

## Dielectric Behavior of Solutions of Electrolytes in Solvents of Low Dielectric Constant I. A Calorimetric Method for Measuring Losses

A. H. Sharbaugh, C. Schmelzer, H. C. Eckstrom, and C. A. Kraus

Citation: *J. Chem. Phys.* **15**, 47 (1947); doi: 10.1063/1.1746287

View online: <http://dx.doi.org/10.1063/1.1746287>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v15/i1>

Published by the [AIP Publishing LLC](#).

---

### Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT

**SHARPEN YOUR  
COMPUTATIONAL  
SKILLS.**



Subscribe for  
**\$49** | year



**computing**  
in **SCIENCE & ENGINEERING**

Scientific  
Computing  
with GPUs

# Dielectric Behavior of Solutions of Electrolytes in Solvents of Low Dielectric Constant

## I. A Calorimetric Method for Measuring Losses<sup>1</sup>

A. H. SHARBAUGH, JR.,<sup>2</sup> C. SCHMELZER,<sup>3</sup> H. C. ECKSTROM, AND C. A. KRAUS  
*Metcalf Research Laboratory, Brown University, Providence, Rhode Island*

(Received October 16, 1946)

The experimental equipment and method used to determine calorimetrically the energy absorption in a radiofrequency field by several electrolytes in solvents of low dielectric constant is described. The dipole conductivity and the loss factor for these systems are then calculated from the experimental data.

FOR some time, the attention of this laboratory has been directed toward a thorough investigation of the behavior of electrolytes in solvents of low dielectric constant. Such investigations are of interest because of the large interionic attractive forces which cause association into ion-pairs and other increasingly complex aggregates. One of the more important aspects of the theory accounting for the behavior of these solutions was the postulation of the existence of the ion-pair, or dipole.<sup>4</sup> Such postulation became fact when dielectric constant measurements yielded values for the dipole moments of a number of quaternary and ternary ammonium salts in benzene which required separation of unit electronic charges by distances of the order of molecular dimensions.<sup>5</sup>

To gain complete insight into these low dielectric constant systems, it has been necessary to investigate their properties by means of several methods, *viz.*, conductance, dielectric constant, and cryoscopic measurements. The method to be described here was developed to give still another approach which would yield information as a direct consequence of the existence of the ion-pair. Certainly, it is to be expected that these large and highly polar molecules dispersed in non-polar solvents should exemplify systems with

large dielectric losses at readily accessible radiofrequencies. Therefore, the quantity of heat generated as a result of energy absorption in a radiofrequency field by several quaternary and ternary ammonium salts in solvents of low dielectric constant have been investigated calorimetrically. This has been accomplished by placing the solution in a two-electrode cell to which is affixed a capillary thermometer tube; thereby, any temperature change in the fluid may be observed directly by a change in the level of the capillary liquid. This method has the advantage of being simple in principle and of giving an absolute measure of dielectric losses of the cell and its contents. It is not a new procedure, having been originated by Harms in 1901,<sup>6</sup> and used more recently by Schmelzer,<sup>7</sup> Oncley,<sup>8</sup> and Conner.<sup>9</sup>

### PRINCIPLES OF THE METHOD

Let an alternating voltage,  $V = V_{\max} \sin \omega t$ , be imposed on a thermometer cell which contains the fluid to be investigated. If the fluid-filled cell presents a resistance  $R$ , the amount of heat generated in  $t$  seconds is given by

$$Q = \int_0^t V^2/R dt. \quad (1)$$

If one neglects the change in resistance caused by the small temperature change during the flow of current, Eq. (1) becomes

$$Q = V_{R.M.S.}^2 t / R = V_{R.M.S.}^2 t \kappa / z, \quad (2)$$

where  $\kappa$  is the specific conductance of the solution

<sup>1</sup> This paper is based on a portion of a thesis submitted by A. H. Sharbaugh, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Brown University, June, 1943.

<sup>2</sup> Metcalf Fellow in Chemistry at Brown University, 1941-42. Present address: General Electric Research Laboratory, Schenectady, New York.

<sup>3</sup> Anthony Fellow in Chemistry at Brown University, 1937-38 and 1938-39. Address: 14a Heindenheim/Brenz, Württemberg, 2 Theodor Schaeferstrasse, American Zone, Germany.

<sup>4</sup> R. M. Fuoss, *Chem. Rev.* **17**, 27 (1935).

<sup>5</sup> Geddes and Kraus, *Trans. Faraday Soc.* **32**, 585 (1936). Kraus, *J. Frank. Inst.* **225**, 687 (1938).

