DIPOLE MOMENTS OF OLEFINIC ESTERS

APPROVED:

R. B. Escue
Major Professor

George Copp
Minor Professor

L. F. Connell, Jr.
Director of the Department of Physics

Jack Johnson
Dean of the Graduate School

DIPOLE MOMENTS OF OLEFINIC ESTERS

THESIS

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Horace M. Poteet, B. S.

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CHAPTER I

INTRODUCTION

Original Work

This thesis was begun as a faculty research project, repeating some experiments and attempting to verify some values obtained by Floyd Shipley[1] for the dipole moments of some olefinic esters. The experimental procedure was identical to that used by Shipley, and described in detail by Spalding.[2] In brief, this method consisted of measuring the dielectric constant, $\epsilon_{1,2}$, and the density, $d_{1,2}$ of a solution of a polar compound in a non-polar solvent at a number of different temperatures, calculating the total polarization, $P_{1,2}$, by means of the Debye equation[3]

$$P_{1,2} = \frac{\epsilon_{1,2} - 1}{\epsilon_{1,2} + 2} \frac{M_1 C_1 + M_2 C_2}{d_{1,2}}, \qquad (1-1)$$

and calculating the dipole moment of the polar compound, μ, from the slope, K_1, of the plot obtained when the total

[1]Floyd D. Shipley, "Dipole Moments of Olefinic Diesters," Unpublished Master's thesis Department of Physics, North Texas State College, 1951.

[2]Dan W. Spalding, "Dipole Moments of Diphenyl Compounds With Conjugated Double Bonds," Unpublished Master's thesis, Department of Physics, North Texas State College, 1950.

[3]Peter Debye, Polar Molecules, p. 45.

polarization was plotted versus the reciprocal of the absolute temperature. Theoretically, such a plot should result in a straight line, the slope of which is related to the dipole moment of the polar solute. In the case of measurements taken on polar compounds in the vapor state, the relationship is

$$\mu = 0.0128\sqrt{K_1} \times 10^{-18} \text{esu.} \qquad (1\text{-}2)$$

This is the equation used by Shipley in his work. It will be shown, however, that when the vapor-phase theory is applied to measurements made on dilute solutions, the correct relationship between the slope and the dipole moment is:

$$\mu = 0.0128\sqrt{K_1/c_1} \times 10^{-18} \text{esu.}, \qquad (1\text{-}3)$$

where c_1 is the mole fraction of the solute.

Following the procedure outlined above, data were taken and calculations were carried out on four compounds: diethyl maleate, dimethyl maleate, dimethyl fumarate, and dimethyl phthalate. The resulting polarization versus inverse temperature plots were linear, but the dipole moment values obtained from their slopes were not consistent. For example, the moments of diethyl and dimethyl maleate should be approximately the same, whereas the experimental results show a value of 4.28×10^{-18} esu. for the former, and a value of 22.21×10^{-18} esu. for the latter.

Purpose of This Thesis

It is the purpose of this thesis to investigate the applicability of the Debye equation to measurements dipole

moments of polar compounds in dilute solutions of non-polar solvents more fully than has been done by previous workers at this institution.

The primary work contained in this thesis is: (1) a brief theoretical treatment of the problem of measuring dipole moments; (2) a resumé of the original work done, together with a qualitative discussion of the results; (3) a discussion of procedures more adaptable to the problem of measuring dipole moments in dilute solutions, and presentation of experimental results from the application of one such method to dipole moment measurements; (4) an evaluation of the thesis as a whole, together with suggested changes in experimental apparatus and procedures which might be carried by further workers.

It is not intended to discuss the theoretical concepts underlying the idea of dipole moments, but rather to apply the equations resulting from these theoretical considerations to the physical problem of measuring dipole moments.

CHAPTER II

THE PROBLEM OF MEASURING DIPOLE MOMENTS

Several methods have been proposed for the experimental determination of the dipole moment of polar compounds. It is the purpose of this chapter to discuss several of these methods and some of the advantages or disadvantages of each. In order to obtain an understanding of the problems involved in these measurements, it becomes necessary to discuss more fully the various proposed methods.

When molecules of a gas are so far removed from one another that there is negligible interaction between them, the polarization, P, is given by [1]

$$P = \frac{4\pi N \mu^2}{9kT} \qquad (2-1)$$

where N is Avagadro's number, μ is the dipole moment of the gas molecules, k is Boltzman's constant, and T is the absolute temperature. This equation is true only in the absence of any external field. However, in order to measure the polarization it becomes necessary to apply a sinusoidal external field. Under the influence of this applied field, there will be two new contributions to the polarization as stated in equation (2-1). First, there will be a contribution due to the

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[1] Samuel Glasstone, Textbook of Physical Chemistry, p. 545.

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displacement of the electron orbits in the direction of the applied field. This results in a change in the centers of positive and negative electric charges in the molecule. The polarization induced in this manner is called the electronic polarization and is denoted by the symbol P_E. The second polarization term P_A, induced in the molecule by the electric field is due to the orientation of the atoms themselves. While the moment of inertia of a single electron is small, thus allowing it to be displaced at rather high frequencies, the moment of inertia of an atom is much larger, which permits a very limited displacement when the applied field varies at frequencies of the order of one megacycle per second. It may then be seen that the magnitude of the electronic polarization term will be large compared with the atomic polarization term. It has been estimated that the latter is of the order of from 5 to 10 per cent of the former.[2] Since even the electronic polarization is small compared to that produced by the permaent dipole moment of even moderately polar compounds, a small error in the evaluation of the atomic polarization will cause little error in the calculation of the dipole moment. In view of the above discussion, it is possible to write

$$P_T = P_E + P_A + P = P_D + \frac{4 \pi N \mu^2}{9k\,T} \qquad (2\text{-}2)$$

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[2] R. J. W. Le Fevre, Dipole Moments, p. 13.

for the total polarization, P_T, which would be obtained from experimental measurements. The total polarization can also be calculated from the dielectric constant, ϵ, the density, d, and the molecular weight M. of the vapor by means of Debye's equation:[3]

$$P_T = \frac{\epsilon - 1}{\epsilon + 2} \; \frac{M.}{d}$$ (2-3)

Calculation of the dipole moment from equation (2-2) involves calculating the total polarization and the distortion polarization. In order to evaluate the distortion polarization, P_D, reference is made to equation (2-2). The measured polarization, P_T, is the sum of three terms. The first two of these comprise the distortion polarization, while the third is the polarization due to the orientation of the whole molecule. Since the molecule is made up of many atoms, its moment of inertia is much greater than that of a single atom, and very greater than that of an electron. Considering this, it is possible to increase the frequency of the measuring field until the molecular dipoles no longer have sufficient time to orient themselves with each cycle. Thus the third term in equation (2-2) is eliminated, and the measured polarization is the distortion polarization. The frequency at which the orientation of the molecular dipoles becomes negligible lies somewhere in the infra-red region for most molecules. If the total polarization were measured with infra-red radiation

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[3] Debye, op. cit., p. 12.

as the exciting field, the value obtained would represent the distortion polarization. Since the procedure is generally impractical further steps must be taken. If the frequency of the measuring field is increased further until it falls in the visible range, even the atomic dipoles do not have time to orient themselves between oscillations of the field. In this case, the measured polarization consists entirely of the electronic polarization, P_E. According to electromagentic theory, the dielectric constant of a material is equal to the square of its index of refraction if both are measured at the same frequency.[4] Thus:

$$\epsilon = n^2, \tag{2-4}$$

where n is the index of refraction. Sustitution of this value into equation (2-3) gives:

$$P_E = P_{T(visible)} = \frac{n^2 - 1}{n^2 + 2} \frac{M.}{d} \tag{2-5}$$

This quantity is generally called the molar refractivity of a compound, and is denoted by R_λ, where λ is the wavelength of the radiation with which the index of refraction was determined.

The approach to the question of the dipole moment of a polar compound is straightforward. A determination of the

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[4] John C. Slater and Nathaniel H. Frank, Electromagnetism, p. 93.

dielectric constant and the density in the vapor phase make
it possible to calculate the total polarization, P_T, from
equation (2-3). Then the electronic polarization can be calcu-
lated from index of refraction and density measurements on
the polar compound. Finally, the total distortion polarization
can be approximated by the equation:

$$P_D = P_E + 0.05P_E. \qquad (2-6)$$

Substituting these values into equation (2-2) make it possible
to solve for the dipole moment, μ.

An alternate method of determining the dipole moment
makes use of the linear dependence of the total polarization
upon the inverse of the absolute temperature. Since the dis-
tortion polarization, P_D, is independent of the temperature
it can be seen from equation (2-2) that the total polarization,
when plotted against the reciprocal of the absolute temperature,
will yield a straight line. The slope of this line b, is:

$$b = \frac{4\pi N \mu^2}{9k}, \qquad (2-7)$$

and the intercept on the polarization axis, m, is:

$$m = P_D. \qquad (2-8)$$

Thus, if the total polarization of a compound in the vapor
state is found as a function of the temperature, and plotted
versus the reciprocal of the absolute temperature, the dipole
moment, μ, can be found from the slope of the resulting
straight line, and the distortion polarization can be evaluated

from the intercept on the axis of polarization. It was by
this experimental means that P_A was proved to be small as
compared to P_E, and that equation (2-6) was proved a satis-
factory approximation of the total distortion polarization
for most cases.[5] In the event that the compound under con-
sideration has a very small dipole moment, the distortion
polarization is then of the same order of magnitude as the
molecular polarization, and the approximation is no longer
valid.

