The Elimination of Errors due to Electrode Polarization in Measurements of the Dielectric Constants of Electrolytes

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fluoride, 0.92A, obtained from its band spectroscopy.[9] Another way of making the comparison is to say that the distance (l) from the ion center to the potential minimum would be 0.22A (1.14−0.92) if the proton remains at the same equilibrium distance from the fluorine nucleus in the FHF⁻ ion as in HF. These various possibilities are summarized in Table I. It appears that these values check sufficiently well to warrant the belief that the doublet under consideration is due to the "tunnel effect." It is to be expected in FHF⁻ and a further calculation of the potential hill also favors this view. The height of the potential barrier can be obtained from

$$V_{x=0} = \tfrac{1}{2}(h\nu_0 q^2) = 38{,}750 \text{ cal./mole,}$$

with $\nu_0 = 3719.7$ cm⁻¹ and $q=2.7$. The zero-point energy is one-half the fundamental frequency ν_3 multiplied by Planck's constant and amounts to 5316 calories. The barrier has a value of 33,400 calories. This quantity can be compared with the potential hill formed when two Morse curves for HF are approached in such a

[9] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 488.

TABLE I.

		Distance	Remarks
a	$\frac{1}{2}$ (F–F)	1.13A	Crystal structure of KHF$_2$
b	H–F	1.15	$k=0.4$ megadyne/cm from 3719.7 cm⁻¹ and Badger's rule (Really $\frac{1}{2}$ (F–F) distance!)
c	$\frac{1}{2}$ (F–F)	1.14	Average: a and b
d	H–F	0.92	In HF monomer (band spectra)
e	l	0.22	c minus d
f	l	0.26	Tunnel effect
g	H–F	0.88	HF distance in FHF⁻; c minus f.

way as to make the F−F distance 2.25A (see Fig. 3). The height calculated is 38,065 calories/mole. For the Morse curve[10] the data on HF given by Herzberg[9] were used. The heat of dissociation of HF is 6.4 ev and $\omega_e = 4141.305$ cm⁻¹. The zero-point energy is calculated to be 5918 cal./mole. Hence the potential hill intervening is 32,150 calories/mole. This height is of the same order as the barrier in FHF⁻ as was to be expected. The problem of the FHF⁻ ion has been discussed by Pauling.[11]

[10] Reference 9, pp. 108–9.
[11] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, chapter 9.

The Elimination of Errors due to Electrode Polarization in Measurements of the Dielectric Constants of Electrolytes

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An investigation was made of the errors resulting from electrode polarization in measurements of the dielectric constants of solutions containing electrolytes. The applicability of two methods, one used by Fricke and Curtis and the other by Oncley, to eliminate these errors, was considered. There is introduced a modification of Oncley's method, which was found applicable at higher electrolyte concentrations than Oncley's method. The relative effectiveness of the modified method and that of Fricke and Curtis was tested by employing the two methods to correct experimental data obtained for aqueous solutions of glycine containing various amounts of electrolytes. The measurements were made at frequencies ranging from 10 to 5000 kc, and at conductivities ranging from 0.29×10⁻⁴ to 1.74×10⁻⁴ ohm⁻¹ cm⁻¹. The corrected values of the dielectric constant were compared with known values in the literature and found to be in good agreement. The limitations of the methods are considered and the usefulness of the methods in cases where the dielectric constant varies with frequency is discussed.

I. INTRODUCTION

THE polarization of dielectric constant cell electrodes is an important source of error in the determination of the dielectric properties of dilute electrolyte solutions. This phenomenon becomes increasingly important as the frequency is lowered and as the conductivity of the solution is raised. Where precise dielectric constant

determinations are desired steps must be taken either to reduce the magnitude of the polarization to the point where it may be neglected or appropriate correction measures must be employed. It is a common practice to reduce the amount of polarization by using platinized electrodes and for many purposes this procedure constitutes an acceptable solution to the difficulty.

For measurements on biological systems platinized electrodes have several disadvantages. They require frequent rechecking because of the instability of the platinization and they may effect, catalytically, a change in the system under investigation.[1] Furthermore, even though platinized electrodes are used, for precise measurements at low frequencies electrode polarization may still be significant. For these reasons the elimination of electrode polarization errors for bare platinum electrodes was investigated.

Aqueous solutions of glycine, containing known amounts of electrolytes, were studied. Two methods were employed to correct the experimental data for electrode polarization. As a test of the effectiveness of the polarization correction methods the dielectric constants calculated from the experimental measurements were compared with known values.

II. ELECTRODE POLARIZATION CORRECTION METHODS

The problem of correcting dielectric cell capacitance measurements for electrode polarization capacity is complicated by the fact that the frequency dependence of the polarization capacitance is not definitely known. Although it varies with the kind of electrodes and with the solution used, the polarization capacitance C_p, for limited ranges of frequency, can usually be expressed by an equation of the form

$$C_p = M\nu^{-m}, \qquad (1)$$

where ν is the frequency, and M and m are empirical constants.[2]

When the capacitance of a dielectric cell is measured it is usually represented electrically in terms of an equivalent parallel capacitance C. This capacitance is thus a measure of both the electrode polarization capacitance and the capacitance of the solution contained between the cell electrodes. In general the dielectric constant of the solution depends on the frequency of measurement,[3] and this of course causes a corresponding dependence of the capacitance of the solution contained between the cell electrodes. Since the polarization capacitance of the electrodes is also frequency dependent, as Eq. (1) indicates, the variation of the cell capacitance with changes in frequency may be exceedingly complex.

