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THE DIELECTRIC RESPONSE OF ORGANIC
LIQUIDS AT HIGH FREQUENCIES

EDWIN M. RUDZIS

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THE DIELECTRIC RESPONSE OF ORGANIC
LIQUIDS AT HIGH FREQUENCIES

by

Edwin M. Rudzis

Major, United States Marine Corps

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

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ABSTRACT

The dielectric properties of organic liquids were examined by means of a high frequency technique. The range of the oscillations were from 31.8 to 66 megacycles. The prime motives of the investigation of the dielectric response were (1) to determine if the organic molecules provided signatures, which would result in the identification of compounds, (2) information was also desired concerning the capability of determining concentrations in binary systems. Due to the anomalous behavior of alcohols, binary systems of alcohols in polar and non-polar solvents were investigated. To provide the high frequencies desired, a simple inexpensive instrument was designed and constructed.

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1. Introduction.

From a study of the literature, the use of high frequency electronic circuits in the field of chemical analysis gained impetus in the United States after the work of F. W. Jensen and A. L. Parrack in 1946.¹ Since that time, many investigations led to the use of this type of instrument in conjunction with titrations of acid - base solutions. Other aspects of chemical analysis were considered and applied, such as studying the composition of complex ions, measuring the rate of diffusion of electrolytes, detection of water in substances such as chemicals, foods, wood, textiles etc., and in the biological field, determining between fertilized and unfertilized eggs of sea urchins and starfish. Kinetics of chemical reactions were also investigated by these devices. A project of particular interest was the heterodyne beat method for the identification of liquid organic compounds by P. W. West, T. S. Burkhalter, and L. Broussard in 1950.² Operating initially at a frequency of four megacycles, the frequency shift caused by various organic compounds was measured by a heterodyne beat method.

¹Jensen, F. W. , Parrack, A. L., Ind. Eng. Chem. Anal. Ed. 18, p595 - 598 (1946)

²West, P. W., Burkhalter, T. S., Broussard, L. ; Anal. Chem., Vol. 22, p469 - 472 (1950)

2. Oscillator Design

The basic device for the production of high frequencies is an electronic oscillator circuit. The need in analytical work in which great accuracy is desired necessitates an oscillator which will operate over extended periods of time with extreme stability. The heart of the oscillator is the tank circuit containing the chemical solution in a cell. It is from this tank circuit that the effects of the high frequency oscillations on the compounds are produced to allow measurements to be made concerning the dielectric properties of the solution. Two general methods have been used to investigate the dielectrical properties of solutions. One is the use of an inductance coil placed around the cell containing the solution. The other makes use of the capacitive effects provided by the solution in which the cell is constructed as a capacitor. A simple sketch of both types is shown below in figure 1.

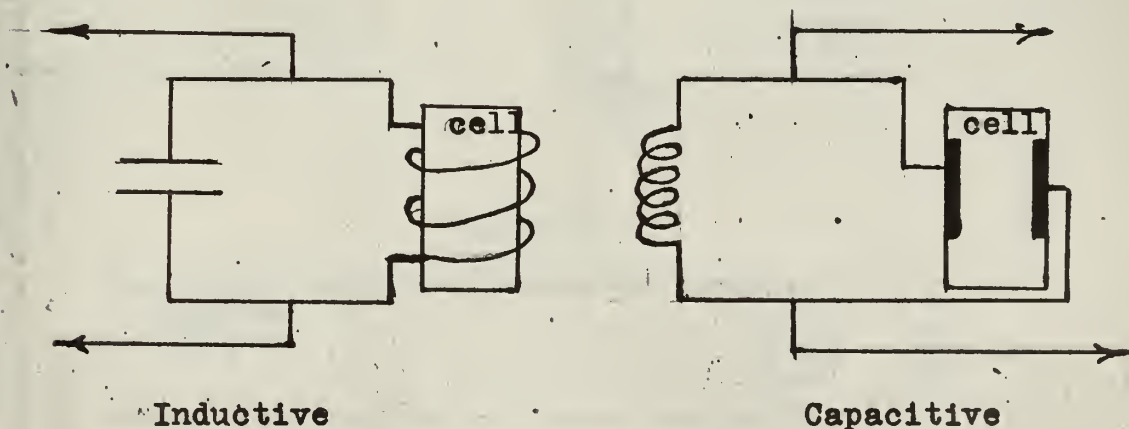


Figure 1.

3. Very High Frequency Variable Oscillator. (VHFVO)

The tuned grid, tuned plate circuitry was used in the construction of the VHFVO. The tank circuit of the plate section was of the capacitive type. Consisting of a glass cell to contain the organic solution and copper metal plates affixed to the sides of the cell. This cell then participated as one of the capacitors of the plate tank circuit. Schematically the VHFVO is shown below as figure 2. Both the grid and plate circuits must be adjusted to resonate at approximately the same frequency for oscillations to take place.

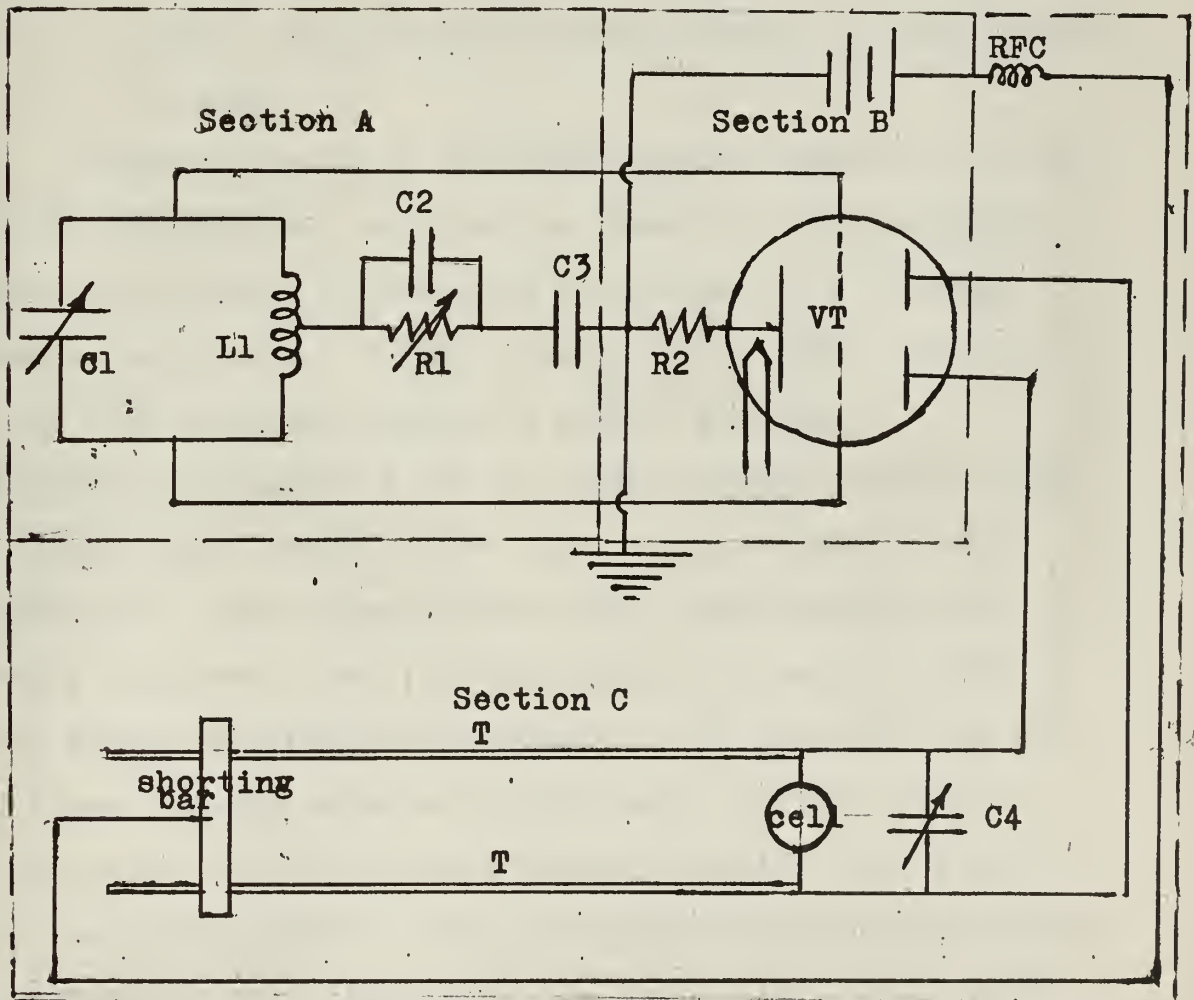


Figure 2

The parts list of the VHFVO are as follows:

- C1, C4 - 36 micro-micro farad variable capacitor
- C2 - 1500 micro-micro farad capacitor
- C3 - 1000 micro-micro farad capacitor
- R1 - 10 k. ohm variable resistor
- R2 - 220 ohm resistor
- VT - 6J6 vacuum tube
- L1 - .5 micro henry inductance coil
- RFC - 2.5 millihenry radio frequency choke coil
- TT - 3/8 inch diameter copper tubing, 40 centimeters long

Section A made up the tank circuit connected to the grids of the tube, as shown in figure 2. The inductance coil L1 was made by wrapping nine turns of # 14 gauge copper wire on a 1/2 inch plastic form, eight turns per inch with 1/8 inch center to center spacing.

