Electrode Polarization in Dielectric Constant Measurements

BY WILLIAM G. SMILEY AND ALLAN K. SMITH

Introduction

In studying the dielectric dispersion of protein solutions, it is necessary to measure dielectric constants over a range from audio to high radio frequencies. The experimental difficulties inherent in this wide frequency range are greatly increased by the fact that most protein solutions have considerable conductivity. For this reason complete dispersion curves have been obtained chiefly on alcohol-soluble[2] and water-soluble[3,4] proteins, although Oncley and his associates[5] have studied some globulins in glycine solutions.

The most persistent difficulty in dielectric constant measurements on conducting solutions at low frequencies is the so-called electrode polarization. The importance of this effect in conductivity work has long been recognized, and it has been extensively studied.[6] In dielectric constant measurements, however, errors from this source are far larger, since the reactance due to the dielectric constant is itself only a very small fraction of the impedance of the cell, at low frequencies. Any additional reactance at the electrodes, therefore, even though it may be quite negligible compared to the resistance of the cell, will still have a large effect on the apparent capacitance. This is the case, in fact, with solutions of low enough conductivity to make dielectric constant measurements possible. The conductance of the cell remains substantially constant throughout the low frequency range, while the capacitance rises rapidly with decreasing frequency.

Oncley[4a] seems to have been the first to take this phenomenon into account in dielectric constant measurements on proteins. Probably most other workers have not used low enough frequencies or high enough conductivities to encounter large polarization effects. Oncley has attempted to eliminate the effect in two ways, by designing the cell to minimize it, and by using an empirical correction which will be discussed later in this paper. At best, however, the effect still prevented accurate results below 10 kc.

It is planned in this Laboratory to make measurements on protein solutions having higher conductivity than those used by Oncley, so that polarization effects will be still more troublesome. Because practically no data have been published on the polarization effect in very dilute solutions or at other than low audio frequencies, a study of this subject was undertaken with the object of finding what relationships exist between polarization capacitance, frequency, and solution composition. Capacitance measurements have been made on a cell with platinum electrodes using very dilute solutions of electrolytes both alone and with some organic substances. This paper presents the results of these measurements and discusses their significance.

Experimental

Bridge Circuit.—The bridge circuit used was essentially the same as Oncley's.[4a] A General Radio[7] Type 516-C r. f. bridge was used with its variable resistor and condenser in parallel. In the adjoining arm of the bridge the cell could be placed in parallel with the resistance and capacitance standards—General Radio Type 670-F compensated decade resistor and Type 722-D precision condenser. A substitution method was used, the cell being switched in and out of the circuit as described later. In series with the decade resistor were a 100-ohm fixed resistor and a 0.1-ohm slide wire for fine adjustment, making the available range 100.0 to 211.1 ohms, which permits the measurement by difference of conductances up to 5260 μmho. A calibrated mica plug-in condenser was used to extend the capacitance range to 1600 μμf.

Power Supply.—At radio frequencies, a Clough–Brengle Model OCX signal generator[8] was used. For the lower frequencies, a General Radio Type 377 oscillator[9] was coupled to the bridge through a 12-volt doorbell transformer which served to match the output impedance of the amplifier contained in the Type 377 with the much lower impedance of the bridge. The oscillator was calibrated

(1) A coöperative organization participated in by the Bureaus of Agricultural Chemistry and Engineering and Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

(2) Arrhenius, *J. Chem. Phys.*, **5**, 63 (1937); Elliott and Williams, THIS JOURNAL, **61**, 718 (1939).

(3) Errera, *J. chim. phys.*, **29**, 577 (1932); Arrhenius, *Physik. Z.*, **39**, 559 (1938); Fricke and Jacobson, *J. Phys. Chem.*, **43**, 781 (1939).

(4) (a) Oncley, THIS JOURNAL, **60**, 1115 (1938); (b) Ferry and Oncley, *ibid.*, **60**, 1123 (1938).

(5) Oncley, *J. Phys. Chem.*, **44**, 1103 (1940); Ferry and Oncley, THIS JOURNAL, **63**, 272 (1941).

(6) For a discussion of the history of this subject see Jones and Christian, ref. 20.

(7) General Radio Company, Cambridge, Massachusetts.

(8) Clough–Brengle Company, Chicago, Illinois.

(9) This oscillator, which is no longer manufactured, was loaned by the Electrical Engineering Department of the University of Illinois for this research.

at points from 1 kc. to 70 kc. against a 1000-cycle fork (General Radio Type 813) by obtaining stationary Lissajous figures on an oscilloscope.