Two methods have been used to treat the problem of electrode polarization effects in the measurement of dielectric constants of solutions. The first method to be discussed was described by Fricke and Curtis,[4] and was used in a study of the dielectric properties of suspensions. In their work platinized electrodes were used but the method, in principle, is applicable to either bare or platinized electrodes. The second method was described by Oncley[5] and was used in studies of the dielectric properties of protein solutions using a cell with sandblasted platinum electrodes.

In the method described by Fricke and Curtis measurements of the capacitance of the dielectric cell are made for two different spacings of the cell electrodes. When this is done the dielectric constant of the solution can be obtained without knowing the absolute value of the polarization capacitance. The latter appears only as a parameter in the calculations, and is eliminated.

The dielectric constant ϵ of the solution is calculated from the measured capacitances C_1 and C_2, corresponding to the electrode spacings d_1 and d_2, by means of the equation[6]

$$\epsilon = [d_2{}^2(C_2 - C_0) - d_1{}^2(C_1 - C_0)]/[K(d_2 - d_1)]. \qquad (2)$$

Here C_0 and K are constants for the particular dielectric cell. Their significance and evaluation are discussed in Section III of this paper.

Oncley's method, referred to previously, makes use of an empirical equation to correct for electrode polarization. The dielectric constant is

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[1] J. W. Mehl and C. L. A. Schmidt, J. Gen. Physiol. **18**, 467 (1935).

[2] I. Wolfe, Phys. Rev. **27**, 755 (1926).

[3] P. Debye, *Polar Molecules* (Chemical Catalogue Company, New York, New York, 1929).

[4] H. Fricke and H. J. Curtis, J. Phys. Chem. **41**, 729 (1937).

[5] J. L. Oncley, J. Am. Chem. Soc. **60**, 1115 (1938).

[6] A derivation of this equation and a statement of the conditions under which it is valid are given in the Appendix to this paper.
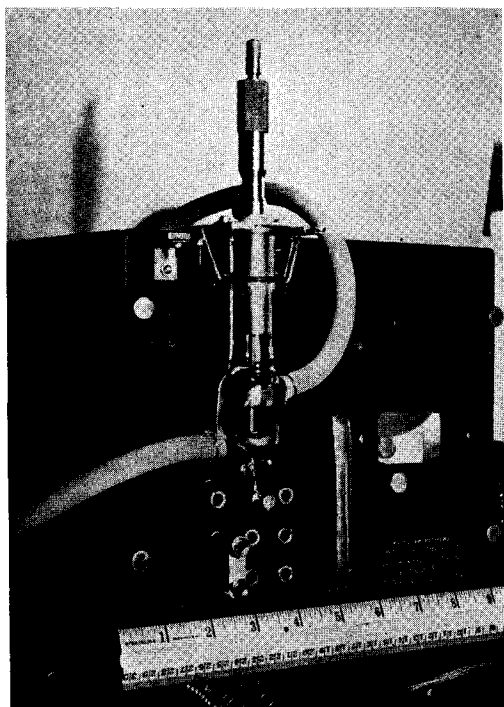
FIG. 1. Photograph of micrometer type cell showing lead and switching arrangement.

calculated by means of the equation,[6]

$$\epsilon = (C - C_0 - A G^2 \nu^{-\frac{3}{2}}) d/K, \qquad (3)$$

where C is the observed cell capacitance for an electrode spacing d, C_0 and K are constants of the cell, and $A G^2 \nu^{-\frac{3}{2}}$ is the correction term for polarization. In the correction term, G is the cell conductance, ν is the frequency, and A is a constant for the solution under consideration. The value of A is the slope of the straight line obtained when $(C - C_0)$ is plotted against $G^2 \nu^{-\frac{3}{2}}$ in a frequency region where the dielectric constant does not vary. When measurements are extended to a region where the dielectric constant varies with frequency, it is assumed that the same value of A still prevails.

Oncley found that the polarization term $A G^2 \nu^{-\frac{3}{2}}$ allowed accurate corrections for electrode polarization to be made only for frequencies greater than 25 kc. For lower frequencies it was found that the simple correction term $A G^2 \nu^{-\frac{3}{2}}$ was not valid and the curves were no longer linear.

In a recent paper Smiley and Smith[7] have reported a study of electrode polarization in the frequency range 1 to 30 kc. These authors conclude from their studies, as reported by Ferry and Oncley,[8] that at frequencies less than 25 kc the correction term $A G^2 \nu^{-\frac{3}{2}}$ is not applicable.

