[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Dielectric Polarization of Liquid and Solid Formic Acid[1]

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The dielectric constant of liquid formic acid has been measured from 40° to 8.4° (m.p.), and the dielectric relaxation in the solid to $-50°$ over the frequency range 20 cycles/sec. to 3 megacycles/sec. The large direct current conductances of both liquid and solid give rise to large electrode polarization effects for which a method of correction was developed and tested by comparison of results for different cell geometrics. The large dielectric constant of the liquid, 56.1 at 25° and its temperature dependence both indicate that one must have a significant contribution from polar configurations of molecules, rather than a system composed entirely of non-polar dimers. The dielectric relaxation in the solid is described by the empirical arc function found for a variety of dielectrics and the temperature dependence of the frequency range is described by a rate expression with an energy of 13 kcal./mole. The static dielectric constant of the solid increases from a value of 13.7 at 0° to 39 at $-40°$, a behavior again characteristic of polar molecules rather than of a structure with dimer molecules as the only units. More detailed analysis of the results must await more direct evidence about the structure, but the large conductances suggest the possible importance of a proton transfer mechanism.

The ability of carboxylic acids to form stable dimers in the vapor phase and in dilute solutions with non-polar solvents has been confirmed by a variety of evidence, including dipole moment studies. Electron diffraction studies[3] of formic acid vapor led to a structure in which the molecules are joined by two hydrogen bonds, and the assumption that this non-polar structure exists also in dilute solution led to a consistent interpretation of dielectric polarization data[4] for benzene and heptane as solvents. The few reported dielectric constant values for liquid formic acid are, however, of the order 50 to 60[5] and are thus much too large to be explained except by a strongly polar arrangement of the molecular units and their immediate surroundings. This situation is in contrast to that in liquid acetic acid for which Smyth and Rogers[6] found a dielectric constant value of 6.1 at 20° and only a small temperature coefficient.

The only reported values of dielectric constant for solid formic acid[7] were obtained many years ago at frequencies of 25 megacycles/sec. or higher, and only one value (19 at 500 mc./sec. and 2°) at temperatures above $-150°$. One can thus infer nothing with any assurance about the equilibrium properties, particularly if dielectric relaxation effects occur.

The scarcity of data on either liquid or solid formic acid is undoubtedly to be attributed to the high specific conductance, the value of 25° for the liquid being 6×10^{-5} mho/cm. The difficulties attending accurate determinations of dielectric constants of conducting dielectrics are well known, and arise not only from insensitivity or inaccuracy of the measuring technique, but also from systematic errors as a result of electrode or interfacial polarization effects. The interesting situation suggested by the inadequate available data led us to a rather comprehensive investigation, as a result of which we have been able to correct for these effects satisfactorily and obtain reasonably accurate values of the dielectric properties for the temperature range -50 to $+40°$ and frequency range 20 cycles/sec. to 3 megacycles/sec.

Purification of Materials

The starting material, 98% Baker and Adamson C.P. formic acid, was purified by a series of distillations under reduced nitrogen pressure.

The observed melting point, 8.4 ± 0.1°, agrees well with values reported by Timmermanns,[8] Coolidge[9] and others. Specific conductances in the range $6.0–6.2 \times 10^{-5}$ mho/cm. were obtained, in agreement with values reported by Schlesinger and Coleman[10] and by Lange[11] after correction for difference in temperature of measurement. The purified material was stored as a solid until used to prevent decompostion, but conductance of the liquid increased only slightly over a period of a day.

Experimental Methods

The electrical measurements of capacitance and conductance were made with an admittance bridge which has been described elsewhere.[12] Two types of sample cell were employed, both of electro-polished stainless steel construction with Teflon (polytetrafluoroethylene) insulation and fitted with guard electrodes. The first with coaxial cylindrical electrodes is essentially the one described by Gross and Taylor,[13] but either of two inner, high potential electrodes of diameters $^3/_8$ inch and $^3/_4$ inch could be used. The outer electrode had a diameter of one inch and electrode gaps of $^5/_{16}$ or $^1/_8$ inch could thus be used. In the second cell, parallel plate electrodes of 25 cm.^{2} area and separation adjustable from $^1/_4$ to $1^1/_4$ inches were used, these being mounted in a cylindrical container. This cell was designed to permit measurements at several separations in order to test for and eliminate electrode polarization effects by taking differences of the apparent values observed. This hope was largely frustrated by the difficulty of freezing homogeneous samples between the more widely spaced electrodes and usually only data for $^1/_4$ and $^1/_2$ inch separations were satisfactory. The cells were placed in an acetone-bath in a large dewar flask and measurements made over the frequency range at fixed temperatures measured by a copper-constantan thermocouple. The temperatures could be held to 0.1° by judicious addition of solid carbon dioxide, as judged by the thermocouple e.m.f. and reproducibility of the electrical data.

