AN INVESTIGATION OF THE "LEAK EFFECT" IN MEASURING DIELECTRIC CONSTANTS

AND

DIELECTRIC CONSTANTS AND POLARIZATIONS OF SOME BINARY MIXTURES OF ACETONE

A THESIS

by

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Discussion of Results

Introduction

The lower members of the fatty acid series are quite conductive when they are dissolved in a material, like water, which has a high dielectric constant. Thwing (1) attempted to measure the entire range of binary mixtures of acetic acid in water but encountered considerable difficulty in making capacitance measurement because of the conductance effect. Mixtures containing less than 30% acetic acid gave the most uncertain results. These dielectric constants were measured by the bridge method which is suitable for conductive materials. Dielectric constants of aqueous solutions of various electrolytes have been determined largely by the resonance and the Furth (2) ellipsoid methods.

Graffunder and Weber (3) had used succesfully, by resistance compensation, the heterodyne method to measure the dielectric constants of polar mixtures like: water in ethyl alcohol; and, chloroform and water in acetone. Akerlof (4) using the resonance method had determined the dielectric constants of many polar mixtures.

The dielectric constants of fatty acids had been determined in non-polar solvents which have a low dielectric constant.

However, no dielectric constant measurement had been made of fatty acids in a polar material with a high dielectric constant, compared to non-polar materials, like acetone. It was thought that a parallel between the action of acetone on fatty acids and the action of water on fatty acids would exist. This has recently been demonstrated by

Kateswaram (5) who found a shift in the Raman spectrum when acetic acid is dissolved in acetone which is comparable to the Raman spectrum shift observed when acetic acid is dissolved in water.

If the acetone, because of its dielectric constant, ~~is going to~~ causes the fatty acids to ionize the effect should be observed in the resultant dielectric constants and polarizations of the mixtures.

It ~~was~~ is also evident that ~~if an ionizing effect is going to function then~~ the conductance of the material will increase.

Now since the heterodyne method gives questionable results when used to measure conductive materials it ~~was therefore~~ is necessary ~~to~~ either to eliminate or measure the conductance effects which may cause serious error in the dielectric constant determined in this way. The apparatus was so designed as to decrease the conductance effect. An expression, derived from theoretical considerations, to correct the "leak effect" proved to be untenable, but a graphic relationship was finally obtained by making non-conductive materials artificially conductive. This was done by placing a series of different size resistors over the cell and observing the effect on the capacitance of the cell.

The work on the binary mixtures was then undertaken but in no case was the conductance so great as to necessitate a capacitance correction.

Nevertheless it was later shown that the leak effect is considerable even for slightly conducting materials if the apparatus is of a certain design.

For comparisons with acetone fatty-acid mixtures, dielectric constant and polarizations were measured for acetone - benzene, toluene and propionaldehyde.

PART I

AN INVESTIGATION OF THE "LEAK EFFECT" IN MEASURING DIELECTRIC CONSTANTS.

METHOD AND APPARATUS FOR MEASURING DIELECTRIC CONSTANTS

SECTION I

The determination of dielectric constants of non-conductive and conductive materials.

The methods used in measuring dielectric constants may be divided into two groups; those used for measuring dielectric constants of non-conductive materials; and, those employed for conductive materials. There is a certain amount of over-lapping as some methods can be used, with modification in most cases, for both types of materials.

Dielectric constants of non-conductive materials have been determined by methods based on three different principles.

1) When the electric force acting through a medium is measured the dielectric constant may be calculated therefrom by means of Coulomb's Law. Silow (6) calculated dielectric constants from the ratio of the electrometer needle angles made by the material and air with a given potential. This method was improved by Perot (7) and later Carman (8). Quincke (9) measured the electric force by means of a balance and air blast. This has also been used by Michaud and Balloul (10).

2) Drude (11) measured dielectric constants by determining the velocity of propagation of electromagnetic waves through a material. A wave of this nature is inversely proportional to the refractive index which in turn is directly proportional to the square root of the dielectric

constant of the material through which the wave is moving. This method has been improved by Holborn (12), Mesny (13) and Wachsmuth (14).

3) By measuring the capacitance of a condenser in some material and then empty, the dielectric constant is obtained by the ratio of the two capacitances. All methods using this principle employ an alternating current in the condenser, and are based on tuning.

The bridge method for measuring capacitances was used by Nernst (15) to arrive at dielectric constants. Nernst at first used a low frequency current but later employed higher frequencies. Hertwig (16), and later Joachim (17) developed the high frequency bridge.

Determining capacities by the resonance method is used chiefly for conducting solutions and will be discussed later.

The heterodyne beat method has been used by Herweg (18), Isnardi (19), Hojendahl (20), Williams (21) and others (22) for non-conducting liquids.

Dielectric constants of conductive materials have been measured by methods which may be placed in three groups.

Furth (2) and others (23), (24), (25), have determined dielectric constants of dilute aqueous solutions of strong electrolytes by observing the extent of rotation in an electrical field of an ellipsoid which was made of a material with a dielectric constant different ~~to~~ from the dielectric constant of the liquid that is to be measured.

The Baretter bridge method has been used by Neise (26) to measure both conducti~~ng~~ity and capacitance of electrolytic solutions.

To find dielectric constants of conducting solutions by the resonance principle, two methods of obtaining resonance have been used. A circuit may be "tuned" for maximum current, which can be detected on a galvanometer, and determining the capacitance with good accuracy. However considerable manipulation and correction is necessary to arrive at the true capacitance of the material in the condenser. This method has been used by Tank (27), Falkenberg (28), Jerzewski, M Wierzbicki and J. Kamecki (29) and others (30), (31), (32).

Latty and workers devised and used a voltage "tuning" method which eliminates some of the difficulties of the current tuning method. (33) (34).

Sach (35) and Williams (36) have used the comparitor-resonance method which accomplishes a comparison simultaneously of conductance and dielectric constant of two solutions, a standard and an unknown.

The Heterodyne beat method had been considered unsatisfactory for conducting materials but Graffunder and Weber (3) used a variable resistance across the cell and adjusted it to give the same damping effect as obtained with the conductive liquid in the cell. A valve voltmeter was employed to control the energy of the circuit and the variable resistance was built up from two radio tubes giving a change in resistance by adjusting the filament current.

Besides the methods outlined for measuring dielectric constants others (37), (38) have been used.

For this investigation the heterodyne method was used with some modifications to measure capacitances of conducting materials.

E_1 = 135 volts

E_2 = 2 ''

E_3 = 1.5 ''

E_4 = 6 ''

E_5 = 3 ''

E_6 = 45 ''

E_7 = 135 ''

E_8 = 90 ''

C_1 = 3000mmfd.

C_2 = 1000 ''

C_3 = Cell

C_4 = 8730 ''

C_5 = 7000 ''

C_6 = 0.01mfd.

C_7 = 0.1mfd.

C_8 = 0.00025mfd.

E_9 = 27 volts

C_9 = 8mfd.

C_{10} = 0.0025mfd.

C_{11} = 0.01mfd.

R_1 = 50000 ohms

R_2 = 6 ohms

R_3 = 25 megohms

R_4 = 5 ''

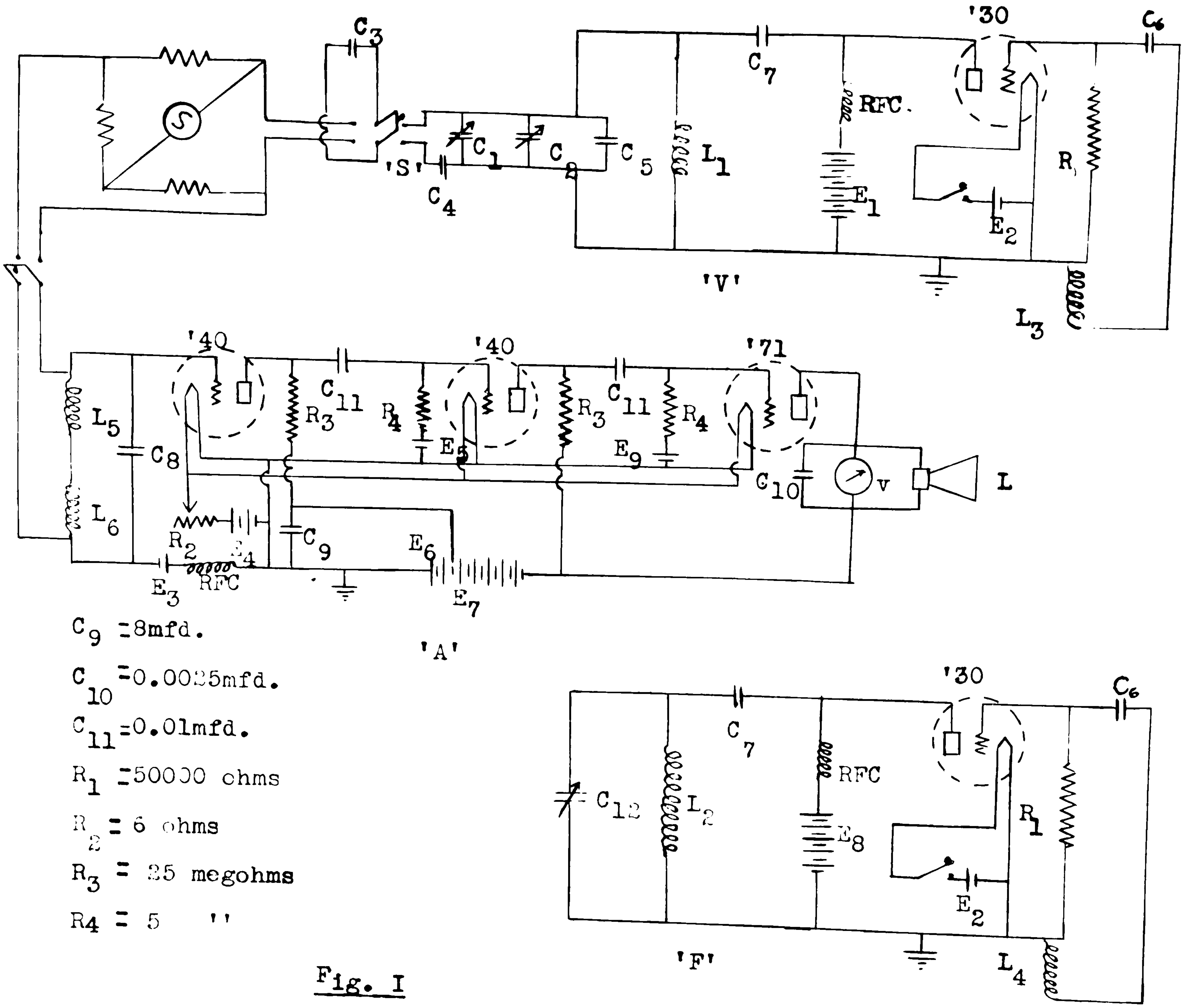


Fig. I

APPARATUS.

The hererodyne beat method for capacitance measurements was used in this work.

When two high frequency oscillators of the vacuum tube type are loosely coupled through an amplifier, beats of an audible frequency may be heard if the frequencies of the two oscillators are near one another. The pitch of the beat decreases as the two oscillators approach the same frequency, and finally a silent point is obtained when both oscillators operate at the same frequency. If the inductance and the resistance in an oscillating circuit are kept constant then the frequency of the oscillator will depend only on the capacitance. Hence by keeping one oscillator at a fixed frequency an unknown capacitance may be measured by inserting it into the circuit of the second oscillator parallel to a standard condenser which may be reduced until both oscillators are again working at the same frequency.

The difference of the two readings on the standard condenser being the capacitance of the unknown. This apparatus has been used by Smyth (22), Williams (21) and others (3), (39).

The oscillator circuits as shown in Fig. 1. are varied somewhat from those previously used (39). The "B" battery was shifted from its series position with the plate coil, L, to a parallel position. A radio frequency ~~coke~~ choke was placed between the "B" battery and the plate of the tube and condenser thereby decreasing the direct current voltage on the condenser plates. This gave a strong oscillation and heterodyning could be obtained with fewer harmonics. A six volt storage battery was tapped to provide two volts for the UX-230 tubes. The same six volt battery was used for the detector amplifier unit (A).

Since a large capacitance was desirable in the variable oscillator (V) to deal with somewhat conducting solutions, the inductance had to be decreased to remain at the same frequency. In place of using sixty-four turns on L_1 and thirty-two on L_3 the new inductance coils had six and thirty turns respectively (39). This gave the circuit a total capacitance of about 10,000 mmf. for the same frequency as the fixed oscillator. The "B" battery voltage was increased from ninety to one hundred and thirty-five volts. The two oscillators were coupled more tightly by using five hundred and fifty turns as compared to four turns. The detector amplifier was the same as that described by Smyth (22) and modified by Deluca (39).

When the original coils of the variable condenser, with larger inductance, were placed in the circuit, and a "B" battery of one hundred and thirty-five volts, a strong beat could be obtained in the loud speaker of the amplifier but resistances of only two thousand ohms could be put across the condensers. With a ninety volt "B" battery the signal again was good but the circuit again ceased oscillating, with parallel resistances smaller than two thousand ohms.

With the new coil and the higher "B" voltage, resistances as low as four hundred ohms could be placed parallel with the condensers. The voltmeter needle deflections were smaller and the null region wider, nevertheless, readings on the standard condenser scale could be duplicated.

For an oscillating circuit with a high capacitance the series resistance R in

$$R = \frac{1}{r} \times \frac{L}{C}$$

where: r is parallel resistance,
L is inductance,
C is capacitance,

will be small even with low resistances of the parallel resistors (r). That is, more leak will be tolerated by the oscillating circuit with a high "C" than with a low "C".

In effect since

$$f = \frac{1}{2\pi\sqrt{LC}}$$

where: f is the frequency,
"L" has been made small, and
"C" has been made large,

to retain the same small frequency the factor $\frac{L}{C}$ becomes small and therefore small resistances in parallel give a smaller equivalent series resistance than with a small "C" and a large "L".

However, the damping effect D in

$$D = \frac{R}{2\pi fL}$$

becomes larger due to the smallness of L and hence a certain broadness of tuning results. In addition as the "leak" through the condenser becomes greater R increases and therefore even greater broadening of tuning is observed.

The standard condenser C, of three thousand mmf. (General Radio Co., Type 246-M) was placed in the center of a circular table eighty inches in diameter and a small mirror was mounted on the end of the main condenser rator shaft. A beam of light was reflected from the mirror and focused onto a scale which was attached to the edge of the circular table. Readings to within one millimeter could be taken readily.

It was latter found that the range of the standard condenser was too large for the size of the cell condenser adopted. To increase the sensitivity of capacitance measurements a number of the condenser plates were rotated on the rator shaft through 180°. This gave the condenser a constant large capacity but the variable capacity was decreased to two thousand mmf. Later more plates were rotated and the range was decreased to about one thousand mmf. To avoid body capacitances a system of verniers and pulleys was arranged to control the standard condenser from outside the edge of the table.

For calibration purposes C_2, three variable parallel condensers were placed parallel to the standard condenser. Two of these condensers had a total capacitance of one thousand mmf. The third condenser had a capacitance of only twenty mmf., and was controlled with a delicate vernier, which could duplicate fractional variations of the standard condenser. The purpose and method of operation of C_2 will be taken up under the topic of calibration.

To deal with conducting solutions C_4 was placed in series with the cell, C_3, to prevent a leak effect also in the standard condenser. This necessitated having C_4 large in order to minimize the loss of accuracy in reading on the standard condenser. Because of this arrangement it was required to calculate the true capacitance from the standard condenser reading and the series condenser. This will be discussed further in Section I, (3).

Since the capacitance of the oscillating circuit had been made large the standard condenser was insufficient and hence further condensers were placed parallel to the standard condenser bringing the total capacitance up to about ten thousand micromicrofarads.

The oscillators and amplifier were mounted on metal bases and each unit together with its "B" batteries was enclosed in a metal box. The amplifier box was larger than the other two and a separate compartment was made in it for the "A" battery.

The leads of L_5 and L_6 were run through holes in the metal shielding. The metal boxes were grounded and kept closed while readings were made thereby avoiding body capacitances.