To meet this difficulty at low frequencies, Ferry and Oncley[8] assumed that the polarization correction could be considered as the sum of two terms: one, a function of the conductivity of the solution, and the other, a function of the nature of the solute. The difference in polarization of two solutions of equal conductivity was then found proportional to $\nu^{-\frac{3}{2}}$. Accordingly, then, polarization corrections could be made by comparing the unknown solution with a known salt solution of equal conductivity. With this method, Oncley and Ferry have made corrections for polarization in protein solutions with conductivities ranging up to 40×10^{-6} ohm^{-1} cm^{-1} at frequencies as low as 10 kc.

It will be shown later, in the present paper, that Oncley's original correction scheme can be retained and the use of a comparison solution avoided, even at frequencies as low as 10 kc and for conductivities of the order 200×10^{-6} ohm^{-1} cm^{-1}.

III. EXPERIMENTAL

Apparatus

The cell used in this investigation is shown in Fig. 1. This cell is of the micrometer type with two circular platinum sheet electrodes, one mounted on the spindle of a micrometer screw, and the other fixed. This type of cell is especially useful for making electrode polarization corrections according to Fricke's method. The electrode spacing may be varied from 0.05 to 10.0 mm with a precision of setting equal to ±0.002 mm. The temperature of the cell was controlled to within ±0.1°C by circulating mineral oil from a thermostat through the glass jacket enclosing the cell. The volume of solution ordinarily used is 2 ml.

By mounting the cell on the condenser used as a capacitance standard, as shown in Fig. 1, several advantages were derived. Short direct leads resulted in a low value of lead inductance, and a rigid and easily reproduced cell mounting resulted in constant lead capacitances.

[7] W. G. Smiley and A. K. Smith, J. Am. Chem. Soc. 64, 624 (1942).

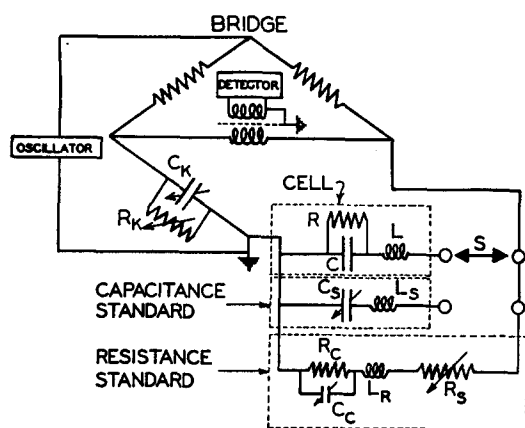[8] J. D. Ferry and J. L. Oncley, J. Am. Chem. Soc. 63, 272 (1941).

FIG. 2. Schematic diagram of bridge circuit arranged for substitution measurements. Components used in set-up are: *Bridge*, General Radio Type 516–CS1; *Oscillator*, General Radio Type 684A; *Detector*, Sargent Radio Model 11VA and Dumont Oscilloscope Type 168 equipped with General Radio Type 814 Amplifier and 8 Type 814P filters; *Capacitance Standard*, General Radio Precision Condenser, Type 722D; *Resistance Standard*, General Radio Decade Resistance Box equipped with inductance compensating network, R_C, C_C (see reference 8). *Cell*, see Fig. 1.

A bridge substitution method was used to determine the capacitance and the resistance of the cell. At each of the various frequencies employed, a precision variable condenser was substituted for the cell by means of the switch S, indicated in Fig. 2, which is a schematic diagram of the circuit used. After the substitution the bridge was rebalanced by adjustment of the precision condenser and an inductance-compensated resistance box.[9] The various items of equipment making up the circuit have been identified on the diagram. It should be noted that in the electrical set-up employed in this paper all lead inductances are measured from the terminals of the precision condenser. The latter may then be considered as the reference terminals of the system.

The use of a substitution method effectively eliminates from the measurements errors which arise from the bridge proper. The further errors which must be considered are those due to the inductances L, L_S, L_R, of the leads between the capacitance and resistance standards and the cell. These inductances affect both the cell resistance and capacitance obtained by the substitution method. In the work reported in this paper only the low frequency measurements

of resistance are used, for which lead inductance effects are negligible. The following discussion is therefore directed to the elimination of errors in the measured capacitances.

The effect of lead inductances on a capacitance determination may be represented by the equation

$$C_S = C + \Delta C_a + \Delta C_b + \Delta C_c + \Delta C_d + \Delta C_e, \quad (4)$$

where C_S is the capacitance setting of the precision condenser, C is the true terminal capacitance of the cell, and the delta terms are capacitance errors to be described below.

The series inductance L of the cell contributes capacitance errors, ΔC_a and ΔC_b. This inductance is in series with the unknown capacitance C of the cell and gives rise to the capacitance increment $\Delta C_a = [C - C/(1 - \omega^2 L C)]$ for a frequency $\nu = \omega/2\pi$. Further, since L is in series with the resistance R of the cell, it gives rise to a capacitance increment $\Delta C_b = (-L/R^2)$. The equations expressing the delta terms are valid when $R^2 \gg \omega^2 L$, which condition holds for the frequencies and resistance values involved here. A detailed treatment of lead errors is given by Davies.[10]

The inductance of the standard condenser L_S behaves in a manner similar to L. At high frequencies the capacitance of the standard condenser is increased by an amount $\Delta C_c = [C_S - C_S/(1 - \omega^2 L_S C_S)]$. Because the standard condenser has a high parallel resistance, the correction ΔC_d, due to the condenser resistance being in series with L_S, is very small and can be completely neglected in the work discussed here.

