped films tend to exhibit the same behavior as the Na$^+$ non-stoichiometric films the neutral films show a slightly different behavior. The neutral films although exhibiting the same trend of increased $\varepsilon'$ with increased moisture content fail to extrapolate to the mutual intersection observed for the non-stoichiometric or treated films.
It is suspected that the similarity in behavior between the treated films and the non-stoichiometric films from this study arises from a similarity in charge transfer mechanism. Charge transfer—that is—d.c. conductivity is felt to play a less important part in the observed dielectric behavior as the moisture content is decreased, however, it still is a major factor at the moisture contents studied in both this and Falkenstein's study. The reduced slope in 15a and 15b observed for neutral film is due to the reduced mobility of charge in this matrix. The charge carrier in this system may be a $H_3O^+$ ion, or residual impurities. It is expected that the increased inter-atomic drag forces would reduce the charge transfer (diffusion) ability of this structure thus reducing the d.c. conductivity and in turn the observed dielectric constant.

With increased frequency the family of curves appear to shift to higher moisture contents. The intersection however occurs at approximately the same level of dielectric constant. It appears likely that the "effective" domain size decreases with increased frequency since the charge carrier motion is restricted. Addition of water to the matrix is thought to "plasticize" the structure reducing the drag forces on the charge carrier. The increased mobility of the charge carrier in this "plasticized" structure compensates for the decreased "travel time" allotted the ion in a given half cycle. (Analysis of this shift factor may give an activation energy for ion motion). Thus the tendency for frequency to decrease the domain size and hence lower the dielectric constant is counterbalanced by the increased moisture content and the dielectric constant remains approximately constant.

(2) As related to residual ion type and content

The effect of ion type is shown in Figures 12, 13, and 14. From these graphs, it would seem that the effect of changing the ion type (particularly at low humidity levels) is to shift the $\varepsilon'$ vs frequency curve along the frequency axis. (Note Figure 12). The curves shown for the treated film product formed from both the original 1.64 H$^+$ and 0.81 H$^+$ base films reveal that at a given frequency the H$^+$ ion produces the highest value of $\varepsilon'$ followed in order by Na$^+$ and Ca$^{++}$. At higher humidity conditions (Figure 13) the 1.64 H$^+$ and 1.64 Na$^+$ curves tend to overlap while the 1.64 Ca$^{++}$ data still falls substantially below the other samples.
The shift of the curves to higher frequencies indicates a trend toward shorter relaxation times. It is suggested that the ability of a domain structure to follow the oscillations of the field is related in some fashion to the basic aqueous solution mobility of the ions (H⁺, Na⁺, Ca⁺⁺).

With regard to the influence of ion content on the value of \( \varepsilon' \), Figures 21 and 22 show that a distinct increase in \( \varepsilon' \) exists with an increase of residual ion content. In the case of the sodium ion it would seem that at 33% R.H. the increase in \( \varepsilon' \) follows the same general pattern as at 65% for a given frequency, however, the curves are shifted to lower \( \varepsilon' \) values with increasing frequency.

As briefly mentioned earlier it is thought that a discrete domain is formed by a hydrated ion. Further it is believed that each domain acts as a polarizable element. Increasing the ion content increases the number of polarizable elements and since each element possesses a finite dipole contribution at a given field strength, the dielectric constant increases. Simultaneously however the existence of a greater number of ions could lead to increased electrode polarization since charge transfer thru the polyanion matrix should increase. Further discussion of this point is reserved for a later section.

(3) As a function of frequency

Every specimen investigated in this study exhibited decreasing dielectric constant (\( \varepsilon' \)) and loss factor (\( \varepsilon'' \)) with increasing frequency. In this respect the samples behaved in an analogous manner to the sodium bromide treated films studied by Falkenstein. The incremental change in both \( \varepsilon' \) and \( \varepsilon'' \) for the frequency interval \( 10^2 \) to \( 10^{10} \) c/s was approximately the same for the monovalent ions (H⁺, Na⁺) while that for the divalent ion (Ca⁺⁺) was substantially lower (two to three decades). Furthermore, in general, the incremental change in \( \varepsilon' \) and \( \varepsilon'' \) decreased with decreasing degree of non-stoichiometry.

As shown in Figures 4 thru 11, the incremental change (\( \Delta \log \varepsilon' \)) in dielectric constant (\( 10^2 - 10^{10} \) c/s) ranged from 2.2 to 6.5 if the effects of both ion and moisture content are considered. The effect of increased moisture content in general caused the slope of the \( \varepsilon' \) and \( \varepsilon'' \) vs frequency curves to increase. In a specific case, the incremental
change ($\Delta \log \epsilon'$) for Na$^+$ films at 33% R.H. was found to vary from 2.1 to 2.8 for the interval $10^{2}$ to $10^{5}$ c/s. Falkenstein had found that a film (75-B) at 33% R.H. containing 0.23 equiv. sodium bromide/ equiv. polysalt exhibited an incremental change ($\Delta \log \epsilon'$) of approximately 1.8 for the same frequency region whereas a 0.46 equiv. sodium bromide/ equiv. polysalt film (250-C) at the same conditions changed about 2.2. (Falkenstein chose to represent the ion content of his films by the term equivalents sodium bromide/equivalent polysalt where the equivalent weight of the polysalt was taken to be 399 grams).

Table VII shows the equivalents of ion/equivalent of polysalt for the films used in this investigation. Thus 0.23 equivalents sodium bromide/ equivalent polysalt corresponds quite closely to the behavior of the 0.81 Na$^+$ film while the 0.46 NaBr sample corresponds to ion content intermediate between 0.81 Na$^+$ and 1.64 Na$^+$.

From this one might conclude that for approximately the same level of equivalents of Na$^+$/equivalent polysalt the non-stoichiometric films exhibit a greater incremental change than the treated films. However, the effect of H$_2$O content cannot be neglected. The 0.81 Na$^+$ sample had a moisture content at 33% RH of approximately twice (0.20 vs 0.10) that of the 0.23 equiv NaBr/equiv polysalt film at 33% R.H.

As will be shown later moisture content tends to raise the dielectric constant and increase the incremental change ($\Delta \log \epsilon'$) versus frequency. Comparison of the two films at approximately equivalent moisture contents (0.20 gram moisture/gram dry film) reveals that the incremental change is very nearly the same (2.2 for 0.81 Na$^+$ and 2.3 equiv NaBr/equiv P.S.).

As pointed out earlier it is felt that the effect of increased frequency is to reduce the effective path length of the charge carrier. The major cause of the decrease of $\epsilon'$ with frequency at a given moisture content is attributed to reduced electrode polarization. This latter effect is virtually negligible at $10^{10}$ c/s.

The influence of excess water content (equivalents free water/equivalents of ion) (See Table VIII) must be controlled in any study of frequency dependence for ideal results. Failure to control this variable could completely mask the true results particularly at low frequencies.
(4) As related to degree of non-stoichiometry

As shown in Figures 16 and 17 the general trend observed at constant frequency (1 KC or 10 KC in this case) is an increase in $\varepsilon'$ with increasing sulfonate excess in the original as-cast films. The samples exhibited anomalous behavior at 1 KC however this is partially explainable by the tendency toward erratic behavior of the $H^+$ forms at low frequencies. (The rapid change of resistance made balance difficult to establish for the 1,64 $H^+$ forms and the resultant $\varepsilon'$ value is therefore probably in error). At 10 KC, it is observed that irregardless of ion type the incremental change in $\varepsilon'$ with increasing degree of non-stoichiometry remains about the same for a given relative humidity. Furthermore it can be seen that the highest values of $\varepsilon$ are produced by the $H^+$ form followed by $Na^+$ and then $Ca^{++}$. This same trend was true at 1 KC.