<sup>6</sup> F. Harms, *Ann. d. Physik* **5**, 564 (1901).

<sup>7</sup> C. Schmelzer, *Ann. d. Physik* **28**, 35 (1937).

<sup>8</sup> Oncley, Ferry, and Shack, *Ann. N. Y. Acad. Sci.* **40**, 371 (1940).

<sup>9</sup> W. P. Conner, *J. Chem. Phys.* **9**, 591 (1941).

and  $z$  is the cell constant. Therefore, if the rate of heat generation,  $Q/t$ , is observed for a given applied alternating voltage, the conductance of the solution may be readily calculated for the frequency of the voltage in question. Equation (2) may also be rewritten as follows:

$$Q = V_{\text{R.M.S.}}^2 \kappa / z = mc\theta = \pi r^2 \Delta h dc / \alpha, \quad (3)$$

where  $m$  is the mass,  $c$  is the specific heat,  $\theta$  is the temperature rise,  $d$  is the density,  $\Delta h$  is the height of rise in the cell capillary in  $t$  seconds,  $r$  is the radius of the thermometer tube, and  $\alpha$  is the coefficient of expansion of the fluid filling the cell. A subscript 0 will denote quantities of Eq. (3) which are measured at a sufficiently low frequency so that no heat is generated as a result of energy absorption by the ion-pairs or dipoles in the solution. The subscript  $\omega$  will denote these quantities observed in the same conductance cell at another higher angular frequency  $\omega = 2\pi\nu$ . When this is done, we may write

$$V_0^2 t_0 \kappa_0 / V_\omega^2 t_\omega \kappa_\omega = [d_0 c_0 \Delta h_0 / \alpha_0] / [d_\omega c_\omega \Delta h_\omega / \alpha_\omega],$$

from which

$$\kappa_\omega = [V_0^2 t_0 \kappa_0 / V_\omega^2 t_\omega] [\alpha_0 d_\omega c_\omega \Delta h_\omega / \alpha_\omega d_0 c_0 \Delta h_0]. \quad (4)$$

Since only the ratio of voltages is now involved, the r.m.s. subscript will be dropped. Equation (4) is further simplified and thermal irregularities are avoided if the low and high frequency observations are made each time for the same solution and for equal temperature rises. Hence, Eq. (4), under these conditions, becomes

$$\kappa_\omega = V_0^2 t_0 \kappa_0 / V_\omega^2 t_\omega. \quad (5)$$

Furthermore, it will be assumed that the high frequency conductance may be resolved as

$$\kappa_\omega = \kappa_0 + \Delta\kappa = V_0^2 t_0 \kappa_0 / V_\omega^2 t_\omega,$$

where  $\Delta\kappa$  will be referred to as the dipole conductivity. Therefore,

$$\Delta\kappa = [(V_0^2 t_0 / V_\omega^2 t_\omega) - 1] \kappa_0. \quad (6)$$

The tacit assumptions to be kept in mind when using Eq. (6) are that both the low and high frequency voltages should be measured in the same manner (as peak values of sinusoidal voltages in this investigation); that Ohm's law is obeyed within the range of voltages used; and

that  $t_0$  and  $t_\omega$  are the times required for the same amount of expansion in the thermometer cell.

The complex dielectric constant<sup>10</sup>  $\epsilon$  may be conveniently expressed as

$$\epsilon = \epsilon' - j\epsilon'',$$

where the prime and double prime represent the real and imaginary parts according to the usual alternating current vector notation. With reference to a medium,  $\epsilon$  may be defined as the ratio of the admittance of a condenser filled with the medium to the admittance of the condenser when empty.<sup>11</sup> Hence,

$$\epsilon = \epsilon' - j\epsilon'' = Y/Y_0 = [G_\omega + j\omega C_1] / j\omega C_0,$$

where  $G_\omega$  is the equivalent parallel conductance at the frequency  $\omega$ , and  $C_1$  and  $C_0$  represent the equivalent parallel capacity of the filled and empty condenser, respectively. Equating real and imaginary parts,

$$\epsilon' = C_1 / C_0$$

and

$$\epsilon'' = G_\omega / \omega C_0 = \kappa_\omega \times 1.80 \times 10^{12} / \nu,$$

where  $\nu$  is the frequency of the applied alternating voltage in cycles per second and  $\kappa_\omega$  is the specific conductance in reciprocal ohm-cm at a frequency  $\omega = 2\pi\nu$ . Furthermore, it is convenient to separate the a.c. and d.c. in-phase components by defining a loss factor  $\Delta\epsilon''$  as

$$\Delta\epsilon'' = 1.80 \times 10^{12} (\kappa_\omega - \kappa_0) / \nu = 1.80 \times 10^{12} \Delta\kappa / \nu.$$

Thus,  $\Delta\epsilon''$  is a measure of the pure a.c. response of the system, and  $\epsilon'$  is the usual dielectric constant defined by the ratio of the capacitance with a given material dielectric, to the capacitance of the same system with a vacuum as a dielectric.  $\Delta\kappa$  will be called, for convenience, simply the dipole conductivity but, in general, it will be understood that losses dealt with in this investigation may be caused by the existence of higher order complexes, such as quadrupoles, octapoles, etc., as well as to dipoles.