THE DIELECTRIC CELL

To arrive at the dielectric constant of a liquid it was necessary to measure the capacitance of the liquid accurately.

A dielectric cell operating on the principle of a variable condenser was first employed by Hubbard (40) and Williams and Krchma (41), Cuthbertson (42) and Maass used a condenser of semicircular plates.

The rator plates were controlled with a vernier adjustment and when the dielectric constant of a liquid was to be determined the condenser was entirely immersed in the liquid. By changing the position of the rator plates with respect to the plates a new capacitance was measured. The dielectric constant being finally determined from the slope of the increase in capacitance. However, since the end effects of the condenser plates did not entirely cancel out and also because of the difficulty in reproducing capacitance settings this type of cell was abandoned. The bakelite mounting of these cells were an additional objection since they came in contact with the liquid investigated.

A coaxial cylinder cell was designed by Linton (43) and Maass so that the inner cylinder could be substituted with a larger or smaller cylinder thereby varying the distance between the plates. To cancel end effects, the height of the liquid in the cell was varied and the dielectric constant again was determined by the slope of the capacitance readings.

Coaxial dielectric cells with fixed plates and calibrated by means of known liquid have been used by Smyth (14) and others (39). Akerlof (4) measured dielectric constants with a cell that had two flat firmly fixed discs two millimeters apart.

Since in this work binary mixtures of organic acids in acetone were to be investigated it was therefore thought desirable to keep the conductance of the dielectric cell as small as possible.

Washburn (45) advises the use of electrodes of four centimeters diameter, and three millimeters apart for conductivity work with pure water and dilute solutions, but for higher concentrations he recommends electrodes one and one-half centimeters diameter and the same distance apart. The ratio of the electrode area to the separation distance in the last case is roughly as one is to one. In the former case where smaller conductivities are encountered the ratio of the area to the separation distance is forty-four is to one. The electrode area distance ratio for the cell described by Smyth (22) is in the vicinity of seven hundred is to one. A cell of that type would be subject to conductivity effects in measuring capacitances.

In the construction of the cell used in this work three points were kept in mind. First, the resistance of the cell must be as high as possible; second, the capacity of the cell must not be too small as considerable error in capacitance measurements would ensue; and third, the volume of the cell must be kept at a minimum so as not to require too much material.

Using the expression for a coaxial condenser

$$C = \frac{5.55 \times E \times 10^{-13} \times l}{\ln \frac{R}{r}}$$

where: C is capacitance in farads

E is the dielectric constant

l is the length of the larger cylinder

R is the inner radius of the larger cylinder

r is the outer radius of the smaller cylinder

and assuming E to be eight the condenser would measure one hundred mmf. when

$$\frac{R}{r} = e^{0.0444 \times l}$$

If, A is the area of the inside cylinder (not including the ends), and R-r is the distance between the two cylinders,

then: $$\frac{A}{R-r} = \frac{\text{Area of plate}}{\text{separation distance}} = X$$

since $$A = \underline{2\pi rl}$$

$$R = \frac{2\pi rl + Xr}{X}$$

Substituting and rearranging

$$2\pi l + X = Xe^{0.0444 \times l}$$

Taking different values of (X) the last equation was solved graphically for l. X = 120, was finally selected as the plate area distance ratio. This made the coaxial cylinders of the cell eight centimeters in length. The inside radius of the outer cylinder was taken as one centimeter, which made the radius of the solid inner cylinder 0.35 cm. The E = 8 was selected as the mean of the dielectric constants that were to be measured. To minimize errors in end effects, due to the presence in the dielectric field of the material holding the cylinders in place, perforated pyrex caps were fitted to the outside of the outer cylinder on either end. The inner cylinder had thin threaded shafts extending through the caps. After the brass parts were lightly gold-plated the cell was drawn firmly together with the studs from the inner cylinder. The upper stud was attached to a glass tube which was made fast in the stopper of the cell. A platinum wire was attached to the stud in the tube and served as a cell lead. Another platinum wire was attached to the side of the outer cylinder, brought up through the stopper at the top of cell and connected to the ground side of the oscillating circuit. The capacitance cell was suspended in a container made from one inchglass tubing. A gravity overflow, above the upper cap of the cylinders,was made to keep the liquid level the same in all cases. The cell was drained by gravity. Besides the leads a stopcocked funnel, for filling the cell, was passed through the stopper which was snugly fitted into the top of the cell container. The gravity drain and overflow came out of the bottom of the bath. A catch bottle was connected to the overflow tube to which was attached a calcium chloride tube to keep moisture from coming in contact with the liquid in the cell.

The water bath in which the container and cell were thermostated at 25 ± 0.03°C, was heated with a twenty watt show case lamp. The temperature was regulated with a toluene-mercury thermoregulator.

The leads from the cell to the switch and from the switch to the oscillator were encased separately in glass tubing to prevent alteration in the leads capacity due to movement.

To measure the resistance of the solutions in the cell a wheatstone bridge was used. An alternating current for the bridge was supplied by a one thousand cycle hummer. Since the telephone produced a poor minimum sound point for resistance measurements, it was replaced with the amplifier. The minimum sound point was then readily obtained by means of the loud speaker of the amplifier.

2. OPERATION OF THE APPARATUS

The oscillators were started at least an hour before any readings were taken and the room temperature was kept as constant as possible since variations in frequencies of the oscillators ensued with temperature change.

During calibration, frequency alterations had to be avoided but during capacitance measurements of liquids, the dielectric constants which were to be determined, slight changes in frequencies were inconsequential because several readings could be taken from which a mean would be derived.

The double pull double throw switch (S) was open while the standard condenser was varied to bring it to the same frequency as the fixed oscillator which was oscillating at 730 kilocycles (CKAC). The null region was determined with a three volt voltmeter (38). In rotating the standard condenser there are two points where the voltmeter needle begins to swing. One on either side of the null region. With the standard condenser set for 3000 to 1000 mmf. the points were in the vicinity of 0.5 cm. of each other and could be read to within 0.5 mm.

on the scale. When the standard condenser had a range of 3000 to 2000 mmf. the distance on the scale was about 1.15 cm. A mean was then taken of the two null point readings and it was subsequently used in arriving at the capacitance of the material.

When the switch S closed the cell-oscillator circuit the standard condenser was rotated until the two voltmeter null points were obtained and the scale readings recorded. A mean was again obtained. The capacitance value resulting when the first reading is subtracted from the second could not be duplicated on other parts of the scale. It was therefore necessary to calibrate the standard condenser.

Greater ease of getting null point readings obtained when the thermoregulator was disconnected. Since around the null region the make and break of the thermoregulator produced confusingswings in the voltmeter. This procedure however was only necessary when a reading was being taken of a material in the cell, and was less pronounced as the conductance in the cell decreased.

In order to measure the resistance of the material in the cell the switch (S) was thrown across to open the cell-oscillator circuit and to close the cell-bridge circuit (Fig. 1.) A bridge resistance box was used and the resistance was adjusted until a minimum sound was obtained from the loud speaker. The resistance was read in ohms off the resistance box.

The 1000 cycle hummer caused annoyance in determining the minimum point and was finally put in an adjacent room and connected to the bridge with long copper wires.

3. CALIBRATION OF THE STANDARD CONDENSER.

The capacitance of a material need not necessarily be in electrical units since only units of the same kind are required in calculating the dielectric constant. (Section 1, (4)).

In this work two centimeters were taken as a unit of one on the standard condenser scale. As previously mentioned readings could be made on the scale to within one-half a millimeter. Actually an insignificant amount of accuracy was sacrificed when readings were taken to within one millimeter, since the error created by this inaccuracy would produce an error of not more than 0.5±% in measuring the smallest capacitance, viz.,air. This error decreased as the dielectric constant of the material increased.

As already observed the capacitance of the condenser and scale readings are not likely to be in linear relationship, because the condenser may not be in the center of the table and also since some of the plates have been rotated to decrease the capacitance range of the standard condenser.

Linton (43) applied corrections and Deluca (39) calibrated the standard condenser scale with successive displacements of the null point and applied deviation corrections in subsequent measurements.

In this work the calibration was altered somewhat from the method of Deluca in that the fixed condenser was kept at a constant frequency. The original purpose was to avoid the variation of capacitance with frequency. This precaution was unnecessary since a ten percent change in frequency alters the original capacitance only about one tenth of a micromicrofarad.

Since calibration involves the insertion and removal of a fixed capacitance, it is necessary to substitute a capacitance which is equivalent to the amount of capacitance removed upon withdrawing the fixed condenser. To do this the same end positions of the null point were obtained with a substituant capacitance of C_2 as for the small condenser (20 mmf.) which was used for the successive calibration steps. This procedure was followed until a range sufficiently large for capacitance measurements of liquids was obtained. The mean values of each two readings were plotted against a convenient unit. In the first calibration the small fixed condenser was taken to be twenty units and in the second calibration forty units.

FIRST CALIBRATION

TABLE I

SCALE READINGS

LEFT	RIGHT	MEAN	UNITS
50.25	50.75	50.50	0
56.25	56.75	56.50	20
62.80	63.30	63.05	40
69.25	69.75	69.50	60
75.60	76.10	75.85	80
81.90	82.40	82.15	100
88.15	88.65	88.40	120
94.35	94.85	94.60	140
100.50	101.10	100.80	160
106.60	107.10	106.85	180
112.75	113.25	113.00	200
124.80	112.35	125.05	220
130.80	131.40	131.10	240
137.00	137.50	137.25	260
143.10	143.60	143.35	280
155.50	156.00	155.75	300
161.75	162.25	162.00	320
168.05	168.60	168.32	340

As already stated to increase the accuracy of capacitance measurements three more condenser plates were rotated 180°. This necessitated a second calibration.

SECOND CALIBRATION

TABLE II

SCALE READINGS

LEFT	RIGHT	MEAN	UNITS
53.20	54.20	53.70	0
64.50	65.75	65.13	40
75.55	76.70	76.12	80
86.25	87.40	86.92	120
96.65	97.75	97.20	160
106.90	108.00	107.45	200
117.10	118.15	117.65	240
127.10	128.30	127.70	280
137.00	138.10	137.55	320
147.15	148.25	147.70	360
157.20	158.30	157.75	400
167.45	168.65	168.05	440
178.20	179.40	178.80	480
188.80	190.05	189.43	520

In order to obtain reading accuracy of 0.05 units the mean values of the scale were plotted against the capacitance units on a graph paper ten feet long that had been cut and spliced to give the slope corresponding to the slope of the calibration curve. Since the slope of the calibration curve was generally the same and also since the reading accuracy used the entire length of the graph paper with only half the readings necessary, the second half of the calibration curve was placed with the appropriate units just below the first half of the calibration curve.

As previously mentioned the condenser C_4 in series with the cell gives smaller cell capacitance values than they actually are. Before C_3 can be calculated either the units must be converted into mmf. or the condenser C_4 must be converted into scale readings. The second alternative was chosen. This was done by using a 100 ± 1 mmf. condenser which had been standardized with a capacitance bridge.

In the first calibration when this condenser was placed parallel to the standard condenser it gave a displacement of ninety-eight units. Since the capacitance of C_4 was 8730 mmf., determined again by the capacitance bridge method, in units C_4 was 8560. Error of one percent in C_4 and using large cell capacitances produces error only in the second decimal place of the true cell capacitance.

Because the standard condenser had been altered a second value of C_4 was necessary. This time the 100±1 mmf. condenser gave a deflection of 216 units or C_4 was equivalent to 18850 units.

A capacitance in the cell requires a removal of a certain amount of capacitance from the standard condenser. From the amount of capacitance removed from the standard condenser it is possible to calculate the true cell capacitance by

$$\frac{1}{\Delta C_2} = \frac{1}{C_4} + \frac{1}{C_3}$$

where ΔC_2 is the capacitance removed from the standard condenser.

Solving for C_3 :

$$C_3 = \frac{\Delta C_2 \; C_4}{C_4 - \Delta C_2}$$

To speed up the evaluation of C_3 a number arbitrary ΔC_2 readings were calculated to give C_3. ΔC_2 was thenplotted against $C_3 - \Delta C_2$. From the graph resulting differences could be read to the second decimal place. The procedure therefore became to find the difference from the graph of ΔC_2 and adding it to ΔC_2 to obtain C_3.

To show the accuracy and also the necessity of the calibration curves, capacitance readings were taken over different parts of the standard condenser scale and the results compared in units.

The values below are not used in subsequent calculations.

TABLE III

FIRST CALIBRATION CURVE (AIR IN CELL).

MEAN SCALE READING	ΔC_2	C_3
64.68	45.20	
58.34	25.50	
6.34	19.70	19.75
71.41	66.05	
65.11	46.45	
6.30	19.60	19.65
89.00	121.95	
82.88	102.15	
6.12	19.80	19.85

SECOND CALIBRATION CURVE (BENZENE IN CELL)

MEAN SCALE READING	ΔC_2	C_3
93.52	145.50	
73.70	71.15	
19.82	74.35	74.65
102.55	179.95	
83.10	105.55	
19.45	74.40	74.70

4. DIELECTRIC CONSTANT DETERMINATION

A) EXPERIMENTAL PROCEDURE

The purified material, the capacitance of which was to be determined, was introduced into the cell by means of the stopcocked funnel at the top of the cell container. The variable oscillator was now tuned, by removing capacitance from the standard condenser, until the two points on either side of the null region were recorded. The cell was then thrown out of the oscillator circuit by the switch (S), and capacitance was put in with the standard condenser until the null points were again obtained. The mean of the first two readings and the last two were then changed into units from the graph. The difference of the two being the capacitance of the material in the cell and the leads. This procedure was repeated several times.

It was found that the material in the cell came to constant temperature within twenty minutes or half an hour. The temperature effect in the capacitance was very noticeable in the first ten minutes. Since the temperature of the material placed in the cell was always below 25°C the capacitance decreased as the temperature of the material in the cell increased. To arrive at a suitable capacitance a mean of the capacitance values over a period of time was taken. The capacitance values observed in the first ten minutes were usually excluded marked (X) except in cases of low dielectric materials where the temperature effect was less apparent.

When the capacitance of the material in the cell was ascertained the liquid was drained and the cell was washed with Merk, reagent quality, acetone. Dried air was then aspirated through the cell for five to ten minutes before a new material was placed in the cell.

The binary mixtures, with the exception of propionaldehyde and acetone were made gravimetrically: 10, 20, 30, 40, 50, 60, 70, 80 and 90%.

At first the cell was washed with acetone and then with the mixture but it was found that the procedure already outlined gave satisfactory results. Since the cell capacity was about 35c.c. at least 40cc. of each mixture were necessary in order to allow some to overflow.

B) STANDARDIZATION OF THE APPARATUS AND CALCULATION OF DIELECTRIC CONSTANTS

In as much as the work was done with two different calibration curves of the standard condenser two cell standards were found.

Besides this in the last part of the work with the second calibration curve an additional cell standardization was made because the apparatus had been accidentally jolted.

The dielectric constant of a material is given by:

$$\frac{c_A}{c_o} = E$$

where: c_A is the capacitance of the material

c_o is the capacitance of the cell under vacuum

E is the dielectric constant of the material

Because of the nature of the apparatus it is impossible to measure the capacitance c_A or c_o without also measuring a small capacitance due to the leads. Hence the capacitance of the material in the cell may be expressed as

$$c_A = c_3 - c_L$$

where c_L is the capacitance of the leads.

If the leads to the cell are not moved, and they were encased in glass tubing, their capacitance should remain the same. They actually do vary slightly from day to day due to atmospheric conditions but remain the same for the short period of time that observations are made. In the first part of the work the variance of c_L was not recognized but was taken into account with the second calibration. An attempt was made to keep the end effects constant by the construction of the cell. The end effects are also included in c_L.

If c_3' is the capacitance of a material A which has a higher capacitance than c_3'' of material B then

$$c_A - c_B = c_3' - c_3''$$

Now the capacitance is measured with a unit which is proportional to a fraction of the standard capacitance unit (viz., farad).