(5) Humidity Variation Study

The influence of moisture on the dielectric behavior of these poly-electrolyte complexes was also noted in the results of a humidity cycling study.

As shown in Figures 6, 7, and 10 of Table V, it was possible for the $Na^+$ and $Ca^{++}$ films to return to virtually the same values of $\varepsilon$ and $\tan \delta$ at 33% R.H. after a brief exposure to 65% R.H. Essentially the same behavior was noted for the 0.81 $H^+$ film above 1 KC. Below this frequency the problems previously noted (drift, instability, etc) with the $H^+$ films were apparent.

It can be seen in Table VI that the "transient" moisture contents of the reconditioned 33% RH samples were lower than the original 33% RH values by small amounts.

In the transient condition the films contained an appreciable amount of water. It is felt that at these levels of moisture content the restraints placed on moisture gain or loss are relatively loose, (presumably not affecting ion hydration shells, etc.) Thus reversibility of moisture gain or loss seems probable. Finally it is suggested that the domain was not altered by the cycling treatment.
(D) Comments on the Anomalous Dielectric Behavior

Before one can attempt to develop a model for the internal structure of the polya salt materials from dielectric studies it is necessary to consider the various mechanisms by which the observed high dielectric constants and losses, large phase shifts and broad dispersion regions occur. As pointed out in the Introduction (Section II), the development of high dielectric constants coupled with broad dispersion seem to rule out the consideration of homogeneous polarization mechanisms as a total answer. Although heterogeneous systems can exhibit relatively high dielectric constants and broad dispersion, a survey of typical results for purposely prepared heterogeneous systems shows that the non-stoichiometric polya salt materials exhibit significantly greater apparent dielectric values. A further possible mechanism that has not yet been ruled out is that of electrode polarization. This mechanism has been shown to have a considerable effect on the measured dielectric values of biological materials and electrolyte solutions especially at frequencies below $10^5$ c/s. (An excellent review of the dielectric analysis of biological materials by Sedunov (37) has recently been published). As will be pointed out in the following paragraphs the available dielectric data shows only the summation of effects due to electrode polarization, heterogeneous polarization and dipole polarization. Further tests to separate the components of the observed response are necessary before a complete interpretation of the internal structure can be made.

(1) Electrode Polarization

During the course of this study several observations were made that seemed to indicate the possibility of electrode polarization. For example, when attempts were made to balance the Schering Bridge circuit at low ($10^2$ c/s) frequency rapid shift of the resistance and capacitive values were noted with time for the 1.64 H⁺ samples. This drift seemed to indicate that there was an appreciable conductivity that increased with time.
A cursory examination of the D.C. voltage gradients between electrodes for a few films at laboratory ambient condition produced the observation that a linear relationship of voltage across the sample did not exist. Furthermore reversal of the field direction showed that at short times of measurement the measured voltage (. 3 volt) did not immediately change sign. Finally it was observed that the films exhibited significant D.C. conductivities when measured at current densities well within the limitations of ohmic behavior.

Although virtually every dielectric analysis of biological materials and polyelectrolyte solutions (to which the polysalt materials have been compared) has indicated the presence of electrode polarization below \(10^5\) c/s, Falkenstein (7) produced an analysis which he felt proved that electrode polarization effects were not present in the data for neutral films. Since this is the only evidence against the presence of electrode polarization in the polysalt materials a review of this analysis will be given.

Falkenstein analyzed the behavior of 5 films supposedly of identical chemical composition under constant humidity and temperature conditions (51% RH, approx. 25°C) as a function of frequency, using an impedance comparator bridge. The thickness of only one film was measured, all other film thicknesses were established by ratioing the capacitance values at \(10^5\) c/s as shown in the formula

\[
x = \left( \frac{C_x}{C_{\text{known}}} \right) \cdot (t_{\text{known}}) \quad \text{where} \quad C = \text{capacitance}
\]

Following this, Falkenstein observed that the ratios of measured capacitance, conductance and Tan \(\delta\) values for films of various thickness were constant irrespective of frequency. He concluded that the ratios should be constant with frequency and equal if

1. surface effects are small compared to volume polarization
2. the two films in the ratio possess identical volume properties

In his test Falkenstein measured the capacitance \((Cm)\) and resistance \((Rm)\) values required to balance the impedance and phase angle of the sample. At balance the Tan \(\delta\) values were computed from \(Cm, Rm\) for a given frequency using the equation for a parallel circuit (51),

\[
\text{Tan} \delta = \frac{1}{2\pi f \cdot \frac{Cm}{Rm}} \quad \text{where} \quad f = \text{frequency}
\]
Two equivalent RC circuit representations have been used in the literature to describe the behavior of systems containing electrode polarization effects. These circuits are composed of two impedances in series. In the model used by Schwann (34) for biological substances the impedance due to electrode polarization effects is regarded as a capacitance in series with a resistance. Sedunov (37), Shaw (38) and others have modeled the electrode effects as a parallel capacitance and resistance combination. This latter model therefore allows for a finite D.C. conductivity. Since the model assumed by Schwann (34) would suggest that the materials possess an infinite resistance at zero frequency the Shaw model seems better suited to our analysis.

As shown in the equivalent circuit analysis in the Appendix Section D, the model yields the result that the measured capacitance \( C_m = C_s + L \) where \( C_s \) = true sample capacitance and \( L \) = constant due to electrode polarization effects (at a given frequency for a fixed electrode area). Similarly the conductance measured \( G_m = G_s + K \). The value of \( K \) is shown to be small in comparison to \( G_s \) while \( L \) can be approximately equivalent to or greater than \( C_s \) (especially at low frequencies). Thus the ratio procedure fails to introduce any variable effect due to electrode polarization which would modify the observed and predicted constant relationship. Several articles in the literature serve to support this conclusion including studies by Smiley and Smith (40), Schwann (34), Jones and Christian (19) and Oncley (28).

Two questions which now require consideration are: What is the possible magnitude of the electrode polarization capacitance contribution at frequencies below \( 10^5 \) c/s and how can these values be determined?

Shaw (38) has made a systematic analysis of electrode polarization effects in the measurement of electrolyte dielectric constants. In this study it is shown that the polarization error at 1 KC for glycine solutions (conductivities from \( 5 \times 10^{-5} \) to \( 1.8 \times 10^{-4} \) ohm\(^{-1}\) cm\(^{-1}\)) ranges from approximately 17% to 88% of the true corrected value for the smallest electrode spacing studied. The error was found to increase with increasing conductivity and to decrease with increasing frequency. The variable conductivity solutions were formed by purposely adding KCl to the aqueous glycine solutions. An addition of only .0015 mole
KCl/liter solution was found necessary to reach the maximum conductivity studied.

Smiley and Smith (40) have also investigated the influence of electrode polarization on the dielectric constants of conducting solutions. They also observed that the polarization influence decreased with increasing frequency. In this study they assumed that the 500 KC value of capacitance was free from polarization effects and reported the excess capacitance at lower frequencies as totally attributable to electrode polarization. Using this scheme a dilute sodium chloride solution (2 x 10^{-4} N) which had a conductivity of 4. x 10^{-5} ohm^{-1} cm^{-1} had a capacitance increment of 21.0 μf at 1 KC. This value decreased by about 7.1 μfd for every decade increase in frequency. Increasing the solution normality raised the polarization error. Unfortunately the capacitance value at 500 kc was not given so that an estimate of the % error at 1 KC could be established. They further observed that the polarization influence increased with increasing hydrogen ion concentration for a series of solutions with differing pH values.