Null Detector.—A Sargent Model 11-UA receiver[10] was used at all frequencies down to 20 kc. At lower frequencies a Supreme Model 546 oscilloscope[11] was used in conjunction with a B299 audio amplifier.[12] To the vertical amplifier of the oscilloscope the amplified output of the bridge was applied, while the bridge input voltage was fed to the horizontal amplifier. The resulting elliptical pattern became a horizontal straight line at the balance point. At the lower frequencies it was necessary to use a regenerative tuned stage in the amplifier to reduce the higher harmonics, which were greatly exaggerated by the variation of cell capacitance with frequency, the bridge being unbalanced for the higher harmonics when balanced for the fundamental. The tuned circuit, placed between the second and third stages of the amplifier, consisted of the primary winding of a Thordarson Type T-75R47 power transformer[13] in parallel with a General Radio Type 219-M decade condenser. Regeneration was obtained by coupling the high-voltage secondary winding of the transformer to the output of the third stage through a 250$\mu\mu$f. variable condenser. Sufficient selectivity was thus available to permit sharp balance, although in the least favorable cases enough second harmonic was still present to give a "figure 8" instead of a straight line at the balance point. Another important advantage of this circuit is that by proper adjustment of capacitance and regeneration the phase shift can be made such that resistive and capacitive balance are independent. A change in resistance tilts the ellipse while a change in capacitance changes its eccentricity. Thus at 1 kc. the capacitance could be balanced to $\pm 1\ \mu\mu$f. in spite of the fact that thermal fluctuations in cell resistance and changes in contact resistance caused larger unbalances.

Cell.—A Washburn conductivity cell was used. Its smooth platinum disk electrodes were 2 cm. in diameter and less than 1 mm. apart, making the capacitance, when the cell was filled with water at 25°, 424 $\mu\mu$f. It was mounted in a small oil-bath the temperature of which was regulated at 25 $\pm$ 0.05°. Into one of the mercury-filled side arms dipped a link of copper wire the other end of which was immersed in a similar tube of mercury connected to the standard condenser. By raising and lowering the link the cell was inserted in and removed from the circuit. This system reduced the shunt capacitance to about 2 $\mu\mu$f.

Accuracy.—The reproducibility of capacitance values was about $\pm 1\ \mu\mu$f. The conductivity was subject to drift, apparently partly thermal and partly due to diffusion, the maximum change during a single experiment being about 0.3%. The apparent conductivity at radio frequencies was high, no doubt because of dielectric loss and skin effect in the decade resistor.

The largest error with this circuit is caused by the variation in inductance of the compensated decade resistor with different settings. In these measurements this error

was minimized by using the same setting for the balance with the cell out at each frequency. Because the difference in capacitance between different frequencies was the important quantity in this study, the effect of inductance at this setting canceled out. The error in the capacitance difference was probably not more than 2 $\mu\mu$f.

Materials.—All solutions were made up with distilled water of conductivity about 3 × 10^{-6} ohm^{-1} cm.$^{-1}$. Sulfuric acid and sodium chloride solutions were made by diluting standard solutions. Carbonic acid solutions were made by passing tank carbon dioxide into water and diluting. No attempt was made to control the concentration of the acid solutions accurately, the observed conductivity being taken as the best measure of concentration. Glycine was twice recrystallized, decomposed at 232–235° (uncor.), and showed a molar dielectric increment[14] of 22.9.

Calculations.—Measurements were made on each solution at 500 kc. and at a number of lower frequencies down to the point at which the cell capacitance became larger than 1600 $\mu\mu$f., or to 1 kc. if possible. Since preliminary measurements had shown that the capacitance was the same at 500 kc. and at 1000 kc., the value at 500 kc., C_{500}, was taken as the true capacitance in the absence of polarization effects. If the capacitance at a lower frequency, ν, was C, the *series electrode capacitance* C_E was calculated as

$$C_E = G^2/4\pi^2\ \nu^2(C - C_{500}) \qquad (1)$$

where G is the conductance of the cell. This equation is an approximation, valid when the polarization reactance is small compared to that of the dielectric. It is accurate within the experimental error for the experiments reported here.

The electrode polarization *resistance* is not considered here because it is unnecessary to assume such a resistance to account for the observed data. This arises from the relatively high resistance of the dielectric and is not inconsistent with the fact that, in more concentrated solutions, polarization resistance and reactance have been found[6] to be of the same order of magnitude.

Corrections were made for shunt capacitance and the inductance of the resistor, but since the correction in these experiments was practically the same at all frequencies, it could be omitted without error in C_E.