Section B in figure 2 was the power supply and the tube assembly with cathode bias. The tube used was a 6J6, medium mu, twin triode vacuum tube. The power supply was a regulated power supply, Model 71, manufactured by the Lambda Electronics Corporation. It provided the D.C. voltage for the tube and the filament voltage of 6.3 volts A.C. for the cathode heater. Section C in figure 2 is the tank circuit of the plates of the oscillator tube. Included in this circuit is the cell which contains the liquid solutions being investigated. The cylindrical cell, four centimeter diameter, was made of pyrex glass and was constructed so that it measured 14 and 1/2 centimeter

in length with a rounded bottom. At the bottom, a teflon stopcock was fitted to allow removal of the organic solutions without having to remove the cell from its fixed position. Thin metal copper plates, with dimensions of two centimeters by three centimeters were curved by heating the metal, making it soft and malleable, then bending them so that they fit the contour of the cylindrical shaped cell. The copper plates were affixed to the sides of the glass cell by spreading a thin film of petroleum jelly on the plates and then a plastic tape was wrapped around the plates to hold them in position on the sides of the cell. The cell construction is shown in figure 3

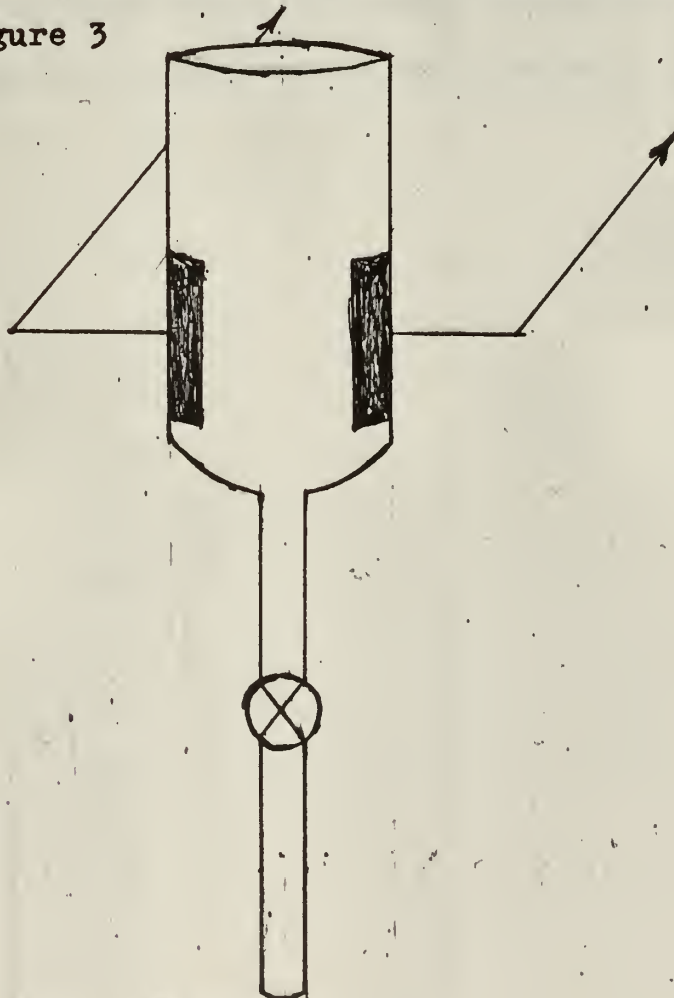


Figure 3

The reason for not permanently bonding the copper metal electrodes to the cell was to allow for interchanging different size electrodes and thus obtain a greater range of frequencies in the operation of the oscillator circuit. The copper tubing elements were placed parallel to each other, 9.5 centimeters apart, they provided inductance and an additional small capacitance to the plate tank circuit. The inductance of this part of the circuit could be varied by moving the copper metal shorting bar to different positions on the copper tubing. A positive potential from the power supply was connected to the shorting bar, passed along the copper tubing and was then connected to the plates of the vacuum tube.

4. Operating Procedures.

Feedback for the oscillating circuit was provided by the interelectrode capacitance between the plate and grid elements. Due to the limitations of the 6J6 tube, it was decided to operate the VHFVO in the frequency range from 30 megacycles to 70 megacycles. The heater element of the tube was allowed a minimum warm-up time of ten minutes. After the warm-up time, a pre-selected frequency was set on the plate tank circuit with the cell empty. The method of setting the frequency was accomplished by adjusting the variable capacitor and/or moving the shorting bar to different positions on the copper tubing. Either or both of these adjustments would allow for various frequencies to be set in the plate tank circuit. The pre-selected frequency set on the plate tank circuit was then checked by a Megacycle Meter (Q-meter, Boonton Instrument Company). A frequency, one to two megacycles lower than that set on the plate tank circuit was placed in the grid circuit by tuning the variable capacitor C1 in that circuit. This too was verified by the Megacycle Meter. The purpose of setting the plate circuit at a slightly higher frequency was to insure that the feedback would be in the correct phase. There are three rapid means of setting various frequencies on the oscillator. Adjusting either of the two variable capacitors will vary the frequency and the third method is by moving the shorting bar to any desired position on the copper tubing. A fourth method which requires more

time to change the frequency, is to interchange the capacitor plates on the side of the cell for a smaller or larger size. The important factor being the area of the plates, which must be either increased or decreased. A fifth method, also more time consuming than the first three mentioned previously was to replace the inductance coil in the grid tank circuit.

The glass cell was constructed of tubing with a teflon stopcock situated approximately six centimeters from the bottom of the cell. At all times when the cell was not in use, a cleaning solution of concentrated sulfuric acid and potassium dichromate was kept in the cell. The cleaning solution kept the inner walls of the cell free from film and most organic liquids ran freely from the cell when the stopcock was opened. This method decreased the time required to go from one test solution to another. With the glass cell empty and the proper frequency set on the oscillator, a positive voltage was applied to the plates of the vacuum tube and the system was ready to have measurements taken.

5. Measurements.

Changes occurring in the plate tank circuit by the introduction of a substance with a specific dielectric constant in the cell could be determined by the following methods; recording the changes in (a) the grid voltage or current, (b) the plate voltage or current, (c) frequency. In order to simplify the electronic circuitry, measurements were made of the grid voltage of the circuit. This was accomplished by use of a vacuum tube voltmeter, (Hewlett-Packard Model No. 410B). This particular model can be used with systems which operate at high frequencies. A particular value of grid voltage by itself had no significance, for what was desired was the change in grid voltage as the dielectric properties of the capacitor cell changed. During the recording of the grid voltages, the settings on the variable capacitors remained fixed, as did the position of the shorting bar on the copper tubing. Therefore any changes occurring in the grid voltage was a function of the dielectric properties of the liquid introduced into the capacitor cell.

In order to provide uniformity to the method of reading the grid voltages and due to the dead space in the bottom part of the capacitor cell, each sample of liquid had a volume of 50 milliliters. A burette was used to measure the amount of liquid placed into the cell. The burette was also cleaned with sulfuric acid-potassium dichromate cleaning solution. The procedure in making

the grid voltage readings were as follows:

(a) The grid voltage was checked with no liquid in the capacitor cell.

(b) Ten milliliters of liquid was released into the cell from the burette, and the grid voltage reading recorded.

(c) Forty milliliters of liquid was released into the cell, making a total of 50 milliliters, the grid voltage again recorded.

The change in grid voltages of interest was the difference between the readings at 10 milliliters and at 50 milliliters. The reason that the volume of interest was maintained at 40 milliliters was due to the fringing effect of the capacitor cell. When 10 milliliters were placed in the cell, the level of the top of the liquid was just below the bottom edge of the capacitor plates. Releasing 40 milliliters more into the cell placed the top of the liquid level slightly above the top edge of the plates. It was found by experimentation that the addition of any more liquid greater than 50 milliliters produce no significant change in the grid voltage. In effect, the dielectric properties of the 40 milliliters of solution between the capacitor plates provided the desired data, which consisted of a change in the grid voltage. This technique was used on all runs made with the VHFVO with one exception, which will be discussed later. The temperature of the liquids was 20 ± 1 degree centigrade at the time the measurements were being recorded.

6. Dielectric Response of Organic Liquids.

A search of the literature on high frequency analysis indicated that a linear relationship did not exist between the response of liquids to high frequency analysis and their dielectric constant. In addition, the dielectric constant of a substance would vary as the frequency varied. Two previous investigations of high frequency analysis on organic liquids gave some indications of the relation between the dielectric response of the compounds and their dielectric constant. One of the investigations was conducted with a commercial oscilloscope, operating at five megacycles, by P.H. Sherrick et al in 1954.³ The results of this investigation are shown in graph form in figure 4.