Hence: $c_3' = k\ C_3'$

$$c_A = k\ C_A$$
$$c_L = k\ C_L$$
$$c_0 = k\ C_o$$

where: c_3', c_A, c_L and c_o are capacitamces in farads and k is the proportionality factor. Similar relationships exist for c_3'' and c_B''

whence: $\frac{k\ C_a}{k\ C_o}$ or $\frac{C_A}{C_o} = E_A$

Where E_A is the dielectric constant of the material A.

C_A, C_o, C_L are capitances in the units selected.

also

$$\frac{C_B}{C_o} = E_B$$

where C_B is the capacitance in units and E_B is the dielectric constant of material B.

Therefore:

$$C_o = \frac{C_3' - C_3''}{E_A - E_B}$$

If the capacitances of the two materials are determined and the dielectric constants of the same materials are known, then C_o for the cell can be evaluated.

Besides air the following liquids were used in the standardization of the cell: benzene, ether, methyl alcohol and in the last standardizations acetone.

PURIFICATION OF MATERIALS FOR STANDARDIZATION OF THE CELL.

Merck's reagent quality benzene, thiophene free, was allowed to stand over sodium until effervescence ceased. The benzene was then fractioned and the portion boiling at

80.2°C. (corr.) was collected and used. The same quality of benzene was subsequently used for the acetone-benzene mixtures.

The ether was first treated with calcium chloride, then given a sulphuric acid treatment, distilled, and placed over sodium wire. When needed the ether was freshly distilled from sodium.

Baker's absolute methyl alcohol-special, was refluxed over lime for fifteen hours and then fractionated. The fraction distilling at 65.5°C. (corr.) was used and had a resistance of 8000 ohms.

Without the lime treatment this alcohol had a resistance of 3000 ohms and a slightly higher capacitance of 346.10 units.

Acetone, Merk reagent quality, was purified according to the method of Åkërlof (4) but the capacitance values were too high for the dielectric constant found by him. Lower capacitance values were obtained when some solid potassium permanganate was dissolved in the acetone and a few drops of concentrated sulphuric acid were added. However, even this gave capacitance values much too high to be in agreement with Åkërlof dielectric constant.

In the first standardization all the liquids mentioned above and air were used. For the two standardizations with the second calibration curve only air, benzene and acetone (E = 19.83) were used.

CAPITANCE OF STANDARD MATERIALS

CALIBRATION CURVE No.1.

TABLE IV

MATERIAL	ΔC_2	C_3
Air	19.95	20.00
Benzene	33.60	33.70
Ether	53.75	54.08
Methyl Alcohol	330.80	344.10
Acetone	213.06	218.50

CAPITANCE OF STANDARD MATERIALS

CALIBRATION CURVE No.2
FIRST STANDARDIZATION
TABLE V

MATERIAL	ΔC_2	C_3
Air (1)	44.50	44.60
Air (2)	45.05	45.15
Air(3)	47.20	47.30
Benzene (1)	74.40	74.70
Benzene (2)	75.15	75.45
Benzene (3)	77.40	77.70
Acetone (1)	479.65	492.05
Acetone (2)	480.35	492.75

Note: 1, 2 and 3 signifies three different days.

The capacitances of 3 are high because the bath had leaked and wet the cell leads. These values were both obtained within a period of half an hour.

SECOND STANDARDIZATION

TABLE VI.

MATERIAL	ΔC_2	C_3
Air (1)	44.50	44.60
Benzene (1)	74.75	75.05
Benzene (2)	74.35	74.65
Acetone (1)	481.10	493.50
Acetone (2)	482.90	495.30

CALCULATIONS OF C_o and C_L

C_o was calculated by using the expression:

$$C_o = \frac{C_3' - C_3''}{E_A - E_B}$$

C_L was obtained from C_3 for air and C_o as:

$$C_L = C_3 - C_o$$

C_o FROM RESULTS OF TABLE IV.

TABLE VII.

C_3'	C_3''	Material A	Material B	E_A	E_B	C_o
54.08	20.00	Ether	Air	4.204 (46)	" 1.006 (47)	10.65
54.08	33.70	Ether	Benzene	4.204	2.276 (22)	10.57
33.70	20.00	Benzene	Air	2.276	1.006	10.78
344.10	54.08	Methyl Alcohol	Ether	"32.0 (48)	4.204	10.43
344.10	33.70	" "	Benzene	32.0	2.276	10.44
344.10	20.00	" "	Air	32.0	1.006	10.46
218.60	54.08	Acetone	Ether	19.1 (4)	4.208	11.03
218.60	33.70	"	Benzene	19.1	2.276	10.99
218.60	20.00	"	Air	19.1	1.006	10.86

(") interpolated.

Taking the mean of the first six values $C_o = 10.55$ and $C_L = 9.45$.

From these values of C_o and C_L the dielectric constant of acetone becomes 19.83.

This value is used in the next standardization. (See Part II, Section II, (1))

C_o FROM RESULTS OF TABLE V.

TABLE VIII.

C_3'	C_3''	Material A	Material B	E_A	E_B	C_o
74.70	44.60	Benzene (1)	Air (1)	2.276	1.006	23.70
75.45	45.15	" (2)	" (2)	2.276	1.006	23.77
492.05	44.60	Acetone (1)	Air (1)	19.83	1.006	23.77
492.05	74.70	" (1)	Benzene (1)	19.83	2.276	23.77
492.75	75.15	" (2)	" (2)	19.83	2.276	23.79
492.75	45.15	" (2)	Air (2)	19.83	1.006	23.78
77.70	47.30	Benzene (3)	" (3)	2.276	1.006	23.93

Mean C_o = 23.80

C_o FROM RESULTS OF TAVLE VI.

TABLE IX.

C_3'	C_3''	Material A	Material B	E_A	E_B	C_o
75.05	44.60	Benzene (1)	Air (1)	2.276	1.006	23.98
495.30	74.65	Acetone (2)	Benzene (2)	19.83	2.2765	23.96
495.30	44.60	Acetone (2)	Air (2)	19.83	1.006	23.94
493.50	75.05	Acetone (1)	Benzene (1)	19.83	2.276	23.84

Mean C_o = 23.90

The dielectric constant is calculated as follows:

$$\frac{C_3 - C_L}{C_o} = E$$

Or using Acetone as an example:

$$\frac{218.60 - 9.45}{10.55} = 19.83$$

SECTION II.

CONDUCTANCE IN THE CONDENSER CELL.

1) THEORETICAL CONSIDERATIONS OF AN OSCILLATING CIRCUIT.

In either the resonance or the heterodyne method a conductance in the measuring cell is going to create an additional capacitance effect which will make the cell capacitance greater than its actual capacitance.

An attempt was made with the help of Professor H. G. I. Watson to find a capacitance correction for the leak effect on the basis of oscillating circuits.

The two circuits:

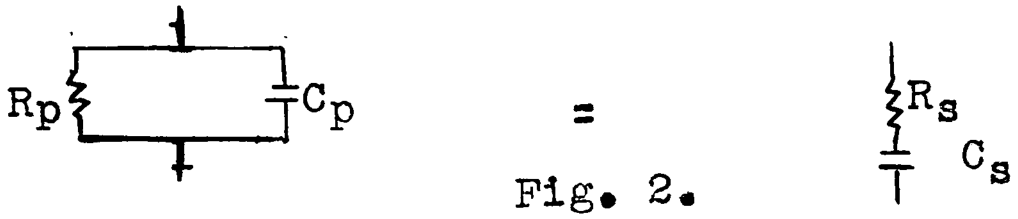


Fig. 2.

are equivalent and hence may be represented as above.

Where R_p is resistance in parallel to the condenser, or the leak resistance.

C_p is the true capacitance of the circuit for a given voltage.

R_s is the effective series resistance which is produced by a parallel resistance Rp.

C_s is the capacitance measured and is greater than the true capacitance due to the decrease in voltage.

As R_s increases R_p decreases whereby C_s is also increased. R_p can be measured as conductance and C_s as capacitance, but R_s and C_p are unknown. An expression is therefore required that will eliminate all terms of R_s and solve for C_p.

Equating voltage drops (Fig. 2.)

(1) $$I \left(R_s + \frac{1}{j\,w\,C_s}\right) = \frac{I_c}{j\,w\,C_p} = I_r \; R_p$$

(2) where: $$I = I_r + I_c$$

$$w = 2\pi f$$

where: f is the frequency.

(3) $$(I_r + I_c)\left(R_c + \frac{1}{j\,w\,C_s}\right) = \frac{I_c}{j\,w\,C_p} = I_r \; R_p$$

Taking the right hand equation of (3).

(4) $$I_c = I_r \; R_p \; j\,w\,C_p$$

Selecting the two ends of (3)

(5) $$(I_r + I_c)\left(R_s + \frac{1}{j\,w\,C_s}\right) = I_r \; R_p$$

Substituting (4) in (5).

$$I_r\,(1 + R_p \; j\,w\,C_p)\left(R_s + \frac{1}{j\,w\,C}\right) = I_r \; R_p$$

Rearranging and multiplying out

(6) $$1 + j\,w\,(C_p R_p + C_s R_s) - w^2 C_s C_p R_s R_p = j\,w\,C_s R_p$$

Equating real and imaginary values in (6).

(7) $$1 = W^2 C_s R_s C_p R_p$$

and

(8) $$C_p R_p - C_s R_p + C_s R_s = 0$$

Solving (7) for R_s and substituting in (8)

(9) $$R_p (C_p - C_s) + \frac{1}{W^2 C_p R_p} = 0$$

Multiplying out, (8) becomes a quadratic of C_p viz.

(10) $$W^2 C_p^2 R_p^2 - W^2 C_p C_s R_p^2 + 1 = 0$$

Solving (10) for C_p and simplifying

(11) $$C_p = \frac{C_s}{2} + \frac{C_s}{2} \sqrt{1 - \frac{4}{W^2 C_s R_p^2}}$$

Assuming that the expression under the root sign remains positive the expression was expanded to two terms and simplified.

$$C_p \doteq C_s - \frac{1}{W^2 C_s R_p^2}$$

To measure C_s it was necessary to keep the leak out of the standard condenser as the standard condenser would be affected in a way similar to the cell. This was done by putting a large condenser C_4 in series with the cell. However, this complicated the problem still more since now the derived expression did not hold. To verify the expression by putting a standard condenser in parallel with a cell would be futile since the leak affects it as already pointed out. There was, therefore, no way, though this was not realized at the outset, that this expression could be tested experimentally.

It was decided that materials in the cell would be made artificially conductive by placing non-inductive and non-capacitive resistances across the cell. To do this ordinary radio resistors were connected by means of mercury cups across the cell and the resistance was measured with the wheatstone bridge apparatus. (Fig.I.)

2) SOME LEAK EFFECT RESULTS

If the leak effect alters the capacitance then by determining the extent of conductance of a solution the capacitance correction due to the leak effect can be made.

Several materials were placed in the cell and a series of resistors were placed across the cell. The general shape of the curve when capacitance was plotted against the reciprocal of the logarithm of the resistance, was the same as in all cases, though as it was found out later it should change slightly with the size of capacitance of the material in the cell. The change mentioned, however, is small and would not be readily recognized.

LEAK EFFECT ON THE CELL CONDENSER WITH RESISTANCES (AIR)

TABLE X.

RESISTANCE	$\frac{50}{\log R}$	C3
	0	19.95
10,000	12.5	19.95
2,220	14.6	20.05
955	16.78	22.20
875	17.00	22.35
800	17.22	23.60
728	17.47	24.20
566	18.16	27.03
483	18.63	29.80
419	19.07	34.05

BENZENE

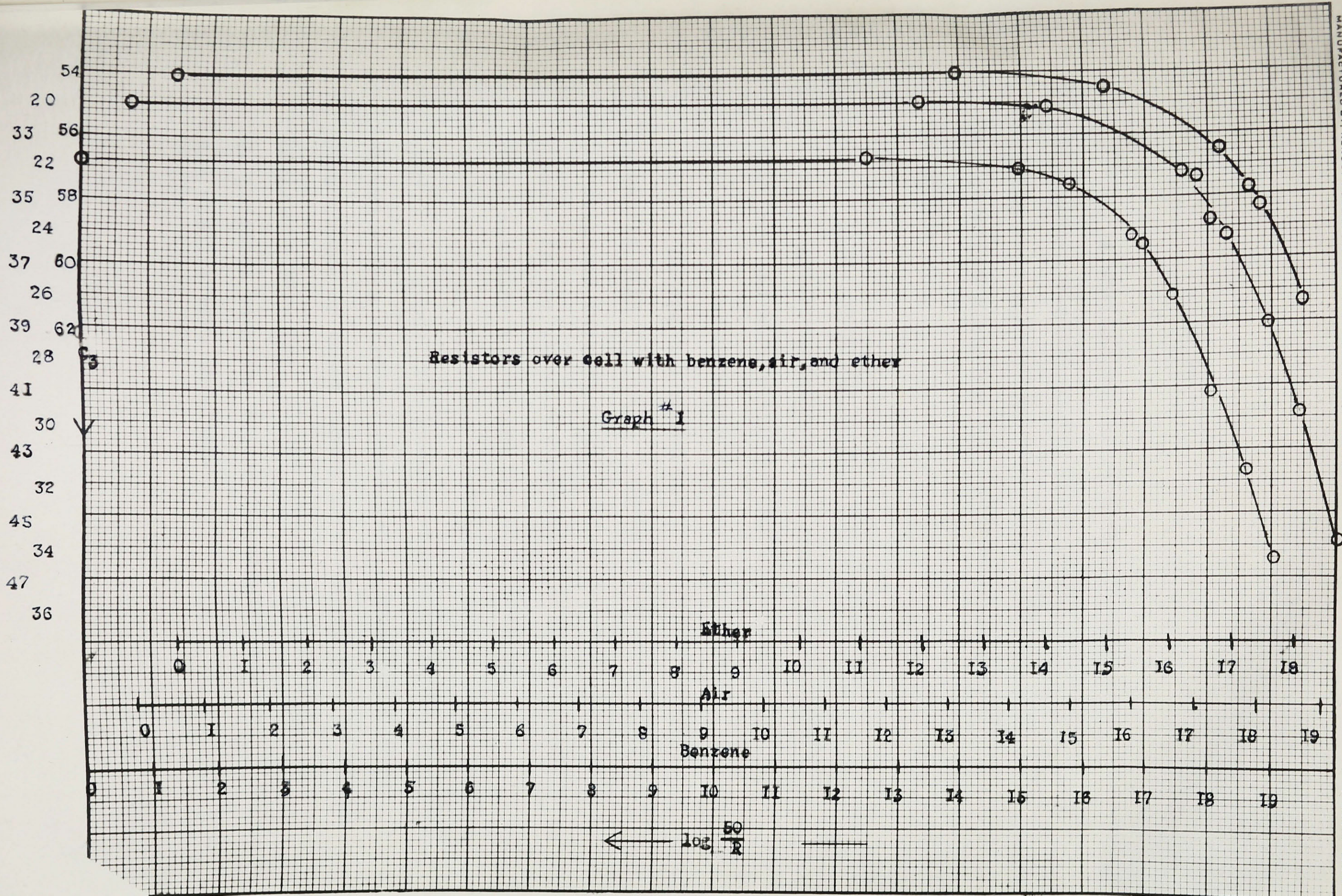
TABLE XI.

RESISTANCE	$\frac{50}{\log R}$	C_3
	0	33.70
10,000	12.5	33.70
2,240	14.93	34.17
1,495	15.73	34.50
956	16.77	36.35
880	16.98	36.50
730	17.47	38.17
569	18.15	41.07
482	18.63	43.67
418	19.07	47.55

ETHER

TABLE XII

RESISTANCE	$\frac{50}{\log R}$	C_3
	0	54.08
10,000	12.5	54.08
2,240	14.93	54.43
956	16.77	56.50
800	17.22	57.65
730	17.47	58.40
567	18.17	61.25


Resistors over cell with benzene,air,and ether

Graph # 1

A similar set of results was obtained with methyl alcohol in the cell. When these results were plotted as C_3 against $\frac{50}{\log R}$ a curve was obtained which was the same in all cases. (Graph I).

3) BEHAVIOR OF THE LEAK EFFECT

After the series of binary mixture determinations had been completed another attempt was made to discover the behavior of the "leak effect".