Considerable care in freezing the solid was found necessary to obtain consistent results. Low values of dielectric constant and conductance, especially at the higher frequencies, were observed for samples in which the presence of voids was suspected or observed. On the other hand, slight contamination of the samples invariably led to anomalously high

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[1] Based on a thesis submitted by J. F. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] L. Pauling and L. O. Brockway, *Proc. Natl. Acad. Sci.*, **20**, 336 (1934).

[4] H. A. Pohl, M. E. Hobbs and P. M. Gross, *Ann. N. Y. Acad. Sci.*, **40**, 389 (1940).

[5] The following data are given in the "International Critical Tables," Vol. VI, p. 83: 58.5 at 16°C. (Drude, 1897), 62.0 at 15°C. (Thwing, 1894), and 47.9 at 18.5°C. (Dobroserdov, 1911).

[6] C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52**, 1824 (1930).

[7] Reference (5).

[8] J. Timmermanns and Mme. Hennaut-Roland, *J. Chim. Phys.*, **27**, 420 (1930).

[9] A. S. Coolidge, THIS JOURNAL, **50**, 2166 (1928).

[10] H. I. Schlesinger and C. Coleman, *ibid.*, **38**, 271 (1916).

[11] J. Lange, *Z. phys. Chem.*, **187A**, 30 (1940).

[12] R. H. Cole and P. M. Gross, Jr., *Rev. Sci. Inst.*, **20**, 252 (1949).

[13] P. M. Gross, Jr., and R. C. Taylor, THIS JOURNAL, **72**, 2075 (1950).

values, especially at low frequencies, as a combined result of the large direct current conductance and electrode polarization effects. These results were attributed to the presence of small regions of supercooled liquid, which were observed in two samples and in these cases found to have such an effect, as, indeed, is to be expected. For these reasons, samples which showed residual ohmic conductance values exceeding the best ones by a factor of three were excluded from further consideration. The possible errors from these causes were judged by comparison of data on different samples measured in the two types of cell. The use of different electrode spacings in the tests also permitted comparison of results in which electrode polarization effects were appreciably different and this afforded tests of the correction method.

In the liquid phase, difficulties from homogeneity are, of course, not met and the absence of dielectric constant dispersion—or absorption conductance—made determination of the true dielectric constant relatively simple. A minor correction for shunting of the bridge ratio arms[14] by the high guard circuit conductance of the cell was applied and checked by direct measurement with known shunting conductances. Data on the apparent frequency dependence of the dielectric constant as a result of electrode polarization were taken as a matter of interest and for assurance that values reported from measurements at 300 kc./sec. were free of such errors.

Analysis of the Data and Results

As already mentioned, the combined effect of d.c. conductance and electrode polarization gives rise to serious errors in the observed apparent values of dielectric constant and absorption conductance. The magnitudes of these effects are shown in Fig. 1 and Table I for the liquid and solid, respectively. The observed dielectric constant at 20° for the liquid is seen from Fig. 1 to rise rapidly with decreasing frequency and varies as $1/\omega^2$, where $\omega = 2\pi$ frequency, in the limit $\omega \rightarrow 0$, as shown by the dashed line of slope -2 on the log–log plot which is approached asymptotically. The conductance change, not plotted, is less than 1% over the frequency range.

These results are accounted for by assuming an electrode impedance in series with the dielectric which is a pure capacitance $(C_{el})_0$, for, as the more general analysis below shows, the observed dielectric constant ϵ_{app} can be written

$$\epsilon_{app} = \epsilon + G^2/\omega^2 C_0 (C_{el})_0 \qquad (1)$$

Subtraction from ϵ_{app} of the values corresponding to the dashed line of Fig. 1 (which represents a correction of the form const/ω^2) gives the constant values indicated as crosses and the electrode capacitance $(C_{el})_0$ calculated from the correction is 30 μf. per cm.^{2} of electrode surface.