Although several investigators such as Schwann (33) and Mandel (20) have commented on the necessity for eliminating electrode polarization they have not included in their reports any indication of the magnitude of the polarization errors for their systems.

Two methods have been mentioned in the literature to eliminate the polarization error. The most popular technique appears to be that described by Shaw (38) which was developed by Fricke and Curtis (12). Two capacitance measurements are made on a given specimen, each measurement at a different electrode spacing. It should be evident from the analysis in Appendix Section D that subtraction of the smaller capacitance value from the larger one eliminates the constant electrode polarization influence. Calculations can then be based on the volume of sample contained in the region formed by the difference in electrode spacings. This approach has been employed by investigators concerned with dielectric behavior of electrolyte solutions with notable success. The utilization of such a method for materials such as the non-stoichiometric polyanion will require a consideration of the effects of the increased sample resistance. Since the buildup of the polarization layer is a time dependent process
an increase in sample length will increase the time necessary for the layer to develop to an equivalent size. For small electrode spacings (microns) as utilized in Falkenstein's study this equilibration effect should be negligible. However when the spacings approach those used in this investigation (2.5 cm) it may be expected that the polarization error will become thickness dependent.

Oncley (28) proposed that the polarization error could be eliminated by the correction $AG^2 \sqrt{\nu}^{-3/2}$ where $A$ is an empirical constant, $G$ the cell conductance and $\nu$, the frequency. The value of $A$ is the slope of the straight line obtained when the observed cell capacitance $C$ minus the cell constant $C_0$, $(C-C_0)$, is plotted against $G^2 \sqrt{\nu}^{-3/2}$ in a frequency region where the dielectric constant does not vary. It is then assumed that the value of $A$ can be used in regions where the dielectric constant varies with frequency. Oncley found that this method of correction was suitable only for frequencies greater than 25 KC. Shaw has analyzed the accuracy of this approach versus that of the variable electrode spacing method (33). His conclusion was that the variable electrode spacing (Fricke and Curtis) method was superior since the Oncley method requires measurements for at least two frequencies outside the dispersion region of the material under investigation. The Fricke and Curtis method could be utilized at a single frequency.

The electrode polarization effect; superimposed as it is on the other mechanisms of polarization makes any attempt to model the structure of the polysalt system with the available data a highly questionable operation. A careful re-evaluation of the dielectric behavior using the Fricke Curtis method on samples with low moisture content appears necessary to minimize the polarization errors. The fragility of the specimens at low moisture contents and the related problems of establishing good contact at the electrodes undoubtedly will be the significant experimental problems in this approach.
(2) Voltage Gradient Analysis

In an attempt to confirm the hypothesis that electrode polarization effects were dominating the dielectric behavior, a qualitative investigation of the A.C. voltage gradient profile was made by Mr. William Westphal (Laboratory for Insulation Research). A sample 1.64 H⁺, at lab. ambient condition (approx. 25°C, 60% RH) was placed between electrodes in a similar manner to the low frequency dielectric tests. A.C. voltage was then superimposed on the specimen (approximately 1 volt). A traveling probe was then placed in contact with the specimen and the voltage to the probe compared to the total imposed voltage.

This test was repeated at both 10 KC and 100 KC. A large voltage drop was noted in all cases within a very small distance of the electrodes.

The qualitative results of this test confirm the suspicion that electrode polarization effects dominate the observed dielectric response.

E. General Observations

(1) Test Specimens

It was quite evident while cutting test specimens that major mechanical property differences existed between the various films, particularly between ion types. For a given ion type there was a definite reduction in elastic modulus as the degree of non-stoichiometry was increased (for a given humidity level). The Ca⁺⁺ films as a group had a higher elastic modulus than either the Na⁺ or H⁺ films. Fabrication of specimens was easiest with the Na⁺ films.
The specimens used in these tests were purposely selected to be as void free as possible. In virtually every case the film samples used were transparent with a color and clarity approximating that of commercial polycarbonate film of equivalent thickness.

The mechanical property behavior of the films is attributed to two factors, the film density and the moisture content. The shrinkage experienced with Ca++ coupled with its low moisture content are felt to be responsible for the increased stiffness.

The observed clarity of the non-stoichiometric films did not differ appreciably from that noted with neutral film. These materials undoubtedly are amorphous systems due to the depression of crystallinity by the presence of the ionic forces.

(2) Testing Procedure

Based on the dielectric test problems experienced by previous investigators, it was felt that a test technique was needed that would

(a) eliminate need for extremely accurate thickness measurements
(b) minimize electrode polarization
(c) avoid surface contact area variations
(d) eliminate need for painting silver electrodes, etc. on specimens
(e) utilize thin film specimens

Discussions with W. B. Westphal revealed that a cell of the type shown previously in Figure 3 should meet all these requirements for the $10^2$-$10^7$ c/s frequency measurements. This cell provides for measurements in the plane of the specimen.

Attempts to use the susceptance - variation method revealed that at the $10^7$ c/s frequency level the technique could not establish a dielectric constant value. This was primarily due to the extremely high cell capacitance. The sample capacitance ($C_s$) was equal to the difference between the measured ($C_m$) capacitance and the cell capacitance ($C_h$). Unfortunately there was sufficient error in establishing $C_m$ and $C_h$ that $C_s$ often did not exist (difference went negative). At this point it was decided to test the specimen on the Schering Bridge equipment. Here extremely accurate differences could be measured. However, the cell constant fluctuated somewhat with frequency and as a result particularly at high frequencies the cell constant variation overrode the sample capacitance and dielectric constant values could not be calculated.
VI Conclusions

1. The water content of the non-stoichiometric films at a given humidity level increased with increasing sulfonate excess in the as-cast film. This data extrapolates in a reasonable manner to the data developed by Falkenstein for neutral polysalt. The water content appeared to increase in a linear fashion for the humidity range 33-65% R. H. in agreement with similar observations for neutral polysalt. In this region the incremental water content above the 33% RH level appears to be present as "free" water - that is - water not associated with an ion hydration shell.

2. By comparison to recent moisture sorption studies by Gray, the vacuum drying operation is felt to have been insufficient to remove all moisture from the specimens. This same error appears to have been incorporated in Falkenstein's data. The error is attributed to the collapse of the polysalt network at the polymer - air interface which significantly retards moisture transfer.

3. The counter-ion conversion procedure was successful as excellent agreement was noted between the residual ion content and the mill-equivalent excess sulfonate in the as-cast films. The Ca\(^{++}\) ion is thought to associate with two pendant anion groups based on the data. This "crosslinking" mechanism is believed to be responsible in part for the decreased dielectric response of the Ca\(^{++}\) films and for the pronounced shrinkage during drying.

4. The observed dielectric data while in agreement with trends predicted by the discrete domain hypothesis used in the analysis of salt laden films by Falkenstein are concluded to arise primarily from electrode polarization effects. A review of the experimental procedures used to determine the existence of electrode polarization by Falkenstein revealed that the method was not sensitive to the presence of electrode polarization. Voltage gradient analysis confirmed several qualitative observations which pointed to a dominate electrode polarization mechanism at frequencies below approximately 10\(^5\) c/s.