Before the capacitance C_4, had been placed in series with the cell, resistors were placed across the cell and instead of getting an increase in capacitance in the standard condenser due to the leak effect, actually a decrease had been observed.

When the fixed oscillator, with a total capacity of about five hundred micromicrofarads, was connected with a standard condenser in parallel a total capacitance of about twenty five hundred mmf. resulted. Resistors were then placed across the cell which was in parallel with the standard condenser and the following results were obtained.

RESISTANCE PARALLEL TO CELL AND STANDARD CONDENSER (AIR)

TABLE XIII

RESISTANCE	C3 (NO.2 CALIBRATION)
None	44.5
2,220	42.5
1,500	30.5
955	- 4.5
875	- 10.00
800	- 14.5

The standard condenser is large in capacitance while the capacitance of the cell is small. It was thought that though the resistance does cause an increase in capacitance in the small condenser the proportional increase in the large condenser would be much greater and therefore it would actually be necessary to take out a part of the standard condenser to bring the total capacitance of the circuit to the value that it had previously. If this were the case, then, a cell capacitance which is large compared to the standard condenser should give a positive capacitance effect. This was tested in the following manner. The large condenser was removed from oscillator circuit and a small condenser of five hundred micromicrofarads was put in its place and parallel to the cell. To have as little of the capacitance of the new condenser in the circuit as possible the oscillator was made to interfere with a radio set on a station in the low capacitance range. The cell was filled with acetone to give it a large capacitance, then a resistor was placed across the cell. To again cause the same radio interference it was necessary to turn the new condenser in the direction of more capacitance. Therefore the leak effect causes a greater increase on the larger condenser of the two condensers when they are parallel.

Hence if measurements are made with a condenser in parallel to the remaining capacitance, after the necessary capacitance for the cell has been removed, the capacitance of which is greater than the capacitance of the cell, a negative leak effect will be observed. But if the capacitance remaining of the standard condenser is less than the capacitance of the cell a positive leak effect will be observed.

Still using the fixed oscillator as the variable one resistors were put across the cell with the large condenser (8730 mmf.) in series. The leak effect was magnified considerably.

SERIES CAPACITANCE 8730 mmf. AND TOTAL OSCILLATOR CAPACITANCE OF 2500 mmf. (AIR).

TABLE XIV

RESISTANCE	C_3
none	47.5
2,220	67.5
935	90.0
875	101.0
800	116.0

The capacitance C3 has more than doubled itself in this case. The leak effect is much greater than with a large oscillator capacitance (Cf. Tables X, XI and XII).

Using the same total oscillator capacitance the series capacitance C_4 was replaced with a capacitance of 3034 mmf. the leak effect was magnified even more.

SERIES CAPACITANCE 3034 mmf. AND
TOTAL OSCILLATOR CAPACITANCE of 2500 mmf.(AIR)

TABLE XV

RESISTANCE	C_3
None	46.5
10,000	51.5
2,220	61.5
1,500	142.5
955	241.5
875	268.5
800	No oscillation

Here the capacitance increased to six times the original capacitance of air without a resistance. The corresponding ratio increase with air, using 8730 mmf as C_4 and a total capacitance of about 10,000 mmf. in the oscillator is about one and one fifth ~~increase~~.

PART II

DIELECTRIC CONSTANTS AND POLARIZATIONS OF SOME BINARY ACETONE MIXTURES.

SECTION I.

DIELECTRIC AND DIPOLAR PROPERTIES OF BINARY MIXTURES OF ACETONE

The dielectric constants and polarizations for many polar materials in non-polar materials have been determined (22). Also many dilute solutions of polar materials in non-polar solvents have been determined over a temperature range in order to calculate the dipole moment of the polar material. Dipole moments have also been calculated from the results obtained with polar solvents.

Drude (49) had determined the dielectric constants of acetone - benzene mixtures using the resonance method at a frequency of 4 x 10^9 cycles. He pointed out that Silberstein's (50) mixing rule did not hold but failed to give the results. The dielectric constants of this series were therefore redetermihed.

Smyth and Rogers (46) have measured the dielectric constants and calculated the polarizations of benzene - acetic and butyric acid mixtures. The dielectric constant curves were concave and the polarization curves were convex with respect to the composition axis.

The dielectric constants and the polarization curves of MIXTURES OF two components which are both polar have not been studied as extensively as the ~~cases~~ MIXTURES where one of the ~~media~~ COMPONENTS is non-polar since the relationships are considered too complicated to interpret (51).

Thwing (1) determined the dielectric constants of acetic acid - water mixtures; from the nature of the dielectric constant curve, he argued that hydrates were formed. The general shape of the curve, however, was somewhat convex.

The dielectric constants of acetone - water mixtures were determined by Åkerlof (4). He observed a concave dielectric constant curve but the polarizations of these mixtures gave a linear relationship.

Kerr (52) and Graffunder (53) both found that the dielectric constants of binary mixtures of acetone and chloroform gave a convex curve in place of a concave one, which is the general rule for a polar and associated material in a non-polar medium.

The acetone - nitrobenzene dielectric constant curve was observed by Graffunder and Heyman (53) to be convex while the polarization relationship of these components was a straight line.

Since water mixtures of the fatty acids would have considerable conductance compared to the conductance of these acids in non-polar media, it was thought desirable to use a material with a moderate dielectric constant, at least at the outset, as one of the media. Acetone was selected as the one component of all the mixtures, which besides having a moderate dielectric constant was also soluble in non-polar media.

In addition to the acetone-fatty acids the dielectric constants of mixtures of three other materials were undertaken for reference purposes.

SECTION II

EXPERIMENTAL RESULTS

1) THE DIELECTRIC CONSTANT OF ACETONE

As previously mentioned acetone purified according to the method of Åkerlöf (4) was first used. The fraction boiling between 56.5 and 56.7°C (corr.) was collected and placed in the cell. The resistance of this acetone was 5,100 ohms and had a C_3 of 227 units. C.P. Stock acetone was placed over freshly burned lime and allowed to stand for twenty four hours. It was then refluxed for twenty-one hours over the lime. The first fraction collected distilled at 56.5°C (corr.) and had a capacitance of 224.6 units. The second fraction 56.5 to 56.7°C (corr.) had a capacitance of 226.5 units. The resistance of these portions was about 18,000 ohms.

It was observed, as already stated, that solid potassium permanganate and a few drops of sulphuric acid gave acetone with lower capacitance. The first fraction distilling at 56.4°C (corr.) had a capacitance of 221 units. The second and third fractions distilled at 56.35°C (corr.) had a capacitance of 221.5 units.

Acetone treated in the above manner was then refluxed for fourteen hours over lime but gave a higher capacitance of 230.5 units.

Merk, reagent quality, acetone treated with permanganate and acid distilled at 56.4°C (corr.) had a capacitance of 218.60 units. This acetone capacitance value was reproduced consistently with other lots of acetone. Acetone used in subsequent work was of the same quality and treated in the same way before being used.

ACETONE CAPACITANCE

TABLE XVI

TIME	Δ C_2	C_3
1.30 P.M.	213.15	218.60
2.03 "	213.25	218.70
2.35 "	213.20	218.65
2.45 "	213.10	218.55
3.00 "	213.05	218.50
3.05 "	213.25	218.70
3.30 "	212.70	218.15
3.37 "	212.95	218.40
4.10 "	212.90	218.35
	Mean	218.50

These results are from calibration curve

No. 1 C_o = 10.55, C_L = 9.45.

DIELECTRIC CONSTANT OF ACETONE

TABLE XVII

((i) interpolated)

AUTHOR	METHOD	F.(KC)	λ(M.)	TEMP. (C)	E.
Drude (54)	Audio	-	-	19°	20.7°
Walden (55)	Bridge	-	-	20°	21.4
"	"	-	-	50° (i)	18.7
"	"	-	-	25°	19.95
Int.Critical Tables ([illegible]	"	-	-	20°	21.3 ± 1
Graffhunder (53)(56)	Heterodyne	-	450-500	20°	21.4
"	"	-	" "	25°	20.87
Kerr (52)	Heterodyne	3,000	95	17°	20.89
Lunt &Rau (85)	Bridge	42	-	25°	20.2
"	"	872	-	25°	20.6
"	"	883	-	25°	20.4
Albright (57)	-	-	-	25°	20.74
L.B.R.S.p.C.T. (58)	Resonance	-	81-84.5	25°	20.88
Åkerlöf (4)	"	2,000	-	25°	19.10
This work	Heterodyne	730	-	25°	19.83

The dielectric constant for acetone obtained by most workers is somewhat over twenty. Lunt and Rau purified their acetone only with calcium chloride and then fractionated. Graffunder used pure Merk acetone, but does not describe any particular method of purification. Albright mentions that he was not able to get the same dielectric value as that obtained by Åkerlöf. Higher dielectric values were obtained with acetone purified according to method of Åkerlöf. ~~were obtained in this work.~~ Acetone so purified had a capacitance of 227 which gives an E of 20.62. This value is in keeping with other workers. It is thought that the method of treatment of the acetone is responsible for the ~~lower~~ dielectric constant being smaller than that obtained by most workers. However, the low dielectric constant as obtained by Åkerlöf is probably due to the leak effect already mentioned.

2) DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE - BENZENE MIXTURES.

Acetone and benzene were purified in the manner already described. The mixtures were made in percentages of multiples of ten. These and subsequent mixtures were made in the following way. 125 CC pyrex **erlenmeyer flasks** were cleaned with chromic acid, washed and rinsed with distilled water and then thoroughly dried over a bunsen burner before being used for storing the mixtures. The weights necessary to make a given percentage of the first component were placed on the balance pan after the flask was counterbalanced. The liquid was poured into the flask until the balance point was nearly reached then the remainder of the liquid was introduced with a long medicine dropper. As soon as the balance point was obtained the weights for the second component were placed on the balance pan and the same procedure was followed in adding this material. Speed was necessary to avoid acetone evaporation and also to prevent the hygroscopic materials from picking up water.

The mixtures for this series were made in sufficient volume to fill the cell twice and to have a few cc for rinsing the cell between fillings. This procedure, however, was not necessary as the capacitance of the first and second fillings were in good agreement if the cell were thoroughly dried after an acetone wash before a second mixture was placed in it. All values marked with an (x) are not used in obtaining the mean capacitance.

ACETONE - BENZENE MIXTURES.

TABLE XVIII (a)

90% Acetone and 10% Benzene
Thermostated at 7.15 P.M.

TIME	C_2	C_3
7.15 P.M.	196.90	201.40 (X)
7.25 "	197.85	202.35
7.35 "	197.55	202.05
7.45 "	197.65	202.15
	Mean	202.20

TABLE XVIII (b)

80% Acetone and 20% Benzene

Thermostated at 8.45 A.M.

TIME	Δ C_2		C_3
9.20 A.M.	176.50		179.20
9.30 "	176.60		179.30
10.45 "	176.25		178.95
12.15 "	175.95		178.65 (a)
12.17 "	176.10		178.80 (a)
12.20 "	176.20		178.90
		Mean	179.10

(a) not used as some of the mixture evaporated and more had to be added. To prevent evaporation in subsequent work the overflow was closed with a screw clamp.

TABLE XVIII (c)

70% Acetone and 30% Benzene
Thermostated at 1.25 A.M.

Time	Δ C_2		C_3
1.25 A.M.	157.30		160.20 (x)
1.53 "	157.85		160.75
2.10 "	157.90		160.80
3.00 "	157.60		160.50
3.10 "	157.60		160.50
3.30 "	157.40		160.30
		Mean	160.55

TABLE XVIII (d)

60% Acetone and 40% Benzene

Thermostated at 8.00 P.M.

TIME	Δ C_2	C_3
9.05 P.M.	138.90	141.20
10.50 "	139.10	141.40
11.07	139.80	142.10
11.15	139.20	141.50
11.20	139.60	141.90
11.30	139.30	141.60
	Mean	141.60

TABLE XVIII (e)

50% Acetone and 50% Benzene

Thermostated at 11.40 P.M.

TIME	Δ C_2	C_3
12.15 A.M.	119.75	121.45
1.45 "	120.55	122.25
2.45 "	120.20	121.90
2.55 "	120.35	122.05
3.05 "	120.25	121.95
	Mean	121.90

TABLE XVIII (f)

40% acetone and 60% Benzene

Thermostated at 3.25 A.M.

TIME	Δ C_2	C_3
3.25 A.M.	102.05	103.15 (x)
4.15 "	101.90	103.00
4.30 "	101.80	102.90
6.20 "	101.70	102.80
6.25 "	101.80	102.90
		102.90

TABLE XVIII (g)

30% Acetone and 70% Benzene

Thermostated at 6.30 A.M.

TIME	Δ C_2	C_3
6.30 A.M.	83.25	84.15 (x)
6.40 "	83.45	84.25
8.50 "	83.05	83.85
8.55 "	83.30	84.10
9.20 "	83.15	83.95
		84.05

TABLE XVIII (h)

20% Acetone and 80% Benzene

Thermostated at 9.55 A.M.

TIME	Δ C_2		C_3	
9.55 A.M.	51.85		66.35	(X)
10.20 "	65.85		66.35	
10.50 "	65.90		66.45	
11.15 "	65.90		66.45	
		Mean	66.40	

TABLE XVIII (i)

10% Acetone and 90% Benzene

Thermostated at 11.18 A.M.

TIME	Δ C_2		C_3	
11.18 A.M.	50.05		50.35	(x)
11.37 "	50.00		50.30	
11.45 "	50.00		50.30	
12.50 P.M.	49.90		50.20	
12.57 "	50.00		50.30	
		Mean	50.30	

Beside determining the dielectric constants of this series of mixtures the polarizations $P_{1,2}$, were also calculated. The polarizations of mixtures is given by the expression:

$$P_{1,2} = \frac{E-1}{E+2} \cdot \frac{f_1 M_1 + f_2 M_2}{d}$$

where

E is the dielectric constant of the mixture
f_1 is the mole component with molecular weight M_1
f_2 is the mole fraction of the component with molecular weight M_2
d is the density d_4^{25}

when the polarization of a pure liquid is calculated this expression is reduced to the Clausius - Mosatti equation

$$P = \frac{E-1}{E+2} \frac{M}{d}$$

The density valuesused to evaluate $P_{1,2}$ were those obtained from the work of Ebersole (59). The densities (d_4^{25}) were plotted against the percentages given and the percentages necessary for the calculations were obtained by interpolation. Bingham and Brown (60) determined acetone - benzene mixture densities at twenty and thirty degrees. The densities for twenty-five degrees were obtained by the mean value method and were found to be in agreement with the densities given by Ebersole. Acetone - benzene densities were measured by Herz (61) at 16°C. When these values were plotted next to those of Ebersole a parallel relationship was observed.

The dielectric constants and polarizations are summarized in Table XIX. When the dielectric constants were plotted against mole fraction a slightly concave curve was obtained (Graph No.2, Curve I), but plotting polarization against mole fraction gave a convex curve with respect to the composition axis (Graph.No.3, Curve I).

TABLE XIX

DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE - BENZENE MIXTURES

% ACETONE	% BENZENE	f_1	f_2	C_3	d_4^{25}	E	$P_{1,2}$
100	00	1.0000	0.000	218.50	0.7862	19.83	63.87
90	10	0.9237	0.0763	202.20	0.7943	18.27	63.94
80	20	0.8433	0.1567	179.10	0.8032	16.08	63.91
70	30	0.7582	0.2416	160.55	0.8120	14.32	63.22
60	40	0.6686	0.3314	141.60	0.8219	12.52	62.46
50	50	0.5735	0.4265	121.90	0.8292	10.66	61.31
40	60	0.4728	0.5272	102.90	0.8370	8.86	59.36
30	70	0.3656	0.6344	84.05	0.8454	7.07	56.07
20	80	0.2516	0.7484	66.40	0.8547	5.40	50.83
10	90	0.1300	0.8700	50.30	0.8655	3.87	41.83
00	100	0.000	1,0000	33.70	0.8736	2.298	27.00

f_1 = mole fraction of acetone
f_2 = mole fraction of benzene
M_1 = 58.05
M_2 = 78.05

C_o = 10.55
C_L = 9.45

3) DIELECTRIC CONSTANT OF isoButyric ACID

Eastman Kodak Co., isoButyric acid was first fractionated with a Hempel column filled with 6 mm. glass beads. This gave a wide boiling range and only a small fraction of the total volume had a boiling point near the correct value. However, when the Hempel column, eight inches in length, was packed with glass single turn helices, about one millimeter thick and one quarter inch in diameter, much better fractionations could be obtained. On distilling the acid with this column about one-half of the acid gave a boiling range of 153.5° to 154° C (corr.). Since the available volume of the acid was small the fraction distilling between 110 and 153.5°C was again fractionated. Roughly one-half of this volume of acid had the same boiling.range as the fraction from the first distillation and hence it was added to it.