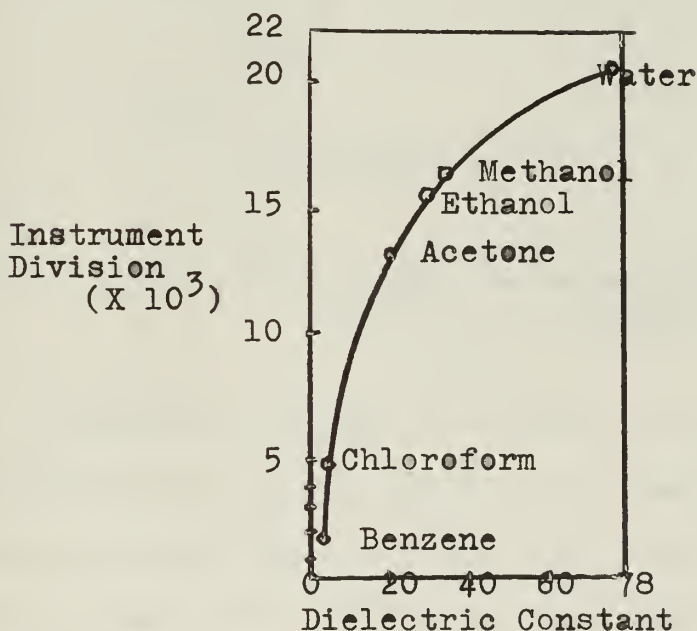


Figure 4

³Sherrick, P. H. ; Dawe, G. A. ; Karr, R. ; Ewen, E. F., "Manual of Chemical Oscillometry", E. H. Sargent, Chicago 1954

The other investigation made use of the heterodyne beat method mentioned earlier, by West, Burkhalter and Broussard. In order to correlate the data of the two investigations on some of the same compounds, a graph was constructed similar to figure 4 and is shown below as figure 5.

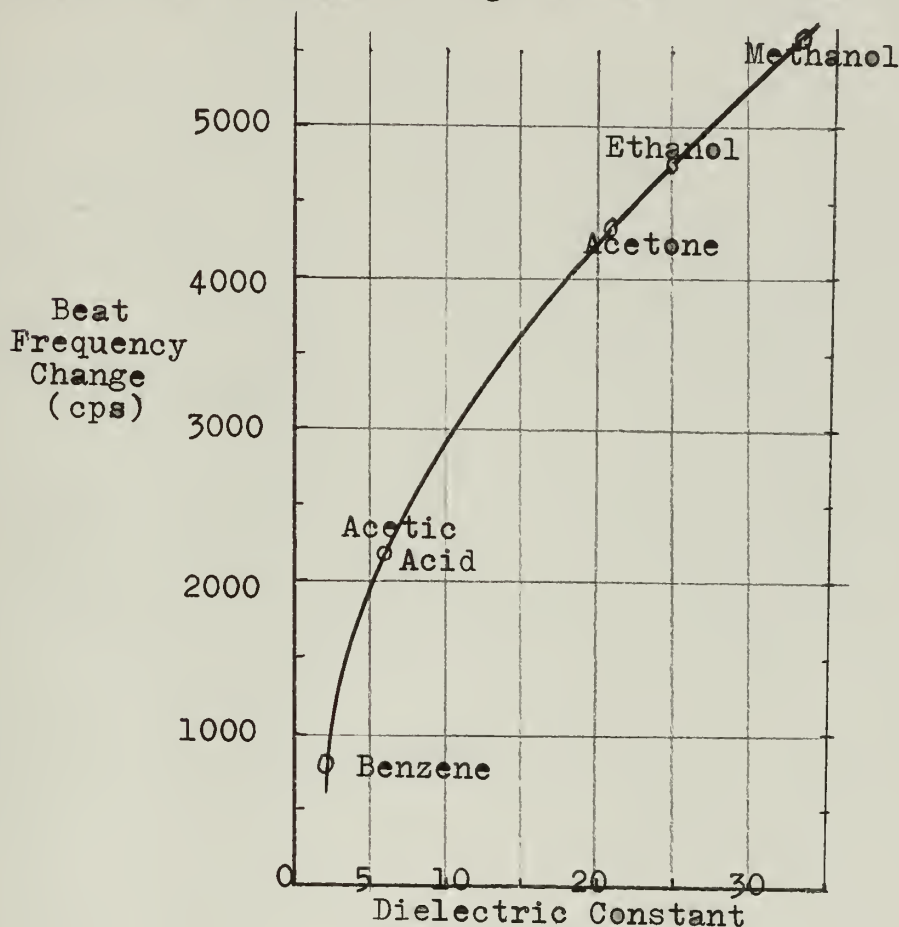


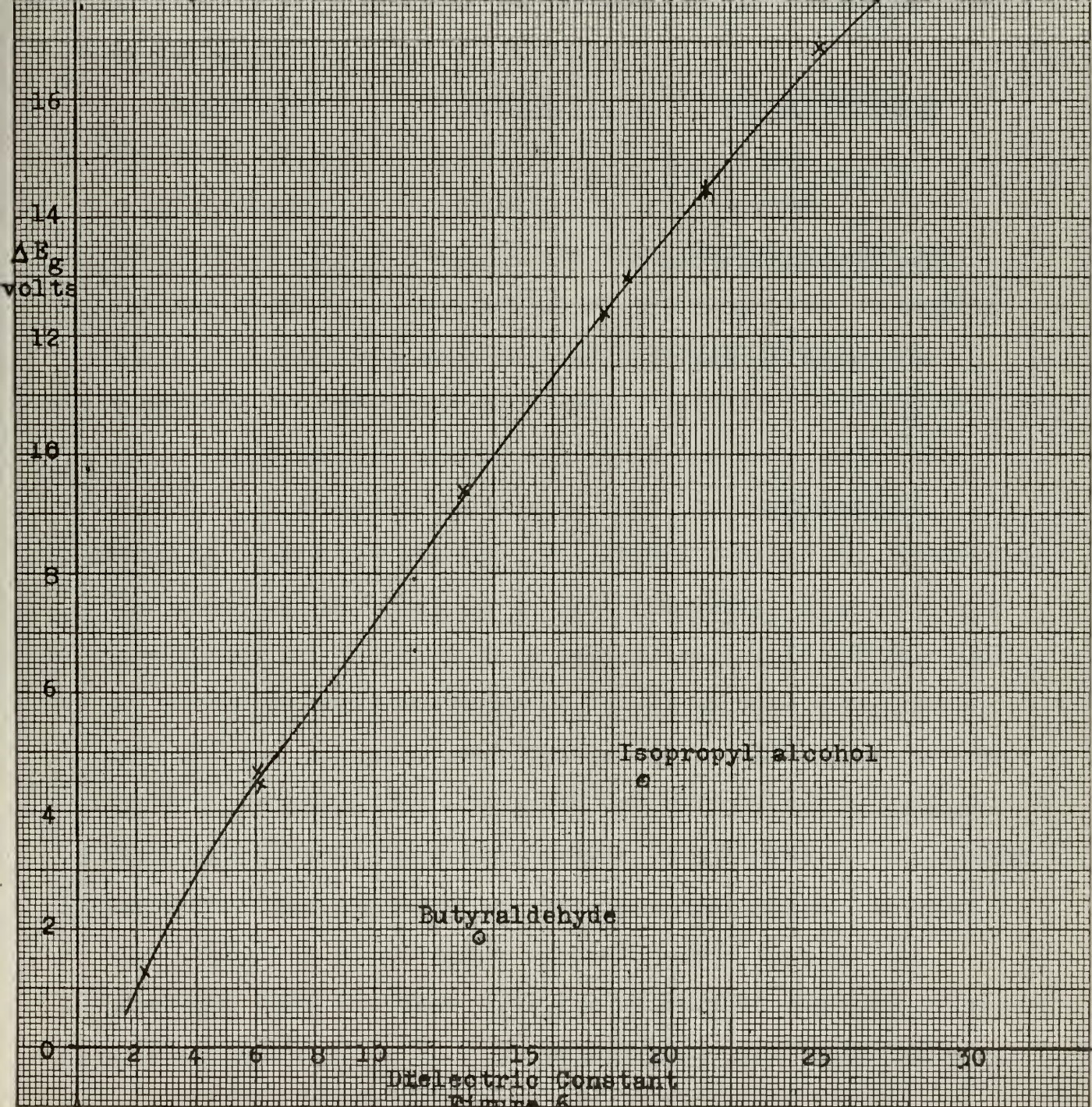
Figure 5

The VHFVO was used to conduct a similar investigation on the ability of the device to be used in chemical analysis work. The oscillator was tuned at 41 megacycles, plate voltage set at 100 volts, and measurements of the grid voltages were recorded as mentioned in section 5. Two runs were made of each substance and the results are shown in figure 6.