## EXPERIMENTAL EQUIPMENT

High frequency energy was furnished by a conventional three-stage short wave generator,

<sup>10</sup> P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).

<sup>11</sup> Hubert H. Race, *Phys. Rev.* **37**, 430 (1931).

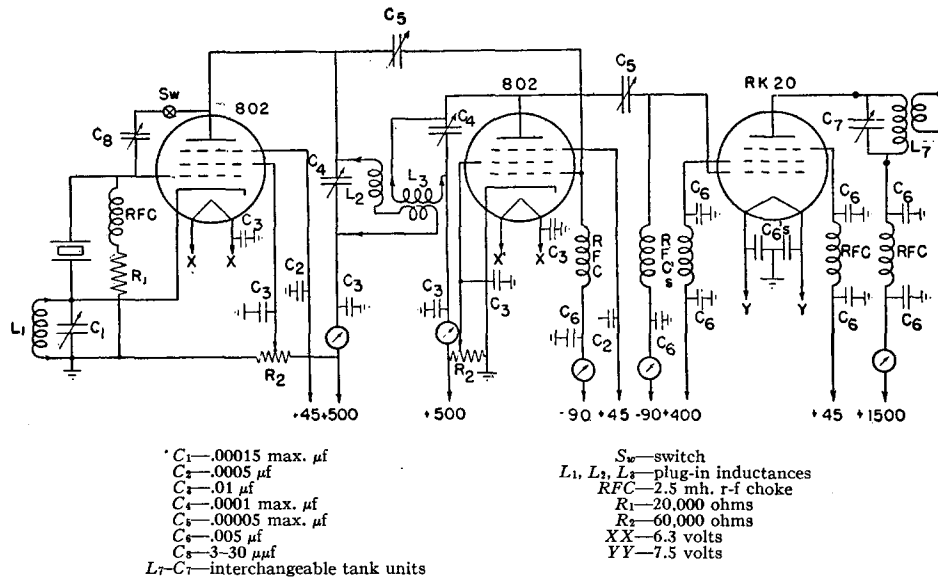


FIG. 1. High frequency generator.

shown in Fig. 1, capable of delivering up to about 50 watts useful output. Frequencies were controlled by three crystals and, by virtue of frequency multiplication in the Tri-tet oscillator stage, as well as in the buffer-multiplier stage, useful output could be obtained on crystal harmonic frequencies through 28 Mc. The frequencies actually used were 1.83, 3.50, 7.04, 10.51, 14.09, 21.13, and 28.18 Mc. The d.c. voltage supplies consisted of two units: one of 500 volts, to operate the oscillator and multiplier stages and, secondly, a 2000-volt supply for the final amplifier and another low frequency transmitter to be described later. A type 83 and a pair of 866 tubes served as rectifiers for the low and high voltage supplies, respectively. The voltage

furnished by the high voltage supply was made continuously variable by means of a Variac inserted in the primary circuit of the high voltage plate transformer. The 115-volt a.c. source was a 500-volt-ampere Sola Constant Voltage transformer. This insured a steady output from the generators since the Sola transformer delivered 115 volts  $\pm 1$  percent for a total primary variation of about 20 percent.

A second generator was constructed for the special purpose of supplying low radiofrequency energy. The Hartley oscillator circuit of Fig. 2 was selected because of its simplicity and the convenience with which the lower frequencies may be obtained, since both plate and grid inductances are shunted by the tuning condenser. Plug-in coils and variable air condensers served to vary the frequency, if desired, although during this investigation, a frequency of 0.1 Mc was principally used. Critical circuit elements were varied until a cathode-ray oscilloscope indicated a substantially pure sine wave output. Frequencies could be set to within  $\pm 3$  percent with a General Radio Type 574 wave meter.

The third source of cell voltages was that of the 60-cycle power mains. An arrangement for supplying this consisted of a Variac whose output could be connected directly to the cell or first stepped up by a transformer. All 60-cycle voltages were measured with a Weston 341 voltmeter.

