MEASUREMENT OF THE DIELECTRIC CONSTANT AND INDEX OF REFRACTION OF WATER AND AQUEOUS SOLUTIONS OF KCL AT HIGH FREQUENCIES

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(Received February 10, 1930)

Abstract

Dielectric constant of distilled water.—The dielectric constant of distilled water was measured with a vacuum tube source of voltage throughout a range of periods extending from about $T=1.31\times10^{-8}$ second to $T=8.49\times10^{-8}$ second corresponding to vacuum wave-lengths of 3.918 meters to 25.47 meters. The value obtained for the dielectric constant is $\epsilon=78.57$ at 25°C and is independent of the period within the above range of periods.

Temperature coefficient of dielectric constant for distilled water.—The values of the dielectric constant ϵ obtained for various temperatures t between 10°C and 60°C satisfy the empirical equation

 $\epsilon_t = 78.57 \left[1 - 0.00461 (t - 25) + 0.0000155 (t - 25)^2 \cdots \right].$

Between 4°C and 10°C the applicability of this equation is somewhat uncertain.

Dielectric constant of conducting solutions.—With distilled water, tap water, and aqueous KCl solutions of conductivity ranging from 0.97×10^7 e.s.u. to 178×10^7 e.s.u., and separating the conduction effects from the dielectric effects, we found the dielectric constant only slightly dependent on the ionic concentration of the solution and nearly the same as that of pure water. The errors of measurement are of the order of 0.1 percent for low conductivities but, because of attenuation, become of the order of 1 percent at the high concentrations of the salt.

Method.—The method employed consists in the measurement of standing electric waves between a pipe and a wire concentrically located within the pipe. The liquid is the dielectric between the wire and the pipe. The frequencies employed were accurately measured by a piezo crystal standardizing a zero beat method, and the half wave-length within the dielectric were obtained by moving a piston in the liquid and observing reactions on the source.

A theoretical discussion of the method is given.

INTRODUCTION

SOON after the discovery of piezoelectric oscillators and their adaptation to the production of constant frequencies of oscillations¹ we began an investigation of waves on wires. The frequencies of an electric oscillator were determined by comparison with the piezoelectric standard and the lengths of the resulting standing waves on two parallel wires were measured. In this way

¹ G. W. Pierce, "Piezoelectric Crystal Resonators and Crystal Oscillators Applied to the Precision Calibration of Wavemeters," Proc. Am. Acad. of Arts and Sciences **59**, No. 4 (1923). "Piezoelectric Crystal Oscillators Applied to the Precision Measurement of the Velocity of Sound etc." Ibid. **60**, No. 5 (1925).

an absolute determination of the ratio of the electro-magnetic to the electrostatic unit of electric quantity was attempted. After about a year of work on this problem it became apparent that the influence of surrounding objects led to errors and uncertainties which could not be sufficiently reduced with the parallel wire system.

To avoid this stray-field trouble it occurred to us to confine the field to the space between a central wire and a surrounding tube. This apparatus we have now had in operation for several years. The investigation with air or vacuum as the dielectric is not yet good enough for publication since on account of certain small mechanical inequalities of the pipe-system the precision desired has not been attained. We have, however, obtained accuracies better than one-tenth of one percent, and as a by-product to the primary research on the ratio of the units we have employed a similar apparatus in the present investigation.

DETAILS OF THE CONCENTRIC PIPE SYSTEM

The present method of determining the index of refraction of poorly conducting liquids resembles the older well-known scheme of measuring the index by comparing the length of the standing waves on Lecher wires immersed in the liquid with the length of the corresponding air waves. The method is, however, here refined by replacing the wires of the Lecher system by a brass pipe having a copper wire centrally within it along the axis of the pipe, with the solution in the pipe. The pipe and wire are excited by a vacuum tube oscillator at frequencies accurately known by their harmonic relationship with a piezoelectric quartz standard. A movable brass plunger making spring contacts with the pipe and wire and carrying a calibrated rod of the same material above it permits accurate settings at the positions of maximum reaction, which are half a wave-length apart. A sensitive galvanometer, recording changes in the plate current of the oscillator exciting the pipe and wire, indicates the half wave positions as the plunger moves along the pipe. From the known frequencies and the wave-length in the dielectric the velocity of the electric waves in the dielectric is computed.

