TABLE V

THERMODYNAMIC FUNCTIONS FOR THE ACTIVATED COMPLEXES AT 298.16°K.

	$\Delta H^{\ddagger}$, cal./mole	$\Delta F^{\ddagger}$, cal./mole	$\Delta S^{\ddagger}$, cal./mole. deg.
RCl-Cl⁻	20,220	24,280	−13.6
RCl-Br⁻	15,040	23,000	−26.7
RBr-Cl⁻	17,280	21,400	−13.8
RBr-Br⁻	17,440	19,780	− 7.8

with the least precise of the sets of velocity determinations. Unpublished results obtained independently in this Laboratory appear to confirm this specific effect. A similar large difference has been found between the entropies for the nitrobenzyl chloride–bromide ion and the nitrobenzyl bromide–chloride ion reactions in a 95–5 (by volume) acetone-methanol solvent containing about 0.6% water. More work is necessary on this point before a complete discussion can be given. An analogous system of reactions investigated in a very precise fashion by Young and Olson[6] shows no such large entropy differences. It should, however, be pointed out in this connection that the halogen of the substituted acetic acids investigated by these workers has a very different reactivity from that of the benzyl halides of the present work. Comparisons between such different compounds are on a very insecure basis.

Summary

1. The rates of the exchange reactions between *p*-nitrobenzyl chloride and *p*-nitrobenzyl bromide and the chloride and bromide ions have been measured in acetone water solutions over various temperature ranges.

2. The results have been analyzed from the point of view of the theory of the activated complex.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. XV. Electrolytes in Plastics[1]

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I. Introduction

In-phase components of current give rise to a.c. power losses in dielectrics; they can be produced either by ionic conductance or by relaxation phenomena of one sort or another. Measurements by a.c. methods give total losses, while d.c. measurements can only give currents produced by actual transport of charged particles. As a first approximation, the relaxation effects can be determined by subtracting the d.c. current from the total a.c. in-phase current; however, as we pointed out early in this series,[2] the difference may still contain contributions due to the electrolyte present. Best proof of this statement is found in the fact that both dielectric constant and a.c. loss factor vary in a systematic way with d.c. conductance, when appreciable quantities of electrolyte are present.

In our early work, the electrolyte was frequently hydrogen chloride of unknown concentration produced by pyrolysis of polyvinyl chloride during the preparation of the samples. In other cases, the nature of the electrolyte was also unknown; it could have been traces of catalysts or emulsifiers, for example. We therefore started a systematic study of the problem, using known concentrations of known electrolytes in plastics as the solvent medium.

It is the purpose of this paper to present some exploratory work on the system polyvinylchloride–diphenylmethane (80:20)–tetrabutylammonium picrate (10^{-4} to 0.05 *N*), which was done before pressure of war work caused us to postpone further studies. We are not yet able to describe the results in terms of a molecular model, but we have at least succeeded in defining conditions under which reproducible a.c. and d.c. results can be obtained on high-loss dielectrics, a problem of considerable technical importance.

II. Experimental

The polyvinyl chloride was similar to sample A5 which has been described previously.[3] Diphenylmethane[4] was chosen as plasticizer, because it is relatively high-boiling and non-polar. Tetrabutylammonium picrate[5] was selected as a typical strong electrolyte which is soluble in non-aqueous systems.

Samples for the electrical measurements were disks 5 cm. in diameter and usually 2–3 mm. thick. Polymer and plasticizer were weighed out separately in proportions 80:20, and salt (or a 1% or 0.1% solution of salt in Ph_2CH_2) was weighed into the plasticizer. The amounts of salt were taken to give round values of concentration, calculated on a normality basis using 1.316 as the density[4] of the 80:20 plastic. No correction was made for the volume of salt because the highest concentration was only 0.05 *N* (23.52 g./l.). Several volumes of methanol were added (petroleum ether, used in our previous work,[4] precipitates the picrate) to dilute the salt solution, which was then added to the polymer, and a little more methanol was used to complete the quantitative transfer. The mixture was stirred five minutes to distribute salt and plasticizer uniformly, and then the methanol was evaporated by

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[1] Paper XIV, THIS JOURNAL, 65, 2067 (1943).

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[2] Fuoss, THIS JOURNAL, 61, 2329 (1939).

[3] Fuoss, *ibid.*, 63, 2401 (1941).