Dielectric Constant Vs. ΔE_g

41 Megacycles

| ΔE_g | Compound |
|--------------|----------------------|
| 20.00 | Methanol |
| 16.9 | Ethanol |
| 14.5 | Acetone |
| 13.0 | 2-Butanone |
| 12.4 | 1-Butyl Alcohol |
| 9.4 | Benzyl Alcohol |
| 4.7 | Ethyl Acetate |
| 4.5 | Acetic Acid |
| 1.3 | Carbon Tetrachloride |



Dielectric Constant

Figure 6

Two of the compounds indicated an abnormally low change in voltage. The chemicals were obtained from reagent bottles in the organic chemical storeroom and a doubt arose with regards to their purity. The two compounds were butyraldehyde and isopropyl alcohol. Samples were taken from the reagent bottles and a check was made of their refractive indices on an Abbe Refractometer, readings were as follows:

| <u>Substance</u> | <u>Handbook Value</u> | <u>Actual Reading</u> |
|-------------------|-----------------------|-----------------------|
| isopropyl alcohol | 1.37757 | 1.4424 |
| butyraldehyde | 1.38433 | 1.4086 |

The results of the check on the refractive indices cast further doubt about the purity of the compounds, therefore it is felt that the grid voltage readings of those two compounds can be viewed with some suspicion.

A comparison of figures 4,5 and 6 indicate that these curves have a common factor, in that they are gentle sloping curves and are similar. It was decided to investigate the shape of the curve at another frequency. This time the oscillator was tuned to 31.8 megacycles, plate voltage set at 150 volts, grid voltages recorded. At this frequency, not all the compounds were tested, as in the investigation at 41 megacycles. The compounds, chloroform and benzene were substituted for butyraldehyde, ethyl acetate and carbon tetrachloride. In addition, the isopropyl alcohol sample was taken from a different reagent bottle than in the previous test. The data from the reading of the grid voltages and a graph similar to figures 4,5 and 6 are shown in figure 7.

Dielectric Constant Vs. ΔE_g
31.8 Megacycles

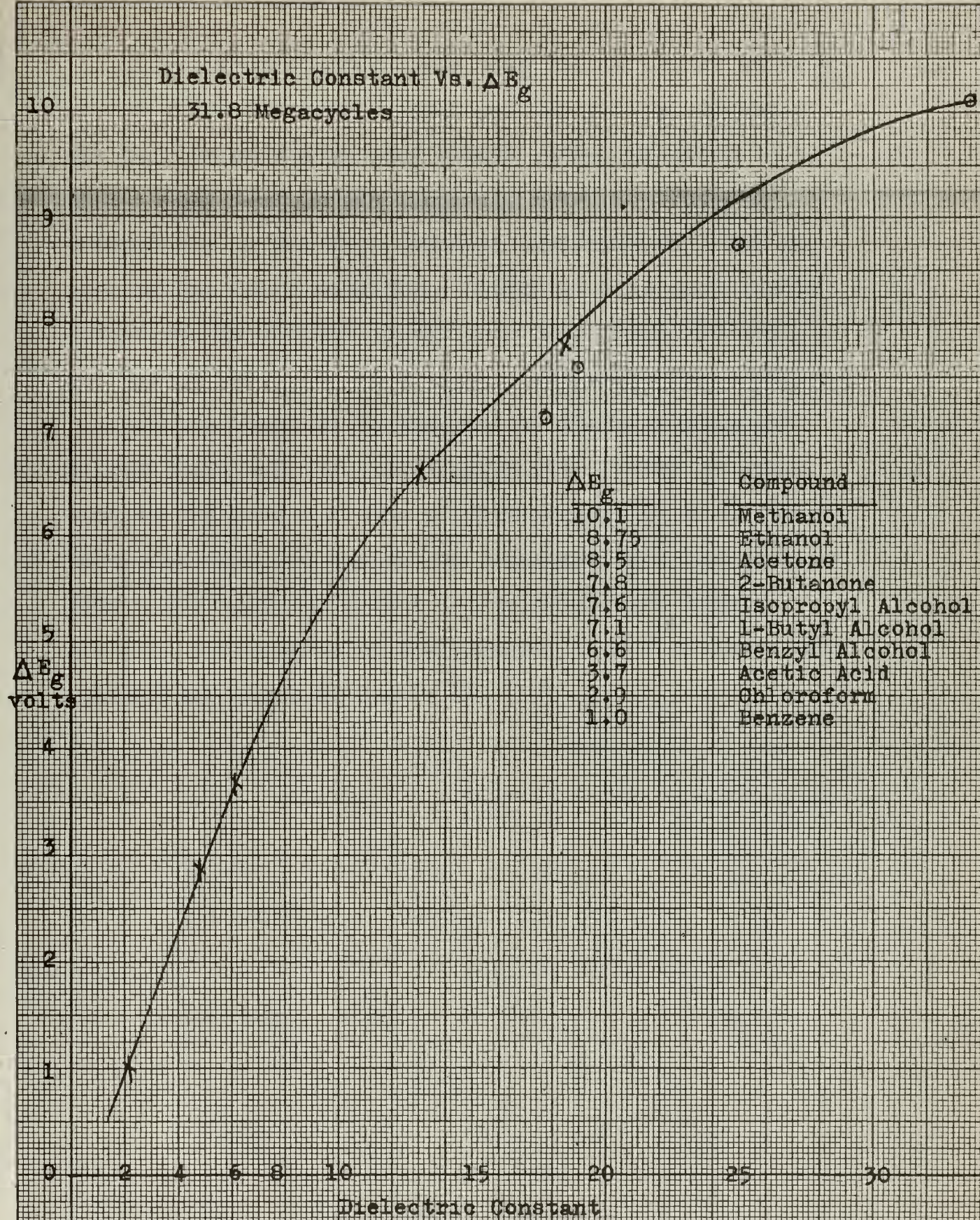
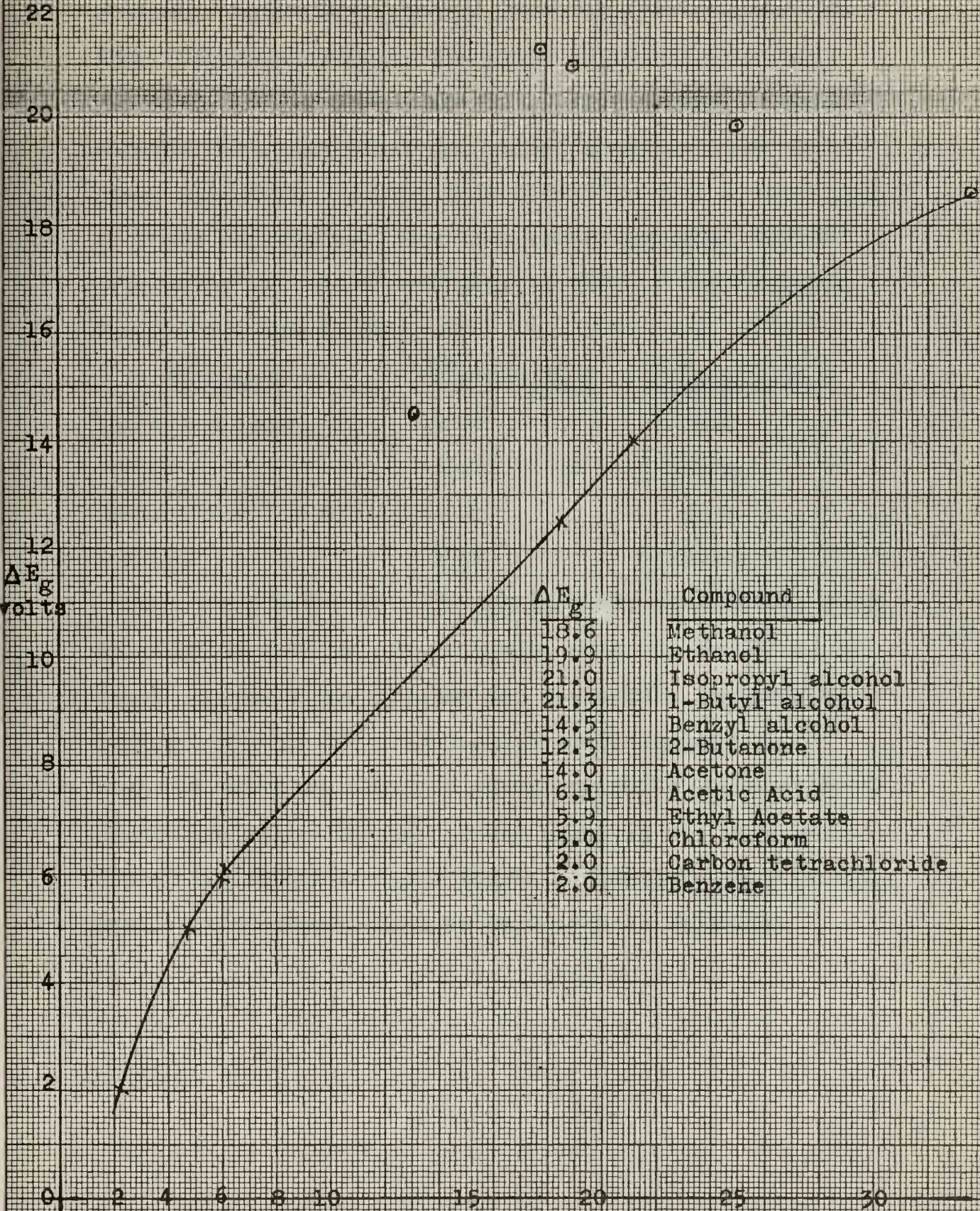


Figure 7

It is interesting to note that the values of ΔE_g of the compounds ethyl, isopropyl and n-butyl alcohols all fall below the general smooth curve. It would appear that some of the alcoholic molecules respond differently to the high frequency oscillations, than do some of the other seemingly, dielectrically more stable molecules. To further investigate this trend, it was decided to oscillate at a higher frequency. The oscillator circuit was tuned at 54 megacycles, plate voltage set at 150 volts and the same samples were tested as where used in the previous runs at 31.8 megacycles with the exception that two additional compounds were included in this investigation, carbon tetrachloride and ethyl acetate. The results of the changes in grid voltages are graphed and shown as figure 8.