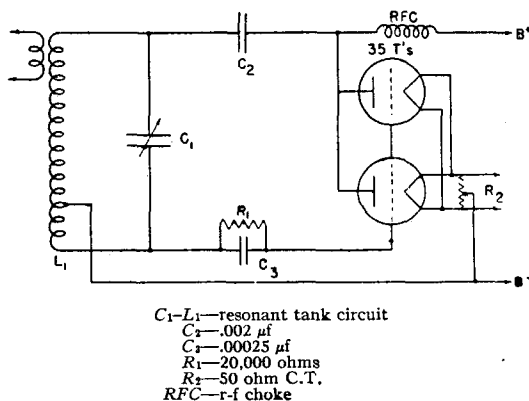
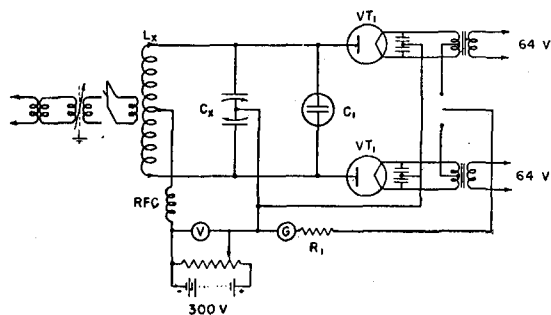


FIG. 2. Low frequency generator.



$L_x$ —plug-in coils  
 $VT_1$ —G.E. custom built water-cooled diodes, 1.60 heater volts  
 $C_x$ —140  $\mu\text{f}$  per section  
 $C_1$ —thermometer cell  
 $R_1$ —1, 2, or 3 megohms  
 $RFC$ —r-f choke  
 By-pass condensers .005  $\mu\text{f}$

FIG. 3. Cell circuit.

Radiofrequency voltages were determined by voltmeter tubes as used in the circuit of Fig. 3. The circuit is similar to that used by Schmeltzer<sup>7</sup> and consists of two diodes in a symmetrical rectifying circuit with provision to exactly compensate the peak radiofrequency voltage with a bank of "B" batteries.

Since the calculation of the dipole conductivity requires the ratio of two voltages measured at very different frequencies, careful consideration was given to frequency dependent errors. A serious source of error may arise because of the voltage drop resulting from the self-inductance of the leads working in conjunction with the electrode capacity of the voltage measuring apparatus. This is easily shown by a consideration of the equivalent circuit shown in Fig. 4. Let  $L_1$  and  $L_2$  = self-inductance of leads,  $V$  = desired high frequency voltage,  $V_a$  = apparent voltage operating in the measuring device, and  $C$  = capacity of the measuring device. By a general application of Ohm's law:

$$V_a/V = Z_c/Z,$$

where

$$Z = j(\omega[L_1 + L_2] - 1/\omega C) \quad \text{and} \quad Z_c = -j/\omega C.$$

Therefore,

$$V/V_a = \omega C(1/\omega C - \omega L),$$

where

$$L = L_1 + L_2.$$

Finally,

$$V = V_a(1 - \omega^2 LC).$$

Estimating  $L$  to be  $0.1 \mu\text{h}$  and  $C$  to be  $0.6 \mu\text{f}$ , the

error in the apparatus described here would be only about +0.2 percent at 28 Mc.

Calculation also reveals that the transit time of the electrons need not be considered with the tubes (about 1.5 mm electrode spacing) and voltages used in this investigation up to frequencies of about 50 Mc.

Because of electron pressure, a very small "resting" current ( $<10^{-6}$  amp.) flowed in the d.c. circuit when no potential was applied to the diodes. The reading of the galvanometer under this condition served as the null point for future balances of the r-f voltage by the biasing d.c. voltage. The two tubes had slightly different "rest" currents; hence, for convenience, when rapidly obtaining cut-off voltages, a single null position was established for both tube balances, and then, later, a small correction could be applied if necessary.

The cut-off voltages were measured on a calibrated Weston Model 45 voltmeter. Currents were indicated by a "loop" galvanometer similar to that described by Deubner.<sup>12</sup> The movement is a piece of aluminum foil (about 1 micron thick), shaped as a "U" and held in the field fissure of a permanent magnet. The loop of foil is protected from air currents by a glass housing and the entire assembly is completely shielded. Observation of the loop displacement as a result of current flow is done subjectively by a telescope (80 $\times$  magnification) containing an ocular scale, illumination being furnished by a lamp within

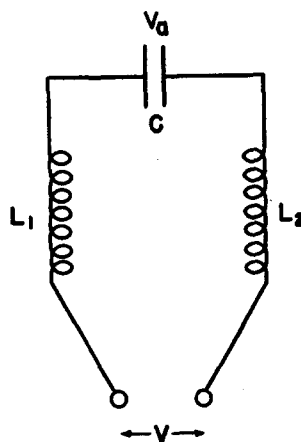


FIG. 4.