The inductance L_R of the standard resistor R_S gives rise to an effective capacitance $C_e = (-L_R/R_S^2)$. In making a substitution measurement of the cell capacitance, the initial bridge balance is obtained with the standard resistance set at its maximum value, equal to 260.2 ohms. After the cell is removed from the circuit and the standard condenser substituted for it, R_S is reduced from its maximum value to another value, which depends on the cell resistance. Hence the effective capacitance C_e of the standard resistor changes during a given cell capacitance measurement and may cause large

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[9] J. L. Oncley, J. Phys. Chem. **44**, 1103 (1940).

[10] R. M. Davies, Phil. Mag. **20**, 75 (1935).

errors if ignored. This effective capacitance *change* ΔC_e was reduced to less than ± 0.7 $\mu\mu$f for frequencies between 5000 and 10 kc by means of a modification of the inductance compensation scheme described by Oncley.[9] A description of the method used to evaluate the capacitance errors in the resistance standard is being prepared for publication.

For the cell shown in Fig. 1, L was found to be 0.11×10^{-6} henry. This value was calculated from measurements of the variation in effective capacitance of the cell at high frequencies. This value of L is sufficiently small that the capacitance ΔC_b may be neglected for all values of the cell resistance R used in the present measurements. For a minimum value of R equal to 450 ohms, the maximum value of ΔC_b is approximately 0.5 $\mu\mu$f. This value is slightly less than the maximum capacitance error of the standard resistor R_S, mentioned above, and it has therefore been neglected.

The capacitances ΔC_a and ΔC_c remain to be considered. These were caused to cancel each other effectively by adjusting L_s to equal L.[8]

Calibration of the Cell

Calibration measurements were made with water and dilute aqueous potassium chloride solutions as standards of known dielectric constant. A frequency of 1000 kc was used in order to avoid electrode polarization. Measurements were made of the parallel capacitance of the cell for a series of electrode spacings between 0.0200 and 0.6000 cm. The cell capacitance C is given by the equation[11]

$$C = C_0 + K\epsilon/d, \qquad (5)$$

where C_0 is the distributed capacitance, K is *approximately* equal to the electrode area divided by 4π, ϵ is the dielectric constant of the cell contents, and d is the electrode spacing. The constants C_0 and K were evaluated from straight line graphs of C plotted as function of $1/d$. The average values obtained were $C_0 = 3.5 \pm 0.5$ $\mu\mu$f and $K = 0.1700 \pm 0.0005$ $\mu\mu$f cm. They were used in reducing the capacitance measurements, for the glycine solutions, to dielectric constants as discussed subsequently.

[11] K. S. Cole and H. J. Curtis, Rev. Sci. Inst. **8**, 333 (1937).

Materials

Glycine was chosen for the dielectric constant measurements for two reasons. First, the dielectric constants of aqueous glycine solutions are known with considerable accuracy[12] for all obtainable concentrations of the material. They serve, therefore, as convenient standards to evaluate the adequacy of the methods for making polarization corrections. Second, glycine solutions were to be used as solvents in a study of the dielectric properties of lactoglobulin in this laboratory over the same frequency range employed in the present investigation and it was desirable, therefore, to know the behavior of the cell when filled with glycine solutions.

The glycine was obtained from the Eastman Kodak Company and was recrystallized once from 90 percent methanol. The solutions studied contained 0.5, 1.5, and 2.5 moles of glycine per liter. In order to vary the conductivity of the solutions, they were made up to contain from 0.0001 to 0.0015 mole per liter of potassium chloride. In this way the conductivity of the solutions was caused to vary from 29×10^{-6} to 174×10^{-6} ohm^{-1} cm^{-1}.

IV. RESULTS

Tables I, II, and III summarize the results for nine solutions of glycine. For the sake of

TABLE I. Summary of cell capacitances and dielectric constants for glycine solutions. Electrode polarization corrections made by the Fricke and Curtis method.

1	2	3	4	5	6	7	8	9	10
	Observed capacitance, $\mu\mu$f						Dielectric constant ϵ		
	$(C - C_0)$			$(C - C_0)$					
	Electrode spacing, d								
	$d = 0.123$ cm		$d = 0.173$ cm	$d = 0.273$ cm			[Eq. (2)]		
Frequency in kc				Solution[a]					
	D	E	F	D	E	F	D	E	F
5000	158.4	158.5	112.6	71.4	71.7	71.8	114.7	115.5	116.8
1000	158.2	159.0	113.5	71.1	71.5	71.3	113.9	114.6	113.0
500	158.8	158.3	113.6	71.1	71.5	71.9	113.6	115.0	115.5
100	159.5	160.7	115.9	71.2	72.0	72.7	113.5	115.1	114.9
50	160.6	166.9	121.3	71.5	73.2	74.6	113.6	114.9	113.8
40	161.5	171.2	124.8	71.7	74.1	75.9	113.7	115.0	113.3
30	163.2	179.6	131.4	72.0	75.7	78.6	113.6	114.7	113.5
20	166.8	201.7	149.0	72.9	80.4	85.9	114.1	115.3	114.5
10	185.7	306.3	232.0	76.7	102.3	120.2	114.0	117.2	118.8

[a] Solutions *D*, *E*, *F* contain 1.5 *M* glycine and have conductivities of 55.7, 139, and 174×10^{-6} ohm^{-1} cm^{-1}, respectively. Conductivities were brought to these values by the addition of KCl.