Results

It was found that when the electrode capacitance C_E was plotted against log ν, in some cases a straight line was obtained, while in others the graph was straight at low frequencies, but curved downward at higher frequencies. Figure 1 shows

(10) E. M. Sargent Company, Oakland, California.
(11) Supreme Instruments Corporation, Greenwood, Mississippi.
(12) Audio Development Company, Minneapolis, Minnesota.
(13) Thordarson Electric Manufacturing Company, Chicago, Illinois.
(14) Wyman, *Chem. Rev.*, **19**, 218 (1936).

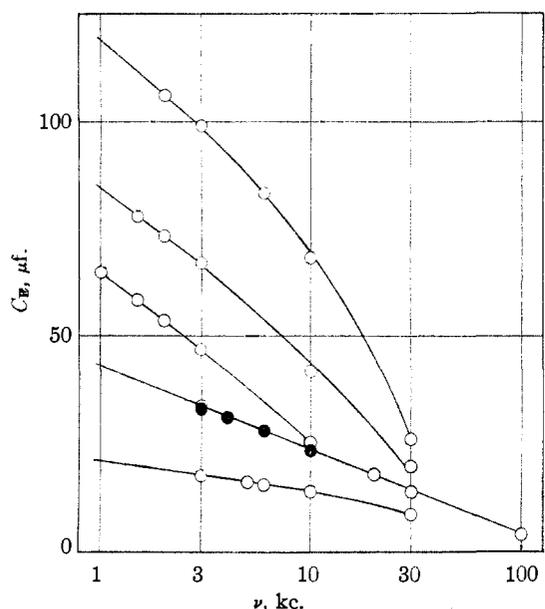some examples, including both the straightest and most curved.

Fig. 1.—Polarization capacitance against log ν: open circles, top to bottom, Experiments 84, 73, 81, 71, 86; filled circles, Experiment 72.

The results of all the measurements are presented in Table I. The first three columns give experiment numbers for identification, the composition of the solution, and the conductance G (the average of the values at the three lowest frequencies at which measurements were made). In the next four columns are given the values of C_E at 1, 3, 10, and 30 kc. The values in parentheses are extrapolated or interpolated from the graph against log ν; the others are as observed. A blank indicates that no measurement was made or that $(C - C_{500})$ was too small to give accurate results. The last column gives the limiting slope at low frequencies, C_N, of the C_E vs. log ν curve (in μfd. per tenfold frequency change).

Further inspection of the curves shows that the deviation from the straight line is approximately proportional to the frequency, so that the data could be represented quite well by an empirical equation of the form

$$C_E = C_1 - C_2 \log\nu - C_3\nu \qquad (2)$$

where C_3 is relatively small or zero. Since this equation has no apparent use or theoretical significance, constants for it have not been calculated. It should be noted that it cannot hold at much higher frequencies than those for which data are given, since C_E cannot become zero.

TABLE I

POLARIZATION CAPACITANCE AT 25°

Expt.	Solution	$G,^a$ μmho	1 kc.	3 kc.	10 kc.	30 kc.	C_N, μfd.
71	Dilute H_2SO_4	3454	(43.0)	33.9	(23.6)	14.0	19.5
72	Same as 71	3438	(43.0)	33.2	23.5	..	19.5
73	Dilute H_2SO_4	2238	(84.5)	67.0	41.9	20.0	36.5
74	Soln. 73 + 0.01% gelatin	2121	(61.9)	48.1	30.2	12.6	28.9
75	Soln. 73 diluted	854	42.4	31.3	18.2	..	24.2
76	H_2O	199	15.2	8.6	..	..	13.7
77	Soln. 71-72 diluted	1932	(32.5)	25.7	18.3	11.6	14.2
78	Soln. 73 washed with N_2	2139	(86.9)	70.0	44.4	18.3	35.4
79	Soln. 73 washed with O_2	2194	(89.2)	71.3	43.3	16.8	37.5
80	CO_2 soln.	2242	(90.2)	69.7	42.4	15.6	42.5
81	Diluted CO_2 soln.	1298	64.9	47.0	25.3	..	37.4
82	Diluted CO_2 soln.	1043	55.6	38.7	23.0	..	35.0
83	CO_2 soln. + <0.001% gelatin	1218	35.0	25.2	15.8	..	19.2
84	Dilute H_2SO_4	4317	(119.0)	99.0	68.3	26.2	42.0
85	4×10^{-4} N NaCl	3760	(23.5)	(19.8)	15.8	11.1	7.7
86	2×10^{-4} N NaCl	2684	(21.0)	17.6	13.9	8.8	7.1
87	0.1 M glycine	908	37.4	27.0	15.0	..	22.4
88	2×10^{-4} N NaCl in 0.1 M glycine	2375	(36.7)	29.1	21.1	12.2	15.6
89	1×10^{-4} N NaCl in 0.1 M glycine	1621	(35.5)	27.0	18.1	9.2	17.5
90	1.6×10^{-4} N NaCl in soln. 73	3250	(72.4)	58.5	39.9	17.5	29.2
91	1×10^{-4} N NaCl in soln. 73	2846	(73.8)	60.0	39.5	16.3	29.0
92	2×10^{-4} N NaCl in 0.02 M glycine	2561	(29.5)	24.6	18.5	10.9	10.2
93	Soln. 73 + 2 vol. % acetone	2020	(77.7)	63.4	41.3	14.4	30.0
94	1×10^{-4} N NaCl + 2 vol. % acetone	1796	(20.2)	16.5	12.2	7.0	7.8
95	2×10^{-4} N NaCl + 2 mg./l. gelatin	2612	(17.0)	(14.3)	11.5	7.7	5.5