As a device for producing standing electric waves the system of pipe, wire, and plunger has the outstanding advantage of confining the electric field to the medium between the pipe and wire. Suppose, for example, a set of parallel wires is immersed in a water tank. If the tank is small, an appreciable part of the electric field associated with the charges on the wires may be quite outside the water; difficulties also arise from reflections at the boundaries of the water; and an increase in size of the tank only reduces and does not eliminate these disturbances. For the longer waves in the present experiments the tank would need to be enormous. In the case of the pipe and wire system, on the other hand, the electric currents are confined to the inner surface of the pipe and the outer surface of the wire, so that the electric field has radial symmetry and is completely within the dielectric.

Fig. 1 shows in detail the experimental arrangements adopted. The brass pipe, 3.7 meters long and having an inside diameter of 4.1 cm and a wall-

thickness of 0.32 cm, was mounted vertically against a wall between two neighboring floors of the Cruft laboratory. A hard-drawn copper wire 0.163 cm in diameter was centrally fixed in the pipe held at the lower end by a canvas bakelite cap, and at the upper end by a bakelite strip. In order to make a watertight joint at the lower end, the bakelite cap was screwed to the end of the pipe hard against a thin cardboard gasket which had been boiled in paraffin. The pipe was filled from the top and emptied through a small hole (normally closed with a bakelite plug) in the bakelite cap.



Fig. 1. Arrangement of apparatus.

Two electric oscillators were used to cover the range from 4 to 25 meters vacuum wave-length: one, an oscillator designed particularly for high frequencies, covered the range from 4 to 5 meters; the other, an ordinary Hartley circuit oscillator with parallel plate supply, was used from 5 to 25 meters. These two oscillators and the piezo-electric oscillator, employing a quartz crystal mounted in vacuum, were placed in a sheet iron box at the lower end of the pipe. The pipe protruded below the cover of this box about 10 cm, and made good contact with the cover by means of a bronze flange clamped about the pipe and bolted to the cover. Shielded cables included all electrical connections from the observing position at the top of the pipe to the various oscillators in the box below. The electric oscillator was coupled to the lower end of the pipe-wire by a single lead through a small condenser, which was variable in order to permit equal coupling at all frequencies. The adjustment to zero beat between the electric oscillator and a harmonic of the crystal oscillator was accomplished by varying a condenser of the electric oscillator for course adjustment; and finally, for fine adjustment, a resistance in the plate circuit of the electric oscillator was varied.

The reflection of waves at the input end occurs principally at the lower surface of the water column, that is, the upper surface of the bakelite cap, due to the large discontinuity in dielectric constants here. The waves are reflected at the other end by a solid brass plunger making spring contact at its lower face with the pipe and wire, and moved by a brass rod 0.6 cm in diameter firmly fixed to the plunger, and upon which are cut marks 50 cm apart. As the piston is moved the current in the plate circuit of the driving oscillator remains constant until the piston is in the neighborhood of a potential node, and then shows a marked change in value as the node is passed due to the reaction of the waves on the oscillator. These nodal positions can be determined with an accuracy of about 0.1 mm with water as dielectric.

STANDARD OF FREQUENCY

The length of a wave in vacuum was computed from the velocity of light and the frequency of the particular harmonic employed. The piezoelectric crystal used as a standard vibrates at a temperature of 25°C with a frequency $f_0 = 5.886 \times 10^6$ cycles per second. In Table I are given the periods and half

TABLE I. Periods and vacuum half wave-lengths for different harmonics of the crystal standard.