The result for the liquid makes plausible the expectation that a similar correction to measured values for the solid would account for electrode effects and give values characteristic of the dielectric only, but this turns out not to be the case. Instead, we have found that the necessary form of electrode impedance to give concordant results is a complex function Z_{el} similar to that found for a number of electrolytic solutions and various metal electrodes.[15] This may be written $Z_{el} = Z_0(i\omega)^{-n}$, in which the constant Z_0 is characteristic of the electrode–dielectric interface, and the exponent n has the value 0.5 in the present case.

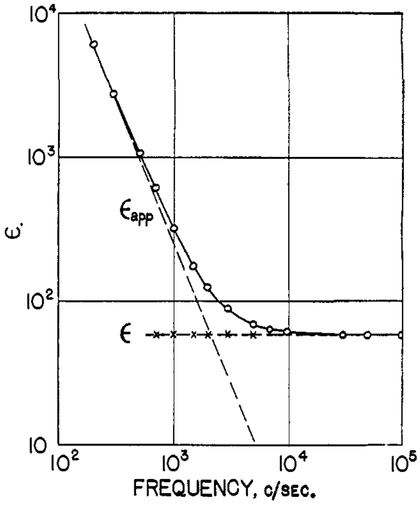

Fig. 1.—Dependence of apparent dielectric constant on frequency for liquid formic acid at 20°.

If the dielectric in a cell of air capacitance C_0 has a true dielectric constant ϵ' and reduced conductance G/C_0,[16] then the apparent values by measurement when an electrode impedance Z_{el} is in series with the sample are given by

$$G_{app}/C_0 + j\omega\epsilon'_{app} = \frac{G/C_0 + j\omega\epsilon'}{1 + Z_{el}(G/C_0 + j\omega\epsilon')} \qquad (2)$$

This result is the consequence of the elementary formula for the equivalent admittance Y_{app} of the admittances $Y = G + j\omega\epsilon' C_0$ and $1/Z_{el}$ in series, Y_{app} being by definition expressed as $Y_{app} = G_{app} + j\omega\epsilon'_{app}C_0$. For the data to be considered, we have $G \gg \omega\epsilon' C_0$ for all frequencies at which Z_{el} is significant and also $|Z_{el}|G \ll 1$, where $|Z_{el}|$ is the modulus of the complex function. With these approximations, we obtain from Eq. (2) with $Z_{el} = Z_0(i\omega)^{-n}$ the relations

$$G_{app}/C_0 = G/C_0 - (Z \cos n\pi/2)\omega^{-n}\, G^2/C_0$$
$$\epsilon'_{app} = \epsilon' + (Z_0 \sin n\pi/2)\omega^{-(n+1)}\, G^2/C_0 \qquad (3)$$

When corrections of these were tested on the experimental data, it was found that asymptotically constant values of *both* G/C_0 and ϵ' were obtained at low frequencies by a suitable choice of Z_0, *provided* the value $n = 0.5$ was used.

The data in Table I are representative values for ϵ' and G/C_0 at low frequencies from three runs at 0° and the values found after applying corrections of the form (3) with the one parameter Z_0 and the value $n = 0.5$. It is seen that the values of ϵ' do not vary significantly below 500*c*, and are in fairly good agreement for the three runs. The values of G/C_0 also are constant to within 0.1% below 500*c*, but the values differ considerably for the three samples. Despite a variety of measures to prevent contamination and to obtain a homogeneous solid, we were unable to obtain consistent limiting conductance values and believe the variability is largely due to small regions of supercooled liquid in which impurities become concentrated.

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[14] For a discussion of the coupled ratio arm circuit and this shunting effect, see reference (12).

[15] See, for example, G. Jones and S. M. Christian, This Journal, 57, 272 (1935).

[16] This reduced conductance differs from the specific conductance as ordinarily defined merely by a conversion factor depending on the units chosen. For example, k (μ mho/cm.) = 0.0885 (G(μ mho)/C_0($\mu\mu$f.)).