5. The simultaneous presence of at least two polarization mechanisms, electrode polarization and heterogeneous polarization, prevents any interpretation of the available data in terms of a molecular model. The trends noted with ion content (increased \(\varepsilon', \varepsilon''\) with increased ion content) moisture content (increased \(\varepsilon', \varepsilon''\) with increased moisture content), ion type (increased \(\varepsilon', \varepsilon''\) with increased ion mobility) and with
frequency (decreased $\varepsilon'$, $\varepsilon''$ with increased frequency) could be interpreted with equal success by either mechanism. Additional studies in this area will be required to separate and determine the magnitude of the two effects.
VII Recommendations

(1) The existence of polarization effects due to electrode polarization must be eliminated prior to any analysis of the data in terms of models such as the O'Konski or Schwarz models. This can be accomplished by adopting the correction procedure recommended by Shaw (38). The possibility of stray field errors must be minimized by procedures such as those shown by Schwan (35). In each measurement several checks should be made with increasing time to insure that equilibrium is established. Finally in future tests bright platinum contacts should be incorporated in the cell design to further minimize electrode polarization effects.

(2) An analysis of the magnitude of electrode polarization effects in these systems should prove valuable to new investigators in this area. Data of this type are not presently available in the literature. It would be interesting to see whether the polarization effect could be reduced to a negligible level at humidity conditions such as used in investigations by prolonged electrodialysis of the as-cast films to remove all residual impurities.

(3) The investigation of the true dielectric behavior in the low humidity region might provide a means of determining the disposition of water in the matrix. The dielectric behavior of a system with unfilled hydration shells should differ from that where the ions are totally hydrated. The shift of this break point between filled vs unfilled hydration shells with frequency should supplement the standard dielectric data as a function of frequency, humidity, ion type and ion content. From these data a better interpretation of the local microstructure should be possible.
VIII APPENDIX
### APPENDIX A

**TABLE**

**Moisture Content Data**

**Weight in grams**

<table>
<thead>
<tr>
<th>Sample</th>
<th>33% R. H.</th>
<th>65% R. H.</th>
<th>Dry***</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Dielectric Tests</td>
<td>After* Dielectric Tests</td>
<td>Long term*** Reconditioned (70 hours further conditioning)</td>
</tr>
<tr>
<td>1.64 H⁺</td>
<td>.0446</td>
<td>.0421</td>
<td>.0403</td>
</tr>
<tr>
<td>1.33 H⁺</td>
<td>.0440</td>
<td>.0421</td>
<td>.0400</td>
</tr>
<tr>
<td>0.81 H⁺</td>
<td>.0883</td>
<td>.0866</td>
<td>.0826</td>
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<tr>
<td>1.64 Na⁺</td>
<td>.0520</td>
<td>.0487</td>
<td>.0448</td>
</tr>
<tr>
<td>0.81 Na⁺</td>
<td>.0732</td>
<td>.0717</td>
<td>.0673</td>
</tr>
<tr>
<td>0.005 Na⁺</td>
<td>.0571</td>
<td>.0546</td>
<td>.0527</td>
</tr>
<tr>
<td>1.64 Ca⁺⁺</td>
<td>.0785</td>
<td>.0770</td>
<td>.0735</td>
</tr>
<tr>
<td>0.81 Ca⁺⁺</td>
<td>.0624</td>
<td>.0608</td>
<td>.0586</td>
</tr>
<tr>
<td>0.005 Ca⁺⁺</td>
<td>.0686</td>
<td>.0664</td>
<td>.0640</td>
</tr>
</tbody>
</table>

* Time elapsed between measurements = 12 hours during which each sample was removed from dessicator for period no longer than 1 hour (in sealed cell)

** Time elapsed between measurements = 11 1/2 hours, during which each sample was removed from dessicator for period no longer than 1 hour (in sealed cell).

*** Following 65% R. H. treatment samples were returned to 33% dessicator for period of 70 hours.

**** Samples dried under vacuum continuously for 100 hours in vacuum dessicator.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. % Transmission</th>
<th>Wt. Sample @33%RH(Grams)</th>
<th>Dry Wt. (grams)</th>
<th>Concentration of solutions(ppm)</th>
<th>Total grams Ion in 25ml sol.</th>
<th>Grams Ion Gram Dry Polysalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run #1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.005 Na⁺</td>
<td>73.9</td>
<td>.1509</td>
<td>.1127</td>
<td>37.3</td>
<td>$9.32 \times 10^{-4}$</td>
<td>$8.27 \times 10^{-3}$</td>
</tr>
<tr>
<td>.81 Na⁺</td>
<td>57.3</td>
<td>.0915</td>
<td>.0649</td>
<td>28.9</td>
<td>$7.22 \times 10^{-4}$</td>
<td>$1.11 \times 10^{-2}$</td>
</tr>
<tr>
<td>1.64 Na⁺</td>
<td>98.3</td>
<td>.0456</td>
<td>.0294</td>
<td>49.6</td>
<td>$12.40 \times 10^{-4}$</td>
<td>$4.22 \times 10^{-2}$</td>
</tr>
<tr>
<td>40 ppm Std.</td>
<td>79.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run #2</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.005 Na⁺</td>
<td>34.2</td>
<td>.1377</td>
<td>.1030</td>
<td>18.2</td>
<td>$4.55 \times 10^{-4}$</td>
<td>$4.42 \times 10^{-3}$</td>
</tr>
<tr>
<td>.81 Na⁺</td>
<td>98.9</td>
<td>.1131</td>
<td>.0804</td>
<td>53.1</td>
<td>$13.27 \times 10^{-4}$</td>
<td>$1.65 \times 10^{-2}$</td>
</tr>
<tr>
<td>40 ppm Std.</td>
<td>75.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run #3</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.81 Ca²⁺</td>
<td>35.0</td>
<td>.1000</td>
<td>.0727</td>
<td>47.7</td>
<td>$11.91 \times 10^{-4}$</td>
<td>$1.64 \times 10^{-2}$</td>
</tr>
<tr>
<td>1.64 Ca²⁺</td>
<td>70.9</td>
<td>.1110</td>
<td>.0796</td>
<td>96.5</td>
<td>$24.13 \times 10^{-4}$</td>
<td>$3.03 \times 10^{-2}$</td>
</tr>
<tr>
<td>40 ppm Std.</td>
<td>29.4</td>
<td></td>
<td></td>
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</table>