<sup>12</sup> A. Deubner, Zeits. f. tech. Physik 11, 163 (1930).

the housing. Three degrees of freedom are furnished by sliding carriages so that the loop can be located at will with respect to the ocular scale. It was found that observation of the movement was facilitated by having a small glass fiber cemented to the foil. This galvanometer is especially suited to its application here because of the extremely small inertia of the loop movement. The specifications are: total time of oscillation, 0.2 sec.; loop resistance 5–10 ohms; sensitivity,  $7 \times 10^{-7}$  amp. per scale division.

The cell circuit was link (inductively) coupled to the radiofrequency generators through a Faraday shield as shown in Fig. 3. Various inductances could be plugged into this circuit to obtain resonance at the different frequencies. (Also additional shunt capacity was necessary in the case of 0.1 Mc.) A measurement of some of the amplitudes of the harmonics present in the cell circuit showed them to be less than 2 percent of the fundamental if they were measurable at all; hence, a tuned intermediate resonant circuit between generator and cell circuit seemed unnecessary.

The thermometer cell bulb and associated components were immersed in a constant temperature air-bath. The temperature of the vessel was controlled by a flow of constant temperature water supplied from a large reservoir, the temperature of which could be held to 25°C within  $\pm 0.001^\circ$  for a day at a time. This water was circulated continuously by two pumps; one line supplied the top cover of the air bath and water jackets of the voltmeter tubes (which were located in the air-bath with the cell in order to obtain the shortest possible leads), and the other line supplied a copper water jacket at the sides and bottom of the air thermostat. Pipe lines, as well as air bath, were thermally insulated to minimize the effect of the ambient temperature. Over a period of several hours, the air bath

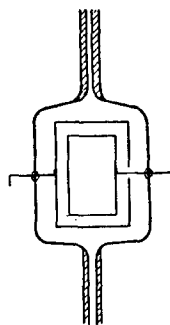


FIG. 5. Thermometer cell.

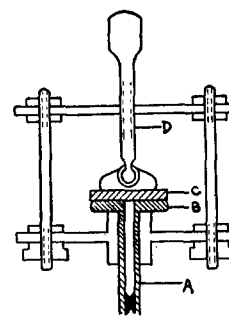


FIG. 5a. Method of closure of thermometer cell on bulb end. A, capillary leading to bulb; B, plane glass surface; C, optically plane glass plate; D, screw arrangement for holding C against B.

temperature varied on the average by less than  $0.01^\circ\text{C}$ , depending on room temperature fluctuations and the quantity of heat lost from the cell.

Three thermometer cells of the type shown in Fig. 5 were used in the investigation. The characteristic constants of these cells are listed in Table I, where benzene is the filling liquid. In order to avoid losses by evaporation, each thermometer cell was equipped on the bulb end with an optically plane glass surface which could be fitted against a similar surface of a glass disk for closing (see Fig. 5a) or to a suction apparatus for filling. With such an arrangement, having an air gap next to the polished glass surfaces, a solution could be kept for weeks without any noticeable evaporation. The capillary of the cell projected from the air-bath where the fluid meniscus could be viewed with a telescope. While in use, the open end of the capillary was connected to a glass bulb containing vapor of the investigated fluid. The dimensions of all these cells were negligibly small in comparison to one-quarter of the shortest wave-length used (10 meters). This, of course, refers to the wave-length in the fluid-filled cell which is smaller than the wave-length in free space by the factor  $(1/\epsilon')^{\frac{1}{2}}$ .

Rising times of the capillary fluid were measured with a synchronous-motor Cenco timer. These times ranged from about 4 sec. to 100 sec., depending on the field strength and conductance of the solution in the cell. To make a continuous time record of a rising meniscus in the capillary, a "Visasig" was used. This instrument delivered a

TABLE I. Cell characteristics.