Dielectric Constant Vs. ΔE_g
54 Megacycles



| ΔE_g | Compound |
|--------------|----------------------|
| 18.6 | Methanol |
| 19.9 | Ethanol |
| 21.0 | Isopropyl alcohol |
| 21.3 | 1-Butyl alcohol |
| 14.5 | Benzyl alcohol |
| 12.5 | 2-Butanone |
| 14.0 | Acetone |
| 6.1 | Acetic Acid |
| 5.9 | Ethyl Acetate |
| 5.0 | Chloroform |
| 2.0 | Carbon tetrachloride |
| 2.0 | Benzene |

Dielectric Constant
Figure 8

With the exception of methyl alcohol, the alcoholic compounds again have strayed from the smooth curve. At this frequency however, the graph indicates that the greatest deviation was made by n-butyl alcohol, isopropyl alcohol next, and ethyl and benzyl alcohols show the least deviation. Because this seemed unusual a verification of trend was desired. The oscillator was tuned for 58 megacycles and tests were made on four of the alcohols. The results are as follows:

| <u>Substance</u> | <u>ΔE_g (58 Mc.)</u> | <u>ΔE_g (55 Mc.)</u> |
|------------------|---|---|
| methyl alcohol | 23.9 | 18.6 |
| ethyl " | 25.0 | 19.9 |
| isopropyl " | 26.0 | 21.0 |
| n-butyl " | 26.6 | 21.3 |

The trend seems to indicate that the more carbon atoms which go to make up the molecule, with the exception of benzyl alcohol, the greater the dielectric response to oscillations in the neighborhood of 55 megacycles. It might be expected that the benzyl molecule would be an exception, since the six carbon atoms in the ring structure of the molecule would behave differently than if they were in a straight chain as an aliphatic molecule.

7. Binary Solutions.

The odd behavior of the alcohols in an oscillating field led to the investigation of their response in a binary solution. The alcohol being paired with a non-polar solvent. The oscillator was tuned to 41 megacycles with a plate voltage of 100 volts. The first pair to be examined was ethanol and carbon tetrachloride. Two runs were made with each sample and the first measurements were of pure carbon tetrachloride. Each succeeding set of measurements were made on an increased amount of alcohol in the non-polar solvent. Table A below shows the values of the measurements with their corresponding per cent of alcohol, by weight.

Table A.

| <u>ΔE_g</u> | <u>% Ethanol, by weight</u> |
|--------------------------------|-----------------------------|
| 1.3 | 0.0 |
| 1.6 | 2.54 |
| 2.0 | 5.22 |
| 2.6 | 8.03 |
| 4.1 | 11.0 |

A second series of measurements were made at the same frequency on another pair of compounds. Again the same non-polar solvent, but the second liquid this time was methanol. Table B shows the data of the second series of measurements.

Table B.

| <u>ΔE_g</u> | <u>% Methanol, by weight</u> |
|--------------------------------|------------------------------|
| 1.3 | 0.0 |
| 1.5 | 1.27 |
| 1.9 | 2.56 |
| 2.1 | 3.89 |
| 2.7 | 5.25 |
| 3.3 | 6.66 |
| 4.9 | 8.10 |
| 6.9 | 9.60 |
| 10.7 | 11.10 |

The data from tables A. and B. were plotted in graph form with the changes in grid voltage on the ordinate and per cent alcohol, by weight, on the abscissa. This is shown in figure 9.

E_g
volts

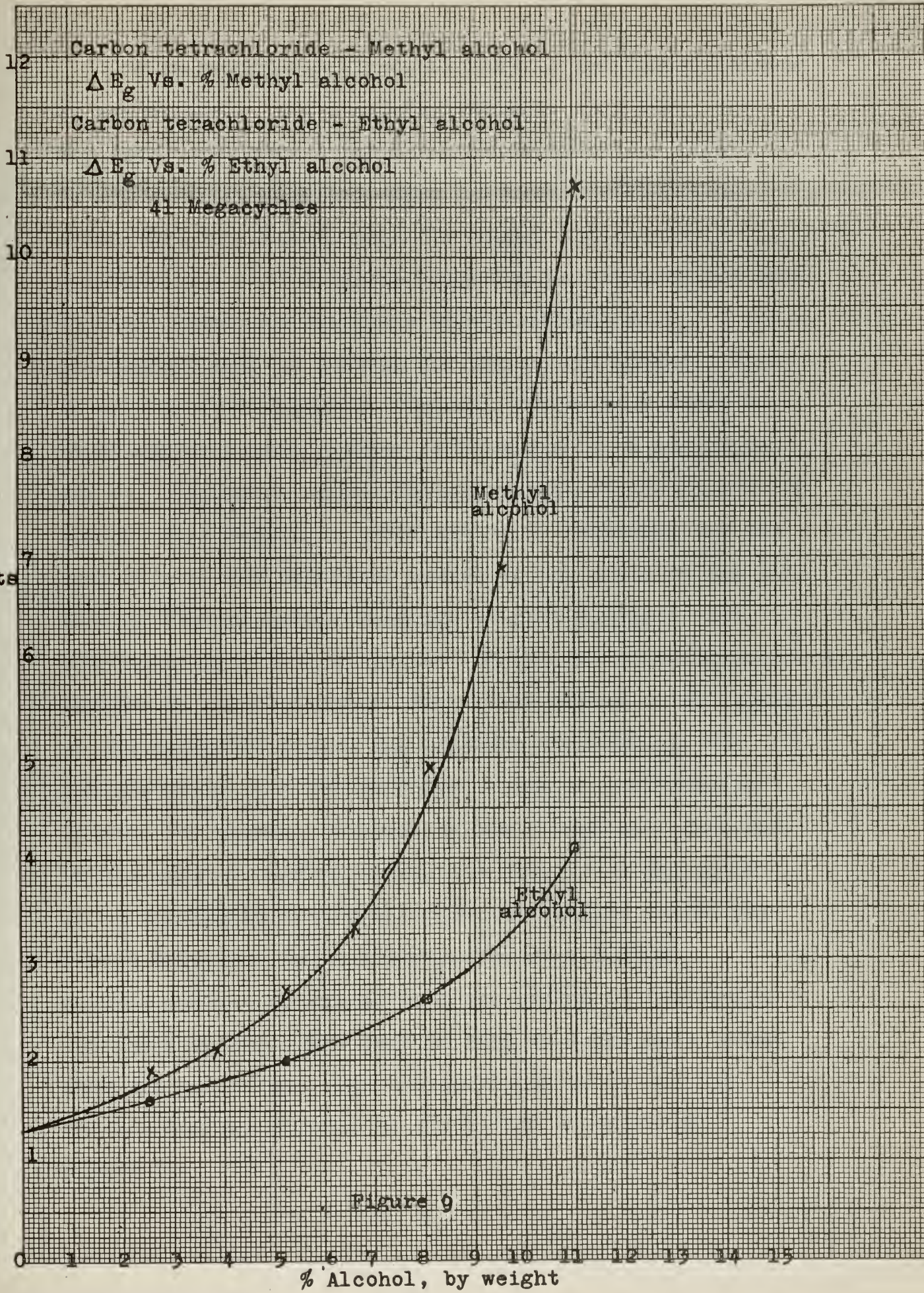
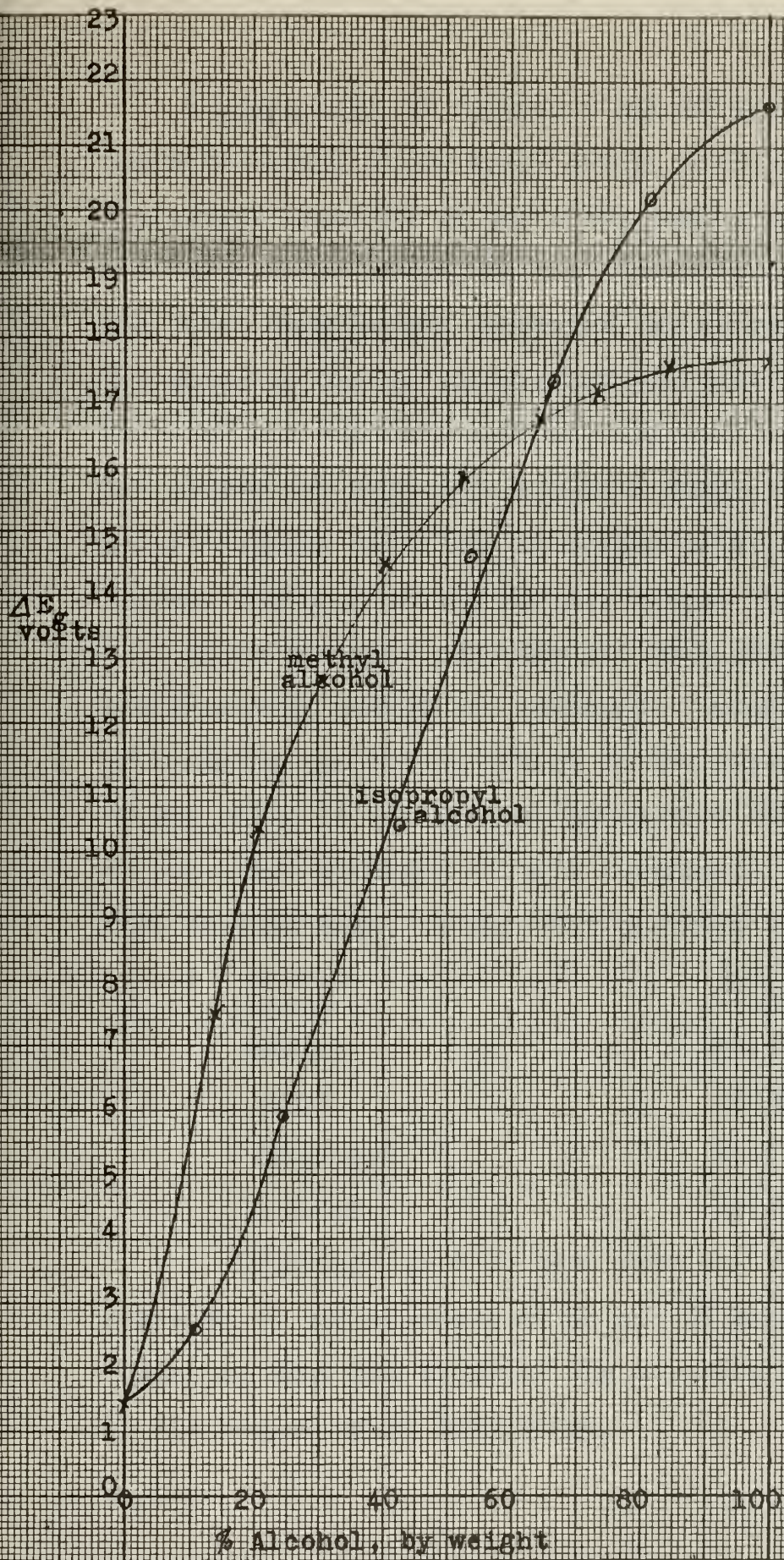