Unfortunately, measurements of the dielectric constants
refractive indices, and densities of compounds in the vapor
state present a difficult problem. Reduced pressures would
be necessary if the vapor pressures of the compounds were
low or if attempts to vaporize them resulted in serious
decomposition. In addition to these considerations, very
precise measurements are necessary. Considering these dis-
advantages, it seems profitable to attempt to modify the
above procedures to apply to dilute solutions.

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[5] Le Fevre, _op. cit._, pp. 16-17.

CHAPTER III

APPLICATIONS TO DILUTE SOLUTIONS

General Considerations

The methods of dipole moment measurement considered in
the preceding chapter apply strictly only when the inter-
action between the molecules of the polar compound can be
neglected. In the case of polar liquids, this is obviously
not true, since molecules of polar liquids exert repulsive
and attractive forces on each other which depend upon their
orientation with respect to each other. Since the configu-
ration in which the attraction is greatest is favored, there
is a tendency for the molecules to associate, forming groups
which behave as one double or triple molecule instead of as
two or three single molecules. This tendency is opposed by
the random motion due to thermal agitation.

In order to disperse the polar molecules sufficiently
so that association will be destroyed by thermal agitation,
it has been suggested that dilute solutions of polar solutes
in non-polar solvents be employed. This procedure necessi-
tates the revision of the vapor phase theory to apply to
dilute solutions.

It has been known for years that the molar refractivity of a liquid mixture is given by the expression

$$R_{1,2} = c_1 R_1 + c_2 R_2 = \frac{n_{1,2}^2 - 1}{n_{1,2}^2 + 2} \quad \frac{M_1 c_1 + M_2 c_2}{d_{1,2}}, \qquad (3-1)$$

where c is the mole fraction, d is the density, M is the molecular weight, n is the index of refraction, and R is the molar refractivity. The subscript, 1, denotes properties of the solute, 2, properties of the solvent, and, 1,2, properties of the mixture.

Adapting equation (3-1) to measurements of polarizations at radio frequencies, by means of equation (2-4) gives:

$$P_{1,2} = c_1 P_1 + c_2 P_2 = \left(\frac{\epsilon_{1,2} - 1}{\epsilon_{1,2} + 2} \quad \frac{M_1 c_1 + M_2 c_2}{d_{1,2}} \right). \qquad (3-2)$$

This equation can be solved for the solute polarization, P_1, in terms of the total polarization, $P_{1,2}$, and the solvent polarization, P_2, which can be calculated from measurements made on the pure solvent by the expression:

$$P_2 = \frac{\epsilon_2 - 1}{\epsilon_2 + 2} \quad \frac{M_2}{d_2}. \qquad (3-3)$$

Assuming that the polar molecules dispersed in the non-polar behave as if they were in the vapor state, that is, that interactions are negligible between them, equation (2-2) may be applied to this case, where P_T now denotes the total polarization of the solute, which is exactly the same as P_1. Thus, solving equation (3-2) for P_1 and equating it to P_T in equation (2-2), it is seen that

$$\frac{1}{c_1} \left\{ P_{1,2} - c_2 P_2 \right\} = P_D + \frac{4 \, \pi \, N \, \mu^2}{9KT}. \qquad (3\text{-}4)$$

From this equation, the dipole moment may be determined by two methods analogous to those discussed in connection with the vapor phase determinations.

The Temperature Variation Method

An examination of equation (3-4) reveals that if the solute polarization, P_1, is plotted versus the reciprocal of the absolute temperature, a straight line should result. In order to actually calculate P_1 as a function of temperature, it is necessary to measure the density and the dielectric constant of the solution at various temperatures, and to measure the density and dielectric constant of the non-polar solvent at a single temperature. The solvent polarization is independent of the temperature, and may thus be evaluated from a single set of measurements.

The polar compounds used in this determination were: dimethyl phthalate, Amend Drug and Chemical Company; dimethyl maleate, Carbide and Carbon Chemicals Corp.; diethyl maleate, Carbide and Carbon Chemicals Corp.; dimethyl fumarate, Chas. Pfitzer and Co. All of these compounds were of technical quality, and were purified as discussed below. The dimethyl maleate was recrystallized several times, a mixture of dry ice and acetone being used to cool it below its freezing point of about -19°C. The dimethyl fumarate was recrystallized several times, first from benzene, and later from chloro-

chloroform. Both the dimethyl phthalate and the diethyl maleate were purified by fractional distillation.

One solution was prepared from each of the compounds listed above, the concentrations being of the order of two grams of the polar solute to eighty grams of benzene. This corresponds to a mole fraction of the solute of about 0.01, for compounds whose molecular weight is about 150. About fifty milliliters of each solution was prepared, and each solution was stored in a plainly marked, tightly stoppered flask. The data concerning the four solutions prepared are shown in Table 1. In the table headings, W_1 is the weight of the solute, W_2 is the weight of the benzene, and C_1 is the mole fraction of the solute.

TABLE 1

CONCENTRATIONS OF SOLUTIONS USED IN
TEMPERATURE VARIATION METHOD

Solution Number	Compound	W_1 grams	W_2 grams	C_1
1	Diethyl Maleate	2.6605	81.6085	0.02182
2	Dimethyl Maleate	2.0329	84.0480	0.01609
3	Dimethyl Fumarate	2.0802	78.8070	0.01050
4	Dimethyl Phthalate	1.0763	49.1522	0.00983

The density and dielectric constant of each solution, as well as of the pure solvent, were then measured at various temperatures. Since in this case benzene was used as the solvent, and since its melting point is about $5^{\circ}C$, and its boiling point is about $78^{\circ}C$, the maximum usable temperature

range was from about 10°C to about 70°C. Since dielectric
constant characteristics at or near the boiling and melting
points may be erratic, it was decided to use only the temper-
ature range from 20°C to 60°C. Dielectric constant and
density determinations were made at 5°C temperature intervals
in this range.

Measurement of Density

The density at each temperature was obtained in the
usual manner by weighing a sample of each solution in a
pycnometer whose volume had been determined at each temper-
ature by weighing it filled with water. The pycnometer used
was of the type having a ground glass stopper containing a
fine capillary. As long as room temperature was less than
the temperature of the measurement, negligible evaporation
occurred from the capillary. When the temperature of the
measurement was less than room temperature, however, some of
the liquid expanded from the capillary and immediately evapo-
rated, making density measurements at such temperatures im-
possible. Fortunately, the density was in each case a linear
function of the temperature, and extrapolation into this
temperature range was not difficult. The accuracy of the
density determinations as a whole is estimated to be better
than two units in the fourth decimal place.

The volume of the pycnometer, V_p, is shown in Table 2
for various temperatures, while Table 3 gives the density of
each solution, $d_{1,2}$, at each temperature.

TABLE 2

PYCNOMETER VOLUME

t	V_P cc
20°C	4.9893
25	4.9902
30	4.9911
35	4.9919
40	4.9926
45	4.9933
50	4.9942
55	4.9950
60	4.9960

TABLE 3

DENSITY OF SOLUTIONS

t	Density grams/cc			
	Solution Number 1	Solution Number 2	Solution Number 3	Solution Number 4
20°C	0.88216	0.88008	0.88907	0.88722
25	0.87635	0.87499	0.88533	0.88157
30	0.87355	0.87104	0.87944	0.87684
35	0.86804	0.86567	0.87547	0.87155
40	0.86291	0.86084	0.86928	0.86564
45	0.85778	0.85657	0.86438	0.85995
50	0.85218	0.85016	0.85864	0.85552
55	0.84762	0.84497	0.85301	0.84968
60	0.84146	0.82651	0.84870	0.84428

Measurement of Dielectric Constant

The dielectric constant of a material is defined as
the ratio of the capacitance of a condenser filled with the
material to the capacitance of the condenser in a vacuum.
Corrections must be made for capacitances due to leads and
spacers. If the dielectric constant of air is assumed to
be unity, then it can be shown that the dielectric constant,
ϵ_x, of an unknown solution is given by the equation

$$\epsilon_x = \frac{C_x - C_{air}}{C_a} + 1, \qquad (3\text{-}5)$$

where C_x is the capacitance of the test capacitor, or test
cell, filled with a solution of dielectric constant ϵ_x,
C_{air} is the capacitance of the test cell filled with air,
and C_a is the true air capacitance of the test cell, defined
by the relationship

$$C_a = \frac{C - C_{air}}{\epsilon - 1}, \qquad (3\text{-}6)$$

where C is the capacitance of the test cell filled with a
liquid of known dielectric constant ϵ^1. Benzene was used
as a standard in this investigation because its dielectric
constant as a function of temperature is accurately known.

The three most widely used methods for determining the
capacity of a condenser, and hence for measuring the die-
lectric constant of a dielectric material filling the con-
denser, are the bridge method, the resonance method, and

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[1] Spalding, op. cit.

the heterodyne-beat method. The first two methods have the advantage that they can be used on solutions of relatively high specific conductance. Since the solutions used in this investigation had very low specific conductances, and since a reasonably accurate apparatus of the heterodyne-beat type was readily available, having been constructed and modified by previous workers in this field, the heterodyne-beat method was chosen.