**TABLE XI**

Residual Ion Content
### Table XII

<table>
<thead>
<tr>
<th>Humidity</th>
<th>Frequency</th>
<th>Capacitance</th>
<th>Resistance or dissipation factor in</th>
<th>Resistance or dissipation factor out</th>
<th>Calibration units factor</th>
<th>f/f₀ Bridge</th>
<th>Measurement order</th>
</tr>
</thead>
<tbody>
<tr>
<td>33%</td>
<td>10⁴*</td>
<td>222.2 µµf</td>
<td>924000</td>
<td>503750</td>
<td>ohms</td>
<td>GR 716</td>
<td>1</td>
</tr>
<tr>
<td>33%</td>
<td>10³</td>
<td>22.9</td>
<td>3180000</td>
<td>2003000</td>
<td>ohms</td>
<td>GR 716</td>
<td>2</td>
</tr>
<tr>
<td>33%</td>
<td>10⁴</td>
<td>20.4</td>
<td>1000000</td>
<td>1670000</td>
<td>ohms</td>
<td>GR 716</td>
<td>3</td>
</tr>
<tr>
<td>33%</td>
<td>10⁵(A)</td>
<td>7.351</td>
<td>821.3</td>
<td>631.4</td>
<td>Dial</td>
<td>7.93 x 10⁻⁵</td>
<td>New (4)</td>
</tr>
<tr>
<td>33%</td>
<td>10⁶</td>
<td>.3956</td>
<td>693.1</td>
<td>496.0</td>
<td>Dial</td>
<td>7.93 x 10⁻⁵</td>
<td>New (5)</td>
</tr>
<tr>
<td>33%</td>
<td>10⁷</td>
<td>.0350</td>
<td>.8742</td>
<td>1.7621</td>
<td>cm(LV)</td>
<td>2.09 x 10⁻⁵</td>
<td>New (6)</td>
</tr>
<tr>
<td>65%</td>
<td>10²*</td>
<td>6293</td>
<td>57000</td>
<td>45000</td>
<td>ohms</td>
<td>GR 716</td>
<td>1</td>
</tr>
<tr>
<td>65%</td>
<td>10³</td>
<td>31.7</td>
<td>.265</td>
<td>.046</td>
<td>DF Dial</td>
<td>GR 716</td>
<td>3</td>
</tr>
<tr>
<td>65%</td>
<td>10⁴</td>
<td>22.3</td>
<td>1.30</td>
<td>.024</td>
<td>DF Dial</td>
<td>GR 716</td>
<td>4</td>
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<tr>
<td>65%</td>
<td>10⁵</td>
<td>1.609</td>
<td>598.3</td>
<td>495.1</td>
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<td>7.93 x 10⁻⁵</td>
<td>New (5)</td>
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<tr>
<td>65%</td>
<td>10⁶(A)</td>
<td>.0434</td>
<td>433.3</td>
<td>356.7</td>
<td>Dial</td>
<td>7.93 x 10⁻⁵</td>
<td>New (6)</td>
</tr>
</tbody>
</table>

(A) C'' = 575.7 µµf

* Sample acted unstable at these frequencies
**TABLE XIII**

Schering Bridge Data

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Frequency</th>
<th>Capacitance</th>
<th>Corrected Capacitance</th>
<th>Resistance or dissipation factor in</th>
<th>Resistance or dissipation factor out</th>
<th>Units</th>
<th>Calibration</th>
<th>f/fo Bridge</th>
<th>Measurement order</th>
</tr>
</thead>
<tbody>
<tr>
<td>33%</td>
<td>$10^2$</td>
<td>1499.9 $\mu F$</td>
<td>122800</td>
<td></td>
<td>100738</td>
<td>ohms</td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 New</td>
<td>3</td>
</tr>
<tr>
<td>33%</td>
<td>$10^3$</td>
<td>166.09 $\mu F$</td>
<td>80305</td>
<td></td>
<td>100722</td>
<td>ohms</td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 New</td>
<td>2</td>
</tr>
<tr>
<td>33%</td>
<td>$10^4$</td>
<td>9.91 $\mu F$</td>
<td>130400</td>
<td></td>
<td>100300</td>
<td>ohms</td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 New</td>
<td>4</td>
</tr>
<tr>
<td>33%</td>
<td>$10^5$ (A)</td>
<td>1.541 $\mu F$</td>
<td>215.5</td>
<td></td>
<td>725.0</td>
<td></td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 New</td>
<td>5</td>
</tr>
<tr>
<td>33%</td>
<td>$10^6$</td>
<td>0.0892 $\mu F$</td>
<td>152.5</td>
<td></td>
<td>637.2</td>
<td>cm(LV)</td>
<td>2.09 x 10^{-3}</td>
<td>1 New</td>
<td>6</td>
</tr>
<tr>
<td>33%</td>
<td>$10^7$</td>
<td></td>
<td>7323</td>
<td></td>
<td>1.3350</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65%</td>
<td>$10^2$</td>
<td>3252.5 $\mu F$</td>
<td>20120</td>
<td></td>
<td>51000</td>
<td>ohms</td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 GR 716</td>
<td>6</td>
</tr>
<tr>
<td>65%</td>
<td>$10^3$</td>
<td>544.9 $\mu F$</td>
<td>20120</td>
<td></td>
<td>55150</td>
<td>ohms</td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 GR 716</td>
<td>5</td>
</tr>
<tr>
<td>65%</td>
<td>$10^4$</td>
<td>46.89 $\mu F$</td>
<td>20095</td>
<td></td>
<td>80410</td>
<td>ohms</td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 GR 716</td>
<td>4</td>
</tr>
<tr>
<td>65%</td>
<td>$10^5$</td>
<td>2.74 $\mu F$</td>
<td>19.900</td>
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<td>103,100</td>
<td>ohms</td>
<td>Dial 7.93 x 10^{-5}</td>
<td>1 GR 716</td>
<td>3</td>
</tr>
<tr>
<td>65%</td>
<td>$10^6$ (A)</td>
<td>1.040 $\mu F$</td>
<td>642.2</td>
<td></td>
<td>492.7</td>
<td>cm(LV)</td>
<td>2.09 x 10^{-3}</td>
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<td>2</td>
</tr>
<tr>
<td>65%</td>
<td>$10^7$</td>
<td></td>
<td>355.7</td>
<td></td>
<td>468.2</td>
<td></td>
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(A) $C'' = 575.7 \mu F$
<table>
<thead>
<tr>
<th>Sample thickness</th>
<th>0.0082 cm</th>
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<tbody>
<tr>
<td>Test temperature</td>
<td>24-26°C</td>
</tr>
</tbody>
</table>

**TABLE XIV**

Schering Bridge Data

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Frequency</th>
<th>Corrected Capacitance</th>
<th>Resistance or dissipation factor in</th>
<th>Resistance or dissipation factor out</th>
<th>Co: $9.06 \times 10^{-4} \mu \mu$</th>
<th>Calibration factor</th>
<th>f/f₀</th>
<th>Bridge</th>
<th>Measurement order</th>
</tr>
</thead>
<tbody>
<tr>
<td>33%</td>
<td>$10^2$</td>
<td>337.7 (\mu \mu)</td>
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*Sample unstable

(a) C" = 5075.7 \(\mu \mu\)
(b) C" = 575.7 \(\mu \mu\)
TABLE XV
Schering Bridge Data

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<th>Relative Humidity</th>
<th>Frequency</th>
<th>Corrected Capacitance</th>
<th>Resistance or dissipation factor in</th>
<th>Resistance or dissipation factor out</th>
<th>units</th>
<th>Calibration factor</th>
<th>f/fo</th>
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(a) $C'' = 575.7 \mu \mu f$

(b) $C'' = 5075.7 \mu \mu f$

Sample: $1.64 \text{Na}^+$

$C''$: 75.7 unless otherwise noted ($\mu \mu f$)

Co: $8.25 \times 10^{-4} \mu \mu f$
**TABLE XVI**

Schering Bridge Data

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<th>Relative Humidity</th>
<th>Frequency</th>
<th>Corrected Capacitance ( \mu F )</th>
<th>Resistance or dissipation factor in ( \mu F )</th>
<th>Resistance or dissipation factor out ( \mu F )</th>
<th>units</th>
<th>Calibration factor ( f/f_0 )</th>
<th>Bridge</th>
<th>Measurement order</th>
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Sample: \( .81 \text{ Na}^+ \)