[4] Mead, Tichenor and Fuoss, *ibid.*, 64, 283 (1942).

[5] Mead and Fuoss, *ibid.*, 61, 2047 (1939).

drying in vacuum for thirty to forty-five minutes at 60°. Complete removal of the methanol was checked by weighing. Then the powder was placed in a hot mold, suction applied to remove air, and the sample was pressed for five minutes at 120° and 4000 psi. That no plasticizer was lost was checked by weighing.

Control samples were made by exactly the same procedure except that no salt was added with the methanol and diphenylmethane. By duplicating the thermal history and other treatment of the samples containing salt, we were able to correct empirically for electrolyte present as impurity and for that produced by pyrolysis of polymer.

Usually, aqua-dag electrodes[6] were painted on the samples. Some experiments were also made in which tin foil, rubbed on with a small amount of vaseline or glycerol, was used to eliminate the air film which is present between samples of solids and the electrodes.[7]

Bridges,[6,7,8] cell[9] and thermostat[9] have been described in previous papers of this series. Measurements were made at 65, 55 and 45°.

III. Results and Discussion

The first results seemed hopelessly erratic, since both a.c. and d.c. properties continued to change with time for days. Going on the (possibly erroneous) assumption that ionic equilibria characteristic of the press temperature were "frozen in" when the samples were rapidly cooled in the mold, we tried annealing the samples for one hour at 90° in the cell, before starting the 65° measurements. The drifts in a.c. properties were very much reduced by this procedure; the remaining few tenths per cent. or less per hour could easily be allowed for by interspersing 60 cycle measurements during a series of other measurements and correcting all of the data back to an arbitrary reference state.[2]

After stabilizing the a.c. properties by annealing, it was found that *the d.c. conductance depended primarily on the previous d.c. history of the sample.* On application of d.c. voltage, the apparent conductance of the cell immediately started to decrease; in general, the initial rate of decrease was more rapid the lower the voltage, although the high voltage curves soon crossed the low voltage ones, probably indicating a lower limiting value for the higher voltage. If the voltage were reversed, the conductance very quickly returned to its original value, remained practically constant a while and then started to decrease again. The t = 0 value of the d.c. conductance always checked within experimental error the conductance obtained by extrapolating the a.c. conductances at that temperature to zero frequency. We finally learned that reproducible d.c. results could be obtained if we always started measurements from a "neutral" state; *i.e.*, starting with a fresh sample, if a given d.c. voltage were applied for a certain time in the forward direction, and immediately followed by the same voltage for the same time in the reverse direction, the sample would give consistent results at different voltages.

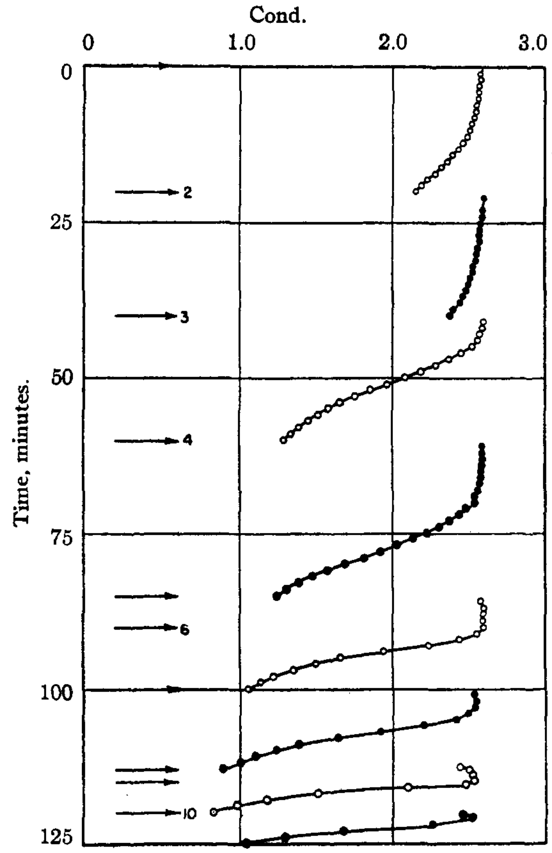

Fig. 1.—Polarization curves for 0.02 N sample at 55°. Open circles forward voltage; solid circles, reverse voltage.