Figure 9

% Alcohol, by weight

It is reasonable to expect that at low concentrations of the alcohols in a non-polar solvent, that the solutions will behave normally, since there are fewer molecules of alcohol per cubic centimeter of solution. Also, that the alcohol with the higher dielectric constant will show a greater response in changing the grid voltage, therefore the slope of the curves, $d(\Delta E_g) / d(\text{concentration})$ will be greater for the methyl alcohol. This is evident from figure 8. However, the problem seems to be at higher concentrations, approaching pure compounds and at frequencies around 55 megacycles. It was decided to explore this region. A modification in technique was put into effect. The capacitor plates on the sides of the cell were shifted slightly. Readings of grid voltages were made at 15 milliliters, instead of 10, and at 45 milliliters instead of 50 milliliters. The fringe effect of the edges of the capacitor plates was ignored, thus taking into consideration only the response of the liquid actually between the plates. Eliminating the fringe area response in the grid voltage readings. The oscillator was tuned at 55 megacycles with a plate voltage of 125 volts. The binary solutions to be investigated were carbon tetrachloride - methyl alcohol and carbon tetrachloride - isopropyl alcohol. The grid voltage readings were taken with the slight modification mentioned above and the information was plotted in graph form as shown in figure 10.



| <u>% alcohol</u> <u>isopropyl</u> | <u>ΔE</u> <u>v</u> |
|--------------------------------------|-----------------------|
| 0.0 | 1.45 |
| 10.9 | 2.6 |
| 24.7 | 5.9 |
| 42.5 | 10.4 |
| 53.5 | 14.6 |
| 66.4 | 17.35 |
| 81.6 | 20.2 |
| 100.0 | 21.6 |

| <u>% alcohol</u> <u>methyl</u> | <u>ΔE</u> <u>v</u> |
|-----------------------------------|-----------------------|
| 0.0 | 1.45 |
| 14.25 | 7.5 |
| 21.75 | 10.4 |
| 30.6 | 12.7 |
| 40.7 | 14.5 |
| 52.3 | 15.9 |
| 64.7 | 16.75 |
| 73.4 | 17.15 |
| 84.5 | 17.56 |
| 100.0 | 17.65 |

% Alcohol, by weight

Figure 10

A comparison of figures 9 and 10 show that at low concentrations, it is again methyl alcohol, with a higher dielectric constant in the lower megacycle region, which has the greater slope. As the concentration of molecules per cubic centimeters increases, at approximately 25%, the slope of the methyl alcohol solution begins to decrease and the isopropyl alcohol solution is greater in the medium and high concentration range, than that of the methyl alcohol solution. At approximately 65%, the grid voltage readings of the former, exceed that of the latter.

Since the grid response had been examined for two of the alcohols, methyl and isopropyl, using a modification of ignoring the fringe effect of the capacitor plates of the cell, it was decided to measure the grid voltage of two other alcohols at this frequency. The change in grid voltage (ΔE_g) of the four alcohols are as follows:

| <u>Alcohol</u> | <u>ΔE_g</u> |
|----------------|--------------------------------|
| methyl | 17.65 |
| ethyl | 19.35 |
| isopropyl | 21.6 |
| n-butyl | 22.7 |

A comparison of this data with the results of the response of the alcohols at 54 and 58 megacycles, on page 18, indicates that the trend of the alcohols is the same in the region of 55 megacycles.

Another area which was investigated, was a comparison between an alcohol and a polar non-alcohol in a non-polar solvent. The binary solutions selected were benzene-methyl alcohol and benzene-acetone. The oscillator was tuned for 66 megacycles and the plate voltage was set at 100 volts. Grid voltage readings were recorded and the data was plotted as shown on figure 11. The results indicate that the curve of the alcohol - benzene solution is similar to that of the methyl alcohol-carbon tetrachloride solution in figure 9. The high response at low concentrations of alcohols in a non-polar solvent followed the same general pattern. However, the effect of a ketone in a non-polar solvent indicates that in the low and medium concentration range, the response is almost linear. Based on the results of the investigations at 31.8, 41 and 54 megacycles, figures 6, 7, and 8, show that the ketones, both acetone and 2-butanone seem to fall on the general outline of the smooth curve. One might therefore conclude that both acetone and 2-butanone are compounds whose response is predictable in the range of 30 to 70 megacycles and that in a non-polar solvent their response, as the concentration of the solute was increased, would be relatively linear as compared to the alcohols.