The dielectric constant of isoButyric acid was determined twice, once with the first calibration curve and again with the second calibration curve.

isoButyric Acid

TABLE XX (A)

Δ C_2		C_3
36.82		37.05
36.20		36.45
36.35		36.60
36.30		36.65
36.45		36.70
36.45		36.70
	Mean	36.70

No time was recorded but the period of observations was about one and one-half hours.

$C_1 = 9.45$ and $C_o = 10.55$

$E = 2.58$ for isoButyric acid.

This value was low compared to the interpolated value of Piekara (62).

After the standard condenser had been altered and the C_o of the cell determined the dielectric constant of isoButyric acid was measured once more. The day that the measurement had been made some water had leaked out of the bath and had wet the leads. C_3 for air at the outset was 47.75.

hence $C_L = 23.95$

TABLE XX (b)

Thermostated at 11.50 A.M.

TIME	Δ C_2	C_3
12.00 A.M.	86.50	86.90 (x)
12.12 P.M.	86.30	86.70
1.05 "	86.30	86.70
1.40 "	86.40	86.80
2. 05 "	86.35	86.75
	Mean	86.73

TABLE XX (c)

DIELECTRIC CONSTANTS OF isoBUTYRIC ACID

AUTHOR	TEMP.	E
Int.Critical Tables	16°	2.68
Drude (63)	20°	2.65
Piekara & Piekara (62)	25°	2.717 (i)
This work	25°	2.58
" "	25°	2.64

((i) interpolated)

Though the dielectric constants observed in this work is lower than the interpolated value of Piekara, it is comparable considering that most of Piekara's values for fatty acids are somewhat higher than those of other workers (Cf. (46)), also Table XXXI (b))

4) DIELECTRIC CONSTANTS OF ACETONE - isoBUTYRIC ACID MIXTURES.

The isoButyric acid from the standardization work was mixed with acetone according to the procedure already indicated. Since there was not enough acid to make nine mixtures the 70 and 50% mixtures were made from the 90 and 80% mixtures by further dilution with acetone. The dielectric constant obtained for the 50% mixture was high compared to the values of the mixtures on either side. Since all the acid had been used and also since there was some doubt as to the purity of the mixtures remaining, which were higher than 50% in isoButyric acid, because they had turned slightly green (the brass cell was only lightly plated with gold) all the mixtures were collected and distilled. The column already described was used and a good portion of the acid was recovered. Precautions were taken to allow a considerable amount of acid to distill over before the acid was collected as pure. The acid used for flushing the distilling apparatus and that collected had the same boiling range of the acid previously used. The second run of the 50% acid gave a dielectric value in agreement with other mixture values of this series.

ACETONE - isoButyric Acid Mixtures

TABLE XXI (a)

90% Acetone and 10% isoButyric Acid

Thermostated at 2.10 A.M.

TIME	Δ C_2	C_3
2.10 a.m.	444.90	455.40 (x)
2.20 "	442.95	453.45 (x)
2.43 "	441.30	451.80
2.53 "	441.45	451.95
3.00 "	441.40	451.90
		451.88

C_L = 20.40

TABLE XXI (b)

80% Acetone and 20% isoButyric Acid

Thermostated at 1.00 A.M.

TIME	Δ C_2		C_3
1.03 A.M.	409.65		418.55 (x)
1.14 "	408.20		417.10 (x)
1.23 "	407.90		416.80
1.35 "	407.70		416.60
1.53 "	407.70		416.60
		Mean	416.70

C_L = 20.40

TABLE XXI (c)

70% Acetone and 30% isoButyric Acid

Thermostated at 11.50 P.M.

TIME	Δ C_2	C_3
11.50 P.M.	370.25	377.65 (x)
12.00 "	369.00	376.40 (x)
12.12 A.M.	370.20	377.60
12.20 "	369.80	377.20
12.30 "	369.80	377.20
12.45 "	369.75	377.15
		377.18

C_L = 20.40

The temperature of the thermostat went above 25°C after the first reading, it was, however, corrected before the third reading.

TABLE XXI (d)

60% Acetone and 40% isoButyric Acid

Thermostated at 7.35 P.M.

TIME	Δ C_2		C_3
7.35 P.M.	332.35		338.20 (x)
8.00 "	331.35		337.20
8.15 "	331.05		336.90
8.40 "	331.40		337.25
8.45 "	331.60		337.45
		Mean	337.20

C_L = 20.40

TABLE XXI (e)

50% Acetone and 50% isoButyric Acid

(A repeat) Thermostated at 3.15 A.M.

TIME	Δ C_2		C_3
3.15 A.M.	296.40		301.10 (x)
3.22 "	296.55		301.25
3.35 "	295.25		299.95
3.45 "	295.15		299.85
		Mean	300.00

C_2 = 20.40

TABLE XXI (f)

40% Acetone and 60% isoButyric Acid

Thermostated at 5.23 P.M.

TIME	Δ C_2		C_3
5.23 P.M.	260.55		264.15 (x)
5.50 "	260.65		264.25
6.15 "	259.75		263.35
6.25 "	259.40		263.00
6.30 "	259.60		263.20
7.03 "	259.40		263.00
		Mean	263.55

C_L = 20.40

TABLE XXI (g)

30% Acetone and 70% isoButyric Acid

Thermostated at 9.17 P.M.

TIME	Δ C_2	C_3
9.17 P.M.	216.30	218.90 (x)
9.45 "	215.75	218.25
9.57 "	215.85	218.35
10.15 "	215.65	218.15
10.20 "	215.80	218.30
	Mean	218.25

C_L = 20.40

TABLE XXI (h)

20% Acetone and 80% isoButyric Acid

Thermostated at 3.35 P.M.

TIME	Δ C_2	C_3
3.35 P.M.	171.90	173.45 (x)
3.55 "	171.90	173.45
4.22 "	171.50	173.05
4.43 "	171.70	173.25
4.57	171.70	173.25
	Mean	173.25

C_1 = 20.40

TABLE XXI (i)

10% Acetone and 90% isoButyric Acid

Thermostated at 1.45 P.M.

TIME	Δ C_2	C_3
1.45 P.M.	127.00	127.85 (x)
2.05 "	126.80	127.65
2.17 "	126.80	127.65
2.40 "	126.60	127.45
3.10 "	126.70	127.55
		127.57

C_L = 20.40

No density data was available to calculate the polarizations and therefore only the dielectric constants have been tabulated. The dielectric constants are plotted against mole fraction giving a concave curve with respect to the composition axis. (See Graph. No.2 Curve II.)

TABLE XXII.

DIELECTRIC CONSTANTS OF ACETONE - isoBUTYRIC ACID MIXTURES.

% Acetone	% isoButyric Acid	f_1	f_2	C_3	E	R (ohms)
100	00	1.0000	0.000	492.05	19.82	10,000
90	10	0.9316	0.0682	451.88	18.13	7,400
80	20	0.8583	0.1415	416.70	16.65	8,500
70	30	0.7795	0.2206	377.18	14.99	8,400
60	40	0.6946	0.3054	337.20	13.31	10,000
50	50	0.6025	0.3986	300.00	11.75	14,000
40	60	0.5030	0.4970	263.55	10.22	15,000
30	70	0.3939	0.6059	218.25	8.31	55,000
20	80	0.2750	0.7250	173.25	6.42	100,000 (approx.)
10	90	0.1442	0.8558	127.57	4.51	100,000 "
00	100	0.0000	1.0000	" 86.73	2.64	400,000 "

f_1 = mole fraction of acetone

f_2 = " " " isoButyric Acid

C_1 = 20.40 in all cases

except (") where it is 23.95

5) DIELECTRIC CONSTANT OF BUTYRIC ACID

Before mixtures were made of butyric acid and acetone for dielectric constant measurements, the dielectric constant of butyric acid was determined. The butyric acid used was obtained from Eastman Kodak Co., and was fractionated with the Hempel column packed with glass helices. Fractionation with glass beads in the Hempel column gave a very small portion of acid near the correct boiling point. Besides when the acid so purified was placed in the cell the dielectric constant calculated from the capacitance of the acid was too high compared to the results of other workers. (46) (62). Using the column with the helices the boiling point remained at 110° for a while and then quickly went upto the vicinity of the correct boiling point. But with beads in the column the rise in boiling point was more gradual.

The fraction collected and used distilled between 162.0 and 162.7°C (corr.) This boiling range is somewhat lower than that of Smyth and Rogers (46) but it is in agreement with the International Critical Tables of 162.4°C.

BUTYRIC ACID

TABLE XXIII (a)

Thermostated at 7.25 P.M.

TIME	Δ C_2	C_3
7.25 P.M.	89.60	90.00 (x)
7.40 "	88.80	89.20
7.53 "	38.95	89.35
8.07 "	88.75	89.15
8.12 "	88.50	88.90
	Mean	89.20

C_L = 20.10 (C_3 for air is 43.90)

DIELECTRIC CONSTANTS OF BUTYRIC ACID.

TABLE XXIII (b)

AUTHOR	TEMP.	E.
Piekara & Piekara (62)	25°C	3,006 (i)
Smyth & Rogers (46)	25°C	2.966 (i)
Int.Critical Tables	16°C	2,93
" " "	20°C	2.85
This work	25°C	2.90

((i) interpolated)

Though the dielectric constant of butyric acid observed is lower than that of Piekara and Piekara, it is comparable with that of other workers.

6) THE DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE - BUTYRIC ACID MIXTURES.

The first two mixtures that were made had high resistance and the dielectric constants gave almost a linear relationship but the subsequent mixtures made from these gave very low resistances (560 ohms with 10% butyric acid). Besides the dielectric constants did not fall in line with the first two mixtures that were measured. Contamination of some electrolyte was probably responsible for the high conductivity. Nevertheless the butyric acid was recovered from the mixtures as in the case of the isoButyric acid and new mixtures were made for the remainder of the series. A new C_L was also found for the last part of the series since the work was done on another day.

TABLE XXIV (a)

90% Acetone and 10% Butyric Acid

Thermostated at 8.03 P.M.

TIME	Δ C_2	C_3
8.10 P.M.	447.45	458.25 (x)
8.30 "	446.25	457.05
8.43 "	445.80	456.60
8.53 "	445.85	456.65
	Mean	456.77

C_L = 20.40 (C_3 for air is 44.20)

TABLE XXIV (b)

80% Acetone and 20% Butyric Acid

(This mixture was made for 70% Butyric Acid and 30% Acetone).

Thermostated at 9.07 P.M.

TIME	$\Delta\ C_2$		C_3
9.12 P.M.	413.00		422.20 (x)
9.33 "	412.00		421.20
9.47 "	411.90		421.10
		Mean	421.15

C_L = 20.40

TABLE XXIV (c)

70% Acetone and 30% Butyric Acid

Thermostated at 4.32 P.M.

TIME	$\Delta\ C_2$		C_3
4.38 P.M.	378.15		385.80 (x)
4.57 "	376.60		384.25
5.20 "	376.05		383.70
5.35 "	376.15		383.80
		Mean	383.90

C_L = 20.40

TABLE XXIV (d)

60% Acetone and 40% Butyric Acid

Thermostated at 6.50 P.M.

TIME	Δ C_2		C_3
7.10 P.M.	340.10		346.25
7.35 "	340.20		346.35
7.45 "	340.05		346.20
		Mean	346.30

C_L = 20.40

TABLE XXIV (e)

50% Acetone and 50% Butyric Acid

Thermostated at 3.38 P.M.

TIME	Δ C_2		C_3
3.42 P.M.	306.75		311.85
4.00 "	306.80		311.90
4.15 "	306.90		312.00
		Mean	311.90

C_L = 20.40

TABLE XXIV (f)

40% Acetone and 60% Butyric Acid

Thermostated at 5.52 P.M.

TIME	Δ C_2		C_3
5.58 P.M.	271.05		274.95 (x)
6.20 "	270.45		274.35
6.37 "	270.00		273.95
		Mean	274.20

C_L = 20.40

TABLE XXIV (g)

30% Acetone and 70% Butyric Acid

Thermostated at 2.35 P.M.

TIME	Δ C_2		C_3
2.40 P.M.	228.90		231.70 (x)
2.55 "	228.70		231.50
3.10 "	228.80		231.60
3.22 "	228.40		231.20
		Mean	231.45

C_L = 20.40

TABLE XXIV (h)

20% Acetone and 80% Butyric Acid

Thermostated at 1.40 P.M.

TIME	Δ C_2	C_3
1.43 P.M.	183.10	184.95 (x)
2.04 "	182.85	184.70
2.20 "	182.85	184.70
	Mean	184.70

C_L = 20.10 (C_3 for air is 43.90)

TABLE XXIV (i)

10% Acetone and 90% Butyric Acid

Thermostated at 10.10 A.M.

TIME	Δ C_2	C_3
10.10 A.M.	136.45	137.45
10.20 "	136.10	137.10
10.40 "	136.10	137.10
10.53 "	136.20	137.20
	Mean	137.15

C_L = 20.10

Density data for the polarization calculations for acetone - butyric acid mixtures could not be found in the literature. The densities of the mixtures of this series had been measured roughly with a Mohr-Westphal balance. The probable error in these measurements is about one percent.

TABLE XXIV (j)

AUTHOR	Acetone d_4^{25}	Butyric Acid d_4^{25}
Kendall (64)	0.7874	-
Ebersole (59)	0.7862	-
Int.Critical Tables	0.7844	0.9534
This work	0.778	0.947

A density error of one percent will produce an error of about one percent in the polarizations which will alter the polarization curve by only a small amount. If the error is in the same direction and the densities are relatively in agreement, then the effect on the shape of the polarization curve will be even less.

TABLE XXV

ACETONE - BUTYRIC ACID DENSITIES.

% ACETONE	% BUTYRIC ACID	d_4^{25}
100	00	0.778
90	10	0.799
80	20	0.814
70	30	0.830
60	40	0.848
50	50	0.863
40	60	0.881
30	70	0.898
20	80	0.915
10	90	0.932
00	100	0.947

When the densities are plotted against percentages of the mixtures an almost linear relationship is observed. The dielectric constant and polarization results are summarized in Table XXVI and plotted against mole fractions in Graph No.2, Curve III and Graph No.4, Curve III respectively.)

TABLE XXVI

DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE-BUTYRIC ACID MIXTURES.

% ACETONE	% BUTYRIC ACID	f_1	f_2	C_3	d_4^{25}	E	$P_{1,2}$	R (ohms)
100	00	1.0000	0.000	492.30	0.778	19.84	64.37	10,000
90	10	0.9316	0.0682	456.77	0.799	18.35	64.11	10,000
80	20	0.8583	0.1415	421.15	0.814	16.85	64.19	6,000
70	30	0.7795	0.2206	382.70	0.830	15.24	64.32	12,000
60	40	0.6946	0.3054	346.30	0.848	13.70	64.03	10,000
50	50	0.6025	0.3986	311.90	0.863	12.26	63.19	20,000
40	60	0.5030	0.4970	274.20	0.881	10.68	62.64	14,000
30	70	0.3939	0.6059	231.45	0.898	8.88	61.40	70,000
20	80	0.2750	0.7250 "	184.70	0.915	6.90	57.83	250,000
10	90	0.1442	0.8558 "	137.15	0.932	4.90	50.78	100,000
00	100	0.0000	1.0000 "	89.20	0.947	2.90	36.05	200,000

f_1 = mole fraction of acetone

f_2 = mole fraction of butyric acid

M_1 = 58.05

M_2 = 88.06

C_L = 20.10 except (") where C_L = 20.40

7) DIELECTRIC CONSTANT OF PROPIONIC ACID.