	Physical volume (cc)	Effective vol.* (cc)	Cell constant	Separation electrodes (mm)	$\Delta h/\Delta t$ cm/deg. (approx.)	Capillary diam. (mm)	Approx. usable range (ohm <sup>-1</sup> cm <sup>-1</sup> )
Cell No. 1	39.3	4.29	0.002326	1	7.0	0.95	$10^{-3}$ – $10^{-4}$
Cell No. 2	8.5	0.741	0.01347	1	6.0	0.50	$10^{-4}$ – $10^{-5}$
Cell No. 3	3.0	0.354	0.1119	2	2.1	0.50	$10^{-7}$ – $10^{-6}$

\* Calculated volume between the electrodes of the cell.

paper tape at a constant speed on which were marked intervals corresponding to seconds. There could also be recorded simultaneously on the paper indications of a pen actuated by closing a telegraph key. Therefore, a time record of the height of the liquid column as observed by a telescope equipped with an ocular scale could be obtained by measuring the time intervals on this paper tape.

All audiofrequency conductances (assumed to be the conductance at 0.1 Mc) were measured by the substitution method on a special bridge built around the Campbell-Shackelton shielded ratio box by Leeds and Northrup. The conductance cells used with this bridge were cleaned with fuming nitric acid, steamed, and baked in an oven at 140° overnight. While cooling, a current of dry air was blown through them. When making measurements, the cells were placed in an air bath and observations made when temperature equilibrium had been established.

#### PRACTICAL ASPECTS OF MAKING MEASUREMENTS

The determination of dipole conductivity, using Eq. (6), is reduced to measuring two rates of rise of the meniscus—once, at a sufficiently low frequency where  $\Delta\kappa$  is zero; and, again, at the

TABLE II.

	Temp.	$V_0$	$t_0$	$V_0^2 t_0 \times 10^{-5}$
$\nu = 0.1$ Mc	3.835	129.4	30.3	5.07
	3.840	149.0	22.5	4.99
	3.842	173.0	17.2	5.15
	3.847	219.6	11.2	5.40
	3.849	219.4	10.8	5.19
	3.850	309.4	5.46	5.23
	3.852	377.4	12.0*	5.12
	3.853	456.2	8.32*	5.20
	3.852	523.0	6.36*	5.22
	Av. $5.17 \pm 1.6\%$			
	Temp.	$V_\omega$	$t_\omega$	$V_\omega^2 t_\omega \times 10^{-5}$
$\nu = 21.1$ Mc	3.860	44.3	16.9	0.330
	3.860	44.3	16.6	0.325
	3.859	46.0	15.8	0.334
	3.862	103.1	10.2*	0.327
	3.855	103.1	10.2*	0.327
	3.860	105.1	9.74*	0.325
	3.850	138.7	5.59*	0.322
	3.846	156.4	4.55*	0.334
	3.851	159.1	4.39*	0.334
	Av. $0.329 \pm 1.2\%$			

\* For  $\Delta h = 10$  mm where the  $V^2 t$  values have been reduced to a  $\Delta h = 3$  mm rise.

desired higher frequency, each time reading the accompanying voltages. Once a reliable r-f voltage measuring arrangement has been constructed, the experimental determination of the rates of rise presents the greatest problem. The question of constancy of the rising rate arises immediately, since the low and high frequency time measurements must be made under identical conditions to be used in Eq. (6). A number of plots of meniscus height *vs.* time were made with the "Visasig" chronograph for each of the three thermometer cells. These were studied carefully to ascertain within just what limits a linear relationship existed. In general, all determinations were made using actual rising heights from 1 to 10 mm (corresponding to 0.01°–0.2°C), depending on the conductance of the solution and size of cell. For best reproducibility, it was necessary to wait for complete thermal equilibrium between each measurement. However, with the largest cell used, satisfactory results could be obtained by operating the cell slightly above its equilibrium temperature and measuring the rate of cooling. The exponential cooling curve was approximated by a linear relationship and so used to correct the rising rate. It was found unnecessary to correct for any effect of temperature shifts of the air-bath.

Within the range of voltages (0.1–6.0 kv/cm) used and within the experimental error, no variation of the observed high frequency conductance with field strength was found. An apparent decrease in conductance with increasing voltages was initially observed, but the effect was eventually traced back to a zero correction on the voltage measurement. According to Onsager's theory,<sup>13</sup> for uni-univalent salts which are very slightly dissociated, the increase in conductance caused by high field strengths (second Wien effect) is given by

$$\kappa_E/\kappa_0 = 1 + 3.33 \times 10^{-3} e^3 V / 4 \epsilon' k^3 T^2 \\ = 1 + 4.818 V / \epsilon' T^2,$$

where  $V$  is the field strength (average volts  $\text{cm}^{-1}$ ),  $e$  is the electronic charge (statcoulombs),  $\kappa_E$  is the increased conductance due to the field, and the other symbols have their usual significance.

<sup>13</sup> Lars Onsager, J. Chem. Phys. 2, 599 (1934).