^{a} Conductivity (ohm^{-1}cm.$^{-1}$) = 1.640 × 10^{-8}G.

Discussion

Variation of C_E with Frequency.—The empirical Eq. 2 has no apparent relation to any theory of electrode polarization so far proposed. Warburg's[15] theory, confirmed fairly well for low frequencies by the experiments of Neumann[16] and Schönherr,[17] indicates that all electrodes should fall somewhere between two extreme cases: the "completely polarized" electrode, whose capacitance is independent of frequency; and the "unpolarizable" electrode, whose capacitance varies inversely as the square root of the frequency. Schönherr[17] found that platinum electrodes in acid could be made to approach either behavior by various treatments, and Warburg[15b] derived for this system an equation of the form[18]

$$C_E = A(2\nu^{-1} + 2a\nu^{-1/2} + a^2)^{1/2} \qquad (3)$$

which approaches the extreme cases as a becomes very large or very small.

In Fig. 2, the same C_E values given in Fig. 1 are plotted against $\nu^{-1/2}$. The behavior is similar to that of Fig. 1, the curves approaching straight lines at low frequencies, but the curvature is greater and begins at lower frequencies. Moreover, the curves are concave downward, whereas according to Eq. 3 they should be concave upward and become horizontal for high frequencies. Evidently, at frequencies above a few kc., other factors than those considered by Warburg become important. Even the low-frequency straight line does not correspond to direct proportionality between C_E and $\nu^{-1/2}$, but would approach this at lower frequencies.

Warburg's theory also leads to a polarization resistance, which in the extreme case becomes equal to the polarization reactance and varies in the same way with frequency. As already indicated, such a resistance would be too small to be detected in our measurements. Its effect on the apparent capacity would also be within the experimental error.

Variation with Composition.—The measurements on different solutions give results which vary rather irregularly with composition, no doubt because of changes in the condition of the electrode surface. There are, however, some observations that may be made.

(15) Warburg, (a) *Ann. Physik.*, **67**, 493 (1899); (b) **6**, 125 (1901).
(16) Neumann, *ibid.*, **67**, 500 (1899).
(17) Schönherr, *ibid.*, **6**, 116 (1901).
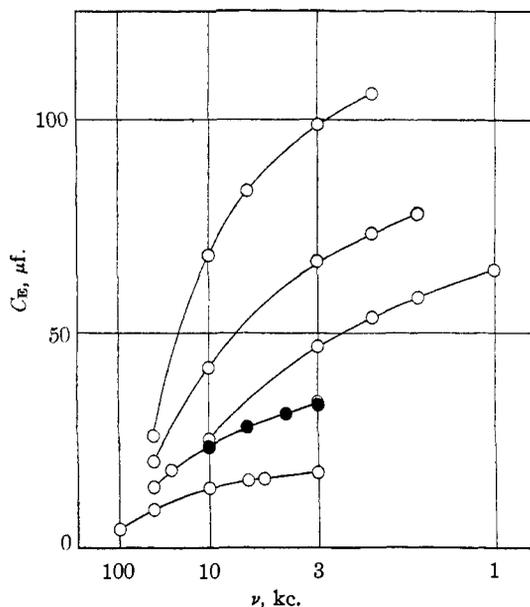(18) On p. 134 of Warburg's article this equation is incorrectly written.

Fig. 2.—Polarization capacitance against $\nu^{-1/2}$, same data as Fig. 1.