[12] J. Wyman, Jr. and T. L. McMeekin, J. Am. Chem. Soc. **55**, 915 (1933).

TABLE II. Summary of corrected capacitances and dielectric constants for glycine solutions. Polarization corrections according to modification of the Oncley method.

1	2	3	4	5	6	7	8	9	10	11	12	13
	Corrected capacitance, C' $\mu\mu f$ [Eq. (6)]						Dielectric constant, ϵ					
	Electrode spacing, d						Electrode spacing, d					
	$d = 0.123$ cm			$d = 0.173$ cm			$d = 0.123$ cm			$d = 0.173$ cm		
	Solution[a]											
Frequency in kc	D	E	F	D	E	F	D	E	F	D	E	F
5000	158.4	158.5	[b]	112.8	113.3	112.6	114.6	114.7	[b]	114.8	115.3	114.6
1000	158.1	159.0		113.1	113.8	113.4	114.4	115.0		115.1	115.8	115.4
500	158.7	158.3		113.0	113.8	113.4	114.8	114.5		115.0	115.8	115.4
100	159.0	157.8		113.2	113.7	113.5	115.0	114.2		115.2	115.7	115.5
50	158.8	157.6		113.3	113.4	113.6	114.9	114.0		115.3	115.4	115.6
40	158.9	157.7		113.3	113.4	113.6	115.0	114.1		115.3	115.4	115.6
30	159.0	157.5		113.3	113.2	113.1	115.0	114.0		115.3	115.2	115.1
20	159.0	157.8		113.5	112.7	113.6	115.0	114.2		115.5	114.7	115.6
10	158.7	163.3[c]		113.5	113.9	113.5	114.8	118.1[c]		115.5	116.0	115.5

[a] Solutions D, E, F contain 1.5 M glycine and have conductivities of 55.7, 139, and 174×10⁻⁶ ohm⁻¹ cm⁻¹, respectively. Conductivities were brought to these values by the addition of KCl.
[b] Measurements not made for solution F at this electrode spacing.
[c] This value is probably in error; not included in averages in Table III.

brevity, detailed data are presented only for the solutions of the 1.5 M glycine.

In Table I, columns 2–7, are shown observed capacitances for three solutions of 1.5 M glycine of different conductivities and for two values of electrode spacing. In columns 8–10 appear the dielectric constants of the solutions calculated from the values of C by means of Eq. (2) according to the method of Fricke and Curtis. The capacitance values in columns 2–7 show clearly the regular increase due to electrode polarization that occurs with decreasing frequency and increasing conductivity. For the solutions of highest conductivity the polarization becomes so large that at low frequencies the observed capacitances are approximately twice the high frequency values. At the three highest frequencies no polarization effects are apparent. The capacitance variations that occur at these frequencies are within the limits of experimental error.

The dielectric constants shown in columns 8–10 should be free from electrode polarization effects if the Fricke and Curtis method is valid. The agreement manifest between the values of ϵ for solutions of different conductivity at high and low frequencies shows this to be the case. No significant trends with frequency or conductivity are apparent, the values of ϵ for the lower frequencies and higher conductivities being in good agreement with the values for the higher

TABLE III. Comparison of dielectric constants of glycine solutions showing effectiveness of methods used to correct for electrode polarization.

1		2	3	4	5	6	7
Solution				Dielectric constant, ϵ			
					Results of present work		
		Conductivity at 10 kc ohm⁻¹ cm⁻¹ ×10⁶	Accepted value[d]	Fricke and Curtis method		Modified Oncley method	
Glycine moles/liter				Mean[a]	Average deviation	Mean[a]	Average deviation
(A)	0.5	29.0		90.9	±0.11	92.2[b] 91.4	±0.06 ±0.07
(B)	0.5	75.4	91.74	91.5	±0.27	91.7 92.1	±0.16 ±0.14
(C)	0.5	135		91.9	±0.19	91.6 91.8	±0.43 ±0.30
(D)	1.5	55.7		113.8	±0.28	114.8 115.2	±0.17 ±0.18
(E)	1.5	139	114.52	115.2	±0.48	114.3 115.5	±0.26 ±0.31
(F)	1.5	174		114.9	±1.42	— [c] 115.3	— ±0.27
(G)	2.5	60.4		139.3	±0.61	136.7 137.4	±0.08 ±0.11
(H)	2.5	99.7	137.30	138.2	±0.24	138.1 138.3	±0.06 ±0.24
(I)	2.5	140		138.1	±1.07	137.2 138.5	±0.44 ±0.22

[a] Mean of 9 values over frequency range 10 to 5000 kc.
[b] In this column the upper figure is for $d = 0.123$ cm; lower figure is for $d = 0.173$ cm.
[c] No measurements were made for $d = 0.123$ cm.
[d] Values for dielectric constant from J. Wyman, Jr., Phys. Rev. 35, 623 (1930) (water); J. Wyman, Jr., and T. L. McMeekin, J. Am. Chem. Soc. 55, 913 (1933) (glycine).

frequencies and lower conductivities, where electrode polarization is negligible. Average values from columns 8–10 of Table I are summarized in Table III, together with similar data for 0.5 and 2.5 M glycine, for comparison with the results obtained by an application of a

modification of Oncley's method to the same experimental data.