The apparatus used, shown in block diagram in Figure 1, consists of a variable frequency oscillator, a fixed frequency oscillator, a mixer, an audio amplifier, and an indicator.
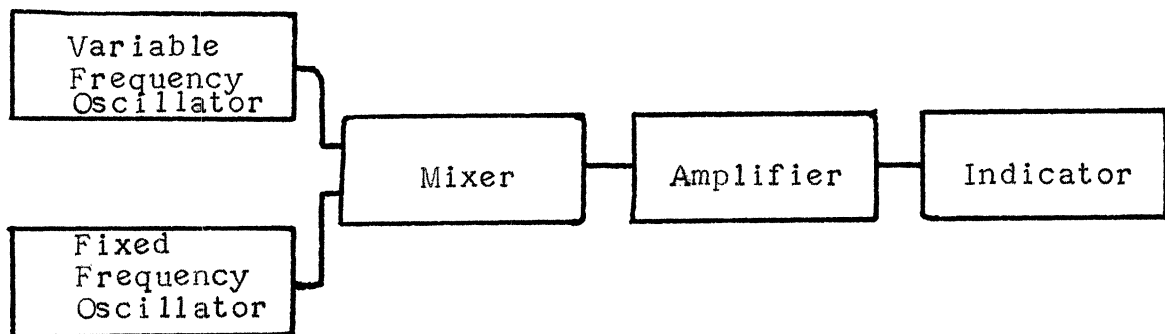
Fig. 1.--Block diagram of
heterodyne-beat apparatus.

The signals from the variable frequency oscillator and the local fixed frequency oscillator are mixed, and the resulting "sum" and "difference", or beat, frequencies are fed into the amplifier. Since the frequency of each of the oscillators is of the order of one megacycle/second, the "sum"

frequency, of the order of two megacycles/second, will be by-passed in the audio amplifier, allowing only the "beat" frequency to be amplified and fed into the indicator. The indicator, which in the apparatus used consisted of a type 6E5 "Magic Eye" indicator tube, is so designed that as long as a signal is supplied to it, the "eye" will remain closed, but if the signal is removed, the "eye" will open to a maximum. Since the signal obtained from the mixer is a difference frequency, it will be zero when the oscillators are at the same frequency. Thus, the variable frequency oscillator can be tuned to the same frequency as the local oscillator by observing the indicator and tuning to a null as indicated by maximum opening of the electron "eye". The local oscillator used in this apparatus was a Bud crystal controlled frequency standard, oscillating at 100 kilocycles per second with harmonics every 100 kilocycles. Care must be taken to use the same harmonic of the local oscillator throughout the determinations.

Since the variation of the frequency of the variable frequency oscillator is effected by variation of a capacitance in a parallel resonant circuit, the magnitude of any capacitance can be determined by connecting it in parallel with the tuning condenser, and by measuring the amount by which the tuning capacitance must be reduced in order to bring the variable frequency oscillator back to the original frequency. This can be accomplished by first bringing the

variable frequency oscillator to zero beat with the local oscillator, connecting the unknown capacitor, and by measuring the increment by which the tuning capacitor must be decreased to bring the variable frequency oscillator back to zero beat with the local oscillator. Since the accuracy with which capacitance measurements may be made depend upon the accuracy of the calibration of the tuning capacitor, a precision capacitor is usually used. In this case, a General Radio type 772 precision capacitor was used, which allowed incremental capacitances to be measured in the range of about 100 micromicrofarads, or in the range of about 1000 micromicrofarads.

The test cell used in this determination was constructed by Fielder.[2] It consisted of three concentric metal cylinders, spaced with thin strips of mica. The inner and the outer cylinders were connected, forming an electostatic shield about the middle, or high potential, cylinder. Connection of the test to the heterodyne beat apparatus was made by beans of stiff metal rods, which dipped into mercury cups located on the cell. Before using the test cell, it was first cleaned in a manner suggested by Fielder. First it was filled with benzene and allowed to stand at a temperature of about 60°C for fifteen minutes. It was then emptied,

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[2] Joseph T. Fielder Jr., "Measurement of Dielectric Constant and Dipole Moment of Liquids," Unpublished Master's thesis, Department of Physics, North Texas State College, 1948.

rinsed with fresh benzene, and the heating process was re-
peated with more benzene. The whole procedure was then re-
peated, using acetone instead of benzene, and the cell was
dried in an oven at 100°C until all traces of the solvent
were removed.

Dielectric constant measurements then consisted of
measuring the capacitance of the test cell filled first
with air to obtain C_{air}, then with benzene to obtain C, and
finally with the dielectric solution to obtain C_x. The die-
lectric constant of the dielectric solution was calculated
by equations (3-5) and (3-6). This procedure was carried
out for each solution at each temperature. The experimental
values of C_{air}, C, and C_x, and the calculated values of C_a
and ϵ are shown in Table 4.

Calculation of Dipole Moments

Having obtained the density and the dielectric constant
of each solution as a function of temperature, the total
polarization, $P_{1,2}$, was then calculated from equation (3-3),
as shown in Table 5. It is possible to solve equation (3-3)
for the solute polarization, P_1, which then may be plotted
versus the reciprocal or the absolute temperature, making
possible the calculation of the dipole moment from the slope
of the resulting straight line. It was decided more con-
venient, however, to derive an expression making it possible to
calculate the dipole moment from the slope of the line

TABLE 4

DATA AND CALCULATED VALUES OF DIELECTRIC
CONSTANT OF SOLUTIONS USED IN
TEMPERATURE VARIATION METHOD

t	Capacitance, in mmF, Test Cell Filled With			C_a mmF	ϵ
	Air	Benzene	Solution		

Diethyl Maleate

t	Air	Benzene	Solution	C_a mmF	ϵ
20°C	115.242	234.915	246.398	93.276	2.4061
25	115.160	234.237	245.397	93.504	2.3928
30	115.034	233.375	244.216	93.624	2.3798
35	114.986	232.410	242.898	93.602	2.3666
40	114.954	231.337	241.695	93.450	2.3587
45	114.924	230.142	240.178	93.181	2.3442
50	114.898	228.932	238.901	93.013	2.3332
55	114.872	227.407	237.348	92.507	2.3240
60	114.852	226.317	235.850	92.348	2.3102

Dimethyl Maleate

t	Air	Benzene	Solution	C_a mmF	ϵ
20°C	115.242	234.915	242.218	93.276	2.3613
25	115.160	234.237	241.006	93.504	2.3459
30	115.034	233.375	239.638	93.624	2.3309
35	114.986	232.410	238.532	93.602	2.3199
40	114.954	231.337	237.418	93.480	2.3101
45	114.924	230.142	235.925	93.181	2.2982
50	114.898	228.932	234.790	93.013	2.2890
55	114.872	227.407	233.347	92.507	2.2807
60	114.852	226.317	232.167	92.348	2.2704

TABLE 4--Continued

Dimethyl Fumarate

t	Capacitance of Test Cell Filled With (mmF)			C_a mmF	ϵ
	Air	Benzene	Solution Number 3		
20°C	115.182	232.688	245.860	91.587	2.4267
25	115.228	231.995	244.828	91.690	2.4135
30	115.247	231.245	243.720	91.771	2.3999
35	115.248	230.282	242.757	91.697	2.3905
40	115.260	229.350	241.718	91.639	2.3800
45	115.245	227.997	240.572	91.186	2.3744
50	115.317	226.535	239.487	90.716	2.3688
55	115.398	225.218	238.218	90.440	2.3602
60	115.477	224.105	237.000	90.227	2.3380

Dimethyl Phthylate

t	Air	Benzene	Solution Number 3	C_a mmF	ϵ
20°C	115.507	235.798	242.090	93.717	2.3501
25	115.516	234.605	241.123	93.641	2.3432
30	115.523	233.920	240.162	93.480	2.3307
35	115.532	232.792	239.105	93.451	2.3221
40	115.541	231.653	237.980	93.249	2.3129
45	115.550	230.318	236.745	92.810	2.3058
50	115.558	228.550	235.298	92.163	2.2992
55	115.563	226.508	233.880	91.204	2.2973
60	115.568	224.580	232.870	90.325	2.2988

TABLE 5

TOTAL POLARIZATION OF TEMPERATURE
VARIATION SOLUTIONS

$1/T$ $\times 10^3$ ($^\circ$Abs)$^{-1}$	$P_{1,2}$ cc			
	Solution Number 1	Solution Number 2	Solution Number 3	Solution Number 4
3.4130	29.922	29.721	28.680	27.646
3.3557	29.512	28.848	28.698	27.726
3.3003	29.167	28.447	28.702	27.785
3.2468	28.786	28.072	28.699	27.738
3.1949	28.501	27.788	28.754	27.783
3.1447	28.123	27.458	28.836	27.871
3.0960	27.788	27.154	28.947	28.006
3.0488	27.567	26.909	29.013	28.080
3.0030	27.187	26.602	28.832	28.282

resulting when the total polarization, $P_{1,2}$, is plotted
versus $1/T$.

Considering equation (3-4), it is seen that the dis-
tortion polarization, P_D, the solvent polarization, P_2, and
the mole fractions of the solute and the solvent, c_1 and c_2
respectively, are all independent of the temperature. Thus,
it is possible to write, from equation (3-4),

$$P_{1,2} = c_1 P_D + c_2 P_2 = \frac{4\pi}{9k} \frac{N\mu^2}{T}, \qquad (3-7)$$

and finally

$$P_{1,2} = K_1 + K_2 \frac{1}{T} \qquad (3-8)$$

where K_1 and K_2 are constants, independent of the temper- ature. Thus, if the total polarization is plotted versus $1/T$, the dipole moment may be calculated by means of the equation

$$\mu = \sqrt{\frac{9k\ K_2}{4\pi c_1 N}} = 0.0128 \sqrt{K_2/c_1} \times 10^{-18} esu \qquad (3\text{-}9)$$

where K_2 is the slope of the resulting straight line.