TABLE I

ELECTRODE POLARIZATION CORRECTIONS FOR FORMIC ACID SAMPLES

Frequency cycles/sec.	Cell 1 Parallel plates $^1/_4''$ separation Obsd.	Cor.	Cell 2 Cylindrical $^5/_{16}''$ separation Obsd.	Cor.	Cell 3 Cylindrical $^1/_8''$ separation Obsd.	Cor.
	Dielectric constant ϵ'					
20	125.3	13.6	....	....	....	....
100	24.4	13.5	42.7	13.7	53.8	13.6
200	17.8	13.7	23.7	13.6	27.2	13.6
500	14.8	13.7	15.9	13.5	16.8	13.6
1000	13.7	13.2	13.8	13.0	14.2	13.2
2000	12.7	12.5	12.6	12.4	12.8	12.4
	Reduced conductance G/C_0 (μmho/$\mu\mu$f.)					
20	3.461	3.475	....	....	....	....
100	3.468	3.475	2.989	3.006	1.931	1.956
200	3.469	3.474	2.993	3.006	1.938	1.956
500	3.473	3.477	3.000	3.008	1.943	1.953
1000	3.479	3.482	3.008	3.013	1.952	1.959
2000	3.493	3.495	3.021	3.027	1.967	1.971

The magnitude of the electrode impedance varied considerably with the sample and electrodes, being consistently larger for samples of high conductance and for more highly polished electrodes.[17] Both types of behavior are reasonably to be expected, but the poorly defined conditions from this point of view make a detailed analysis unjustified. The qualitative behavior does, however, give further support to our conclusion that the large changes and variability in the observed behavior at low frequencies are to be attributed primarily to an electrode effect rather than to volume inhomogeneities.

With the correction procedure outlined it was found possible to obtain consistent values of ϵ' over most of the dispersion range of frequencies for temperatures down to $-50°$. On the assumption that the limiting values of G/C_0 at low frequencies result from a d.c. conductance G_0/C_0, values of absorption conductance $\Delta G/C_0$ and the corresponding imaginary part ϵ'' of the complex dielectric constant were calculated by the reactions

$$\epsilon'' = \Delta G/\omega C_0 = (G - G_0)/\omega C_0$$

The values of ΔG never exceeded $G_0/5$ at the center of the dispersion region and at lower frequencies the difference $G - G_0$ became very small compared to G_0, with progressively greater uncertainty in ϵ'' as a result. The values found for ϵ'' at frequencies much below the center of the dispersion range are thus very sensitive to error in G_0/C_0, and any variations in its value during a run, and were found to scatter quite badly at the lowest frequencies. This variation plus errors from non-reproducibility of samples constituted the major sources of error in defining the complex dielectric constant and its frequency dependence.

The quantity of data obtained in some twenty runs on the solid which gave useful information, each at twenty or more frequencies, is much too great to be more than summarized in a reasonable space. The convenience of a plot of the complex locus of ϵ'' *vs.* ϵ' in analysis of dielectric data has been discussed elsewhere[18] and this method is employed here. Data obtained at four different temperatures from 0 to $-40°$, and for two or more runs at two, are plotted in Figs. 2, 3 and 4. The values of ϵ' at low frequencies obtained after correction for electrode polarization are indicated by the vertical lines at the ends of the circular arcs drawn to pass through the limiting values.

From the plots it is seen that the data are fitted, within the rather large uncertainty of values for ϵ'' at the lower frequencies, by circular arcs with depressed centers. The analytical expression for this functional behavior is[18]

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + (i\omega\tau_0)^{1-\alpha})$$

and the behavior at any temperature is defined by the values of ϵ_0 and ϵ_∞, the limiting low and high frequency dielectric constants, τ_0, a characteristic relaxation time, and the parameter α which determines the depression angle of the arc. The values fitting the data of Figs. 2, 3, 4 and other results are given in Table II, the values for τ_0 having been found from the frequency f_c for which ϵ'' reaches a maximum and $\epsilon' = (\epsilon_0 + \epsilon_\infty)/2$ by the relation $\tau_0 = 1/2\pi f_c$.