In Table II are presented the results obtained when a modification of Oncley's method is used to correct the experimental data for electrode polarization. Oncley's method was modified in order to be able to make corrections at low frequencies without introducing the additional complication of the comparison method that Ferry and Oncley[8] found necessary. When values of the observed capacitance C are plotted as a function of $G^2 \nu^{-1.5}$ or simply $\nu^{-1.5}$, because G^2 changes very little in the frequency region concerned,[13] curves of the type shown in Fig. 3 are obtained. These curves are linear at all except the highest conductivities for frequencies down to about 25 kc. Below this frequency the curves are no longer linear. This behavior was noted by Ferry and Oncley and resulted in their adoption of a comparison method, mentioned previously.

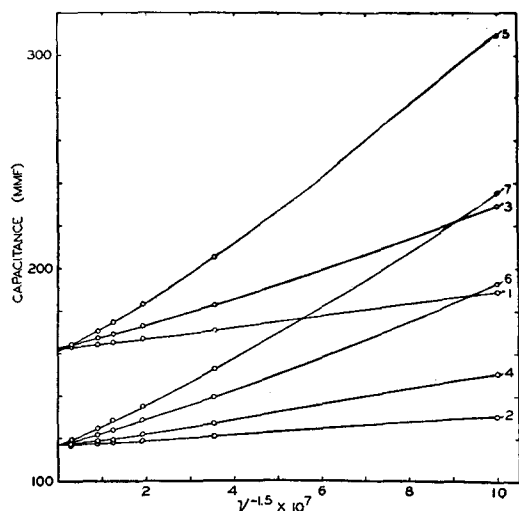In an effort to avoid the additional complication introduced by the comparison method, tests

FIG. 4. Curves showing relation between dielectric cell capacitance C and frequency ν to -1.7 power for 1.5 molar glycine solutions of varying conductivity σ and for different dielectric cell electrode spacings d.

Curve 1, $\sigma = 55.7 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.123$ cm.
Curve 2, $\sigma = 55.7 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.
Curve 3, $\sigma = 91.4 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.123$ cm.
Curve 4, $\sigma = 91.4 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.
Curve 5, $\sigma = 139 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.123$ cm.
Curve 6, $\sigma = 139 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.
Curve 7, $\sigma = 174 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.

were made in the present work to see if the adoption of a different frequency dependence would yield straight lines. By successive trials it was found that when values of C were plotted as a function of $\nu^{-1.7}$, straight lines resulted. This behavior was found not only for the glycine solutions, for which data are reported here, but in addition for aqueous solutions of potassium chloride with concentrations ranging from zero to 0.002 N. Typical curves of C versus $\nu^{-1.7}$ are shown in Fig. 4.

The fact that graphs of C versus $\nu^{-1.7}$ are linear would appear to indicate that the constant m in Eq. (1) is equal to 0.3[14] for the lower frequencies, at least, rather than 0.5 as was assumed by Oncley.[5] That m varies with the frequency is well known. For example, Wolfe[2] reported m to be approximately 0.5 in the upper portion and approximately 0.3 in the lower portion of a frequency range of 0.2 kc to 200 kc. The present results, however, seem to indicate that m is not critical for high frequencies and for low conductivities, and that $m =$ either 0.5 or 0.3 represents the data adequately. At the very low frequencies,

FIG. 3. Curves showing relation between cell capacitance C and frequency ν to -1.5 power for 1.5 molar glycine solutions of varying conductivity σ and for different dielectric cell electrode spacings d.

Curve 1, $\sigma = 55.7 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.123$ cm.
Curve 2, $\sigma = 55.7 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.
Curve 3, $\sigma = 91.4 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.123$ cm.
Curve 4, $\sigma = 91.4 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.
Curve 5, $\sigma = 139 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.123$ cm.
Curve 6, $\sigma = 139 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.
Curve 7, $\sigma = 174 \times 10^{-6}$ ohm^{-1} cm^{-1}, $d = 0.173$ cm.

[13] In all the experiments here reported the total change in conductance amounts to a decrease of 1 percent or less for the frequency range 10 kc to 500 kc.
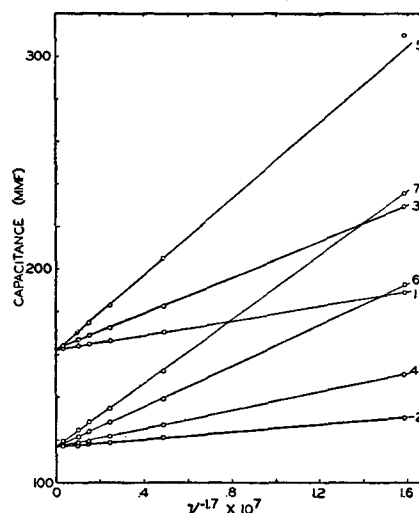
[14] See Appendix 2.

however, as a comparison of Figs. 3 and 4 shows, the smaller value of m is essential.