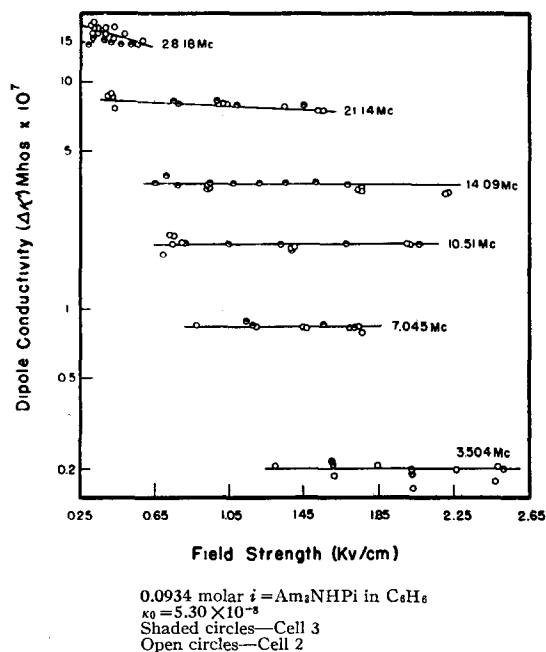


FIG. 6. Dipole conductivity as a function of frequency and field strength.

Thus, for benzene,

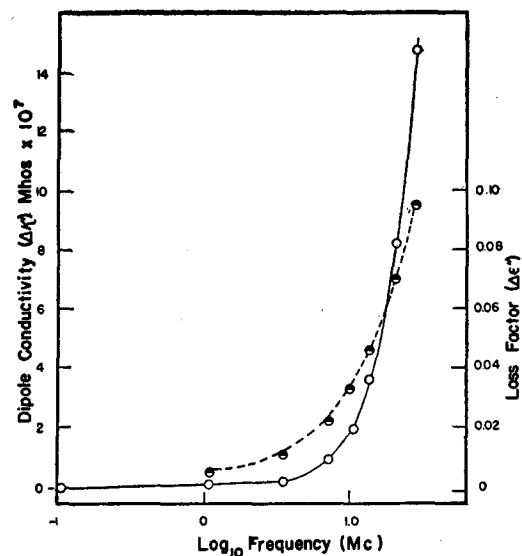
$$\kappa_E/\kappa_0 = 1 + 23.8 \times 10^{-6} V,$$

and in the example cited where  $V = 2(2.5 \times 10^3)/\pi = 1.6 \times 10^3$ , we could expect a maximum of about a 4 percent increase in conductance. However, the Langevin relaxation time, which is the time required to establish equilibrium between charge distribution and the external electric field, is only about 2 microseconds.<sup>14</sup> Our working frequencies correspond to periods of from 0.04–0.6 microsecond so that in this range there was not time for the Wien effect to appear in the cells.<sup>15</sup> However, no systematic increases in conductance with increasing field strengths were observed at 60 cycles or at 0.1 Mc where the periods are long enough to allow the effect to exist. Further work at these frequencies is in progress.

Wherever necessary, a correction was made for the heating of the glass of the cells. These corrections were calculated from data obtained with only pure solvent in the cells with the aid of Eq. (4). Observable heating was found at only the highest frequencies and the correction

<sup>14</sup> L. Onsager, reference 13. For benzene solutions, the Langevin relaxation time  $\tau_L = \epsilon'/72\pi \times 10^{11} \kappa = 10.1 \times 10^{-14}/\kappa$ .

<sup>15</sup> Mead and Fuoss, J. Am. Chem. Soc. 62, 1720 (1940).



0.0934 molar  $i = \text{Am}_2\text{NHPI}$  in  $\text{C}_6\text{H}_6$ .  
 Open circles—observed dipole conductance, ordinates left.  
 Shaded circles—observed loss factors, ordinates right.  
 Solid and dashed curves—theoretical curves for dipole conductance and loss factor, respectively, based on  $\epsilon_0 - \epsilon_\infty = 1.44$ ;  $\nu_0 = 430$  Mc.

FIG. 7. The dependence of dipole conductivity and loss factor on frequency.

amounted to only a few percent except for the very dilute solutions. The apparent glass conductance varied with the first to second power of the frequency depending upon the cell geometry.

For each concentration studied, the density, refractive index, viscosity, and audiofrequency dielectric constant, all pertinent to the Debye theory, were measured. All observations were made at 25.0°C.

Individual rates of rise per volt squared for a constant voltage could be reproduced with a mean deviation of about  $\pm 1$  percent. The rate of rise per volt squared for a two- or threefold voltage increase could be measured with a mean deviation of  $\pm 5$  percent.