Þ	$T \times 10^8$	λ₀/2	Þ	T×10 ⁸	λ₀/2	Þ	$T \times 10^8$	λ₀/2
2 3 4 5	8.49 5.66 4.25 3.40	1273.5849.0636.8509.4	6 7 8 9	2.83 2.42 2.12 1.89	$\begin{array}{r} 424.5\\ 363.9\\ 318.4\\ 283.0\end{array}$	10 11 12 13	$1.70 \\ 1.54 \\ 1.41 \\ 1.31$	$254.7 \\ 231.5 \\ 212.3 \\ 195.9$

wave-lengths in vacuum corresponding to the employed harmonics of this crystal from the second to the thirteenth inclusive. Harmonic numbers are tabulated in the first column under p. The fundamental frequency is characterized by p=1. The periods (T) are in seconds, and the vacuum half wave-lengths $(\lambda_0/2)$ are in centimeters.

Theory

The velocity of propagation of electric waves along coaxial tubes in the ratio of the angular velocity of the exciting current to the retardation angle per unit length of the tubes. That is, if β is retardation angle per unit length of tube, $\omega/2\pi$ the frequency of electric oscillator and v the velocity of electric waves of frequency, $\omega/2\pi$, then

$$v = \omega / \beta. \tag{1}$$

The retardation angle β depends rather simply upon two coefficients of the line: one involving the series resistance and inductance per loop unit length

of the line, and the other involving the capacity and leakage conductance per loop unit.

Let r, l, c, g be respectively resistance, inductance, capacity, and leakage conductance per loop unit of length for the pipe and wire; μ , ϵ be respectively the permeability and dielectric constant of the medium between the pipe and the wire.

$$\eta = r/l\omega$$

$$s = g/c\omega$$

$$f(h) = +\left(\frac{(1+h^2)^{1/2}+1}{2}\right)^{1/2}$$

$$g(h) = +\left(\frac{(1+h^2)^{1/2}-1}{2}\right)^{1/2}.$$
 See Footnote 2.

It will be later shown that in these experiments $\eta S < 1$ so that, since $\mu = 1$, the retardation angle β is given by the leaky-line equation:

$$\beta = \frac{\omega}{c'} \epsilon^{1/2} (1 - \eta s)^{1/2} f(h) \tag{2}$$

where

$$h = \frac{\eta + s}{1 - \eta s}$$
c' = ratio of the units.

Since from Maxwell's theory the velocity of electromagnetic waves in vacuum is numerically equal to the ratio of the units (a fact that we have checked experimentally to better than one part in 3000), the index of refraction, corresponding to Eq. (2), is, in view of (1),

$$N = \epsilon^{1/2} (1 - \eta s)^{1/2} f(h).$$
(3)

The index N is directly measured in these experiments as the ratio of the wave-length is vacuum to the wave-length in the water.

Eq. (3) then gives a means of calculating the dielectric constant ϵ from values of N and the line coefficients η and s. It will be noted that s and h both involve ϵ through c, the capacity per loop unit of length.

With the object of still further simplifying (3) let us examine the magnitudes of η and s for the actual line. By substitution of the values of g and c in terms of the inner radius of the pipe and the outer radius of the wire it may be shown that

$$s = \frac{2\gamma T}{\epsilon}$$

² Cf. G. W. Pierce, "A Table and Method of Computation etc," Proc. Am. Acad. 57, No. 7 (1922), where these functions, which occur frequently in electromagnetic theory, have been computed and tabulated for values of h between 0 and 250.

where γ is the specific conductivity of the medium between pipe and wire in e.s.u. and T is the period in seconds corresponding to angular velocity ω . Since it is known before hand that ϵ is sensibly independent of frequency, s will be a maximum where the product $T\gamma$ is largest. This occurred in our experiments for waves of period 2×10^{-8} second and for a conductivity of 178×10^{7} e.s.u. Since ϵ is approximately 78.5 for water we find

 $s \leq 0.96$.