The values of C', the corrected capacitance of the cell, which appear in columns 2–7 of Table II, were therefore obtained according to the equation

$$C' = (C - C_0 - S\nu^{-1.7}). \tag{6}$$

The constant S was obtained from the straight lines resulting when C was plotted against $\nu^{-1.7}$. The values of C' are seen to be independent of frequency and conductivity. The excellent agreement between high and low frequency values confirms the use of Eq. (6) for the elimination of the polarization effects which occur at the lower frequencies.

The dielectric constants which appear in columns 8–13 of Table II were calculated according to the relation $\epsilon = C'd/K$.

Averages of the values in columns 8–13 have been assembled in Table III for comparison with the results obtained by the method of Fricke and Curtis.

An inspection of Table III reveals that the Fricke and Curtis method and the modified Oncley method are equally adequate to eliminate polarization effects. The dielectric constants obtained by an application of these methods to the experimental data are seen to agree well with the values of Wyman and McMeekin.[12] This is true for solutions with conductivities ranging from 0.29 to 1.74×10^{-4} ohm^{-1} cm^{-1}. No dependence of the dielectric constant on the conductivity of the solution is apparent. The differences between the "mean" and "accepted" values is about the same for the two methods. With one exception these differences are of an order of magnitude consistent with the uncertainty in the cell constants.

The quantities listed as "average deviations" in columns 5 and 7 represent deviations among the values for different frequencies. In most instances these deviations are much less for the modified Oncley method than for the method of Fricke and Curtis. They probably reflect errors arising from incomplete compensation of the lead inductance in the standard resistor, as mentioned earlier. The greater deviation in the case of the results with the Fricke and Curtis method is to be expected since twice as many observations, each subject to the same uncer-

tainty, enter into the calculations, as a comparison of Eqs. (2) and (6) shows.

V. CONCLUSIONS

The data presented demonstrate that errors due to electrode polarization in dielectric constant measurements may be eliminated equally well by the application of the Fricke and Curtis method or the modification of Oncley's method, described in the present paper. This conclusion applies, of course, only for the frequency range and conductivity range investigated. There appears to be no reason why the Fricke and Curtis method cannot be extended to much lower frequencies and to higher conductivities. On the other hand the extension of the modified Oncley method is questionable. Since the frequency dependence of the polarization is known to vary with the frequency, it is quite likely that for a precise correction of the polarization at lower frequencies it would be necessary to take this fact into account.

Of the two methods for eliminating polarization errors, there is no doubt of the more general utility of the Fricke and Curtis method. This is true despite the fact that the dielectric constants obtained with their method are less precise than the values obtained with the modification of Oncley's method. The greater utility arises from the fact that the Fricke and Curtis method can be used to eliminate polarization effects in measurements made at a single frequency only. Oncley's method or the present modification of it, on the other hand, requires measurements for at least two frequencies; moreover, these must lie outside of the dispersion region of the material under investigation. This latter limitation is particularly important in studies of proteins or other high molecular weight compounds where the dielectric constant may show dispersion over an extremely wide range of frequencies. In those instances where this limitation does not apply, Oncley's method would appear preferable on the basis of increased precision and because it may be used for measurements made with a simple cell having fixed electrodes.

APPENDIX 1
Derivation of Eq. (2)

It is desired to find an equation expressing the dielectric constant of a solution in a dielectric constant cell with

MEASURED CAPACITANCES AND RESISTANCES / EQUIVALENT IMPEDANCES

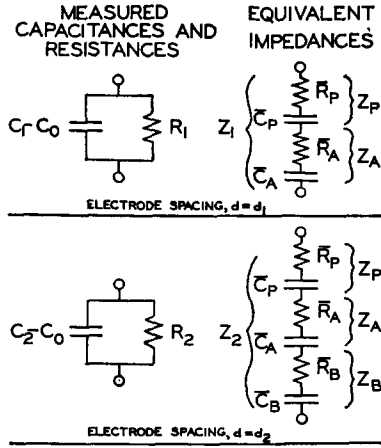ELECTRODE SPACING, $d=d_1$

ELECTRODE SPACING, $d=d_2$

FIG. 5. Schematic diagram showing relation between measured capacitances and resistances and equivalent impedances. C_1, R_1, measured parallel capacitance and resistance of cell for electrode spacing d_1; C_2, R_2, measured parallel capacitance and resistance of cell for electrode spacing d_2; and C_0, distributed capacitance of cell.

Z_p = impedance of electrodes;
Z_A = impedance of solution defined by electrode spacing d_1;
Z_B = increase in impedance of solution due to change in electrode spacing from d_1 to d_2;
Z_1 = total impedance of cell for electrode spacing d_1;
Z_2 = total impedance of cell for electrode spacing d_2.