An example is shown in Fig. 1 for the 0.02 N system at 55°, where conductance in arbitrary units ($\kappa = 22.1 \times 10^{-10}$ at 1.0 on scale) is plotted across the diagram and time increases downwards. At t = 0, 50 volts were applied and left on for twenty minutes, during which time the conductance dropped to 83% of its initial value. At t = 20 minutes (arrow 2), the 50-volt field was reversed; the first reading that could be taken showed practically the original conductance. The conductance then proceeded to drop again. At forty minutes (arrow 3), the field was again reversed and raised to 100 volts. After twenty minutes, the conductance had dropped to 50% of its initial value but rose at once (arrow 4) on reversing the 100 volts. The conductance was followed for twenty-five minutes; the field was again reversed (arrow 5) and left on for five minutes to neutralize the sample. Then (arrow 6), 200 volts was applied forward, reverse and forward (6, 7, 8) and finally 500 volts forward and reverse (9, 10). It will be noted that the conductance drops rapidly on the initial application of voltage to a neutral sample, but that the rate of change is slow at first when the reverse voltage is applied. Occasionally on reversing voltage, a few points could be caught where the conductance was rising, but usually the conductance was back to its a.c. value within about a minute.

(6) Fuoss, This Journal, **61**, 2329 (1939).
(7) Fuoss, *ibid.*, **59**, 1703 (1937).
(8) Fuoss, *ibid.*, **60**, 451 (1938).
(9) Fuoss, *ibid.*, **63**, 369 (1941).

After a sample was polarized by application of d.c. and let stand, it would gradually relax to a neutral state. An example is shown in Fig. 2 (κ = 22.5 $\times$ 10^{-10} at 1.0 on conductance scale) for a 0.01 N sample at 55°. Five hundred volts were applied for twenty minutes, which reduced the conductance to about 13% of its initial value. Then the bridge voltage was turned off, and the conductance was followed for an hour at 10 volts, with bridge current on just long enough for balance—a matter of seconds. It will be noted that most of the spontaneous recovery occurs within the first ten minutes.

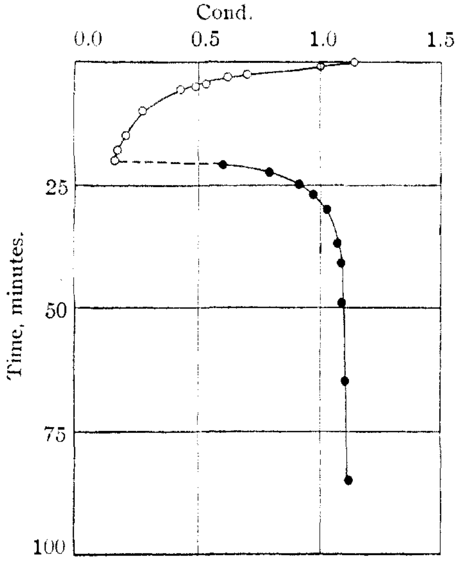

Fig. 2.—Relaxation of polarization: sample polarized at 500 volts (open circles); relaxation followed by flash readings at 10 volts (closed circles).

The a.c. properties of a polarized sample are also a little different from the normal properties. The effects seem to be small, but since they depend on time, and the change from d.c. to a.c. circuits could not be made instantaneously, we can only state that an effect exists. We hope to investigate this phenomenon in more detail, using a commutator circuit, in which the period of commutation will be long compared to the a.c. bridge period but short compared to the time of relaxation of the polarized dielectric.

The changes produced by d.c. are evidently quite complicated, as is shown by the shapes of the various κ-t curves. In Fig. 3 are shown some examples in which conductance (κ = 23.7 $\times$ 10^{-10} at 1.0 on scale) is plotted against the product of Vt, voltage applied times elapsed time, for a 0.05 N sample at 65°. The top half of the drawing is for the first application of a given voltage; the corresponding curve for the reverse voltage is given in the bottom half. (The initial rise at 500 volts is probably due to heating.) To a very rough first approximation, the Vt scale brings the different curves together, indicating either that the total number of coulombs passed is the fundamental independent variable, or that a diffusion mechanism[10] with Vt as independent variable is involved.