The Schuchardt, Gorlitz Germany, propionic acid was fractionated twice. The fraction which was used distilled between 140.2° and 140.7° C (corr.). International Critical Tables give the boiling point of propionic acid as 140.0°C. The column packed with helices was used for these fractionations.

PROPIONIC ACID

TABLE XXVII (a)

Thermostated at 2.00 P.M.

TIME	ΔC_2	C_3
2.20 P.M.	96.15	96.55
2.40 "	96.15	96.55
2.50 "	96.25	96.75
	Mean	96.60

C_L = 20.10 (C_3 of air is 43.90)

DIELECTRIC CONSTANTS OF PROPIONIC ACID

TABLE XXVII (b)

AUTHOR	TEMP.	E
Piekara & Piekara (62)	25°C	3.316 (i)
Int.Critical Tables	17°C	3.21
" " "	19°C	3.19
This work	25°C	3.21

((i) interpolated)

8.) DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE - PROPIONIC ACID MIXTURES.

These mixtures were made from the acid of the same lot as that used in determining the dielectric constant of propionic acid, and the acetone was treated in the manner as previously described. The acetone had a capacitance of 490.55 units. C_3 for air was 43.90.

TABLE XXVIII (a)

90% Acetone and 10% Propionic Acid.

Thermostated at 10.30 P.M.

TIME	ΔC_2	C_3
10.40 P.M.	448.55	459.35 (x)
11.00 "	447.00	457.80
11.12 "	446.40	457.20
11.22 "	445.90	456.60
	Mean	457.20

C_L = 20.10

TABLE XXVIII (b)

80% Acetone and 20% Propionic Acid

Thermostated at 9.22 P.M.

TIME	ΔC_2	C_3
9.35 P.M.	420.25	429.65 (x)
9.50 "	418.35	427.75
10.00 "	417.80	427.20
10.15 "	418.35	427.75
	Mean	427.60

C_L = 20.10

TABLE XXVIII (c)

70% Acetone and 30% Propionic Acid.

Thermostated at 8.35 P.M.

TIME	ΔC_2	C_3
8.35 P.M.	387.85	395.90 (x)
8.55 "	386.45	394.50
9.05 "	386.80	394.85
9.10 "	386.60	394.65
	Mean	394.65

C_L = 20.10

TABLE XXVIII (d)

60% Acetone and 40% Propionic Acid

Thermostated at 7.35 P.M.

TIME	ΔC_2	C_3
7.40 P.M.	353.45	360.05 (x)
8.05 "	351.95	358.55
8.17 "	351.90	358.55
	Mean	358.55

C_L = 20.10

TABLE XXVIII (e)

50% Acetone and 50% Propionic Acid

Thermostated at 6.45 P.M.

TIME	ΔC_2	C_3
6.47 P.M.	319.90	325.40 (x)
7.13 "	319.00	324.50
7.23 "	318.90	324.40
	Mean	324.45

C_L = 20.10

TABLE XXVIII (f)

40% Acetone and 60% Propionic Acid

Thermostated at 11.30 P.M.

TIME'	ΔC_2	C_3
11.37 P.M.	285.15	289.45 (x)
11.48 "	283.90	288.20
11.57 "	283.50	287.80
12.10 A.M.	283.85	288.15
	Mean	288.05

C_L = 20.10

TABLE XXVIII (g)

30% Acetone and 70% Propionic Acid

Thermostated at 5.16 P.M.

TIME	ΔC_2	C_3
5.25 P.M.	245.50	248.70 (x)
5.40 "	245.10	248.30
5.55 "	245.05	248.25
6.14 "	245.00	248.20
	Mean	248.25

C_L = 20.10

TABLE XXVIII (h)

20% Acetone and 80% Propionic Acid

Thermostated at 4.20 P.M.

TIME	ΔC_2	C_3
4.22 P.M.	199.15	201.25 (x)
4.43 "	198.90	201.00
4.58 "	198.80	200.90
	Mean	200.95

TABLE XXVIII (i)

10% Acetone and 90% Propionic Acid

Thermostated at 3.00 P.M.

TIME	ΔC_2	C_3
3.10 P.M.	148.25	149.50 (x)
3.32 "	148.75	150.00
3.57 "	148.70	149.95
	Mean	150.00

$C_L = 20.10$

The densities of these mixtures were determined with the same apparatus as in the case of the acetone-butyric acid mixtures.

ACETONE-PROPIONIC ACID DENSITIES

TABLE XXIX.

% ACETONE	% PROPIONIC ACID	d_4^{25}
100	00	0.778
90	10	0.798
80	20	0.820
70	30	0.835
60	40	0.858
50	50	0.878
40	60	0.898
30	70	0.920
20	80	0.940
10	90	0.963
00	100	0.984

The dielectric constant and polarization results are summarized in TABLE XXX. The graphic relationship of dielectric constant and mole fractions are given in graph No.2 (Curve IV). Mole fractions are plotted against polarization in graph No. 4 (Curve IV). The dielectric constant curve is slightly convex and the polarization curve is considerably less convex than the polarization curve of butyric acid.

TABLE XXX.

DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE-PROPIONIC ACID MIXTURES.

% ACETONE	% PROPIONIC ACID	f_1	f_2	C_3	d_4^{25}	E	$P_{1,2}$	R (ohms)
100	00	1.0000	0.0000	490.55	0.778	19.77	63.25	10,000
90	10	0.9198	0.0801	457.20	0.798	18.37	63.42	7,100
80	20	0.8360	0.1639	427.60	0.820	17.12	62.09	10,000
70	30	0.7485	0.2515	394.65	0.835	15.74	61.78	11,000
60	40	0.6566	0.3433	358.55	0.858	14.22	60.36	14,000
50	50	0.5606	0.4393	324.45	0.879	12.79	59.01	13,000
40	60	0.4493	0.5406	288.05	0.898	11.26	56.96	25,000
30	70	0.3535	0.6465	243.25	0.920	9.53	55.09	32,000
20	80	0.2418	0.7582	200.95	0.940	7.60	51.09	100,000
10	90	0.1241	0.8760	150.00	0.963	5.46	44.74	> 500,000
00	100	0.0000	1.0000	96.60	0.984	3.21	31.92	>500,000

f_1 = mole fraction of acetone

f_2 = mole fraction of propionic acid

C_L = 20.10

M_1 = 58.05

M_2 = 74.05

9.) THE DIELECTRIC CONSTANT OF ACETIC ACID.

Because of its hygroscopisity acetic acid is difficult to purify. Smyth and Rogers (46), starting with glacial acetic acid, crystallized twelve times and finally obtained acetic acid melting at 16.6°C. The same procedure of purification was attempted. After three crystallizations the melting point of the acid was 15.9°C. Three additional crystallizations failed to raise the melting point above 15.9°C. Since the crystallizations were made in the winter time the laboratory windows were opened to bring the temperature to 10°C. Because of the humidity of the air sometimes after a crystallization the melting point of the fraction crystallized was actually lower than that from which the crystallization had taken place.

Since the small column with the helices had given such excellent fractionations with the other acids, it was decided to purify the acetic acid by this method.

General Chemical 99.5% glacial acetic acid was fractionated twice. The final fraction was used for the determination of the dielectric constant of acetic acid and the acetone-acetic acid mixtures distilled between 117.6° and 117.8° C (corr.) Smyth and Rogers (46) fractioned by distillation the acetic acid that had been crystallized twelve times and collected the fraction distilling at 117.8°C. As some of the acid purified by crystallization was on hand the capacitance of it was determined and found to be 231.05 units, which gave a dielectric constant of 8.83. C_3 for air and acetone were 45.15 and 492.75 respectively.

ACETIC ACID.

TABLE XXXI (a)

Thermostated at 2.07 P.M.

TIME	ΔC_2	C_3
2.10 P.M.	166.10	167.65 (x)
2.18 "	165.80	167.35
2.45 "	165.75	167.30
2.55 "	165.85	167.40
3.10 "	166.15	167.75
	Mean	167.50

C_L = 21.35

DIELECTRIC CONSTANTS OF ACETIC ACID

TABLE XXXI (b)

AUTHOR	TEMP.	E.
Piekara & Piekara)(62)	25°C.	6.476 (i)
Smyth & Rogers (46)	25°C.	6.18 (i)
This,work	25°C.	6.14

((i) interpolated)

The dielectric constant of acetic acid from this work is in good agreement with the value obtained by Smyth and Rogers. The dielectric constants of fatty acids determined by these authors are in general lower than those of Piekara and Piekara.

10) DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETIC ACID.

These mixtures were weighed out quickly to prevent absorption of moisture from the atmosphere. Their capacitances were determined within two hours after the solutions had been made up.

TABLE XXXII (a)

90% Acetone and 10% Acetic Acid

Thermostated at 1.53 P.M.

TIME	ΔC_2		C_3	
2.00 P.M.	458.95		470.30	(x)
2.17 "	459.05		470.40	
2.40 "	458.85		470.20	
3.10 "	459.10		470.45	
3.25 "	459.50		470.85	
		Mean	470.50	

C_L = 21.00 (C_3 for air = 44.80)

TABLE XXXII (b)

80% Acetone and 20% Acetic Acid

Thermostated at 12.08 P.M.

TIME	ΔC_2		C_3	
12.15 P.M.	436.80		447.10	(x)
12.55 "	435.20		445.50	
1.10 "	435.50		445.80	
1 .30 "	436.00		446.30	
1.35 "	435.80		446.10	
		Mean	445. 90	

C_L = 21.00

TABLE XXXII (c)

70% Acetone and 30% Acetic Acid

Thermostated at 10.30 A.M.

TIME	ΔC_2	C_3
10.35 A.M.	412.00	421.10 (x)
10.50 "	410.05	419.15
11.07 "	409.70	418.80
11.22 "	410.25	419.30
11.40 "	409.90	418.95
11.55 "	409.85	418.90
	Mean	419.00

C_L = 21.00

TABLE XXXII (d)

60% Acetone and 40% Acetic Acid

Thermostated at 10.05 P.M.

TIME	ΔC_2	C_3
10.08 P.M.	389.70	397.85, (x)
10.20 "	388.20	396.35
10.35 "	387.95	396.10
10.50 "	387.65	395.80
11.00 "	388.25	396.40
11.10 "	387.95	396.15
	Mean	396.15

C_L = 21.35

TABLE XXXII (e)

50% Acetone and 50% Acetic Acid

Thermostated at 8.50 P.M.

TIME	ΔC_2	C_3
8.58 P.M.	362.10	369.10)x)
9.07 "	361.15	368.15
9.23 "	361.00	368.00
9.35 "	361.10	368.10
9.53 "	361.05	368.05
	Mean	368.05

C_L = 21.35

TABLE XXXII (f)

40% Acetone and 60% Acetic Acid

Thermostated at 7.35 P.M.

TIME	ΔC_2	C_3
7.40 P.M.	333.10	338.95 (x)
7.45 "	331.75	337.60 (x)
8.12 "	331.40	337.25
8.30 "	331.40	337.25
8.45 "	331.30	337.15
	Mean	337.20

C_L = 21.35

TABLE XXXII (g)

30% Acetone and 70% Acetic Acid

Thermostated at 6.15 P.M.

TIME	ΔC_2	C_3
615 P.M.	305.10	310.10 (x)
6.30 "	304.25	309.25
7.10 "	303.95	308.95
7.25 "	303.80	308.80
	Mean	309.00

$C_L = 21.35$

TABLE XXXII (h)

20% Acetone and 80% Acetic Acid

Thermostated at 4.37 P.M.

TIME	ΔC_2	C_3
4.37 P.M.	269.85	273.70 (x)
4.53 "	269.10	273.00
5.10 "	269.05	272.95
5.35 "	270.30	274.20
5.40 "	270.20	274.10
5.50 "	269.40	273.30
6.00 "	269.95	273.85
	Mean	273.60

$C_L = 21.35$

TABLE XXXII (i)

10% Acetone and 90% Acetic Acid

Thermostated at 3.25 P.M.

TIME	ΔC_2		C_3
3.25 P.M.	324.40		227.10 (x)
3.45 "	224.00		226.70
3.55 "	223.90		226.60
4.12 "	223.70		226.40
4.25 "	223.95		226.65
		Mean	226.60

$C_L = 21.35$

The densities used in calculating the polarizations of acetone-acetic acid mixtures are the interpolated values of Kendall and Brakeley (64). Densities determined with the Mohr-Westphal balance were comparable with those of Kendall and Brakeley.

The dielectric constants and polarizations of this series are summarized in Table XXXIII and the results are represented graphically Graph. No. 2 (Curve V) and Graph No. 4 (Curve V).

The dielectric constant curve is more convex than the propionic acid curve, which is more convex than the butyric acid curve. The acetone-acetic acid polarization curve is less convex than the acetone-propionic acid polarization curve, which is less convex than the acetone-butyric acid curve.

TABLE XXXIII.

DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE-ACETIC ACID MIXTURES.

% ACETONE	% ACETIC ACID	f_1	f_2	C_3	E	d_4^{25}	$P_{1,2}$	R (ohms)
100	00	1.0000	0.0000	492.75	19.81	0.7874	63.57	17,000
90	10	0.9030	0.0970	"470.50	18.89	0.8094	61.65	2,900
80	20	0.8054	0.1947	"445.90	17.85	0.8347	59.48	2,900
70	30	0.7068	0.2931	"419.05	16.73	0.8570	57.48	3,000
60	40	0.6081	0.3928	396.15	15.75	0.8830	55.42	5,200
50	50	0.5084	0.4917	368.05	14.57	0.9070	53.31	5,100
40	60	0.4080	0.5919	337.20	13.27	0.9340	50.97	6,500
30	70	0.3070	0.6929	309.00	12.06	0.9620	48.58	7,100
20	80	0.2054	0.7946	273.60	10.60	0.9900	45.61	10,000
10	90	0.1030	0.8968	226.60	8.62	1.024	41.93	26,000
00	100	0.0000	1.0000	167.50	6.14	1.0499	36.95	140,000

f_1 = mole fraction of acetone

f_2 = mole fraction of acetic acid

M_1 = 58.05

M_2 = 60.03

C_L = 21.35 except (") where

C_1 = 21.00

11) THE DIELECTRIC CONSTANT OF PROPIONALDEHYDE

Elmer and Amend, New York, propionaldehyde was fractionated and the portion distilling between 48°C and 49°C (corr.) was collected and used. The resistance of the propionaldehyde was somewhat lower than that of pure acetone (see Table XXXV) and dropped from 7,500 to 4,700 ohms within half an hour. Partington and Coomber(65) determined the dipole moment of propionaldehyde but did not determine the dielectric constant of pure propionaldehyde. The International Critical Tables give two values for the dielectric constant of propionaldehyde but neither value is at 25°C. These values were determined by Drude and Thwing.

TABLE XXXIV (a)

PROPIONALDEHYDE

Thermostated at 4.00 P.M.

TIME	ΔC_2		C_3
4.05 P.M.	434.60		444.50 (x)
4.15 "	427.70		437.60
4.20 "	427.40		437.20
4.30 "	427.40		437.20
		Mean	437.30

C_1 = 20.60 (C_3 for air is 44.50)

C_0 = 23.90 (Second standardization)

DIELECTRIC CONSTANTS OF PROPIONALDEHYDE

TABLE XXXIV (b)

AUTHOR	TEMP.	E.
Drude (54)	17°C	18.9 ± 4
Thwing (66)	14°C	14.4
This work	25°C	17.44

The dielectric constant determined is in fair agreement with that of Drude (dielectric constants decrease as a rule with increase of temperature) but is not comparable with that obtained by Thwing.

12) THE DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE-PROPIONALDEHYDE MIXTURES.

Only a small quantity of propionaldehyde was available, 50 cc, and therefore fewer mixtures were made than in previous cases. The 80% mixture of propionaldehyde was used to make the 60% mixture, which in turn was diluted with acetone to make the 40% mixture. The 20% propionaldehyde mixture was made from pure propionaldehyde. The acetone used for these mixtures was prepared in the usual way and had a capacitance of 495.30 and a resistance of 15,000 ohms.