Dashed quantities are equivalent series capacitance and resistance components of corresponding impedances.

polarized electrodes in terms of the measured resistance and capacitance of the cell. Referring to Fig. 5, where the symbols are defined, it can be seen that the impedance of the element of solution, Z_B, of length (d_2-d_1) is given by,

$$Z_B = Z_2 - Z_1. \tag{7}$$

Making use of the well-known relations between the capacitance and resistance of series and parallel equivalent circuits, substitution for the impedances in Eq. (7) yields,

$$\omega^2 C_B R_B^2/(1+\omega^2 C_B^2 R_B^2)$$
$$= [\omega^2(C_2-C_0)R_2^2]/[1+\omega^2(C_2-C_0)^2 R_2^2]$$
$$- [\omega^2(C_1-C_0)R_1^2]/[1+\omega^2(C_1-C_0)^2 R_1^2] \tag{8}$$

and

$$R_B/(1+\omega^2 C_B^2 R_B^2) = R_2/[1+\omega^2(C_2-C_0)^2 R_2^2])$$
$$- R_1/[1+\omega^2(C_1-C_0)^2 R_1^2]. \tag{9}$$

Now for the conditions, which hold for all measurements reported in this paper where the polarization is significant,

$$\omega^2(C_1-C_0)^2 R_1^2 \ll 1, \quad \omega^2(C_2-C_0)^2 R_2^2 \ll 1,$$

and

$$\omega^2 C_B^2 R_B^2 \ll 1, \tag{10}$$

it follows that,

$$C_B = [(C_2-C_0)R_2^2 - (C_1-C_0)R_1^2]/(R_2-R_1)^2 \tag{11}$$

and

$$R_B = (R_2-R_1). \tag{12}$$

Equation (11) may be simplified further. Jones and

Christian[15] have shown that the equivalent series resistances of a cell of the type used here may be expressed,

$$\bar{R}_1 = (d_1/A\sigma) + \bar{R}_P \tag{13}$$

and

$$\bar{R}_2 = (d_2/A\sigma) + \bar{R}_P, \tag{14}$$

where A is the area of the cell electrodes and σ is the specific conductivity of the solution. For the conditions (10), $\bar{R}_1 = R_1$ and $\bar{R}_2 = R_2$. Thus Eqs. (13) and (14) may be substituted in Eq. (11) with the result,

$$C_B = [d_2^2(C_2-C_0) - d_1^2(C_1-C_0)]/(d_2-d_1)^2. \tag{15}$$

Now it follows from the theory for a parallel plate condenser that

$$C_B = \epsilon K/(d_2-d_1), \tag{16}$$

where K is a constant. The elimination of C_B from Eqs. (15) and (16) yields finally,

$$\epsilon = [d_2^2(C_2-C_0) - d_1^2(C_1-C_0)]/K(d_2-d_1). \tag{2}$$

This equation also holds for frequencies where electrode polarization is negligible but for which the condition expressed in (10) is not satisfied. When the electrode polarization is negligible, $(C_1-C_0) = K'/d_1$, $(C_2-C_0) = K'/d_2$, $C_B = K'/(d_2-d_1)$, $R_1 = K''d_1$, $R_2 = K''d_2$, and $R_B = K''(d_2-d_1)$, where for a given cell and solution K' and K'' are constants. If these values are substituted in Eqs. (8) and (9), then

$$C_B = C_1 \cdot C_2/(C_1-C_2). \tag{17}$$

This equation may be used interchangeably with Eq. (2) when electrode polarization effects are absent.

APPENDIX 2

Derivation of Eq. (3)

The cell is assumed to be represented by a measured parallel capacitance $(C-C_0)$ and measured parallel conductance $G=(1/R)$, as Fig. 5 indicates. These quantities are related to the series polarization capacitance $\bar{C}_p$ of the electrodes, and the series capacitance $\bar{C}$ of the solution in the cell by the following equation,

$$(C-C_0) = \{G^2/\omega^2[\bar{C} \cdot \bar{C}_p/(\bar{C}+\bar{C}_p)]\}, \tag{18}$$

which can be obtained by a process similar to that used in Appendix 1, for the condition, $R^2(C-C_0)^2\omega^2 \ll 1$. Assuming that the polarization capacitance may be represented by $\bar{C}_p = M\nu^{-m}$ [Eq. 1] by substitution is obtained,

$$(C-C_0) = (G^2\nu^{-(2-m)}/4\pi^2 M) + (G^2/4\pi^2\nu^2\bar{C}). \tag{19}$$

When $R^2 C^2 \omega^2 \ll 1$ then $\bar{C} = G^2/4\pi^2\nu^2 C$, which when substituted in Eq. (19) yields

$$C' = C - C_0 - A G^2\nu^{-(2-m)}, \tag{20}$$

where C' is the cell capacitance corrected for electrode polarization. Now, making use of the equation for a parallel plate condenser, $\epsilon = C'd/K$, Eq. (20) becomes

$$\epsilon = [C-C_0-AG^2\nu^{-(2-m)}]d/K, \tag{3}$$

which, for $m=0.5$, is the desired equation.

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[15] G. Jones and S. M. Christian, J. Am. Chem. Soc. **57**, 272 (1935).