Plots of the calculated values of $P_{1,2}$ versus $1/T$ for each solution are shown in Figure 2. The values of the slope, K_2, of each of the resulting curves, together with the dipole moment, μ, calculated from each, are shown in Table 6.

TABLE 6

SLOPE OF POLARIZATION VERSUS INVERSE
TEMPERATURE PLOT AND CALCULATED
DIPOLE MOMENTS

Solution Number	K_2 cc-^{o}Abs.	μ Debyes
1	65610.	22.21
2	62683.	25.25
3	356.6	2.36
4	1098.	4.28

Values for the dipole moment of only one of the polar compounds used, diethyl maleate, could be located in the literature. The value obtained from the literature was
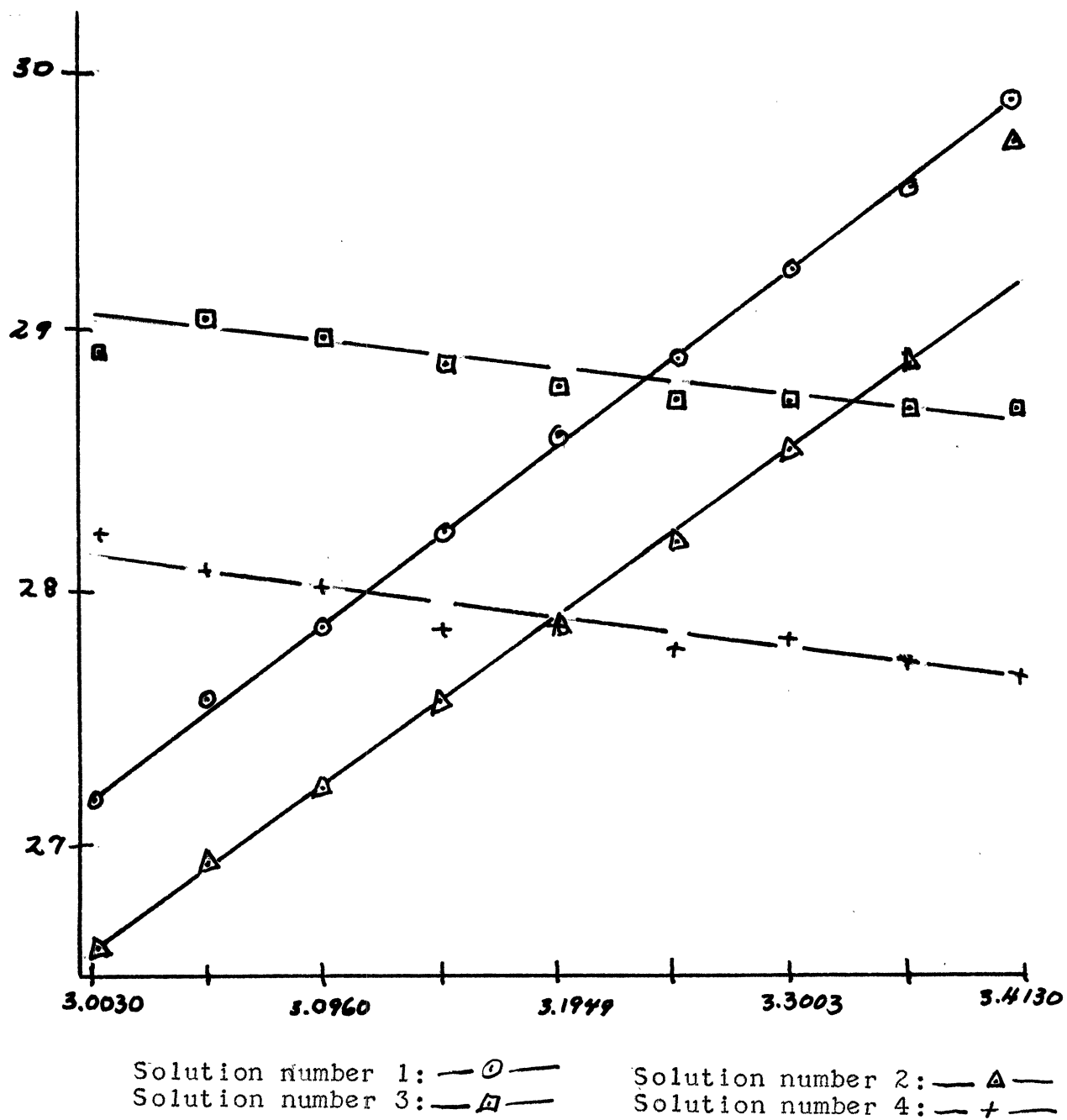
Fig. 2.--Total polarization versus inverse temperature.

2.56 x 10^{-18} esu. Assuming free rotation of the ethyl and
methyl radicals, the dipole moment of dimethyl maleate should
be exactly the same as that of diethyl maleate; also, the
moments of any of the olefins should be of the same order of
magnitude, indicating that the values to be expected would
lie in the region between 2D and 3D, where

$$D = 10^{-18} \text{ esu. cm.} \qquad (3\text{-}10)$$

is defined to be the Debye, or unit of measurement of mole-
cular dipole moments.

As evidenced by the dipole moment values listed in
Table 6, the range of experimental values obtained for the
olefins investigated was much greated than that to be ex-
pected. A review of the assumptions made when modifying
the vapor phase theory to apply to measurements made on dilute
solutions showed several of them to be of doubtful validity.

First, the asumption that non-polar molecules could be
used as a dispersive element for the polar molecules, in
order to eliminate interactions, is not strictly truc. If
the solution is dilute enough, all interactions between the
polar solute molecules will be eliminated, but interactions
between the polar molecules and the surrounding solvent mole-
cules can occur. This results in a polarization or orien-
tation term being induced in the non-polar solvent molecule.
The induced electric moment will oppose the permanent moment
of the polar molecule. To illustrate this, consider Figure
3, which depicts a polar molecule of small size, having an

electric moment of magnitude M in the direction shown by
the arrow. The polar molecule is surrounded by six non-
polar solvent molecules. It is assumed that the influence
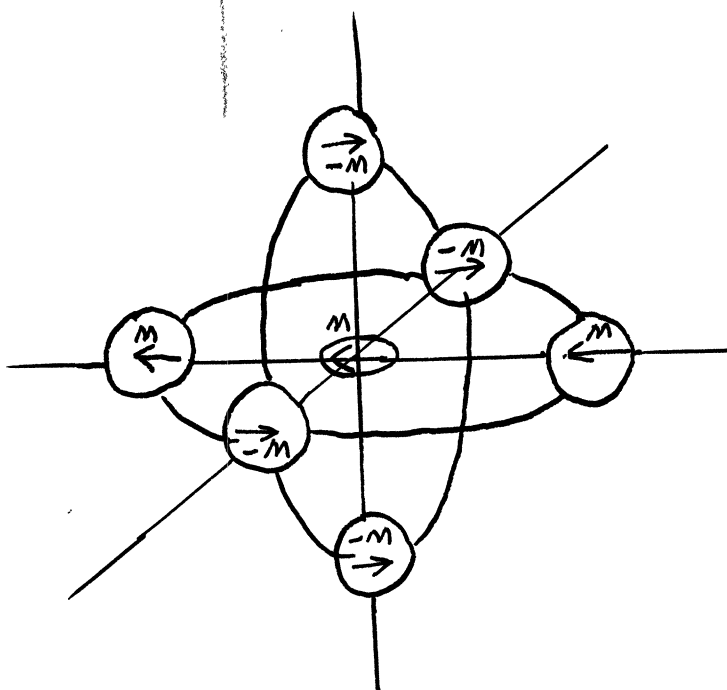
Fig. 3.--Normal solvent effect:
effective moment is -M.

of the solute molecule will not extend beyond the immedi-
ately surrounding molecules. An electric moment, of magni-
tude M, is induced into each of the solvent molecules in
directions shown by the arrows, so that the vector sum of
of the moments is -M. Since it is only possible to measure
the magnitude of the dipole moment, no effect could be de-
tected if interactions of this type actually occurred. If,
however, the polar molecule is large, that is if it extends

Into the space which would normally be occupied by one of the six solvent molecules shown in Figure 3, a very different situation results. Consider as an example, Figure 4.
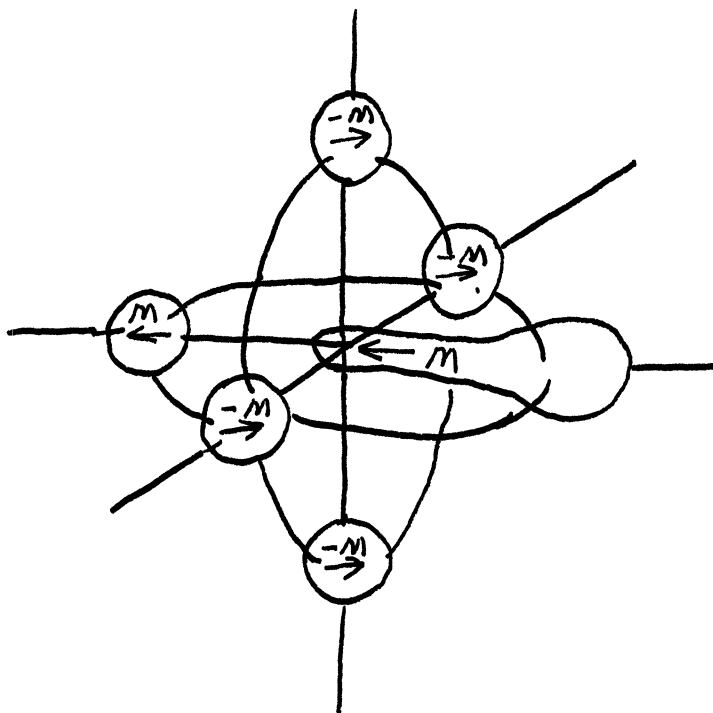
Fig. 4.--Positive solvent effect:
effective moment is -2M.