The exact value of η for a particular frequency cannot be calculated unless the value of the resistance per loop unit of pipe and wire is known. A value of η sufficiently near the actual value to discuss negligibilities in Eq. (3) may, however, be obtained by assuming that the resistance of the pipe is negligible in comparison with the resistance of the wire.

With this approximation it may be shown, by putting in numerical values, that for the conditions in the present investigation

 $\eta \leq 0.0035$

$$\eta s \leq 0.0034.$$

These results permit considerable simplification in Eq. (3). In the first place, it is evident from inspection of tabulated values of the function f(h) that for all values of h for which f(h) contributes to Eq. (3) a multiplier different from unity the expression for h may be reduced to

$$h = s = 2\gamma T/\epsilon$$

without affecting the accuracy by one part in a thousand. Finally, the maximum error which would be produced by neglecting ηs in comparison with unity under the radical of Eq. (3) will be approximately $\eta s/2$ or about one part in six hundred. But so large an error would occur only for the highest conductivities and lowest frequencies, for which, because of high damping, the accuracy of the experimental determinations is reduced to approximately one part in two hundred; so that the final accuracy of computed observations will not be appreciably affected if we write for all cases in these experiments,

where

$$N = \epsilon^{1/2} f(h)$$

(4)

$$h = 2\gamma T/\epsilon$$

Eq. (4) is the theoretical expression for the index of refraction of water and aqueous solutions for the particular frequencies, conductivities, and physical dimensions employed in the work herein described. γ and ϵ are respectively the conductivity in e.s.u. and dielectric constant in e.s.u. of the water or the solution, and T is the period of the electric waves.

Measurements of the Dielectric Constant of Distilled Water in the Range of Periods 1.31×10^{-8} to 8.49×10^{-8} Second

Table II gives a series of results obtained for distilled water at approximately 25°C. The first column contains the number of the harmonic of the

and

standard crystal oscillator with which the electric oscillator was held at zero beat-frequency. From Table I the corresponding values of the half vacuum wave-length $\lambda_0/2$ are taken and are tabulated in column II. Column III contains the temperature, column IV the measured value of half wave-length in the water at temperature *t*, conductivity γ ; column V the half wave-length reduced to 25°C by use of the coefficient obtained below; column VI the value of index of refraction N at 25°C. The next to the last column contains approximate values of $2\gamma T/\epsilon$, in which only a rough value of ϵ is needed. For h = 0.0212, in the top line of the table, the value of f(h) as defined above is 1.00005 and can be replaced by unity. For larger values of $p2\gamma T/\epsilon$ is still nearer unity; so throughout the table the correction for γ is negligible, making ϵ in the last column of this table the same as the square of the sixth column.

Þ	λ₀/2	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	$N(25, \gamma)$	$2\gamma T/\epsilon$	€ 25
2	1273.5	25.5	143.95	143.79	8.856	.0212	78.43
3	849.0	"	95.93	95.82	8.860	.0141	78.50
4	636.8	"	71.89	71.81	8.867	.0106	78.62
5	509.4	"	57.50	57.44	8.868	.0085	78.64
6	424.5	"	47.94	47.89	8.864		78.57
7	363.9	ű	41.08	41.03	8.868		78.64
8	318.4	25.4	35.96	35.92	8.864		78.57
9	283.0	ű	31.97	31.93	8.864		78.57
10	254.7	"	28.77	28.73	8.866		78.61
11	231.5	25.7	26.16	26.13	8.861		78.52
12	212.3	ű	23.97	23.95	8.862		78.54
13	195.9	u	22.11	22.09	8.870		78.68
					$Mean = 78.57$ $Mean departure = \pm 0.05$		

TABLE II. Distilled water, of conductivity $\gamma = 0.97 \times 10^7 \text{ e.s.u.}$

The mean value of ϵ at 25°C is

$\epsilon_{25} = 78.57 \pm 0.05$

for distilled water.