\( C'' = 75.7 \) unless otherwise noted \( (\mu F) \)

\( Co = 9.06 \times 10^{-4} \)
### TABLE XVII

Schering Bridge Data

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<th>Corrected Capacitance</th>
<th>Resistance or dissipation factor in</th>
<th>Resistance or dissipation factor out</th>
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<th>Calibration factor</th>
<th>f/fo</th>
<th>Bridge</th>
<th>Measurement order</th>
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(a) $C'' = 5075.7 \mu F$
(b) $C'' = 2075.7 \mu F$
(c) $C'' = 575.7 \mu F$

* This value taken 1/2 hr. later
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<th>Sample thickness</th>
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**TABLE XVII**

<table>
<thead>
<tr>
<th>Sample thickness: 0.072 cm.</th>
<th>Test temperature: 24-26°C</th>
<th>Sample: L.64 Ca++</th>
<th>Measurement order</th>
</tr>
</thead>
<tbody>
<tr>
<td>33%</td>
<td>10.2</td>
<td>588.6</td>
<td>1</td>
</tr>
<tr>
<td>33%</td>
<td>10.3</td>
<td>640.2</td>
<td>1</td>
</tr>
<tr>
<td>33%</td>
<td>10.4</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>33%</td>
<td>10.5</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>33%</td>
<td>10.6</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>33%</td>
<td>10.7</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>65%</td>
<td>10.2</td>
<td>61.7</td>
<td>1</td>
</tr>
<tr>
<td>65%</td>
<td>10.3</td>
<td>61.7</td>
<td>1</td>
</tr>
<tr>
<td>65%</td>
<td>10.4</td>
<td>61.7</td>
<td>1</td>
</tr>
<tr>
<td>65%</td>
<td>10.5</td>
<td>61.7</td>
<td>1</td>
</tr>
<tr>
<td>65%</td>
<td>10.6</td>
<td>61.7</td>
<td>1</td>
</tr>
<tr>
<td>65%</td>
<td>10.7</td>
<td>61.7</td>
<td>1</td>
</tr>
<tr>
<td>10%</td>
<td>10.2</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>10%</td>
<td>10.3</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>10%</td>
<td>10.4</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>10%</td>
<td>10.5</td>
<td>644.7</td>
<td>1</td>
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<tr>
<td>10%</td>
<td>10.6</td>
<td>644.7</td>
<td>1</td>
</tr>
<tr>
<td>10%</td>
<td>10.7</td>
<td>644.7</td>
<td>1</td>
</tr>
</tbody>
</table>

(a) C" = 57.5.7 μF.
### TABLE XIX
Schering Bridge Data

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>Frequency</th>
<th>Corrected Capacitance</th>
<th>Resistance or dissipation factor in</th>
<th>Resistance or dissipation factor out</th>
<th>units</th>
<th>Calibration factor</th>
<th>f/fo</th>
<th>Bridge</th>
<th>Measurement order</th>
</tr>
</thead>
<tbody>
<tr>
<td>33%</td>
<td>$10^2$ (A)</td>
<td>0.347 μF</td>
<td>5033</td>
<td>0.8098</td>
<td>cm(LV)</td>
<td>2.09 x 10^{-3}</td>
<td>1</td>
<td>New</td>
<td>1</td>
</tr>
<tr>
<td>33%</td>
<td>10³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>33%</td>
<td>10⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>33%</td>
<td>10⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>33%</td>
<td>10⁶</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>33%</td>
<td>10⁷</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>65%</td>
<td>$10^2$ (B)</td>
<td>1.096</td>
<td>656.5</td>
<td>601.5</td>
<td>Dial</td>
<td>7.93 x 10^{-5}</td>
<td>1</td>
<td>New</td>
<td>2</td>
</tr>
<tr>
<td>65%</td>
<td>10³</td>
<td>0.366</td>
<td>777.3</td>
<td>611.0</td>
<td>Dial</td>
<td>7.93 x 10^{-5}</td>
<td>1</td>
<td>New</td>
<td>3</td>
</tr>
<tr>
<td>65%</td>
<td>10⁴</td>
<td>0.048</td>
<td>633.9</td>
<td>608.7</td>
<td>Dial</td>
<td>7.93 x 10^{-5}</td>
<td>1</td>
<td>New</td>
<td>4</td>
</tr>
<tr>
<td>65%</td>
<td>10⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>65%</td>
<td>10⁶</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>65%</td>
<td>10⁷</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

(A) C'' = 575.7 μF
(B) C'' = 2075.7 μF

Sample: 0.81 Ca^{++}
C'' = 75.7 μF unless otherwise noted
Co = 8.0 x 10^{-4} μF

Measurement order:
### TABLE XX
8.5 x 10⁹ c/s Data

Diameter specimen holder 1.0025

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative Humidity</th>
<th>$\Delta X$</th>
<th>$\Delta N$</th>
<th>$d$ (cm)</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.005 Na⁺</td>
<td>65%</td>
<td>.0245</td>
<td>.0235</td>
<td>.0116</td>
<td>4.815</td>
<td>1.997</td>
</tr>
<tr>
<td>.81 Na⁺</td>
<td>65%</td>
<td>.0244</td>
<td>.0189</td>
<td>.0095</td>
<td>4.746</td>
<td>2.418</td>
</tr>
<tr>
<td>1.64 Na⁺</td>
<td>65%</td>
<td>.0214</td>
<td>.0127</td>
<td>.0082</td>
<td>3.916</td>
<td>2.457</td>
</tr>
<tr>
<td>1.64 H⁺</td>
<td>65%</td>
<td>.0266</td>
<td>.0099</td>
<td>.0069</td>
<td>3.702</td>
<td>3.630</td>
</tr>
<tr>
<td>1.33 H⁺</td>
<td>65%</td>
<td>.0316</td>
<td>.0200</td>
<td>.0094</td>
<td>5.006</td>
<td>3.165</td>
</tr>
<tr>
<td>.81 H⁺</td>
<td>65%</td>
<td>.0289</td>
<td>.0171</td>
<td>.0114</td>
<td>3.825</td>
<td>2.395</td>
</tr>
<tr>
<td>.81 Ca ++</td>
<td>65%</td>
<td>.0133</td>
<td>.0103</td>
<td>.0094</td>
<td>3.063</td>
<td>1.342</td>
</tr>
<tr>
<td>.005 Na⁺</td>
<td>33%</td>
<td>.0153</td>
<td>.0169</td>
<td>.0116</td>
<td>3.743</td>
<td>1.242</td>
</tr>
<tr>
<td>.81 Na⁺</td>
<td>33%</td>
<td>.0136</td>
<td>.0168</td>
<td>.0095</td>
<td>4.330</td>
<td>1.348</td>
</tr>
<tr>
<td>1.64 Na⁺</td>
<td>33%</td>
<td>.0123</td>
<td>.0003</td>
<td>.0082</td>
<td>x</td>
<td>1.412</td>
</tr>
<tr>
<td>1.64 H⁺</td>
<td>33%</td>
<td>.0162</td>
<td>.0133</td>
<td>.0069</td>
<td>4.548</td>
<td>2.210</td>
</tr>
<tr>
<td>1.33 H⁺</td>
<td>33%</td>
<td>.0175</td>
<td>.0158</td>
<td>.0094</td>
<td>4.165</td>
<td>1.763</td>
</tr>
<tr>
<td>.81 H⁺</td>
<td>33%</td>
<td>.0179</td>
<td>.0161</td>
<td>.0114</td>
<td>3.659</td>
<td>1.478</td>
</tr>
<tr>
<td>1.64 Ca ++</td>
<td>33%</td>
<td>.0079</td>
<td>.0125</td>
<td>.0087</td>
<td>3.706</td>
<td>.855</td>
</tr>
<tr>
<td>.81 Ca ++</td>
<td>33%</td>
<td>.0082</td>
<td>.0095</td>
<td>.0094</td>
<td>2.903</td>
<td>.821</td>
</tr>
</tbody>
</table>

x Not calculated - sample not correctly placed in cavity.
B. Calculations:

(1) Dielectric Constant

(a) Schering Bridge measurements \((10^2-10^7 \text{ c/s})\)

In this range the sample capacitance \(Cs\) could be determined from \(Cs = \Delta C - C_h\) which was valid for both the resistance-capacitance substitution method and the capacitance substitution method since the last term in the true formula for the latter case was negligible in our tests.

\[
Cs = C - C_h - C'' \left(\frac{Dx-D'}{1+(Dx+0.034)^2}\right)
\]

(26)

\[
C = C_{out} - C_{in}
\]

\[
C_h = C'_{out} - C'_{in}
\]

where

\[
C_{out} \text{ = balance with cell and sample out (farads)}
\]

\[
C_{in} \text{ = balance with cell and sample in (farads)}
\]

\[
C'_{out} \text{ = all-out balance (farads)}
\]

\[
C'_{in} \text{ = balance with empty cell in place (farads)}
\]

\[
C_h \text{ = cell capacitance (farads)}
\]

\[
Dx \text{ = Dissipation balance, sample in}
\]

\[
D' \text{ = Dissipation balance, sample out}
\]

The dielectric constant \(\epsilon'\) was calculated from

\[
\epsilon' = \frac{Cs}{C_0}
\]

where \(C_0\) is the vacuum capacitance

\[
\epsilon' = \left(\frac{9.85 \text{ A/c}}{t}\right) \mu_f
\]

\[
A = \text{specimen area perpendicular to current flow (cm}^2\text{)}
\]

\[
t = \text{thickness parallel to current flow (cm)}
\]

The following sample calculation should illustrate the general procedures:

Sample: \(1.64 \text{ Ca}^{++}\) at 33% R. H. \((10^2 \text{ c/s})\)

Data: (see table XVIII)

\[
C = 7.839 \mu_f
\]

\[
C_h = 7.163 \mu_f
\]

\[
Cs = 0.676 \mu_f
\]

The specimens used in these measurements were 1" x 1" x d" thick

For this sample \(A = (2.54) (.0072) \text{ cm}^2 = .0183 \text{ cm}^2\) while

\(t = 2.05 \text{ cm.} \) \(C_0\) as a result was \(8.0 \times 10^{-4} \mu_f\)

\[
\epsilon' = \frac{Cs}{C_0} = \frac{0.676}{8.0 \times 10^{-4}} = 8.56 \times 10^2
\]
(b) Traveling wave detector measurements \( (8.5 \times 10^9 \text{ c/s}) \)

The general procedure used to calculate the dielectric constant by this technique are very well outlined by W. B. Westphal (49). The procedures defined there are simplified to the following expressions (with little loss in accuracy) for the specimens used in this study (50).

\[
\varepsilon' = \left[ \frac{\Delta N (2.53 W-U)}{dW} \right] + 1
\]

where \( W = U + 1 \)

\[
U = \left[ \frac{\lambda g}{\lambda c} \right]^2
\]

\[
\frac{1}{\lambda_j^2} + \frac{1}{\lambda_c^2} = \frac{1}{\lambda_0^2}
\]

\( \lambda g = \) wavelength air filled guide = 5.608 cm
\( \lambda c = \) constant related to free space wavelength by the
\( \lambda c = \) (Diameter holder) \((3.4126)/(1.27) = 4.355 \text{ cm} \)

For a typical sample \((0.81 \text{ Na}^+ \text{ at 65% R.H.})\) the following data were determined (See Table XX)

\( \Delta N = .0189 \)
\( d = .0095 \text{ cm.} \)
\( U = \left( \frac{\lambda_j}{\lambda_c} \right)^2 = \left( \frac{5.608}{4.355} \right) = 1.809 \)
\( W = U + 1 = 2.809 \)
\( \varepsilon' = \frac{(.0189)(2.53)(2.809) - (1.809)}{(.0095)(2.809)} + 1 = 4.746 \)

(2) Loss Tangent

(a) Schering Bridge Measurements \((10^2 - 10^7 \text{ c/s})\)

Basically two techniques were used to calculate loss tangent values. When the resistance capacitance substitution method was used \( \tan \delta \) was calculated with the following expression:

\[
\tan \delta = \frac{R_x - R'}{\omega C_s R_x R'}
\]

where \( R_x = \) Resistance balance, sample in (ohms)
\( C_s = \) sample capacitance (farads)
\( R' = \) Resistance balance, sample out (ohms)
\( \omega = \) frequency (c/s)

When the capacitance substitution method was used, \( \tan \delta \) was calculated with this expression:

\[
\tan \delta = \frac{C''}{C_s} \left( \frac{D_x - D'}{f^2} \right)
\]
where \( C'' \) = all-out capacitance balance (farads)
\( D_x \) = Dissipation factor balance with sample in
\( D' \) = Dissipation factor with sample out

Typical calculations:

Equation (29) (Resistance-Capacitance Substitution Method)
Sample: (0.81 Na\(^+\) @ 33% R.H.) frequency = 10\(^3\) c/s.

Data: See Table XVI
\( R_x = 3.606 \times 10^6 \) ohms
\( R' = 2.005 \times 10^6 \) ohms
\( C_s = 1.49 \mu F \)

\[
\tan = \frac{(3.606 - 2.005) \times 10^6}{2 \cdot (10^3)(3.606)(2.005)(10^{12})(1.49 \times 10^{12})} = 23.65
\]

Equation (30) Capacitance Substitution Method
Sample: (0.81 Na\(^+\) @ 33% R.H.) frequency 10\(^4\) c/s
Data: See Table XVI
\( D_x = 704.3 \) Dial units Calibration Factor:
\( D' = 611.0 \) Dial units \( 7.93 \times 10^{-5} \) Dissipation Factor unit
\( C'' = 5075.7 \mu F \)
\( C_s = 0.3775 \mu F \)
\( f/f_0 = 0.1 \)

\[
\tan = \frac{(5075.7 \times 10^{-12})(704.3 - 611.0)(7.93 \times 10^{-5})(1)}{(0.3775 \times 10^{-12})} = 9.95
\]

(b) Traveling Wave detector measurements (8.5 \times 10^9 \) c/s

\[
\tan = \frac{\varepsilon''}{\varepsilon'}, \varepsilon' \text{ (dielectric constant was calculated in the previous section, the value for } \varepsilon' \text{ will be calculated in the next section)}
\]

(3) Loss Factor

(a) Schering Bridge measurements (10\(^2\) - 10\(^7\) c/s)

The loss factor can be calculated from the following expression using previously calculated values for \( \tan \xi \) and \( \varepsilon' \)

\[ \varepsilon'' = \tan \xi \cdot \varepsilon' \]
(b) Traveling Wave measurements \((8.5 \times 10^9 \text{ c/s})\)