Again a polar molecule having a moment M is surrounded by solvent molecules, but in this case, due to the size of the polar molecule, only five of the solvent molecules are close enough to actually be in the induction field of the polar molecule. Each of the five has an induced moment, of magnitude M, in directions shown by arrows, so that the vector sum of the system is -2M, which is twice the magnitude of

the polar molecule. A similar situation can be visualized
in which the resultant dipole moment is zero. Such an
orientation is shown in Figure 5, in which the dipole moment
of the polar molecule is perpendicular to the largest di-
mention of the molecule.

Fig. 5--Negative solvent effect:
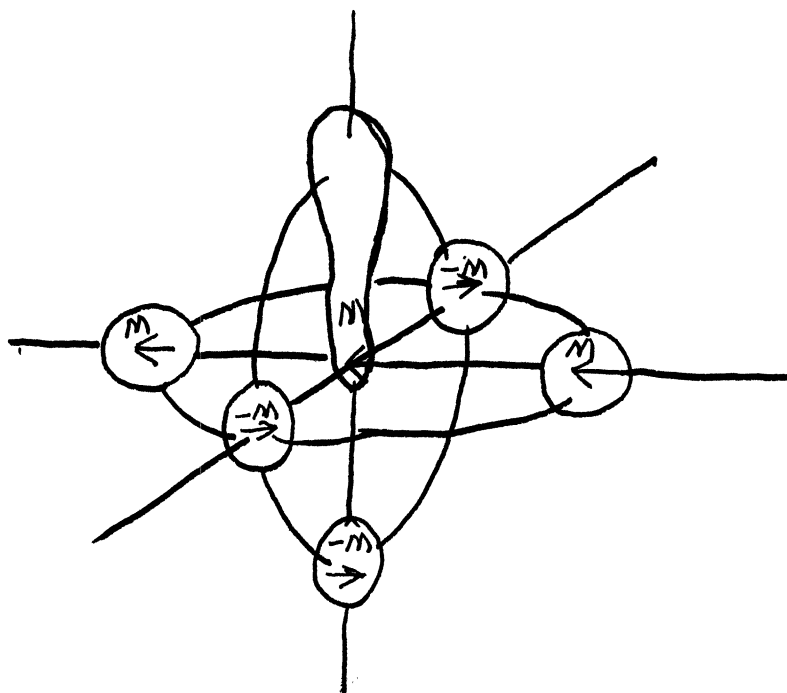effective moment is zero.

In the case of actual solutions, the static cases listed
above would prove to be unsatisfactory approximations to
thermal agitation. Quantitative analasys would involve
kinetic theory applications. For the present case, it suf-
fices to say that the magnitude of the dipole moment of a

polar compound, as measured in dilute solutions of a non-
polar solvent having a dielectric constant greater than unity,
can vary appreciably, depending upon the size of the polar
molecule and the orientation of the electric moment in re-
lation to the greatest dimention of the molecule.

Second, as has already been mentioned, association
can occur between polar molecules. The most commonly oc-
curing types of association orientations can be represented
by Figure 6, and can be described as follows: (a) anti-
parallel and opposing one another, having a moment equal to
M, where M is the moment of a single molecule, while having
a molecular weight equal to 3m, where m is the molecular
weight of a single molecule; (b) colinear and aiding one
another, having an equivalent moment of 3M and an equiva-
lent molecular weight of 3m; (c) and (d) in various rec-
tangular, and polygonal configurations, each having zero
dipole moment, and an equivalent molecular weight of nm,

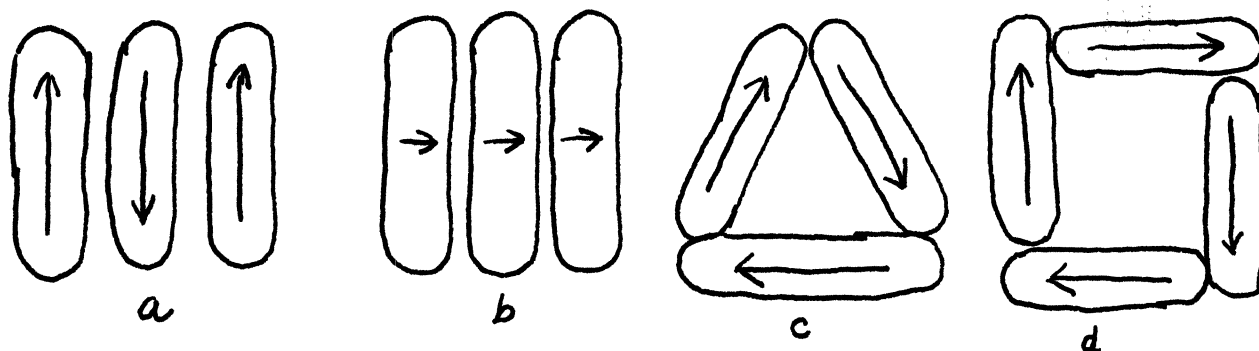Fig. 6.--Molecular association types.

where n is the number of sides of the polygon.[3] In the
case of the experimental procedure discussed previously,
the concentrations used were so small that very little
association of any type was probable. That little associ-
ation occurred is evidenced by experimental results: all
of the above types of molecular association, with the ex-
ception of type (b), which rarely occurs, would yield an
experimental value for the dipole moment which would be
smaller than the value expected, whereas the dipole moment
values obtained in this determination were almost without
exception much larger than anticipated.

Third, experiment has shown that the measured polari-
zation, even in very dilute solutions, varied with concen-
tration. This, together with the experimental fact that the
variation is not the same for different temperatures, is
enough to render the experimental procedure used previously
invalid. In order to determine the correct value of the
polarization, independent of the concentration, it is neces-
sary to measure the molar polarization of the solute at
several different concentrations, and extrapolate the values
to infinite dilution. Such a procedure should yield the
value of the polarization of the pure solute molecules.
In the range of very low concentrations, the extrapolation
is approximately linear, and can be carried fairly accur-
ately with a minimum of difficulty.

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[3] Le Fevre, op. cit., pp. 17-19.

Conflicting opinions are found in the literature concerning the applicability of the temperature variation method to the measurements on dilute solutions. Since the polarization versus concentration relationship is not independent of the temperature, and since the exact quantitative form of the resultant variation is unknown, it would seem safer to use an experimental procedure which proceeded isothermally, thus eliminating any possible error due to temperature variation. Such a procedure results directly from the application of the vapor phase theory of the refractivity method to dilute solutions.

Refractivity Method

In common with the temperature variation method, equation (3-3) was taken as defining the contributions of the solvent and the solute polarizations toward the total polarization of the solution. From measurements made on the pure solvent, the solvent, the solvent polarization, P_2, was evaluated by means of equation (2-3). From these values, the solute polarization, P_1, was calculated by equation (3-3). Due to the dependence of the solute polarization on the concentration of the solution, it was necessarily calculated at several different concentrations, and extrapolation was carried out to infinite dilution.

Having thus obtained a reasonably correct value for the solute polarization, an observation of equation (3-4)

revealed only the necessity of evaluating the distortion polarization, P_D, before the dipole moment could be calculated. This evaluation was accomplished to a fair approximation by equations (2-5) and (2-6), using values of the density and refractive index obtained from measurements made on the pure solute.

Experimental Procedure

In order to carry out the calculations enumerated above, it was necessary to measure both the density and the dielectric constant of each of several solutions of varying concentrations. It was also necessary to measure the density and the refractive index of both the pure solute and the pure solvent. From these data, the value of the solute polarization was calculated, for each solution, the values obtained were plotted versus the concentration, and extrapolation was carried out to infinite dilution. The value of the solute polarization obtained in this manner was then used as the true solute polarization, independent of concentration. In order that the extrapolation be as linear as possible, it was necessary to use very dilute solutions, the most concentrated of which contained about 0.2 grams of the polar solute in about 38 grams of benzene.

To eliminate as nearly as possible all temperature variations, all measurements were carried out at $20^\circ C$ in a water-filled thermostat. The regulation was accomplished

by allowing a mercury thermo-regulator to control an electric
pump which circulated cold anti-freeze through a cooling coil
immersed in the thermostat. The total temperature variation
of the thermostat did not exceed $0.1^{\circ}C$.

Dipole moment measurements were carried out using three
of the four polar compounds on which measurements were made
by the temperature variation method. They were: diethyl
maleate, dimethyl maleate, and dimethyl fumarate. Five
solutions of varying concentrations were prepared for each
of the polar compounds. Each solution was kept in a tightly
stoppered, ;lainly marked flask until used. The data con-
cerning the solutions of each compound are shown in Table 7.
The column headings are as follows: W_1 is the weight of
the solute, W_2 is the weight of the solvent, and c_1 is the
mole fraction of the solute.