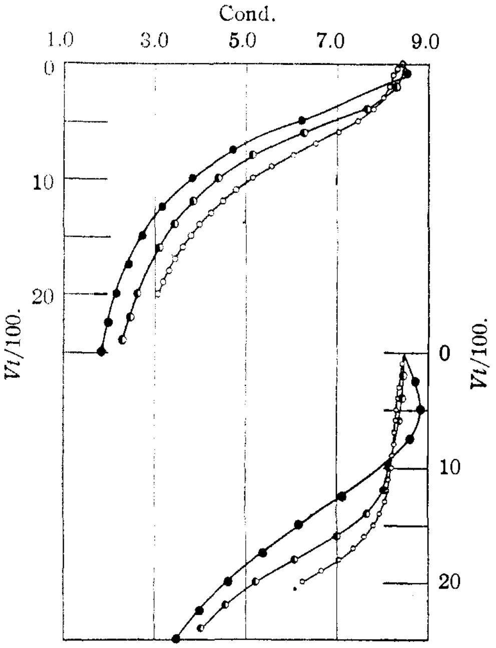

Fig. 3.—Polarization curves for 0.05 N sample at 55°: ○, 100 volts; ◑, 200 volts; ●, 500 volts.

The polarization and relaxation curves depend on voltage, time, temperature and concentration. The time (in minutes) for the conductance to drop to half its initial value gives an approximate measure of the changes; an abstract of these data is given in Table I. As expected, rates are higher at higher temperatures and voltages, and they decrease with decreasing concentration.

Table I

Time in Minutes Required to Halve Conductance

	65°				55°		45°
c	500 v.	200 v.	100 v.	50 v.	500 v.	200 v.	500 v.
0.05	0.5	1.0	4	7	2.8	5.5	15
.02	.7	2.2	5	12.5	2.5	7.5	16
.01	.6	1.3	3	7	3.5	7	30
.005	.8	2.0	6.5	14.5	6.0	14	50
.002	1.3	1.8	3	6	5.5	10	..
.001	3.0	6.7	8.5	14	17.0	..	..

Equivalent conductance as a function of concentration at the three temperatures is shown in Fig. 4. These values were calculated from the t = 0 d.c. (or f = 0 a.c.) specific conductivities. It is interesting to note that the equivalent conductance changes only very slowly with concentration over a 500-fold change of concentration, indicating that the fraction of salt existing as ions is nearly independent of concentration. The molecular mechanics of ion association in media of such high viscosity will probably turn out to be quite different from those in ordinary liquids.

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[10] Fuoss and Elliott, This Journal, **67**, 1339 (1945).

In order to discuss the a.c. properties, it will be necessary to define the contributions of the different components of the system to the measured dielectric constant ϵ' and the loss factor ϵ''. From a conductance κ measured at a frequency f, we calculate the loss factor

$$\epsilon'' = 18 \times 10^{11} \kappa/f \qquad (1)$$

Part of ϵ'' is due to the usual relaxation effects produced by the chlorine dipoles of the polymer; we shall designate this contribution by ϵ''_P. The difference $(\epsilon'' - \epsilon''_P)$ is due to the electrolyte present. The d.c. conductance κ_0 measures the normal ionic conductance, most of which is due to the salt added, but part of which is due to hydrogen chloride and impurities. The conductance of the blanks is thus the analog of "solvent conductance." We can write

$$\kappa_0 = \kappa_h + \kappa_s \qquad (2)$$

where κ_h is ionic conductance due to hydrogen chloride, etc., and κ_s is ionic conductance due to the picrate. From κ_0, we calculate loss factor contributions ϵ''_h and ϵ''_s by equation (1). Now we find that

$$\epsilon'' > \epsilon''_P + \epsilon''_s + \epsilon''_h \qquad (3)$$

i.e., the total observed a.c. loss is greater than the sum of the losses due to polymer relaxation and to normal ionic conductance as measured by d.c. Likewise, the dielectric constant of the plastic containing electrolyte is larger than that of the blank by an amount far in excess of that calculated on the basis of the salt acting as ion-pair dipoles.