TABLE XXXV (a)

80% ACETONE AND 20% PROPIONALDEHYDE

Thermostated at 10.25 P.M.

TIME	ΔC_2	C_3
10.30 P.M.	472.65	484.44 (x)
10.42 "	471.10	483.00
10.50 "	470.55	482.45
10.55 "	470.70	482.65
	Mean	482.65.

C_T = 20.60

TABLE XXXV (b)

60% Acetone and 40% Propionaldehyde

Thermostated at 9.40 P.M.

TIME	ΔC_2		C_3
9.45 P.M.	465.50		473.90 (x)
9.57 "	461.30		472.70
10.08 "	461.05		472.45
10.15 "	461.10		472.50
		Mean	472.55

C_L = 20.60

TABLE XXXV (c)

40% Acetone and 60% Propionaldehyde

Thermostated at 8.45 P.M.

TIME	ΔC_2		C_3
8.50 P.M.	454.50		464.50 (x)
9.00 "	451.05		462.05
9.17 "	452.25		463.25 (x)
9.25 "	452.10		463.10
		Mean	462.55

The temperature dropped 0.2°C between 9.00 and 9.17 and hence the third value was not used in the mean

C_L = 20.60.

TABLE XXXV (d)

20% Acetone and 80% Propionaldehyde

Thermostated at 8.00 P.M.

TIME	ΔC_2		C_3
8.07 P.M.	441.30		451.80 (x)
8.15 "	443.80		454.30 (x)
8.30 "	440.70		451.20
8.38 "	441.05		451.55
		Mean	451.35

C_L = 20.60

Because of the similarity of the two materials the densities were assumed to be in linear relationship and as previously pointed out a one percent error in the densities does not alter the $P_{1,2}$ curve appreciably. The dielectric constants and polarizations are summarized in Table XXXVI and the results are plotted against mole fraction in Graphs No. 2 (Curve VI), Graph No. 3 (Curve VI). Both dielectric constants and polarizations vary almost linearly with mole fraction.

TABLE XXXVI.

DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE-PROPIONALDEHYDE MIXTURES.

% ACETONE	% PROPIONALDEHYDE	f_3	f_2	C_3	E	d_4^{25}	$P_{1,2}$	R_1	R_2
100	00	1.0000	0.0000	495.30	19.86	0.787	63.57	15,000	15,000
80	20	0.8000	0.2000	482.65	19.33	0.802	62.20	5,000	4,000
60	40	0.6000	0.4000	472.55	18.91	0.817	60.85	4,000	3,600
40	60	0.4000	0.6000	462.55	18.49	0.837	59.20	3, 400	3,000
20	80	0.2000	0.8000	451.35	18.02	0.853	57.86	4,400	2 ,300
.00	100	0.0000	1.0000	437.30	17.44	0.865	56.76	7,500	4,700

f_1 = mole fraction of acetone

f_2 = mole fraction of propionaldehyde

M_1 = 58.05

M_2 = 58.05

R_1 = resistance at the beginning of the determination

R_2 = resistance at the end of the determination.

C_L = 20.60

C_o = 23.90

13) DIELECTRIC CONSTANT OF TOLUENE.

Merk reagent quality toluene was allowed to stand over sodium until effervescence ceased. It was then distilled and the fraction distilling at 110.5°C (corr.) was collected and used. International Critical Tables give 110.7°C as the boiling point of toluene.

TOLUENE

TABLE XXXVII (a)

THERMOSTATED AT 3.08 P.M.

TIME	ΔC_2	C_3
3.10 P.M.	76.55	76.90
3.25 "	76.75	77.10
3.47 "	76.20	76.55
4.00 "	76.70	77.05
4.05 "	76.60	76.95
	Mean	76.90

C_L = 20.20 (C_3 for air is 44.10)

DIELECTRIC CONSTANTS OF TOLUENE

TABLE XXXVII (b)

AUTHOR	TEMP.	E
Schupp (67)	18°C	2.31
Int. Critical Tables (68)(69)	20°C	2.387 ± 5
Int. Critical Tables	80°C	2.25
" "	25°C	2.376 (x)
Grutzmacher (70)	25°C	2.36 (x)
Richards & Shipley (71)	20°C	2.335
Hyslop & Carman (72)	21°C	2.39
Williams (73)	25°C	2.370 ± .003
This work	25°C	2.37

((x) interpolated)

The dielectric constant obtained for Toluene is in very good agreement with the value of Williams,who worked at a similar frequency and used toluene distilling between 110.6° and 110.8°C. The results of the other authors are also in close agreement with the dielectric constant measured in this work.

14) THE DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE-TOLUENE MIXTURES.

The acetone-toluene mixtures were made in the usual way. An additional mixture was made in this series to see if any break in the dielectric constant curve took place with a dilute toluene mixture. The acetone-benzene dielectric constant plotted against percentage gave a concave curve except in the dilute benzene mixture (10%) the curve became slightly convex. C_3 for acetone was 493.95 units, and for air 44.10 units.

TABLE XXXVIII (a)

95% acetone and 5% Toluene

Thermostated at 10.55 P.M.

TIME	ΔC_2		C_3
11.00 P.M.	463.10		474.55 (x)
11.35 "	461.00		472.45
11.42 "	461.00		472.45
		Mean	472.45

C_L = 20.20

90% Acetone and 10% Toluene

Thermostated at 4.30 P.M.

TIME	ΔC_2	C_3
4.32 P.M.	433.00	443.30 (x)
4.45 "	436.60	446.90
4.55 "	436.05	446.35
5.00 "	435.65	445.95

C_L = 20.20

TABLE XXXVIII (c)

80% Acetone and 20% Toluene

Thermostated at 5.10 P.M.

TIME	ΔC_2	C_3
5.12 P.M.	389.45	397.60 (x)
535 "	389.15	397.30
5.43 "	388.80	396.95
5.50 "	389.05	397.20
	Mean	397.15

C_L = 20.20

TABLE XXXVIII (d)

70% Acetone and 30% Toluene

Thermostated at 5.55 P.M.

TIME	ΔC_2	C_3
6.00 P.M.	342.65	348.85 (x)
6.14 "	341.75	347.95
6.23 "	341.55	347.75
6.30 "	341.10	347.30
	Mean	347.65

C_L = 20.20

TABLE XXXVIII (e)

60% Acetone and 40% Toluene

Thermostated at 6.40 P.M.

TIME	ΔC_2	C_3
6.45 P.M.	302.30	307.30 (x)
7.05 P.M.	301.45	306.45
7.20 "	302.88	307.88
7.25 "	303.20	308.20
7.35 "	302.85	307.85
	Mean	307.60

C_L = 20.20

TABLE XXXVIII (f)

50% Acetone and 50% Toluene

THERMOSTATED AT 7.45 P.M.

TIME	ΔC_2	C_3
7.45 P.M.	265.40	269.10 (x)
8.15 "	263.95	267.65
8.23 "	264.00	267.70
	Mean	267.70

C_L = 20.20

TABLE XXXVIII (g)

40% Acetone and 60% Toluene

Thermostated at 8.32 P.M.

TIME	ΔC_2	C_3
8.35 P.M.	223.20	225.95 (x)
8.55 "	222.40	223.00
9.05 "	222.55	223.15
	Mean	223.10

C_L = 20.20

TABLE XXXVIII (h)

30% Acetone and 70% Toluene

Thermostated at 9.15 P.M.

TIME	ΔC_2	C_3
9.15 P.M.	183.05	184.85 (x)
9.35 "	182.60	184.40
9.40 "	182.50	184.30
	Mean	184.35

C_L = 20.20

TABLE XXXVIII (i)

20% Acetone and 80% Toluene

Thermostated at 9.50 P.M.

TIME	ΔC_2	C_3
9.53 P.M.	145.65	146.90 (x)
10.10 "	145.45	146.70
10.20 "	145.40	146.65
	Mean	146.65

C_L = 20.20

TABLE XXXVIII (j)

10% Acetone and 90% Toluene

Thermostated at 10.30 P.M.

TIME	ΔC_2	C_3
10.30 P.M.	109.60	110.20 (x)
10.45 "	109.45	110.05
10.50 "	109.35	110.00
	Mean	110.05

C_L = 20.20

The densities tabulated below are based on the density formula of Andersin and Hirn(74) which was obtained from the International Critical Tables. Since the constants of the formula were given only for 13°, 16° and 22°C. the constants were extropolated to 25°C. With the extropolated constants the formula became

$$d_4^{25} = 0.7855 + 0.000726 X$$

where X is the percentage weight of toluene.

To check the densities resulting from the extropolation they were plotted beside the d_4^{22} densities.

The graphs of the densities at both temperatures were entirely of the same shape and were parallel with one another. The density for Toluene obtained by this formula at 25°C is 0,8581, which is in good agreement with 0.8610, the density given by International Critical Tables. The density of acetone also obtained from the formula agrees well with that of Ebersole (59), Kendall and Brokeley (64) and Bingham and Brown (60.)

TABLE XXXIX
ACETONE - TOLUENE DENSITIES

% Toluene	d_4^{25}
0	0.7855
5	0.7897
10	0.7928
20	0.8000
30	0.8073
40	0.8145
50	0.8218
60	0.8290
70	0.8363
80	0.8436
90	0.8508
100	0.8581

The dielectric constants and polarizations of acetone-toluene mixtures are summarized in Table XXXX, and the dielectric constant and polarization, mole fraction relationships are shown in Graphs No. 2 (Curve VII) Graph No. 3 (Curve VII) respectively. The dielectric constant curve is more concave than previous dielectric constant mole fraction relationships. Similarly the polarization curve is more convex than previous polarizations mole fraction results.

TABLE XXXX

DIELECTRIC CONSTANTS AND POLARIZATIONS OF ACETONE-TOLUENE ACID MIXTURES.

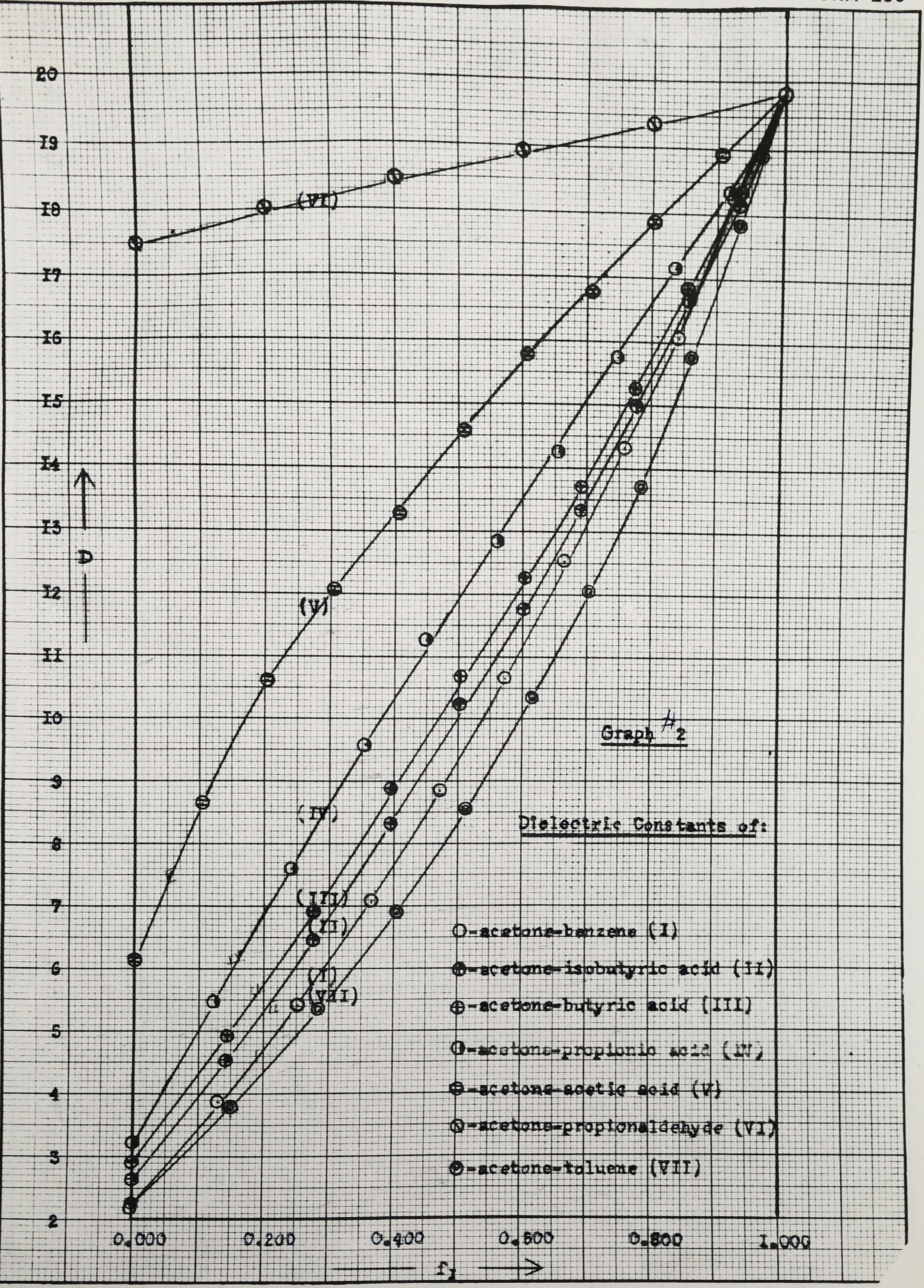
% ACETONE	% TOLUENE	f_1	f_2	C_3	E	d_4^{25}	$P_{1,2}$	R (ohms)
100	0	1.0000	0.0000	493.95	19.83	0.7855	63.75	14,000
95	5	0.9679	0.0321	472.45	18.92	0.7891	64.21	12,000
90	10	0.9345	0.0655	446.50	17.83	0.7928	64.52	12,500
80	20	0.8639	0.1361	397.15	15.77	0.8000	65.13	16,500
70	30	0.7873	0.2127	347.65	13.70	0.8073	65.41	27,000
60	40	0.7040	0.2960	307.60	12.03	0.8145	65.75	23,000
50	50	0.6133	0.3866	267.70	10.36	0.8218	65.60	70,000
40	60	0.5140	0.4861	223.10	8,53	0.8290	64.43	100,000
30	70	0.4046	0.5953	184.35	6.90	0.8363	62.07	>100,000
20	80	0.2839	0.7161	146.65	5.31	0.8436	57.60	>100,000
10	90	0.1498	0.8502	110. 05	3.76	0.8508	48.99	>100,000
00	100	0.0000	1.0000	76. 90	2.37	0.8581	33.63	>200,00