TABLE 7

CONCENTRATIONS OF SOLUTIONS USED
IN REFRACTIVITY METHOD

Solution Number	W_1 grams	W_2 grams	c_1	$M_1c_1 + M_2c_2$ grams/mole
1	0.2061	38.6100	0.002416	78.338
2	0.1571	38.5505	0.001844	78.284
3	0.1201	38.8851	0.001400	78.242
4	0.0874	38.4978	0.001030	78.206
5	0.0428	38.6767	0.000503	78.157

TABLE 7--Continued

Dimethyl Fumarate

Solution Number	W_1 grams	W_2 grams	c_1	$M_1c_1 + M_2c_2$ grams/mole
1	0.2079	38.4804	0.002921	78.303
2	0.1672	38.8401	0.002327	78.264
3	0.0995	38.4975	0.001399	78.203
4	0.0643	38.4185	0.000906	78.169
5	0.0365	38.4828	0.000507	78.145

Dimethyl Fumarate

1	0.2173	38.5373	0.0030477	78.3109
2	0.1586	38.3651	0.002236	78.2568
3	0.1173	38.4680	0.001560	78.2189
4-	0.0795	38.4753	0.001119	78.1839
5	0.0460	38.4892	0.000825	78.1389

Measurement of Density

With the extremely dilute solutions used in this determination, it was essential that very precise density values be obtained. Noting the difficulties experienced in the previous density determinations due to evaporation, and lacking a pycnometer having a ground glass stopper, a pycnometer was constructed. It was fitted with a ground glass stopper, which effectively stopped all losses due to evaporation, and its volume was 16.5820 gm/cc at $20^{\circ}C$. This was determined accurately by weighing the pycnometer filled with distilled water, and by calculating the volume from the known density of water. It was necessary to make a correction for the bouyant effect of the air displaced by the liquid in the

pycnometer. For samples of about the same density, this consisted of a constant term added to each calculated density. The magnitude of the correction term was about 0.0011 gram per cubic centimeter when the density of the sample was about that of benzene. The density determinations are shown in Table 8; $d_{1,2}$ is the density of the solution.

TABLE 8

DENSITIES OF SOLUTIONS USED
IN REFRACTIVITY METHOD

Solution Number	Density grams/cc		
	Diethyl Maleate	Dimethyl Maleate	Dimethyl Fumarate
1	0.87979	0.87998	0.87951
2	0.87961	0.87974	0.87924
3	0.87936	0.87940	0.87908
4	0.87924	0.87922	0.87880
5	0.87914	0.87907	0.87872
Benzene	0.87907	0.87888	0.87846

Evaluation of Distortion Polarization

In the measurement of the distortion polarization, it was necessary to determine the density and the refractive index of the pure solute. The density was measured using the pycnometer just described, and the index of refraction was found by means of an Abbe refractometer. The refractive index measurements were carried out at 20°C using radiation

of the sodium D line. The distortion polarization was then calculated by means of equations (2-5) and (2-6). The distortion polarization is assumed to be independent of the temperature; experiments show that the difference in the values at $20^{\circ}C$ and at $37^{\circ}C$ is less than one unit in the second decimal place, which is negligible, since the polarization extrapolation cannot be accurate beyond the first decimal place.

Since it was impossible to measure the index of refraction of dimethyl fumarate using the experimental apparatus at hand, the molar refractivity was calculated using the accepted values for the bond refractivities. Refractivities obtained in this manner are usually accurate to within a few percent, which is sufficient accuracy for this measurement.

Refractive index data and density data for each compound, and for benzene, together with the calculated values of the density, the molar refractivity, and the distortion polarization, are shown in Table 9.

Measurement of Dielectric Constant

It was evident, when dielectric constant measurements were begun in this series of experiments, that, since much more dilute solutions were used than in the preceeding method, much more precise dielectric constant determinations must be carried out in order to be able to differentiate between

TABLE 9

REFRACTIVITY DATA AND DISTORTION
POLARIZATIONS

Polar Compound	n_D^{20}	d^{20} grams/cc	R_D cc	P_D cc
Diethyl Maleate	1.4401	1.06690	42.541	44.668
Dimethyl Maleate	1.4425	1.16068	26.040	27.342
Dimethyl Fumarate	------	--------	32.749	34.386
Benzene	1.4996	0.87907	27.116	------

solutions of almost the same dielectric constant. Experi-
mental results using the test cell used in the previous pro-
cedure indicated that it could not be applied satisfactorily
to the refractivity method. The differences in capacity
being measured had become smaller than the inherent inaccu-
racies of the test cell itself. Due to its rather open
construction, it was easy for the relative positions of the
leads, or even of the cylindrical plates themselves, to be
slightly displaced as the cell was removed and reinserted
in its outer container. While these changes were admittedly
small, they could not be tolerated in precise measurements
on very dilute solutions. It was thus evident that con-
struction of a new test cell, of a design more appropriate

It was decided to use a variable condenser type of
test cell, since by taking the differences in capacity
from the maximum to the minimum capacitance settings with
the condenser filled first with the dielectric solution,
and later with air, and by taking the ratio of the two differ-
ences, the dielectric constant of the liquid could be de-
termined directly without the necessity of laborious cali-
brations with liquids of known dielectric constant. The
dielectric constant of liquid is given by the equation

$$\epsilon = \frac{\Delta C_x}{\Delta C_{air}}, \tag{3-11}$$

where ΔC_x and ΔC_{air} are the differences in the maximum
and the minimum capacitances of the test cell filled with
a liquid of dielectric constant ϵ, and air, respectively.
This equation is strictly true only if the dielectric con-
stant of air is assumed to be unity. The actual value is
about 1.00059.

An outer container for the variable condenser type
test cell was constructed from heavy gauge galvanized iron
to give good mechanical stability. All of the seams were
silver soldered, and the stator, or high potential lead,
was brought out through the side by means of a feed-through
insulator. The variable capacitor used was a two-bearing
air dielectric variable condenser, having an air capacitance

of about 35 micromicrofarads. Connection of the test cell
to the heterodyne-beat appartus was made by means of heavy
gauge copper wires, one soldered directly to the cell con-
tainer, and the other bolted to the insulated high potential
terminal. A four-pronged male plug was soldered permanently
to the leads, making possible direct connection to the heter-
odyne-beat apparatus without the necessity of intervening
leads, thus reducing the possibility of introduction of
stray incremental capacitances due to slight changes in the
relative positions of the leads. The mechanical stability
of the completed cell was very good; during all of the measure-
ments taken, reproducable maximum and minimum settings could
consistently be obtained. The lid of the cell was constructed
of a small square of galvanized iron, which fitted snugly
over the top. In spite of the evaporation which undoubtedly
must have occurred, control tests indicated that the die-
electric constant of a solution was not changed by a measur-
able amount after being allowed to stand in the cell for
periods of as long as two hours.

Measurement of dielectric constants by means of a test
cell of this type were very simple. First, the quantity
Δ c_{air} was found by measuring the difference in capacity
of the cell between the maximum and the minimum setting.
Then a measured quantity of a dielectric solution was poured
into the cell. The exact quantity of solution used was not
found to be critical as long as all of the condenser plates

were covered, but the same quantity should be used in all determinations. Once the dielectric solution in the cell had reached the temperature of the thermostat, the quantity ΔC_x was found by again measuring the difference in capacity of the test cell between the maximum and minimum readings. Having obtained these two quantities, the dielectric constant of the solution was calculated directly from equation (3-11). It was important that special care be taken in transferring the solutions to the test cell, as air bubbles were sometimes trapped between the condenser plates, giving rise to erroneous capacitance readings. The error was very easily recognized, when the calculated values of the dielectric constant were plotted versus the concentration. However, such errors, and the resulting time consuming repetitions, were eliminated by careful handling of the solutions. The estimated accuracy of the dielectric constant determinations carried out by this method is about one or two units in the fourth significant figure.

Determination of the dielectric constant as a function of concentration showed that for the compounds in question, there existed a linear relationship between these quantities. Since the spread of experimental points was appreciable in most cases, the "best" values of the dielectric constant of each solution at each concentration were found by calculating the "best" straight line through the experimental points by the method of least squares. Table 10 gives the

experimental data, the calculated dielectric constants, ϵ_{exp}, and the values obtained by the least squares method, ϵ, for each solution of each compound.

TABLE 10

DIELECTRIC CONSTANT OF SOLUTIONS USED IN REFRACTIVITY METHOD

Solution Number	Δc_{air} mmF	Δc_x	ϵ_{exp}	ϵ By Least Squares Method
Diethyl Maleate				
1	32.487	74.780	2.3018	2.30209
2		74.720	2.3000	2.29957
3		74.542	2.2945	2.29394
4		74.420	2.2908	2.29138
5		74.303	2.2872	2.28801
Benzene		74.237	2.2851	2.28442
Dimethyl Maleate				
1	32.458	74.980	2.3101	2.31007
2		74.820	2.3051	2.30521
3		74.573	2.2975	2.29762
4		74.430	2.2931	2.29358
5		74.388	2.2918	2.29032
Benzene		74.177	2.2853	2.28617
Dimethyl Fumarate				
1	32.358	74.415	2.3034	2.30333
2		74.375	2.2985	2.29840
3		74.356	2.2948	2.29484
4		74.141	2.2912	2.29081
5		74.097	2.2899	2.28982
Benzene		73.940	2.2850	2.28481

Calculation of Dipole Moments

Using the values of the dielectric constant, together with the density values obtained previously, the total polarization, $P_{1,2}$, was calculated for each solution by equation (3-3). From the dielectric constant and the density of benzene, the polarization of the solvent, P_2, was calculated, and used in conjunction with the equation (3-4) to calculate the solute polarization, P_1, for each solution. Since the value of P_1 was found to increase for decreasing concentration, extrapolation was carried out to infinite dilution to obtain the polarization of the pure solute, P_∞. This value, together with the value obtained for the distortion polarization of each compound, was used together with the equation

$$\mu = \sqrt{\frac{9kT}{4\pi N} \ (P_\infty - P_D)}$$

to obtain the dipole moment of each compound.