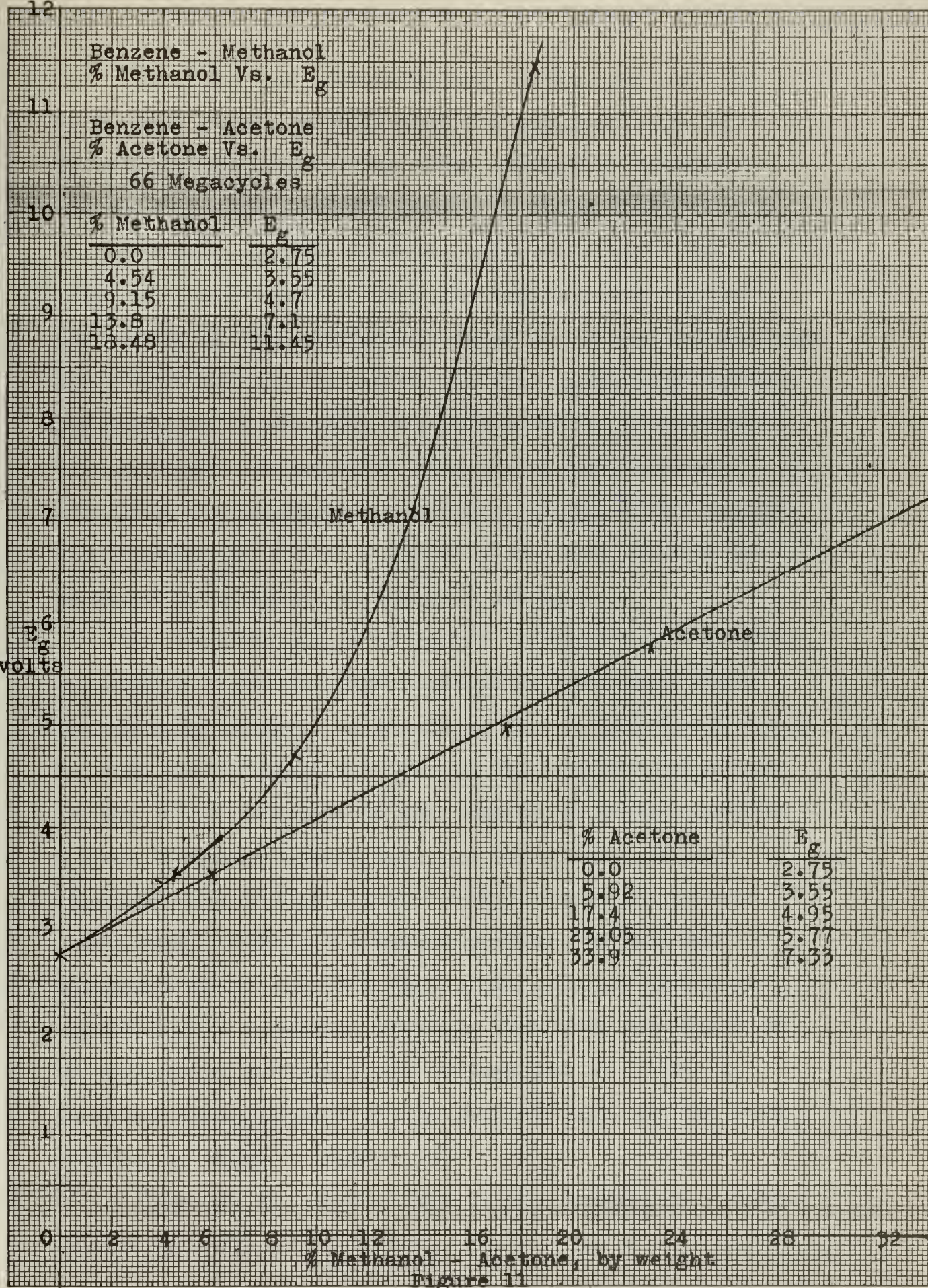
Benzene - Methanol
% Methanol Vs. E_g

Benzene - Acetone
% Acetone Vs. E_g

66 Megacycles

| % Methanol | E _g |
|------------|----------------|
| 0.0 | 2.75 |
| 4.54 | 3.55 |
| 9.15 | 4.7 |
| 13.8 | 7.1 |
| 18.48 | 11.45 |

| % Acetone | E _g |
|-----------|----------------|
| 0.0 | 2.75 |
| 5.92 | 3.55 |
| 17.4 | 4.95 |
| 23.05 | 5.77 |
| 33.9 | 7.33 |

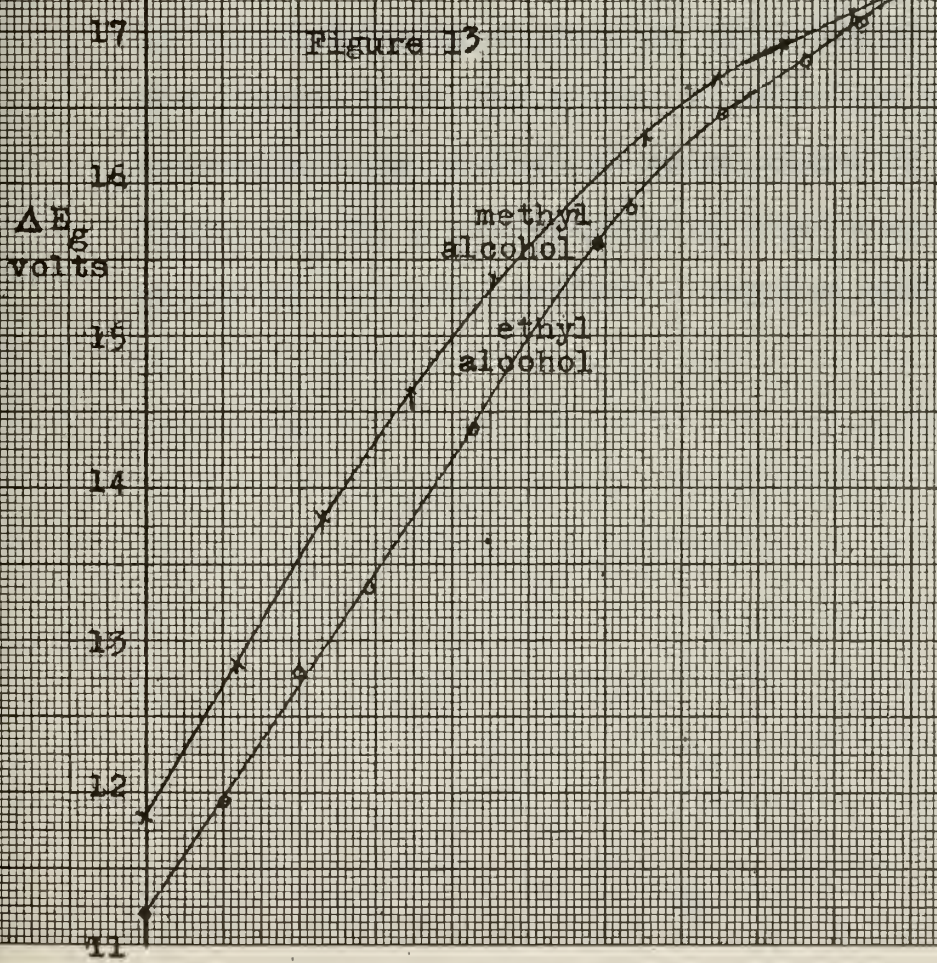
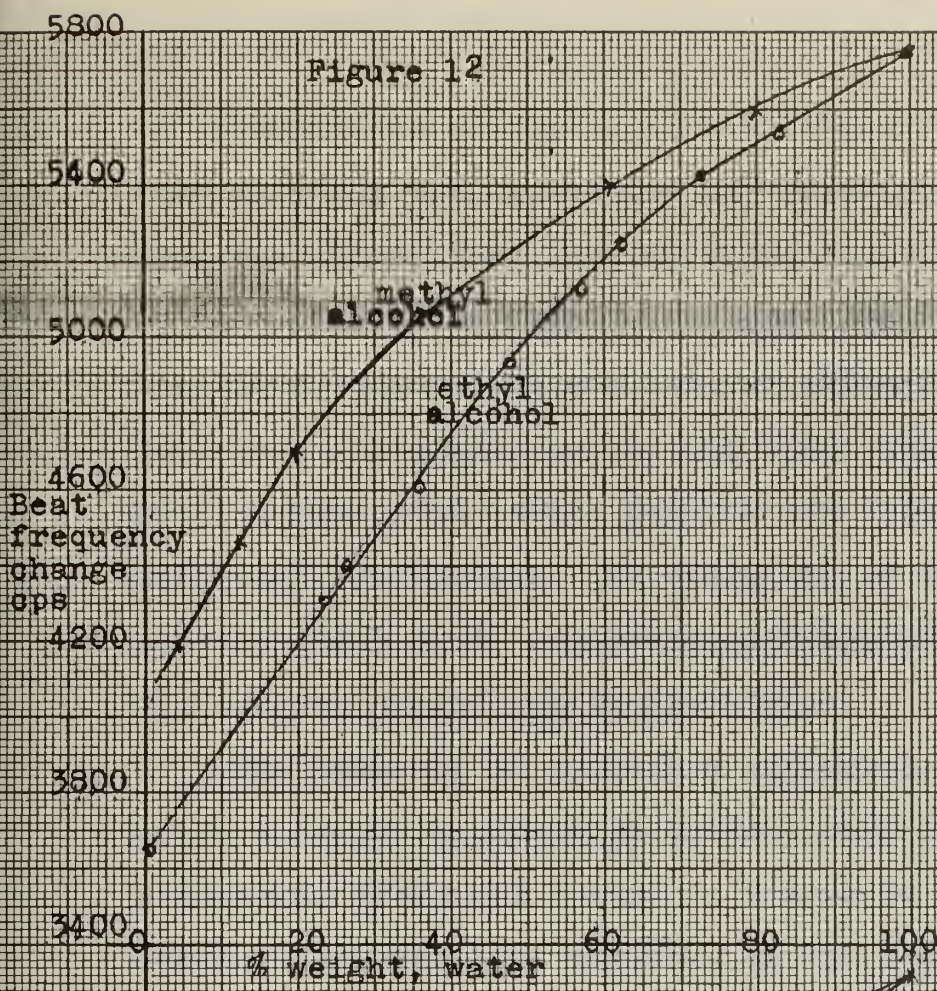


% Methanol - Acetone, by weight.