TABLE II

DIELECTRIC CONSTANTS OF SOLID FORMIC ACID

t, °C.	Electrode separation, inches	ϵ_0	ϵ_∞	$\tau_0 \times 10^6$, sec.	α	G_0/C_0 (μmho/$\mu\mu$f.)
0.6	$^1/_4$	13.7	3.2	4.43	0.44	3.48
1.3	$^5/_{16}$	13.5	3.1	4.30	.46	3.01
0.7	$^1/_8$	13.6	3.0	4.69	.44	1.96
−10.1	$^1/_4$	11.7	3.0	9.36	.42	2.08
−10.1	$^1/_8$	11.7	3.0	8.85	.42	1.76
−15.0	$^1/_8$	12.8	2.7	12.7	.47	1.34
−30.0	$^5/_{16}$	30	3.0	31.8	.50	0.56
−40.0	$^1/_4$	40	2.9	76	.40	0.61
−40.0	1	39	3.0	71	.48	1.04
−40.0	$^1/_{16}$	37	2.9	99	.48	0.31
−50.0	$^1/_4$	50	2.8	159	.40	0.22

The accuracy of the data in Table II is limited primarily by the errors and uncertainties in the large corrections necessary to account for the electrode polarization and to some extent by inhomogeneity of samples. We do not feel justified in considering variations of less than 5% significant, although the reproducibility and internal consistency of data for individual runs are much better than this figure.

Equilibrium dielectric constants ϵ_0 for the liquid obtained as interpolated values at several temperatures are given in Table III.

TABLE III

DIELECTRIC CONSTANTS OF LIQUID FORMIC ACID

t, °C.	8.4 (m.p.)	15	20	25	30	35	39
ϵ_0	62.2	59.7	57.9	56.1	54.5	52.9	51.6

The agreement with the values found by Thwing and Drude[5] is reasonably good, with that of Dobroserdov poor. A figure of 0.5% is a reasonable estimate of the accuracy of the results.

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(17) Attempts to increase the effective surface area by platinization were unsuccessful, as the electrodes invariably peeled or were otherwise unreproducible.

(18) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

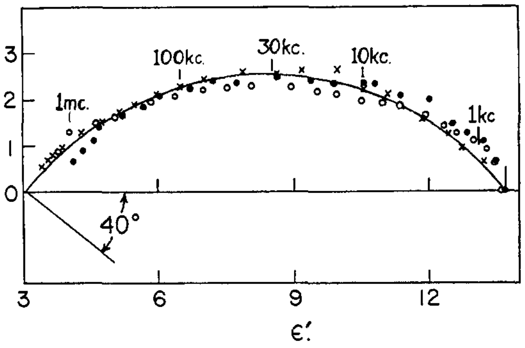

Fig. 2.—Complex plane dielectric constant locus for three solid formic acid samples at or near 0°.

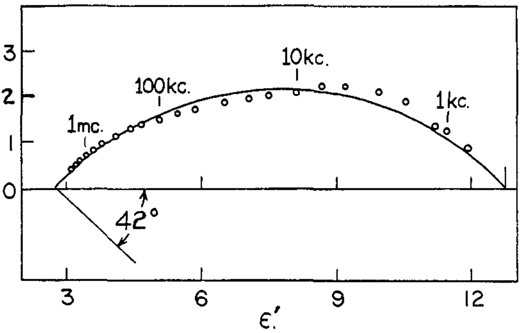

Fig. 3.—Complex dielectric constant locus for solid formic acid at −15°.

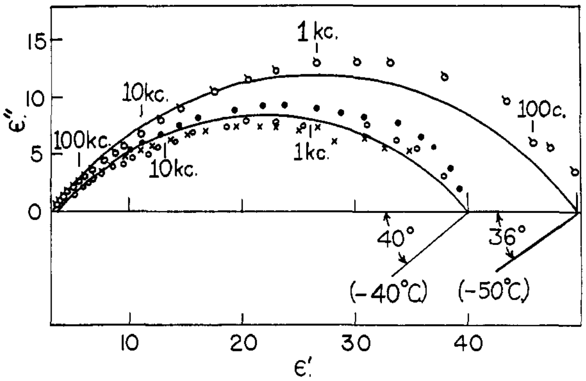

Fig. 4.—Complex dielectric constant loci for solid formic acid at −40° (three samples) and at −50°.