MEASUREMENTS OF THE TEMPERATURE COEFFICIENT OF THE DIELECTRIC CONSTANT OF DISTILLED WATER

Water temperatures from 3° to 60° C were obtained by filling the pipe with water just above the freezing point, allowing the pipe to warm slowly to room temperature, taking velocity measurements as different temperatures were reached. For higher temperatures heat was applied to the pipe by passing current through several coils of resistance wire wound around it, as shown in Fig. 1. The pipe was covered with asbestos packing to prevent rapid temperature changes. This precaution, in addition to the stirring produced by moving the plunger, insured a practically uniform temperature throughout the water in the pipe except near the ends, which regions could not be included in the temperature coefficient measurements. The temperature of the water before and after the wave-length measurement was read by a mercury thermometer provided with a cylinder for collecting water and holding it around the thermometer bulb as the thermometer was raised to read. This method allowed temperatures to be determined within about 0.2°C once the operator developed sufficient speed in pulling up the thermometer and taking readings.

The values obtained for ϵ_t were found to satisfy the empirical equation $\epsilon_t = 78.57[1-0.00461(t-25)+0.0000155(t-25)^2 \cdots]$

for temperatures between 10° and 60°C, as seen by reference to Fig. 2 where the curve is the curve of the equation and the points are observed values of ϵ_i . Three different vacuum wave-lengths λ_0 were employed, and the points for the three different values of λ_0 all fall near the curve in the specified range of temperatures 10° to 60°C.



Fig. 2. Locus of empirical equation for the dielectric constant of distilled water as a function of temperature. Observed values for three wave-lengths are included.

For temperatures between 5° and 10°C there is a significant departure from the curve of the equation and the longer wave-lengths seem to give values of ϵ_i departing farther from the curve. These anomalies appear at values of temperature for which the water has anomalous behavior as to density.

> Index of Refraction and Dielectric Constant of Tap Water and of Aqueous KCL Solutions

Tables III, IV, and V give measured values $\lambda/2(t, \gamma)$ of the half wavelength in tap water of conductivity $\gamma = 11.9 \times 10^7$ e.s.u., aqueous KCl-solu-

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tion of $\gamma = 47 \times 10^7$ e.s.u. and KCl-solution of $\gamma = 178 \times 10^7$ e.s.u., all measured for the various values of $\lambda_0/2$ indicated in the second column of each table. Using the temperature coefficient formula of the preceding section and ex-

Þ	λ₀/2	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	$N(25, \gamma)$	$2\gamma T/\epsilon$	€25	
2 3 4 5 6 7 8 9 10 11	1273.5 849.0 636.8 509.4 424.5 363.9 318.4 283.0 254.7 231.5 212.3	26.6 " " " " " " " " " " " " "	142.66 96.14 71.73 57.36 47.93 41.12 36.01 31.98 28.83 26.15 23.97	$\begin{array}{r} 142.16\\ 95.80\\ 71.48\\ 57.16\\ 47.76\\ 40.98\\ 35.88\\ 31.87\\ 28.73\\ 26.06\\ 73.89\end{array}$	8.958 8.862 8.909 8.912 8.899 8.878 8.874 8.881 8.881 8.885 8.885 8.885	$\begin{matrix} 0.257 \\ .171 \\ .129 \\ .103 \\ .086 \\ .074 \\ .064 \\ .057 \\ .051 \\ .047 \\ .043 \end{matrix}$	78.95 77.91 79.04 79.26 78.85 78.66 78.55 78.71 78.45 78.78 78.78 78.78	
13	195.9	u	22.15	22.08	8.873	.040	78.57	
					$Mean = 78.71$ Mean departure = \pm 0.23			