The difference must be due to additional losses produced by the electrolyte by an a.c. mechanism which at present is unknown. Phenomenologically, it is a polarization out of phase with the applied field. Calling these ϵ''_H and ϵ''_S for the two electrolytes, we then have

$$\epsilon'' = \epsilon''_P + \epsilon''_H + \epsilon''_S + \epsilon''_h + \epsilon''_s \qquad (4)$$

The conductances $\kappa_H = \epsilon''_H f/18 \times 10^{11}$ and $\kappa_S = \epsilon''_S f/18 \times 10^{11}$ cannot be measured by d.c., of course, any more than can $\kappa_P = \epsilon''_P f/18 \times 10^{11}$. Now, given a.c. and d.c. data for a sample and the blank, we calculate the term in the pure a.c. loss due to picrate as

$$\epsilon''_S = (18 \times 10^{11}/f)\,[(\kappa - \kappa_0)_{\text{sample}} - (\kappa - \kappa_0)_{\text{blank}}] \qquad (5)$$

TABLE II

A.C. PROPERTIES OF 0.05 N Bu_4NPi in $PViCl$-Ph_2CH_2, 80:20 AT 45°. $\kappa_0 = 44.9 \times 10^{-10}$

f	$10^{10}\kappa$	ϵ''	ϵ'	ϵ'_S	ϵ''_S
60 c.	48.7	146.1	20.7	13.4	11.4
120	50.5	75.8	16.4	9.4	8.4
240	53.6	40.2	13.55	6.9	6.5
480	58.5	21.93	11.40	5.1	5.1
1 kc.	66.9	12.04	9.06	3.3	3.9
2	79.5	7.16	7.59	2.2	3.1
4	98.9	4.45	6.32	1.4	2.4
8	128.3	2.89	5.26	0.8	1.9

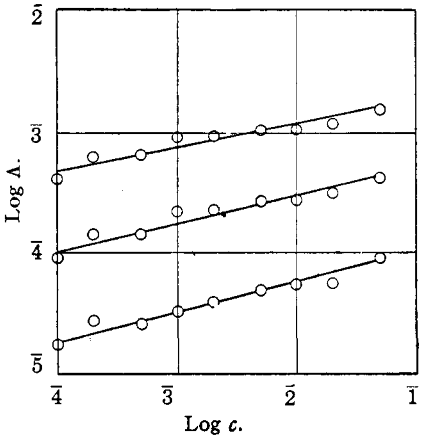

Fig. 4.—Equivalent conductance as a function of concentration, Bu_4NPi in $PViCl$-Ph_2CH_2, 80:20: top curve, 65°, center, 55°, bottom, 45°.

Similarly, the picrate contribution to dilectric constant is given by

$$\epsilon'_S = \epsilon'_{\text{sample}} - \epsilon'_{\text{blank}} \qquad (6)$$

Data for a typical sample are given in Table II, for the frequency range 60 cycles to 8 kilocycles. The precision in ϵ'_S and ϵ''_S is not very high, because both are small differences between larger quantities. Study of the data for a number of samples showed that at a given concentration, temperature and frequency

$$\epsilon'_S = \epsilon''_S \qquad (7)$$

and furthermore, that both varied inversely as the square root of the frequency. The data for the 0.05 N sample at the three temperatures are shown in Fig. 5, where the values of ϵ'_S are shown as open circles and ϵ''_S as solid circles.[11] The concentration dependence is also fairly simple: if we plot the logarithms of the slopes of the $\epsilon_S - f^{-1/2}$ curves against log c, the points approximate a 45° line as shown in Fig. 6. Combining the information of Figs. 5 and 6, we obtain the empirical result

$$\epsilon'_S = Ac/\sqrt{f} = \epsilon''_S \qquad (8)$$

where A depends on the temperature. It probably also depends on the nature of the salt and the plasticizer content of the plastic solvent medium. The above result can be expressed as follows: electrolyte in a plastic solvent exhibits an anomalous high conductance when measured at low frequencies and furthermore produces an increment in the dielectric constant, which must indicate ionic motion out of phase with the field. The presence of the electrolyte makes the dielectric behave as if it were shunted by another dielectric

[11] One set of measurements on an 0.02 N sample was made at 65° over the frequency range 1 kilocycle-1 megacycle; on account of the high conductance, the guard circuit of the high frequency bridge could not be balanced, so the data are in error due to fringe effects. However, the approximate equality of ϵ'_S and ϵ''_S persisted over this extended frequency range. We are indebted to Mr. S. I. Reynolds for these results.