Using the same notation as defined in the dielectric constant calculations the loss factor can be calculated as follows:

\[
\varepsilon'' = \Delta x \frac{(2.53 \text{ W-U})}{dW}
\]  

(32)

Using the same example from the dielectric constant calculation

\[
\varepsilon'' = \frac{(0.024)(2.53)(2.809) - 1.809}{(0.0095)(2.809)(2)} = 2.418
\]

(4) D.C. Conductivity Calculations

\(k = \text{conductivity} = 1/\rho\) where

\[
\text{Resistivity } = \rho = \text{Resistance} \left(\frac{\text{Cross Sectional Area}}{\text{thickness}}\right)
\]

(33)

where Cross Sectional Area is perpendicular to current flow and thickness is parallel to the current flow.

\[
\text{Resistance } = \frac{\text{Voltage}}{\text{Current}}
\]

\[
k = \frac{\text{Thickness} \times \text{Current}}{\text{Voltage} \times \text{Cross Sectional Area}}
\]

(34)

Current density = \(\frac{\text{Current}}{\text{Cross Sectional Area}}\)

Sample:

For 1.64 H+ @ 65% R.H. at \(t = 0\)

\[k = \frac{(2.54 \text{ cm})(6.0 \times 10^{-6} \text{ amperes})}{(2.54 \text{ cm} \times 0.0050 \text{ cm})(3.0 \text{ volts})} = 4 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} \]

\[
\rho = 1 = \frac{1}{k} = \frac{1}{4} \times 10^{-4} = 2500 \text{ ohm cm}
\]

Current density = \(\frac{6.0 \times 10^{-6} \text{ amps}}{(2.54 \times 0.005) \text{ cm}}\)

\[= 4.7 \times 10^{-4} \text{ amps/cm}^2\]
Figure 23  Film History

Films cast from 15.2% (wt.) polysalt ternary solvent solution
.005 H⁺ .81 H⁺ 1.64 H⁺

Placed in 2N HCl to soak
1.64 H⁺ avg. residence time = 30 hours
0.81 H⁺ " " = 26 "  
0.005 H⁺ " " = 10 "

1 film each placed in 2% (wt) NaCl
1 film each placed in 1.9% (wt) CaCl₂

Average bath residence time = 27 hours

65% R.H. → 33% R.H. → Specimens cut 33% R.H.
15 hours 10 hours 14 hours

65% Dielectric tests
33% Dielectric tests

weight measurement
33% R.H. 19 hours 65% R.H. 12 hours 65% R.H. 16 hours

weight measurement (3 specimens)

33% R.H. Dielectric tests (3 specimens) re-run 33%
51 hours

weight measurement → vacuum dessicator → weight measurement → vacuum dessicator → final weight measurement
D. Equivalent Circuit Analysis of the Shaw Model

The sample to be measured is represented by

\[
\begin{align*}
\text{Cp} & & \text{Rp} = \frac{1}{G_p} \\
\text{Cs} & & \text{Rs} = \frac{1}{G_s}
\end{align*}
\]

while the measuring circuit is represented by

\[
\begin{align*}
\text{Cm} & & \text{Rm} = \frac{1}{G_m}
\end{align*}
\]

The condition for balance in the bridge circuit is that the impedance of the measuring circuit must be equal to that of the sample.

Thus the impedance balance yields

\[
\begin{align*}
\frac{1}{G_m + i\omega C_m} &= \frac{1}{G_p + i\omega C_p} + \frac{1}{G_s + i\omega C_s} \\
(35) \\
\frac{G_m - i\omega C_m}{(G_m)^2 + (\omega C_m)^2} &= \frac{G_p - i\omega C_p}{(G_p)^2 + (\omega C_p)^2} + \frac{G_s - i\omega C_s}{(G_s)^2 + (\omega C_s)^2} \\
(36)
\end{align*}
\]

Separation into real and imaginary portions

\[
\begin{align*}
\frac{G_m}{(G_m)^2 + (\omega C_m)^2} &= \frac{G_p}{(G_p)^2 + (\omega C_p)^2} + \frac{G_s}{(G_s)^2 + (\omega C_s)^2} \\
(37) \\
\frac{C_m}{(G_m)^2 + (\omega C_m)^2} &= \frac{C_p}{(G_p)^2 + (\omega C_p)^2} + \frac{C_s}{(G_s)^2 + (\omega C_s)^2} \\
(38)
\end{align*}
\]

Consider the electrode polarization terms to be constants at a given frequency for a given electrode area(34, 38).

Thus

\[
\begin{align*}
\frac{G_m}{(G_m)^2 + (\omega C_m)^2} &= \frac{G_s}{(G_s)^2 + (\omega C_s)^2} + K. \\
(39)
\end{align*}
\]

For a typical sample (Falkenstein's data for film 11-A @ 10^2 c/s)

\[
\begin{align*}
C_m &= 844 \times 10^{-12} \text{ farads} \\
R_m &= 3.16 \times 10^5 \text{ ohms} \\
\left(\frac{\omega C_m}{G_m}\right)^2 &= \left[(2\pi i)(10^2)(8.44 \times 10^{-10})(3.16 \times 10^5)\right]^2 \\
&= (4\pi^2)(10^4)(8.44)^2(10^{-20})(3.16)^2(10^5) \\
&= (4\pi^2)(8.44)^2(3.16)^2(10^{-6}) \\
&\approx (40)(80)(10)(10^{-6}) \approx 3.2 \times 10^{-2}
\end{align*}
\]
\[
\frac{G_m}{1 + \left( \frac{\omega C_m}{G_m} \right)^2} \cong G_m
\]  

(40)

Furthermore since \( R_s \) is believed to be significantly greater than \( R_p \) (19) and \( C_s \) is finite, it is expected that the term \( \left( \frac{\omega C_s}{G_s} \right)^2 \) should also be significantly less than 1.

Therefore \( G_m \cong G_s + K \)  

(41)

Presumably \( C_p \) can approach values which are appreciable fraction of the total observed capacitance for frequencies less than \( 10^5 \) c/s (19, 38).

The magnitude of \( R_p \) for cases where carelu analysis has been made (19) seem \( \omega \) to be low usually from 1-100 ohms. Thus the value of \( K \) should be roughly (at \( 10^2 \) c/s for film 11-A):

Assume \( C_p = 1/2 \ C_m = 422 \times 10^{-12} \) farads  
\( R_p = 100 \) ohms

\[
K = \frac{G_p}{1 + \frac{\omega^2 C_p^2}{G_p^2}} = \frac{1/100}{1 + \frac{4 \pi^2 \cdot 10^4}{(4.22 \times 10^{-10})^2(10^4)}}
\]

\[
= \frac{1/100}{1 + \frac{4 \pi^2 (25)(10^8)(10^{-20})}{1 + (40)(25)(10^{-12})}} = 0.01
\]

\( \therefore \) \( G_m \) is controlled by \( G_s \)

A ratio of \( G_m \) values for films of supposedly different thickness will not show the influence of electrode polarization.

In an analogous manner it can be shown that \( C_m \cong C_s + L \)

where \( L \) = the constant capacitive term due to electrode polarization.

In this case at a given frequency the contribution due to the polarization effects can be appreciable. However since the term (\( L \)) is essentially thickness independent (the basis for Shaw's technique for elimination of electrode polarization), it is readily seen that the ratio of measured capacitance values will be stabilized by the term. The ratio of measured capacitance would again fail to prove the absence of electrode polarization.
E. Literature Citations:

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