Discussion of Results

The values of equilibrium dielectric constant ϵ_0 for liquid formic acid are typical of a strongly polar hydrogen-bonding substance. This can be shown by comparison of the observed value with the prediction of Onsager's theory[19] which is known to work quite well for normal liquids and may be written

$$\epsilon_0 = n^2 + \frac{(n^2 + 2)^2}{2} \frac{4\pi N}{9kTV} \mu_0{}^2 \qquad (4)$$

In this equation, n is the extrapolated index of refraction, μ_0 the dipole moment of the polar unit, V the molar volume, N and kT have the usual significance, and the approximation is made that n^2 is negligible compared with $2\epsilon_0$. If we assume a value $\mu_0 = 1.8$ Debye units, as estimated by Pohl, Hobbs and Gross[4] for the monomer from dilute solution data, and use $n_0 = 1.37$, the value predicted by Eq. (4) is 15 at 25°. If, instead, we take $n^2 = 3.0$, corresponding to the value of ϵ_∞ for the solid, a value of 24 is obtained.

The observed figure of 56 is much greater than either estimate and the reasonable conclusion is that in liquid formic acid a large effect of hydrogen bonding is present. In the absence of any knowledge of the form this takes, all that can be said with assurance from the dielectric data is that the large values of ϵ_0 are not consistent with the existence of the molecules exclusively as non-polar dimers, in contrast to the situation in acetic acid for example.

The values of ϵ_0 for the solid are striking in that a considerable drop on freezing is followed by a rapid rise with decreasing temperature below −10°. The value of ϵ_∞ of 3.0 is of the magnitude frequently found in solid dielectrics. Any examination of the behavior below about −50° by the methods we have used or any obvious alternative procedures would be very difficult, as the frequency ranges of dispersion are very low and, although the d.c. conductance is smaller, electrode effects are as serious as at higher temperatures. The large difference compared to the liquid suggests that the local order about any molecule of the solid must change appreciably on melting but, as in the liquid, the observed values indicate an appreciable polarization by molecular orientation or rearrangement in the presence of an electric field. More direct evidence from X-ray diffraction studies would evidently be valuable and virtually prerequisite to more detailed analysis of the present data.

The variation with temperature of the relaxation times τ_0 given in Table II can be expressed within the accuracy of our measurements by a rate law of the form $\tau_0 = Ae^{E/RT}$ as shown by the plot in Fig. 5 of log τ_0 *versus* $1000/T$, the constants for the straight line as drawn being $A = 1.3 \times 10^{17}$ sec. and $E = 13.2$ kcal./mole. It should be emphasized,

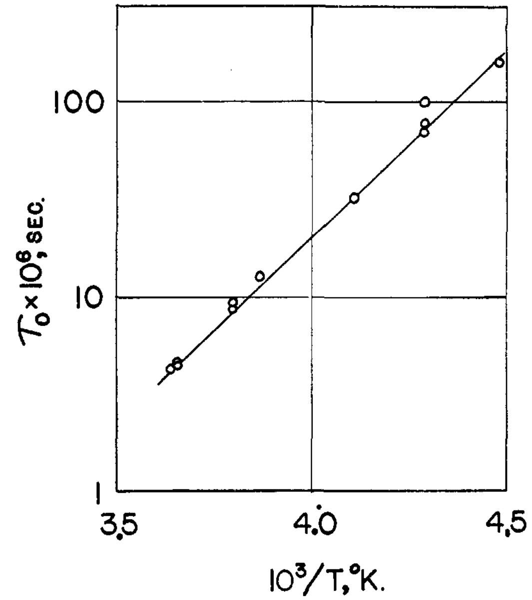

Fig. 5.—Dependence of relaxation time (log scale) on reciprocal temperature for solid formic acid.

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[19] L. Onsager, THIS JOURNAL, 58, 1486 (1936).

however, that the observed dielectric constant locus requires a broad distribution of assumed simple relaxation processes[18] or of activation energies for such processes, a situation encountered in many other dielectrics. The breadth of the distribution, as measured by the parameter α, does not appear to change significantly with temperature over the range 0 to $-40°$.

Some comment about the direct current conductances of both the liquid and solid is in order, as they are orders of magnitude greater than those for most polar liquids and solids. In the case of the liquid, the reproducibility of the measured values and agreement with the data of others confirm the belief that the figure of 6.0×10^{-5} mho/cm. at 25° is characteristic of the pure substance. In measurements on the solid we were unable to obtain consistent limiting values despite a variety of precautions, presumably, because of slight contamination and patches of supercooled liquid, and we can only state upper limits of 2×10^{-7} mho/cm. at 0° and 3×10^{-8} at $-40°$. We do, however, believe that the true figures are not greatly less than these values.