The calculated values of the total polarization, $P_{1,2}$, the solvent polarization, P_2, and the solute polarization, P_1, are shown in Table 11. Table 12 shows the values of P_∞ obtained for each compound, together with the dipole moment of each as calculated from equation (3-12).

The value obtained for diethyl maleate is in excellent agreement with the value found in the literature; also, the dipole moment of dimethyl maleate is also experimentally proved to be approximately equal to that of diethyl maleate.

TABLE 11

TOTAL POLARIZATIONS AND SOLUTE POLARIZATIONS
SOLUTIONS USED IN REFRACTIVITY METHOD

Solution Number	$P_{1,2}$ cc	P_1 cc
Diethyl Maleate		
1	26.9365	175.960
2	26.8958	177.220
3	26.8019	178.922
4	26.7591	180.520
5	26.7004	180.780
Benzene	$(26.6378 = P_2)$	--------
Dimethyl Maleate		
1	27.0480	157.139
2	26.9707	157.452
3	26.8506	157.943
4	26.7861	158.133
5	26.7354	161.541
Benzene	$(26.6670 = P_2)$	--------
Dimethyl Fumarate		
1	26.9664	136.003
2	26.8851	139.311
3	26.8306	146.242
4	26.7638	143.342
5	26.7368	152.242

TABLE 12

SOLUTE POLARIZATION AT INFINITE DILUTION
AND CALCULATED DIPOLE MOMENTS

Compound	P_∞ cc	μ
Diethyl Maleate	182.4	2.57 D
Dimethyl Maleate	158.6	2.51 D
Dimethyl Fumarate	158.1	2.45 D

Finally, due to the shift from the high energy "cis" con-
figuration in the dimethyl maleate to the lower energy
"trans" configuration in the dimethyl fumarate, the dipole
moment value of the latter should be somewhat smaller than
the former. This is also verified by the experimental
results.

Discussion of Results

On the whole, however, the results of this series of
experiments must be classed as non-conclusive. Although
the moments of three polar compounds were determined with
fair accuracy, not all of the intended experiments were
carried out. For example, it was intended to measure, in
addition, the effect of the cis-trans rotation of the C = C
double bonds with the addition of a small amount of iodine
to the dimethyl maleate. This would have required the use
of $C cl_4$, or some other non-polar solvent less reactive

with I_2 than C_6H_6. It would have also required the re-
determination of the value of the dipole moment in the new
solvent, since polar compounds measured in the same solvent
under a similar condition, significance can usually be
attached to differences in dipole moment values of the order
of one per cent or less, but for the same compound measured
in different solvents, the values obtained for the moment
may vary as much as 20 per cent, thus a difference of a few
per cent in the dipole moment as measured in carbon tetra-
chloride from that measured in benzene would have little or
no significance.[4]

The main purpose of this thesis thus becomes a study
of the methods of measuring dipole moments, and some of the
problems encountered in the actral experimental determi-
nations necessary to effect such measurements.

Summary of Work

The original prodedure was obtained from a careful
study of the theses of Spalding,[5] Fielder,[6] and Shipley.[7]
The first experiments, of the temperature variation type,
were based on the procedure thus obtained. As has been

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[4] Ibid., p. 22.

[5] Spalding, op. cit.

[6] Fielder, op. cit.

[7] Shipley, op. cit.

noted previously, the results must be classified as negative, due primarily to the concentration dependence of the solute polarization, and the variation of this effect with temperature. To eliminate this effect, the next method used was the refractivity method, in which the total polarization was measured at a single temperature, and the distortion polarization was evaluated as the molar refractivity by means of the density and the refractive index of the pure solute. The dependence of the solute polarization was eliminated by making polarization measurements at various concentrations, and by extrapolating the values obtained to zero concentration, or infinite dilution. Values of the dipole moment of diethyl maleate, dimethyl maleate, and dimethyl fumarate were found. The value for diethyl maleate was in excellent agreement with that found in the literature, and the values for the other compounds were of the magnitude expected.

Experiments were halted by sudden change in the test cell used, and subsequent inability to obtain reproducable maximum and minimum capacitance settings using it. Although several attempts were made to comstruct another test cell, it was impossible to produce one having satisfactory capacitance settings.

On the whole, although few accurate dipole moment values were obtained, this thesis was successful in that it has paved the way for further work on this subject by uncovering some of the fallacies in procedures used by

previous workers at this institution, and by describing in detail an experimental procedure which should prove successful in future experiments.

CHAPTER IV

SUGGESTED EXPERIMENTAL PROCEDURE

General Considerations

Reasonably accurate results were obtained using the
refractivity method of measuring dipole moments; thus, this
chapter will not consist of presenting a completely new
method, or procedure, but will merely present some suggested
modifications of the existing procedure.

The Test Cell

Construction of a new test cell by further workers
will be necessary due to a breakdown of the original. . Some
of the various advantages and disadvantages of the variable
capacitor type test cell have been discussed in comparison
with the fixed capacitor type. In order to decide which
type of test cell will best fit the experimental needs,
the various advantages and disadvantages of each type will
be discussed in more detail here.

As has been mentioned, the greatest advantage of the
variable capacitor type test cell is that there is no de-
pendence on the knowledge of the dielectric constant of a
standard substance, and that computation is greately simpli-
fied. On the other hand, such a cell must have very

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accurately reproducable maximum and minimum capacitance
settings. In the ordinary variety of variable capacitors,
such characteristics are rare or nonexistent. Most capaci-
tors have maximum and minimum capacitance settings which
are satisfactory for most purposes, but which for the de-
termination of dipole moments, where the reproducability
must be of the order of ± 0.0001 micromicrofarad, they are
entirely unsatisfactory. It must be acknowledged that the
mechanical precision necessary for a condenser having the
characteristics necessary for very precise dielectric con-
stant measurements would be so great as to be prohibitive,
at least financially, in this case. In view of this, the
alternative is to construct a test cell of the fixed capaci-
tor type. A cell of this type was used in the temperature
variation method, but was found to be unsatisfactory for
very precise measurements.

In the design of a fixed capacitor type test cell,
one of the main considerations should be that either the
condenser plates be protected to prevent accidental displace-
ment, or that provision be made for changing the solutions
without the necessity of removing the capacitive element.
The latter of these appears to be the better, so the design
for such a test cell will be proposed which is not, in reality,
radically different from that built by Fielder and used by
subsequent workers.

The main differences may be enumerated, making reference to Figure 7. First, a coaxial cable connector is used instead of the original mercury contact cups. This makes possible connection of the cell to the heterodyne-beat apparatus by means of a coaxial cable, and hence eliminates capacitance variations due to differences in the positions of leads. Second, the mechanical stability is increased, and the losses due to evaporation are decreased by the use of metal-to-glass seals at the points where the leads from the cylindrical capacitive elements enter the cell. Third, two glass tubes are added, T_1, sealed into the top of the cell for the introduction of liquid samples by gravity, and T_2, sealed into the bottom of the cell for the removal of samples. A suggested procedure for cleaning a cell constructed in such a manner consists in filling the cell with clean benzene, heating the temperature bath to about $60^{\circ}C$, and gently bubbling clean, dry air through the benzene. This process should be repeated several times, and the procedure completed by drying the cell by means of a gentle blast of clean, dry, air blown through it. Fourth, a cylindrical copper shield should be soldered tightly about the outside of the cell, completely shielding it. Although the lengths of the cylindrical capacitive elements in the test cell are constructed in such a manner as to afford some shielding, the shielding action would be made complete by a metal shield completely enclosing the cell. In addition