The value of C_E at a given frequency, the slope C_N, and the curvature of the C_E vs. log ν graph, all tend to increase with increasing hydrogen ion concentration. That hydrogen ion is the important factor is shown by the fact that sulfuric and carbonic acids give similar results for the same conductivity, while sodium chloride at comparable concentrations has a relatively small effect (compare Expts. 73, 80, 90, 91; 76, 85, 86). Further, C_E and C_N for the acid solutions are very roughly linear functions of log G, and therefore of pH. The most notable exceptions are Expts. 71, 72, and 77, which give abnormally low results. Since these three solutions were all from the same original stock, it seems evident that some impurity produced this effect.

In connection with possible effects of impurities, Expts. 74, 83, and 95 on gelatin are interesting. In each case the C_E values are lower than those for the same solution without gelatin (Expts. 73, 81, 82, 86). The gelatin may act in various ways, by changing pH for example, but in Expt. 95, at least, it appears that the effect of the very small concentration of gelatin must be due chiefly to adsorption on the electrodes.

Experiments 78 and 79 were made to determine the possible effect of dissolved oxygen. Solutions washed with oxygen and with nitrogen both gave approximately the same results as the original solution (Expt. 73), and a carbon dioxide solution of nearly the same conductivity also agreed quite

well, so that the common dissolved gases cannot be considered important factors in the effect.

Experiment 87 on glycine solution and Expts. 88, 89, and 92 on glycine solutions containing different amounts of sodium chloride give C_E vs. log ν curves which lie close together, but the slopes are somewhat irregular. The curves lie above those for aqueous salt solutions rather than below as would be expected from the pH of 6.1. Apparently the glycine itself has a considerable effect on electrode polarization. Experiments 93 and 94 show that 2% by volume of acetone (about 0.3M) has a relatively slight effect in both acid and salt solutions.

Methods of Correction.—Oncley[4a] introduced a method of correcting for electrode polarization as follows. The apparent cell capacitance C is plotted against the function $G^2\nu^{-2/3}$. If (a) the dielectric constant is independent of frequency, and (b) C_E is proportional to $\nu^{-1/2}$, a straight line will be obtained. If the dielectric constant shows dispersion, but becomes constant at low frequencies, then the curve will become a straight line at low frequencies. This straight line is extrapolated to infinite frequency. By subtracting the resulting infinite-frequency value from the capacity given by the straight line at any frequency, the correction to be subtracted is obtained.

It is evident from what has been said above that assumption (b) has neither theoretical nor experimental foundation. It is true that both Eq. 3 and the experimental curves of Fig. 2, if extrapolated to low enough frequencies, would approach (b) as a limit; but since the error in C caused by a given error in C_E varies inversely as ν^2, this error would increase, not diminish, with decreasing frequency. This is what Oncley[5] actually found to be the case. Even by using a differential method, comparing two solutions of the same conductivity, he was unable to use the method below 10 kc. Thus it appears that Oncley's method is purely empirical and depends on the polarization error being so small that a crude approximation is adequate. It should be noticed that even if a straight line is obtained over a certain frequency range, it could conceivably be due to a combination of dispersion and polarization, thus leading to erroneous results.

Probably no serious error in Oncley's results, or at least in his critical frequencies, arises from the polarization correction. But for higher conductivities, for lower frequencies, and for cases where the behavior of dielectric constant with frequency is more complex, e. g., polydisperse systems, it seems clear that a better method of dealing with electrode polarization is needed. Such a method is suggested by the work of Miller[19] and of Jones and Christian,[20] who used movable electrodes in studying electrode polarization. Measurement of conductance and capacitance for the same electrodes at two or more previously calibrated positions would permit the calculation of dielectric constant and polarization capacitance independently. Some experimental difficulties arise from the close electrode spacing needed for dielectric constant measurements, but these do not seem to be insuperable, and work on the design of such a cell is now in progress.

Acknowledgment.—The authors are indebted to Professor W. H. Rodebush, of the Chemistry Department of the University of Illinois, for suggesting this research and for many helpful discussions.

Summary

1.   An apparatus is described for conductance and capacitance measurements on conducting solutions from 1 kc. to radio frequencies.

2.   Results are given on the polarization capacitance of platinum electrodes in very dilute solutions of sulfuric acid, carbonic acid, and sodium chloride, alone and with glycine, gelatin, and acetone.

3.   In the range from 1 to 30 kc. the polarization capacitance does not follow the "inverse square root law." An empirical equation (Equation 2) is given which does describe the variation of polarization capacitance with frequency.

4.   Polarization capacitance increases with decreasing pH.

5.   The results are discussed particularly with regard to methods of correction in dielectric constant measurement.

(19) Miller, *Phys. Rev.*, **22**, 622 (1923).

(20) Jones and Christian, THIS JOURNAL, **57**, 272 (1935).