f_1 = mole fraction of acetone

f_2 = mole fraction of toluene $\qquad C_L = 20.20$

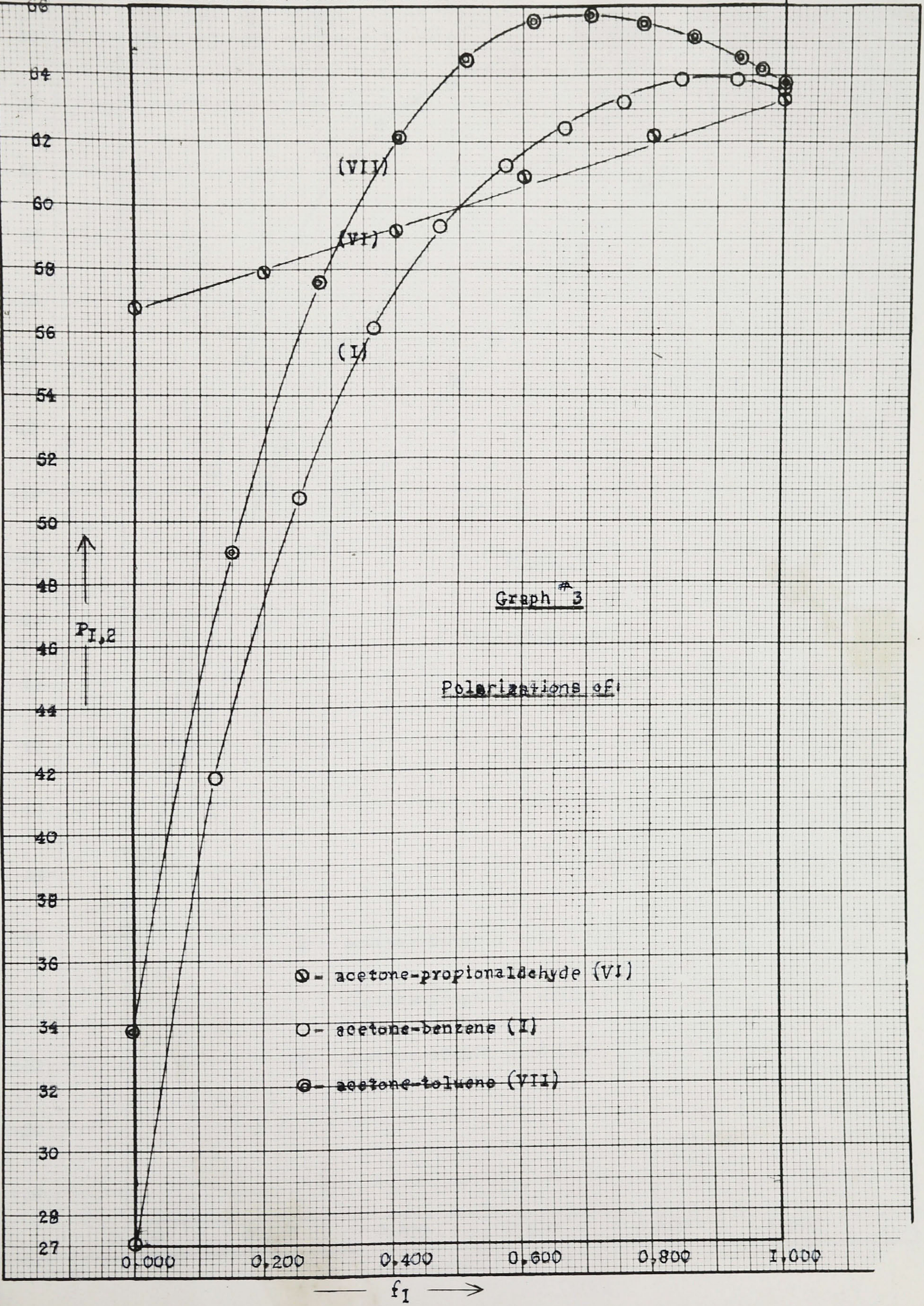
$M_1 = 58.05$

$M_2 = 92.06$



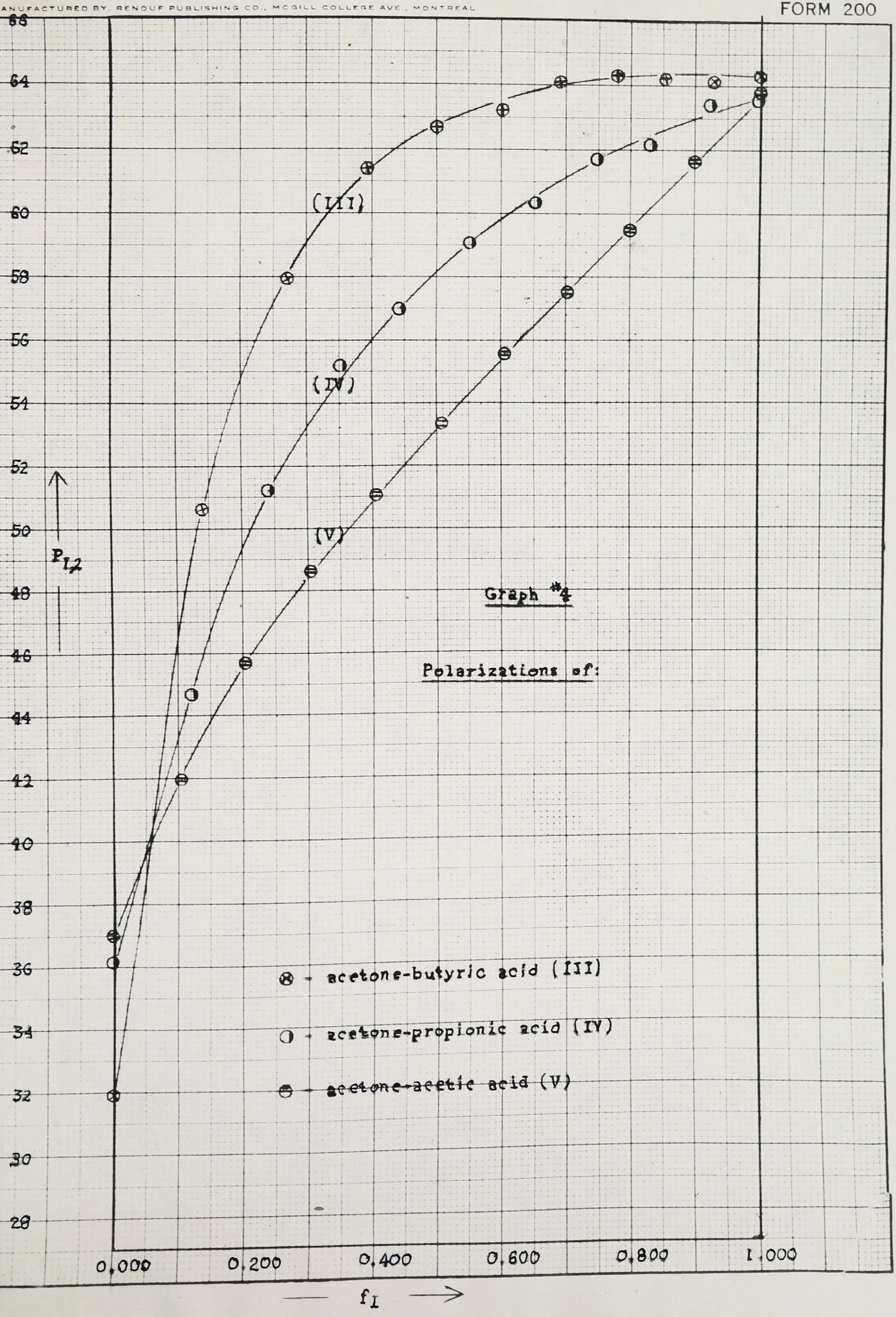
Graph #2

Dielectric Constants of:



Graph # 3

Polarizations of:



Graph #4

Polarizations of:

DISCUSSION OF RESULTS

1) THE LEAK EFFECT

It has been shown that two types of errors may arise because of conductance. When the cell condenser is larger than the standard condenser then the leak effect will be positive. That is the capacitance observed for the cell will be greater than it actually is.

In the apparatus describe by Linton (43) a standard condenser of five hundred micromicrofarads was used. Since this method did not require a standard condenser larger than the cell a fifteen hundred micromicrofarad cell was employed. It is obvious that the conductance effect in such an arrangement is going to give values for the capacitance of the material which are too high. And therefore the dielectric constant will also be too high.

However, the fact that the standard condenser has a higher capacitance than the cell does not mean that in actual measurements the same condition will obtain. Because when the cell is placed in the circuit capacitance must be taken out with the standard condenser to return to the original frequency. In which case the amount of capacitance remaining unremoved from the standard condenser may be small while that removed, because of the insertion of the cell, may be large. Smyth (22) remarks that capacitance errors may be observed with conductance up to 100% with methyl alcohol. If the cell used in that particular measurement was the standard cell employed by that author (22), then the capacitance of the cell, calculated on the basis of methyl alcohol and coaxial cylinder condenser, is about 4,300 mmfd. Now the standard condenser described by Smyth has a capacitance of 1,500 mmf. It is evident that a cell as large as the one described could not have been used. In any event it seems probable that the amount of capacitance remaining,after a sufficient amount has been withdrawn to allow for the cell, will be smaller than the capacitance of the cell, wherefore, the anamolous result obtained may be understood.

A negative capacitance effect results when the standard condenser has a larger capacitance than the cell condenser even when the latter is placed in circuit with the standard condenser. As the material in the cell becomes conductive the capacitance of the cell as measured from the parallel standard condenser will decrease. (See Table XIII).

Akerlof (4) determined the dielectric constant of acetone and measured a series of binary mixtures of that compound. As has already been pointed out his dielectric value is considerably lower than that of other authors. (Part II), Section II,1). The resonance method was used by Akerlof and in the tank circuit the cell was placed parallel to the standard condenser. The standard condenser had a capacitance of 1,500 mmf. The cell as already observed consists of two discs. 5 cm. in diameter and 2 mm. apart. The capacitance of the cell empty is 10.2 mmfd. With acetone (using $E = 20$) the capacitance would be in the vicinity of 200 mmfd. This value compared to 1,300 mmfd. which would be left in the standard condenser, indicates that the leak effect due to conductance would give a negative result in the standard condenser. And, therefore, the capacitance values obtained would be too low and the dielectric values obtained for materials with some conductance and capacitance below 750 mmfd would also be too low. But the greatest error would be with those having a relatively large conductance and a small capacitance compared to the remaining capacitance of the standard condenser. Besides the two effects produced by measuring capacitances with the cell and the standard condenser in parallel, and measurements made with different condensers in series with the cell and with different total capacities of the oscillator, it is apparent that apparatus conditions are important factors in measuring capacitances of materials even with only a slight conductance. ~~The~~ Results obtained therefore of dielectric constant~~s~~ measurements ~~in such~~ obtained under the conditions considered are therefore ~~cases are~~ subject to error, due to the nature of the apparatus. In this work precautions were taken to avoid conductance effects and hence the dielectric values obtained are based on pure capacitances of the materials investigated.

2) BINARY ACETONE MIXTURES.

The measured dielectric constants of the binary mixtures were compared with the results obtained by calculation using Silberstein's (50) volume mixture rule for dielectric constants. Deviations from this rule were observed in all cases except in the case of the acetone-propionaldehyde mixtures where about only one percent discrepancy was observed. The acetone-acetic acid mixtures gave the widest departures from the mixing rule. Kerr (52) observed that this rule did not hold for mixtures of benzene and aniline, benzaldehyde, M-cresol and benzyl alcohol.. The second component of these mixtures is in all case associated in benzene. Thus a simple explanation is available, since Silberstein's formula includes two assumptions: that the capacities are directly additive; and that the molecules of the two components have no dielectric effect on each other. But associated molecules are dipolar and do change even in a non-polar medium. Marrow (75) and others (76) from X-Ray diffraction of liquids have shown that a binary mixture does not show the individual diffraction intensities of the components, but rather as a modification and a single liquid.

When a non-polar material is mixed with a non-polar material the mixture polarization $P_{1,2}$ is a straight line, and since the molecules do not affect one another due to the absence of dipoles, the mixing rule holds. The polarization curves of polar materials in non-polar liquids display varying curvatures. The $P_{1,2}$ curve of benzene-toluene has only a slight hump.

Dissolving a polar and highly associated material like acetone in benzene, deviations from the mixing rule and the $P_{1,2}$ linearity are to be expected. According to Debye dilution increases the number of free dipoles and hence causes the $P_{1,2}$ curve to rise in a convex manner from the composition axis.

Upon diluting acetone in a slightly polar medium, toluene, a greater curvature of the $P_{1,2}$ curve was obtained than in the case of benzene. The acetone-toluene curve rises slightly to a maximum with decreasing acetone concentration while the acetone-benzene polarization curve has no marked maximum. The dipolar effect of the toluene is acting in an additive way to the acetone polarization.

Thus far binary mixtures considered have been: one component associated; and, the second unassociated. Fatty acid dissolved in non-polar solvents are associated much as they are in the pure state. Broughton (77) has shown with cryoscopic data that the extent of association of fatty acids decreases slightly with dilution in a polar medium, cyclohexane, acetic acid exists mainly as double molecules in benzene, but with increasing concentration the polarization rises. In view of Broughton's work more association would be expected to take place as the mixtures increase in concentration of acetic acid which, following Smyth's reasoning, may be due to the formation of a more highly polymerized form possessed of a moment the proportion of which increased with increasing concentration of acid.

When two polar associated materials are mixed two factors at least may be expected to affect the $P_{1,2}$ curves. The extent and kind of association present will define the number of dipoles that will be free to orient themselves in the field which together with the moment of the molecules will fix the amount of polarization that will take place.

Association is usually regarded as a result of cohesive forces. The association which arises from dipolar effects is of two types. First, the molecules may lie side by side in such a way as to tend to neutralize their dipolar effect and produce thereby a quadrapolar unit. Again, association may be an end to end alignment where dipolar effect is additive. Finally, association may be due to Van der Waal forces the limiting condition of which is chemical union.

Kateswaram (78) observed on examining the Raman spectrum of acetic acid dissolved in water, in the pure state, and in a non-polar medium, benzene, that aqueous acetic acid shows clear alterations of the Raman spectrum, However, in the non-polar solution the Raman spectrum remains unaltered. Increasing the temperature of pure acetic acid produces an effect similar to dissolving in water. Since association decreases with rise in temperature it is argued that the solution in water causes a change in the association of acetic acid. If a change has taken place in the association of the acid in benzene it was too small to detect.

When two polar and associated compenents are being diluted one in the other four processes may take place. The association of both materials may remain the same or both may change. On the other hand one may change and the second retain its original degree of association, or the reverse.

The mixture polarization curve of water-acetone is a straight line (4). Both water and acetone are associated. But the Raman line of the carbonyl group of acetone in water is not effected and the frequency is the same in the pure liquid as in the water (79). The fatty acids in water do give a shift which is not due to the carbonyl group of the acid. This shift of the Raman frequency suggests a possibility of an actual chemical change in the structure of the substances. It appears probable that most of the fatty acids, acetic may be taken as typical, exist largely as double molecules, but the presence of two lines of aqueous acetic acid suggests a single and a double molecule of acetic acid.

Acetone-propionaldehyde give a straight line for the polarization mixtures. Propionaldehyde and acetone both have about the same dipole moments, 2.7 (80) and 2.54 (81) $X\ 10^{-18}$ respectively. Calculating the extent of association with the Charborski and Launginescu (82) formula for propionaldehyde, the association was found to be 1.5. This compares favourably with 1.42 the degree of association found by Stakhorski (83). Other values of association of acetone are somewhat higher, but using the same formula for finding the association as used for the propionaldehyde the extent of association is found to be 1.4. Because of the similarity of dipole moments and associations together with carbonyl properties a linear $P_{1,2}$ relationship, which has been found, might have been expected.

The Raman spectrum of acetic acid in acetone has been observed by Kateswaram (5) and was found to be similar to the acetic acid-water spectrum, which is not comparable with the acetic acid-benzene Raman Spectrum.

The dipole moments of the fatty acids, of which the polarization mixture curves were calculated, are of the same order and do not show any marked increase or decrease of moment in the series (84). Broughton (77) has shown that the extent of association in a non-polar medium of acetic, propionic, and butyric acids decreases slightly with increasing molecular weight.

The magnitude of the dipoles of these acids do not seem to be related to the polarization curves but the degree of association of the fatty acids, which is parallel with their ionization constants, does agree with the results obtained, for the $P_{1,2}$ curves of the acetone-fatty acids were found to decrease in curvature as the molecular weight decreased and as the association and ionization constant increased.

CLAIM OF ORIGINAL WORK.

The leak effect has been investigated and apparatus conditions are found to be determinative in the measurement of dielectric constants of materials that have some conductance.

Two cases have been recognized as due to conductance with ordinary oscillating circuits.

a) When the capacitance remaining in the standard condenser after the removal of a capacitance equal to the cell, is small compared to the cell capacitance, then the error in the measurement of the capacitance will be positive and the dielectric constant calculated therefrom will be too large.

b) When the capacitance remaining in the standard condenser is large compared to the cell, the error in the capacitance will be negative and the dielectric constant will be too small.

The apparatus designed was free from these errors and the extent of the conductance effect on capacitance with this apparatus was observed.

Dielectric constants of acetone; isobutyric, butyric, propionic and acetic acids; propionaldehyde and toluene were redetermined and found to be in good agreement with other workers.

Dielectric constants of acetone-benzene; isobutyric, butyric, propionic and acetic acids; propionaldehyde and toluene binary mixtures used investigated. The polarizations of these mixtures give information comparable to the Raman spectrum results.

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