In 1951, the heterodyne beat method was used by P. W. West et al, to determine its applicability for direct measurements of the water content of monohydric and polyhydric alcohols.⁴ Figure 12 shows their results on the binary systems of methyl alcohol - water and ethyl alcohol - water. Along the ordinate are plotted the values of beat frequency change and along the abscissa, the weight per cent of water. In this particular method, the response of the cell to the dielectric properties of the liquid are measured as a change in frequency, utilizing the heterodyne principle. In the VHFVO system, the response of the cell in the plate tank circuit is measured as a change in the grid voltage.

Two purposes would be served in employing the VHFVO to conduct a similar investigation as mentioned above on the water content of alcohols. First, an attempt could be made to correlate the data of the two investigations, to see if the response of one instrument which produces a beat frequency change bore any resemblance to the response measured as a grid voltage change of another instrument (VHFVO). The second purpose, to see how alcoholic molecules in a very polar solvent behave as compared to a non-polar solvent. The VHFVO was tuned to 41 megacycles and the plate voltage set at 75 volts. Readings were recorded of the grid voltage and the data plotted as shown in figure 13.

⁴West, P. W., Burkhalter, T. S., Senise, P. ; Anal. Chem., Vol. 24, p1250 (1952)



| Ethyl alcohol % water | ΔEg |
|--------------------------|-------|
| 0.0 | 11.2 |
| 10.3 | 11.95 |
| 20.2 | 12.8 |
| 29.6 | 13.35 |
| 43.1 | 14.4 |
| 55.9 | 15.6 |
| 63.9 | 15.65 |
| 75.5 | 16.45 |
| 86.5 | 16.8 |
| 93.5 | 17.05 |
| 100.0 | 17.3 |

| Methyl alcohol % water | ΔEg |
|---------------------------|-------|
| 0.0 | 11.85 |
| 12.1 | 12.85 |
| 23.8 | 13.8 |
| 34.9 | 14.65 |
| 45.5 | 15.4 |
| 55.6 | 15.8 |
| 65.3 | 16.3 |
| 74.5 | 16.7 |
| 83.4 | 16.9 |
| 92.4 | 17.1 |
| 100.0 | 17.3 |

Comparison of figure 12 with figure 13 indicates that although the curves are not superimposable, one upon the other, they bear an extremely strong resemblance to each other. One might check for example, the slope of the lines between 10% and 20%, at 80% and 90% and find that they are approximately the same. However one must bear in mind, that these results are from two entirely different instruments, one operating at four megacycles and the other at 41 megacycles and therefore exact duplication should not be expected.

The behavior of alcoholic molecules in a highly polar solvent, as compared to non-polar solvents, indicate a somewhat different trend. In figure 9, with the non-polar solvent, the response produces an "S" shape curve. While in figure 12, one feature is predominant and that is the linearity of the curves at both low and high concentrations. A feature which might be recalled from figure 10, of a dielectrically stable ketone in a non-polar solvent, acetone - benzene system.

8. Associated Liquids.

One aspect of the investigation which was not foreseen was the seemingly erratic behavior of the alcohols at various frequencies. From figure 9, in dealing with the response of the alcohols in a non-polar solvent, it was evident that at low concentrations, methyl alcohol with a dielectric constant of almost twice that of isopropyl alcohol behaves as would be expected. However beyond 25%, the response of the isopropyl alcohol exceeds that of methanol. At 66 megacycles, as shown in figure 10, the acetone solution shows almost a linear dependency as the concentration increases. Not so the methanol, which shows an extremely high rise in response as the number of alcoholic molecules per cubic centimeter becomes greater. To this investigator's knowledge, there is no previous work, dealing with alcohols in the 30 - 70 megacycle range which would either corroborate or contradict this molecular behavior of alcohols. One previous work by C. P. Smyth and W. N. Stoops does lend some credibility to this type of deviation.⁵ However their investigation was in the kilocycle range and dealt with a solution of ethanal in hexane and heptane. Smyth stated that although normally, departure of the dielectric constant or polarization from linear dependence upon concentration is not attributed to molecular association or polymerization, that there are occasions of the strong influence of molecular association upon the behavior of the polarization. He cited as an

⁵C. P. Smyth, W. N. Stoops, J. Am. Chem. Soc., 51, p.3312, 1929

outstanding example, the case of alcohols in which hydrogen bonding between hydroxyl groups produces polymers.

It was desired to provide an explanation for the deviations resulting from the response of the alcohols. It was felt that these deviations were a result of the induced polarization of the alcoholic molecules caused by the alternating field of the capacitor plates. Looking to the Debye equation, it was found that where association, disassociation or changing intramolecular energy occurred, this invalidates the use of the equation. In the semi-empirical equation of van Arkel and Snoek, who had modified the Debye equation by introducing an additional energy term in the denominator corresponding to dipole - dipole interaction, results of polar liquids improved. However associated liquids such as alcohols caused great variations and was extremely approximate. The work of Onsager led to many advances in the field of dielectric theory. He proposed the following equation:

$$\frac{(\epsilon - \epsilon_{\infty})(2\epsilon + \epsilon_{\infty})}{\epsilon(\epsilon_{\infty} + 2)^2} = \frac{4\pi N}{3} \times \frac{u_0^2}{3KT}$$

ϵ = dielectric constant.

ϵ_{∞} = optical dielectric constant, at frequencies so high that permanent dipoles are unable to contribute.

N = number of molecules per cubic centimeter.

k = Boltzmann constant.

T = absolute temperature.

u = permanent electric moment in vacuo.

When ϵ is large in comparison to ϵ_{∞} , then the above equation reduces to the approximation

$$\frac{\epsilon}{(\epsilon_{\infty} + 2)^2} \approx \frac{2\pi N u_0^2}{9KT}$$

An empirical equation, similar to the one by Onsager, developed by J. Wyman

$$p = \frac{\epsilon + 1}{A}$$

where A is an empirical constant ranging from 6.2 to 11 and having the value of 8.5 for a large number of liquids,

$$\text{and } p = \frac{4\pi N \alpha_0}{3} + \frac{4\pi N u^2}{9KT}$$

α_0 = polarizability per molecule

Both the equation by Onsager and Wyman however fail to apply in dealing with associated liquids such as alcohols. Kirkwood had generalized the Onsager theory, coming up with possibly the best equation to deal with the moment induced as a result of the hindered rotation in the spherical region surrounding the molecule, which would affect the induced polarization. Kirkwood showed

that

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \times \frac{M}{d} = \frac{4\pi N}{3} \left(\alpha_0 + \frac{gu^2}{3KT} \right)$$

M = molecular weight of substance.

d = density.

N = Avogadro's number.

u = molecular dipole moment.

Kirkwood pointed out that the departure of the parameter "g" from unity is a measure of the degree of hindered relative molecular rotation arising from the short range molecular forces. That for normal liquids, "g" is very close to unity, but associated liquids give values of "g" significantly far from unity.

Onsager suggested that the formation of a hydrogen bond increased the moment of the group carrying the hydrogen, an increase now known to be usually small and often undetectable, but it was pointed out that complex formation would account qualitatively for

the apparent increase of moment in the pure liquid as compared to the vapor or dilute solution. For example, if N molecules possessing dipole moment u polymerized to form $N/2$ double molecules in which the two dipoles pointed in the same direction to give moment $2u$ to each of the double molecules, the apparent value of the orientation polarization would double and the value calculated for the moment would be $\sqrt{2} u$ even though no change in the bond moment had occurred.

The effect that high frequency oscillations (55 megacycles) have on the dielectric properties of alcohols, on their polarizability, induced dipole moments or molecular association is not known. However the evidence is rather conclusive that the dielectric response of associated liquids tend to produce anomalies.

⁶C. P. Smyth, Dielectric Behavior and Structure, McGraw Hill Book Co. , p.32, 1955

9. Summary.

The original purpose of this work was to investigate the dielectric properties of organic solutions, using a very high frequency variable oscillator. It was necessary to design and build the instrument. Simplicity and flexibility were foremost in design considerations, followed by stability and sensitivity, in that order. The total cost of the instrument was approximately \$8.00.

The prime motive in employing the VHFVO was to investigate the dielectric properties of organic solutions and to determine if it could be applied as a tool in chemical analysis. It was also desired to operate at various frequencies to observe the effect that the frequency had on a property that is dependent on the dielectric constant of the compound. From the data and figures 6,7,8 and 12, resulting from investigations by the instrument as an analytical tool, it is felt that the VHFVO deserves some merit in that particular endeavor. Initially the response of the alcohols were viewed with concern, however the theories of Debye, Onsager, Wyman, Smyth and Kirkwood substantiate the fact that associated liquids will behave much differently than normal liquids.

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