Coaxial Connector

T_1

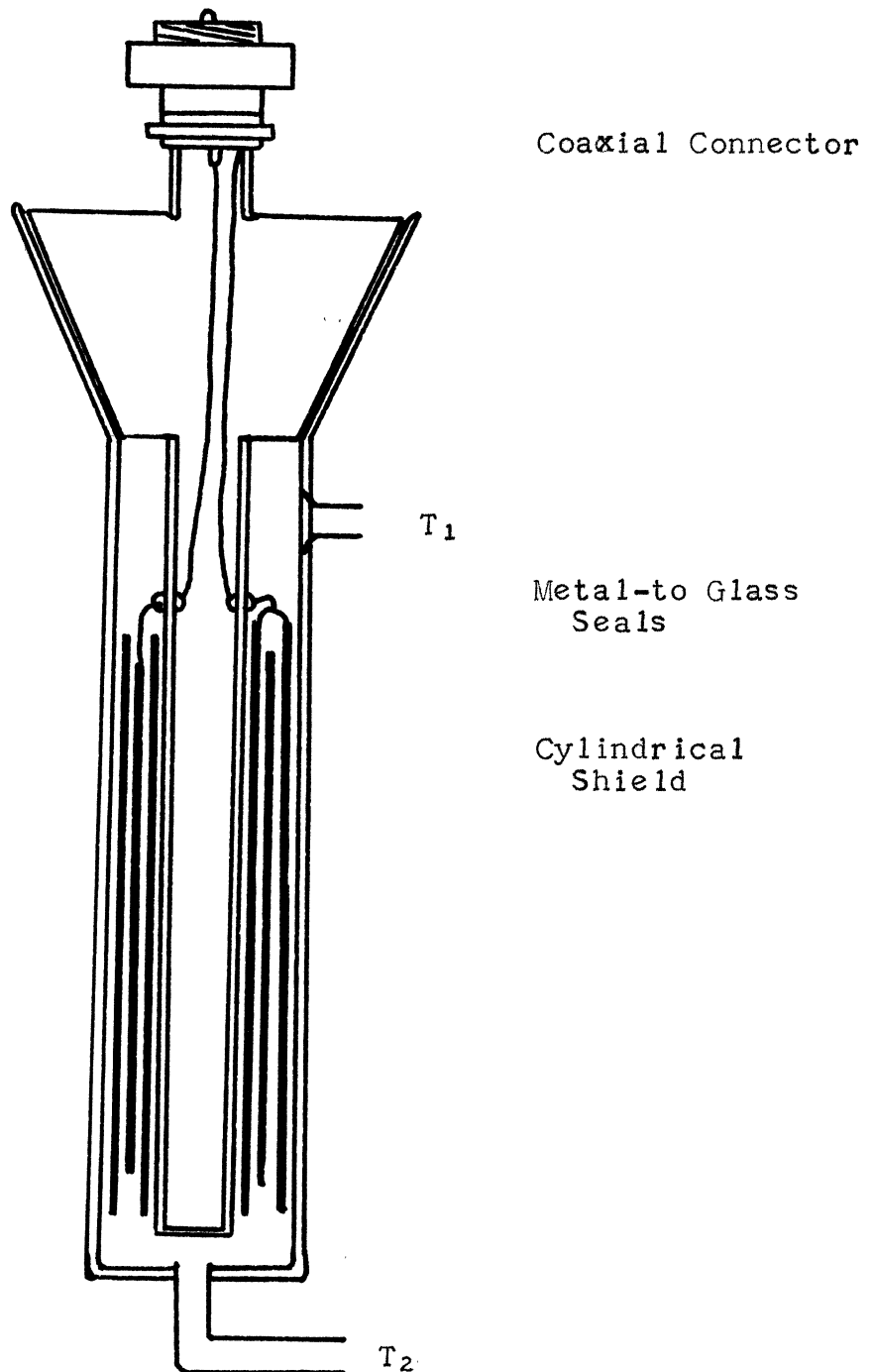Metal-to Glass
Seals

Cylindrical
Shield

T_2

Fig. 7.--Modified test cell.

to this, special care should be taken that the water in
the thermostat used to maintain the constant temperature
is grounded, and that the water level is maintained constant.

With the exception of the four changes enumerated
above, the construction of this test is exactly the same as
that described and constructed by Spalding.

The Heterodyne-beat Apparatus

The heterodyne-beat apparatus available was constructed
by Spalding[1] and modified by Fielder.[2] It is fairly accurate,
the drift being negligable over short periods of measure-
ment. The most prominent difficulties experienced arose
due to fluxuations in power line voltage. Since a voltage
regulated power supply was not incorporated in the original
design, and since the Denton commercial power is not noted
for its constancy, considerable difficulty was experienced
at times, not to constant, gradual shift of the oscillators,
but rather to sudden shifts in the oscillator frequencies
as the voltage varied. This was avoided to some extent by
taking much of the dielectric constant data in the early
morning hours, when the voltage fluxuations were at a min-
imum.

For very precise dielectric constant determinations,
however, a more stable apparatus is necessary, but fortu-
nately many excellent designs are available, eliminating

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[1] Spalding, op. cit.

[2] Fielder, op. cit.

the necessity of designing a completely new apparatus. One such design, shown in schematic by Weissberger,[3] utilizes a crystal controlled local oscillator, electron-eye indicatior, and a voltage-regulated power supply, should be entirely satisfactory.

The Precision Condenser

The heterodyne-beat apparatus just mentioned is capable of much greater accuracy than any precision condenser ordinarily available. The precision of the dielectric constant measurements is increased by using, instead of a precision capacitor having a variation sufficient to allow the incremental capacitance to be read directly upon connection of the dielectric-filled test cell, a precision capacitor having a very small capacitance range, say 5 or 10 mmF, in conjunction with several known fixed capacitors connected in parallel with it. In order to measure capacitances using such a capacitance arrangement, a null reading of the precision capacitor is taken with the test cell disconnected; then the test cell is connected, and several of the fixed capacitors are disconnected, until the total capacitance of those disconnected is a little less than that of the test cell. The precision capacitor is then again adjusted to the null, and the capacitance of the test cell is read as

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[3] Charles P. Smyth, "Dipole Moments," Vol. I, Part II, Physical Methods of Organic Chemistry, edited by Arnold Weissberger (2 vols.), pp. 1633-1641.

the sum of the fixed capacitors removed, and the difference
between the initial and final readings of the precision
capacitor. A switching arrangement should be provided for
the rapid connection and disconnection of the fixed capaci-
tors in parallel with the test cell. Figure 8 shows in
schematic a proposed configuration which should prove satis-
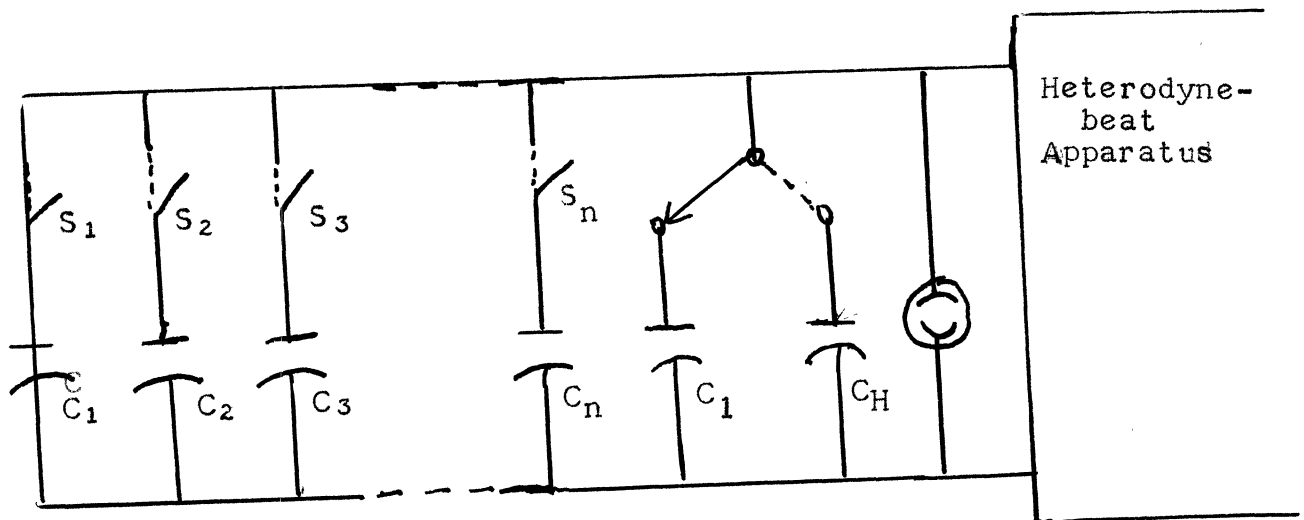factory. In the figure, C_1, C_2, C_3, ------ C_n are small

Fig. 8.--Proposed Capacitance configuration.

capacitors, which may be switched in and out of the circuit
by means of the anti-capacity type switches, S_1, S_2, S_3,
------ S_n. They are chosen so that their total capacitance
when connected in parallel will be greater than the maximum
capacitance of the test cell filled with a dielectric solution.

Also, they must have values allowing adjustment of the capacitance to within 5 or 10 mmF. of the capacity of the test cell by their removal, so that the remainder of the incremental capacitance can be measured with the low range capacitor, C_1. It would be convenient to also provide a switching arrangement to allow either the low range capacitor, C_1, or a high range capacitor, C_H, having a capacitance range of about 110-1100 mmF., to be connected as desired. The latter would be useful for measuring approximately the capacitance of the test cell in order to estimate the number of fixed capacitors to remove.

A low range precision capacitor can either be made directly, or obtained by the modification of a higher range precision capacitor. As the simplest solution to the problem, it is suggested that a General Radio precision condenser, model 772, be modified by removal of all but three of the stator plates and two of the rotor plates of the 10-110 mmF. section. This should result in a capacitor having a capacitance variation of about 10 mmF. in about 2500 scale divisions. Before a capacitor so constructed can be used, however, calibration is necessary. This rather tedious process is best carried out by a procedure given by Smythe.[4]

Once calibration is accomplished, the precision condenser can be used, in conjunction with the heterodyne-beat apparatus, to measure the capacitance of the fixed capacitors,

4
Ibid, pp. 1645-1647.

which may consist of small two-bearing air padder condensers, having screwdriver adjustments. The final calibration should take place with them mounted on the apparatus, and with the switches in place.

Experimental Procedure

With the exception of the substitution of the apparatus described above, the experimental procedure is exactly the same as that described earlier for the refractivity method. With the apparatus described, however, appreciably more accurate dielectric constants should be obtained, and consequently, more accurate dipole moment values.

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