The conductance values for both liquid and solid are so large that a proton transfer mechanism is more reasonable than for hydrogen-bonding substances which have conductances orders of magnitude smaller. If intermolecular proton transfer is important, one might expect the magnitude of the conductance to be limited by the time required for molecular reorientation, of which the dielectric relaxation time is a measure. Under these conditions, the Maxwell time $\theta = \epsilon/4\pi k$ for relaxation of a charge distribution in a conducting dielectric ought to be comparable with the time τ_0 obtained from the dielectric constant locus. If the values of ϵ_0 and k for solid formic acid from Table II are used to calculate θ, the values obtained are found to be of the same magnitude as τ_0 over the temperature range (0 to $-50°$). This comparison is made graphically in Fig. 6 in which values of θ and τ_0 for the various runs are plotted against each other, and the points are seen to scatter about the line $\tau_0 = \theta$. The correspondence would be more convincing if more reproducible direct current conductances had been obtainable, but is sufficiently good to give some support to the possibility of a proton-transfer process, which thus merits further consideration when information about the solid structure becomes available.

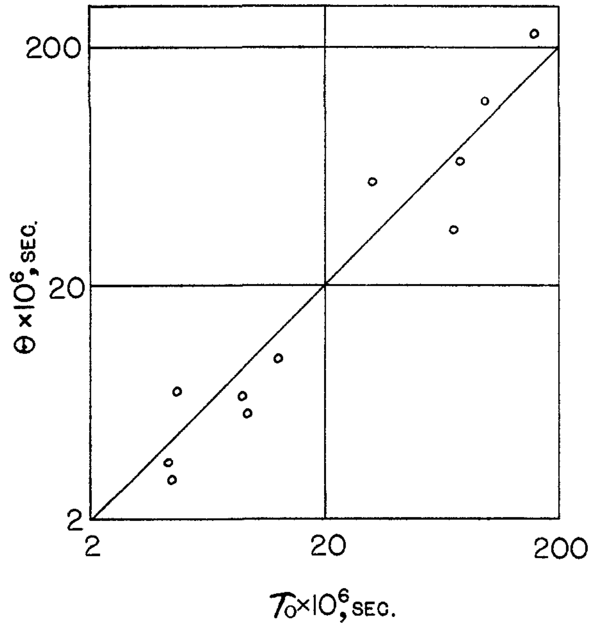

Fig. 6.—Correlation of dielectric relaxation time τ_0 with Maxwell relaxation time θ for solid formic acid.

Finally, it is of interest to consider the difference in behavior of the electrode-polarization effect for liquid and solid. In the liquid, the equivalent electrode impedance is within experimental error that of pure capacitance, and for the solid an expression of the form $Z_{el} = Z_0(i\omega)^{-1/2}$ accounts for the data. Although this appears odd at first sight, simple considerations suggest that the great difference in conductances of the two phases is responsible.

If a diffusion process limits the development of space charge, near the dielectric–electrode interface, then an equilibrium charge distribution leading to an equivalent capacitance of the Gouy type will be realized. At sufficiently high frequencies, however, this equilibrium will not have time to become established, and a solution of the diffusion equation such as that discussed by Ferry[20] shows that the limiting equivalent impedance is of the form $Z_{el} \sim (2\theta/i\omega)^{1/2}$ where θ is the Maxwell relaxation time already defined. The transition between the two asymptotic forms for such a model would be expected at frequencies for which $\omega\theta$ is of the order unity. These would be much lower in the solid than the liquid because of the smaller conductance and so are consistent in this respect with the observed difference. Quantitatively, however, the model fails for the solid because the transition in behavior is predicted to occur in the dielectric dispersion range when θ and τ_0 are comparable, while, in fact, the variation as $\omega^{-1/2}$ persists to the lowest frequencies of measurements for the solid. This lack of agreement is not surprising in view of the crudeness of the model and similar difficulties in its applications to other situations are discussed by Ferry. We have discussed it here merely to suggest that the observed electrode behavior is not unreasonable.

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(20) J. D. Ferry, *J. Chem. Phys.*, **16**, 737 (1948).