The conductances measured at 60 cycles and 0.1 Mc agreed within the allowable experimental error.

#### EXAMPLE OF A MEASUREMENT

In Table II, is presented a typical set of data for a 0.0934 molar solution of tri-*iso*amylammonium picrate in benzene in Cell No. 2. The solution was allowed to return to temperature equilibrium between each application of the voltage. A temperature value of 3.854, in the



second column, corresponds to 25.000°C;  $V$  = peak voltage of the field;  $t$  = time in sec. for  $\Delta h = 3$  mm or 10 mm rise, as indicated;  $\kappa_0$  = audiofrequency conductance =  $5.30 \times 10^{-8}$  ohm $^{-1}$  cm $^{-1}$ ; density = 0.8825 g cm $^{-3}$ ; viscosity = 0.00657 poise; dielectric constant (1000 cycles) = 3.60; and index of refraction = 1.5000.

According to Eq. (5), the values of the dipole conductivity and loss factor at 21.1 Mc would be

$$\begin{aligned}\kappa_\omega &= V_0^2 t_0 \kappa_0 / V_\omega^2 t_\omega = (5.17)(5.30 \times 10^{-8}) / 0.329 \\ &= 83.4 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1},\end{aligned}$$

$$\begin{aligned}\Delta\kappa' &= \kappa_\omega - \kappa_0 - \kappa_{\text{glass}} = (83.4 - 5.30 - 0.3) \times 10^{-8} \\ &= 78.0 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1},\end{aligned}$$

$$\begin{aligned}\Delta\epsilon'' &= \Delta\kappa'(1.80 \times 10^{12})/\nu \\ &= (78.0 \times 10^{-8})(1.80 \times 10^{12})/21.1 \times 10^6 \\ &= 6.65 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}/\text{cycle}.\end{aligned}$$

Plots of the dipole conductivity *vs.* voltage and frequency for this solution are shown in Figs. 6 and 7. In Fig. 7, the experimental values are represented by the plotted points while the course of the solid curves is determined by calculation based on the Debye theory.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 15, NUMBER 1 JANUARY, 1947

## Dielectric Behavior of Solutions of Electrolytes in Solvents of Low Dielectric Constant.

### II. Dielectric Absorption<sup>1</sup>

A. H. SHARBAUGH, JR.,<sup>2</sup> H. C. ECKSTROM, AND C. A. KRAUS

*Metcalf Research Laboratory, Brown University, Providence, Rhode Island*

(Received October 16, 1946)

The dielectric losses in solutions of salts in several low dielectric constant solvents are studied as a function of frequency and concentration, using the calorimetric method. The results are interpreted according to the Debye theory, and critical frequencies, molecular radii, and dipole moments are evaluated wherever feasible. Solutions of tri-*iso*amylammonium picrate in benzene and diphenylmethane behave as a monodisperse system having a single well-defined polar structure relatively independent of concentration. Corresponding solutions of tetra-*n*-butylammonium thiocyanate, in contrast, show a marked departure from theoretical behavior for a monodisperse system, having a broad distribution of relaxation times and a high degree of association strongly dependent on concentration. Di-*n*-butyldioctadecylammonium thiocyanate shows monodisperse behavior at low concentrations, with more physically and electrically different polar bodies appearing as the concentration is increased. These results are in good agreement with polarization, conductance, and cryoscopic measurements for these systems.

THE experimental approach for measuring the dipole or "absorption conductivity" of solutions of electrolytes described in Part I of this series has been used for the study of solutions of tri-*iso*amylammonium picrate, tetra-*n*-butylammonium thiocyanate, di-*n*-butyldioctadecylammonium thiocyanate, di-*n*-butyldioctadecylammonium octadecylsulfate, tetra-*n*-butylammonium bromide, and *n*-butyl alcohol. Benzene and diphenylmethane were selected as solvents

because their dielectric constants are sufficiently low to cause marked ion association and the difference in their viscosities also provides a check against theory. These results are interpreted on the basis of the Debye theory of polar molecules.<sup>3</sup>

### EXPERIMENTAL

Commercial, thiophene-free benzene was purified by stirring with successive portions of concentrated sulfuric acid until the acid was no longer colored. The acid was removed by stirring with dilute sodium hydroxide solution, followed

<sup>1</sup> This paper is based on a portion of a thesis submitted by A. H. Sharbaugh, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Brown University, June, 1943.

<sup>2</sup> Metcalf Fellow in Chemistry at Brown University, 1941-42. Present address: General Electric Research Laboratory, Schenectady, New York.

<sup>3</sup> P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).