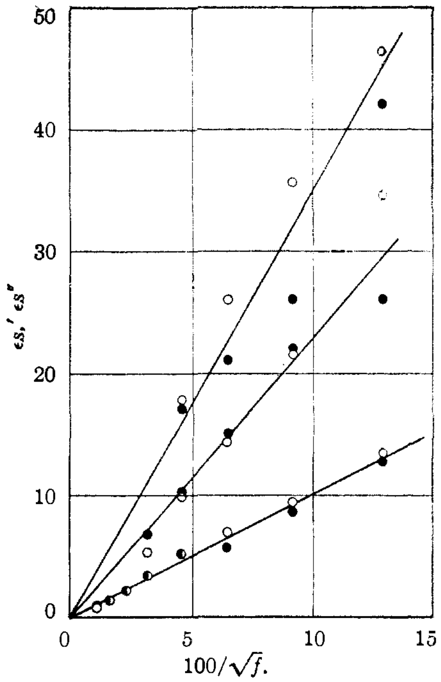

Fig. 5.—Linearity of ϵ'_S and ϵ''_S in $1/\sqrt{f}$: top curve, 65°; center, 55°; bottom, 45°.

of constant phase angle ($\varphi = \pi/4$), whose magnitude is proportional to salt concentration.

At present, we are unable to suggest a mechanism to account for the results. Part of the unusual behavior is an interface effect at the electrodes, because different absolute values of ϵ', ϵ'' and κ_0 were obtained using aqua-dag, foil-vaseline or foil-glycerol electrodes, and, also, the values of these quantities depended on the thickness of the sample. The equality of ϵ'_S and ϵ''_S, however, persisted, as did the linearity in $f^{-1/2}$, as these experimental conditions were changed. The complete reversibility of the d.c. results seems to rule out electrolysis as an explanation of the phenomena. All that can be stated at the moment is that both volume and surface (electrode) effects are present, which contribute to an extra out-of-phase polarization when electrolyte is dissolved in the dielectric.

Several experiments on other systems were made which deserve brief mention, because they show that the anomalous dielectric behavior due to added electrolyte is highly specific. A 0.01 N solution of tetrabutylammonium picrate in polystyrene gave at 65° and 60 cycles $\epsilon'_S = 0.3$ and $\epsilon''_S = 0.03$. With increasing frequency, ϵ'_S decreased while ϵ''_S *increased*. Also, a 0.05 N solution of tributylammonium picrate in PViCl-Ph_2CH_2 (80:20) gave $\epsilon'_S = 4$, $\epsilon''_S = 0.5$ at 65° and 60 cycles, and again ϵ'_S decreased while ϵ''_S increased with increasing frequency up to 8 kc. These two systems have one point of similarity: the first is a strong salt in a solvent of low dielectric constant and the second is a weak salt in a solvent of intermediate dielectric constant, so both are systems in which the ionic concentration is very low.[12]

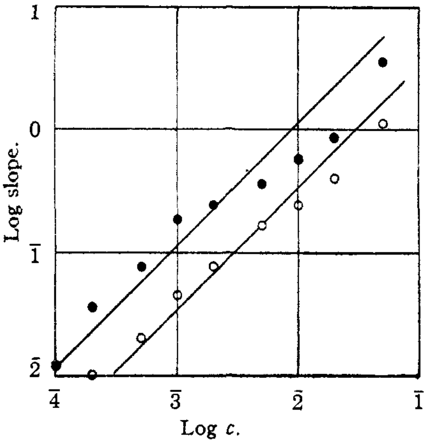

Fig. 6.—Dependence of polarization on concentration: ○, 45°; ●, 65°.

Summary

1. The electrical properties of the system polyvinyl chloride–diphenylmethane (80:20), containing tetrabutylammonium picrate (10^{-4} to 0.05 N) have been measured at 45, 55 and 65°, with d.c. and with a.c. over the range 60 cycles to 8 kilocycles.

2. The losses of these dielectrics are ***greater*** than the sum of polymer losses plus those due to normal ionic currents. Also the dielectric constant is higher than that of a salt-free dielectric.

3. The increment in loss factor equals that in dielectric constant at a given concentration, frequency and temperature; both increase approximately proportional to salt concentration and decrease inversely proportional to the square root of frequency.

4. Both surface and volume effects are involved.

SCHENECTADY, N. Y. RECEIVED MAY 15, 1945

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[12] Fuoss, *Chem. Rev.*, **17**, 27 (1935).