TABLE III. Tap water, of conductivity $\gamma = 11.9 \times 10^7 \text{ e.s.u.}$

Þ	$\lambda_0/2$	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	$N(25, \gamma)$	$2\gamma T/\epsilon$	€25
2 1 3 4 5 6 7 8 9 10 11 12 13	1273.5849.0636.8509.4424.5363.9318.4283.0254.7231.5212.3195.9	26.6 " " 26.8 26.7 26.9 27.1 27.3 27.4 27.3	90.63 68.77 55.82 47.16 40.69 35.79 31.86 28.80 26.15 23.96 22.18	$\begin{array}{r} &\\ & 90.31\\ & 68.53\\ & 55.62\\ & 46.97\\ & 40.53\\ & 35.66\\ & 31.73\\ & 28.67\\ & 26.02\\ & 23.83\\ & 22.07\end{array}$	9.401 9.292 9.159 9.038 8.977 8.928 8.919 8.884 8.898 8.898 8.906 8.877	$\begin{array}{c}$	79.92 81.21 80.62 79.44 78.84 78.45 78.45 78.45 78.45 78.45 78.45 78.5 78.68 78.32
					$Mean = 79.24$ $Mean departure = \pm 0.88$		

TABLE IV. KCl solution, about 1/270 normal, of conductivity $\gamma = 47 \times 10^7 \text{ e.s.u.}$

TABLE V. KCl solution, about 1/70 normal, of conductivity $\gamma = 178 \times 10^7 \text{ e.s.u.}$

Þ	λ₀/2	t	$\lambda/2(t, \gamma)$	$\lambda/2(25, \gamma)$	Ν(25, γ)	$2\gamma T/\epsilon$	€25	
8 9 10 11 12 13	318.4 283.0 254.7 231.5 212.3 195.9	25.6 " "	32.87 29.64 27.06 24.66 22.78	32.83 29.60 27.02 24.63 22.75 21.23	9.698 9.560 9.427 9.401 9.331 9.228	0.960 .856 .770 .697 .639 .593	78.73 78.94 78.57 79.56 79.56 78.70	
					Mean = 79.01 Mean departure = ± 0.33			

tracting the square root we have the approximate relation $\Delta\lambda/\lambda = -0.0023\Delta$ for change of wave-length with change of temperature, and have reduced the measured values of $\lambda/2$ to the values at 25°C recorded in the column marked

" $\lambda/2(25, \gamma)$." Dividing this into $\lambda_0/2$ we obtained $N(25, \gamma)$. Then employing the formula $N = \epsilon^{1/2}f(h)$, which has above been shown to be a correct approximation within the limits of period and conductivity here occurring, we have calculated the values of ϵ given in the last columns of the tables. In examining these results it should be borne in mind that large conductivities and long waves have a higher attenuation and introduce greater difficulties of measurement, which accounts for the fact that departures of readings from their average values are greater with the larger conductivities and with the longer vacuum wave-lengths. (In fact with the solution of Table V the two nodal points necessary for determining the $\lambda/2$ in the solution could not be obtained for $\lambda_0/2$ greater than 318.4 cm). Taking into account these larger sources of error we see that the addition of salts in sufficient quantity to increase the conductivity from 0.97×10^7 to 178×10^7 increases the index of refraction, in



Fig. 3. Theoretical variation of the index of refraction of tap water $(\gamma = 11.9 \times 10^7)$ and aqueous solutions of KCl $(\gamma = 47 \times 10^7 \text{ and } \gamma = 178 \times 10^7)$ with wave-length, assuming the true dielectric constant ϵ independent of the conductivity. Observed points are included.

a manner dependent on γ and λ_0 , but when the effects of conductivity are eliminated so as to give the true dielectric constant ϵ , the value obtained for ϵ differs from ϵ of distilled water by less than 1 percent. It is not yet known whether this small difference is due to errors introduced by the high attenuation at the higher conductivities; errors which do not arise when water or low-conductivity solutions are employed.

Fig. 3 exhibits graphically as a function of wave-length the values of the index of refraction N taken from the sixth column of Tables III, IV, and V. The smooth curves are the loci of Eq. (4) for the conductivities listed above the tables; and are plotted assuming that ϵ is independent of γ and of the same value as for distilled water. The fact that the observed values lie near these theoretical curves is evidence for the validity of the assumption that ϵ is sensibly independent of γ for the conductivities here employed.