6-1952

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Recommended Citation

Dreyfuss, Robert George, "Determination of the dipole moment of Indole" (1952). *Honors Theses*. 1763.
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DETERMINATION OF THE DIPOLE MOMENT OF INDOLE

by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

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Approved by J D Porter

Date May 23, 1952

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Table of Contents

The purpose of this research was to determine the dipole memoent of indole, by a method that involves using the Yellow Springs Instrument Company's Dielectric Constant Meter.

The application of this new instrument made it necessary to determine its applicability and accuracy in this particular experment. The experimental part of this research is comprised of the determination of the dipole moments of four compounds. The The compounds and solvents used are as follows:

1. meta-dinitrobenzene in benzene
2. paranitrotoluene in dioxane
3. benzotriazole in dioxane
4. D indole in dioxane
   B indole in benzene

The first two compounds were used as standards and the third as a semi-standard, The latter is thus classified due to the fact that only one determination of its dipole moment is mentioned in the literature (8).

Interest in the electrical nature of molecules caused men like Debye (1), at the turn of the century, to undertake the continuation ofthe work of Mosotti(2) and Clausius (3). Work in this field of physical chemistry involves observing theeffects of electrical fields and temperature changes on molecules and determining, from the data thus obtained and from application ofelectrical and thermodynamic calculations, the exact physical nature of the molecules.

The electrical moments of a great many compounds, including most of the common organic substances, have been determined, but research to determine the structure of heterocyclic compounds was not undertaken until about 1940. This was due to the increasing use these chemicals were at that time finding in the pharmaceutical and dye industries. It is interesting to note that in scrutinizing the chemical literature in search of data on heterocyclic nitrogen compounds it was found that not very much was published on the subject before 1938, but that the following is part of what has appeared since;

1938 configurations of some heterocyclic compounds (4)
1940 dipole moments of pyrazole, imidazole, -methyl im~~m~~idazole (5)
1941 dielectric behaviour of heterocyclic nitrogen compounds (6)
1942 dipole moments of various azole compounds (7)
1943 dipole moments of azole compounds (8)

1948 dipole moments of dioxane and pyridine (9)

1948 dipole moments of some pyridine homologs (10)

1949 dipole moments of furazans and diazoles (11)

1941 electric moments of im~~m~~idazolidine derivatives (12)

The fundamental relationship between the molar polarization and the dielectric constant of a substance is the Mosotti-Clausius equation

$$P_T = \frac{e-1}{e+2} \frac{M}{d}$$

where P_T = total polarization

e = dielectric constant

M = molecular weight

d = density

This relationship holds for a non-polar molecule, one that has perfect freedom of orientation in an electric field and has a dipole moment equal to zero.

Debye, in the course of more detailed investigations, showed that the total molar polarization is due to three distinct factors, a) the orientation polarizations, Po; b) the atomic polarization, Pa; and c) the electronic polarization, Pe; all due to the effect of an electric field on the molecule;

$$P_T = Po + Pa + Pe.$$

This can be shown, using the kinetic theory, to be equal to

$$P_T = \frac{4\pi N}{9KT}\mu^2 + Pa + Pe$$

where N = Avagadro's number

k = Baltzmann constant

T = Absolute temperature

μ = dipole moment

According to Le Fèvre (13) the sum of the atomic and electronic polarizations may be approximated by substituting the molar refraction (M. R.) for long wavelength light on the basis that the error thus introduced is less than the error resulting from the wxperimental determination of the total polarization.

$$P_e + P_a = (M.\ R.)$$

and

$$P_T = \frac{4\pi N}{9kT}\mu^2 + (M.\ R.)$$

We thus obrain an expression for the dipole moment in terms of constants and determinable values.

These equations are derived for molecules in the gaseous state and assume complete freedom of orientation in that phase. To determine the polarization in the liquid or dissolved state, as was the method in this work, the fact that the molecule is not entirely free to move in this fashion has to be taken into account. In any real solution molecules are close enough to exert steric and electrical forces upon one another.

The total polarization of a substance (in the gaseous phase) is identical, by definition, to its polarization in an infinitely dilute solution of the substance in a non-polar solvent. It must be remmmbered that the infinitely dilute solution is an abstraction that can only be approximated.

The polarization of molecules in solution is a function of the polarizations of solute and solvent molecules, and their mole fractions, $P_{1,2} = x_1 P_1 + x_2 P_2$

where x = mole fraction

and the subscripts one and two refer to solute and solvent. This relationship may be expressed in the Mosetti-Clausius form;

$$\frac{e_{1,2}-1}{e_{1,2}+2}\,\frac{x_1M_1+x_2M_2}{d_{1,2}}=x_1P_1+x_2\,\frac{e_2-1}{e_2+2}\,\frac{M_2}{d_2}$$

Then to approximate the gaseous state and to determine the molar polarization, P_T , of the solute,~~mole~~ P_1 can be plotted against the solute mole fraction x_1 and the curve extrapolated value is then used in the formula derived above;

$$\mu^2=\frac{9KT}{4\pi N}\left[P_T-(MR)_1\right]$$

when the values for the constants are inserted,

Boltzmann constant, $K = 1.38 \times 10^{-16}$ erg / degree

Avagadro's number, $N = 6.02 \times 10^{23}$

Experimental temperature, $T = 298° K$

we obtain the expression that is used in the calcultions

$$\mu = .2211\sqrt{P_T-(M.R.)_1} \quad \text{debye units}$$

where the debye unit $= 1 \times 10^{-18}$ electrostatic units For most compounds molecular weight, density, and dielectric constant data are available, or may be readily determined and molar refractions may be calcuated from tables of atomic refractions (14), so that the only quantities that remain to be determined for calculation of the dipole moment are the dielectric constant and the density of the solutions.

The detemination of these comprised the experimental work of this research.

There are two particular difficulties in the method of extrapolation to zero concentration. These are the association and solvation of the solute molecules. The first of t these phenomena takes place when molecules come into close contact with each other, and the obvious rememdy is to keep them apart by using very dilute solutions. The solvation of the soluteby the solvent depends on the nature of the two substances. Polarization versus mole fraction are of the same type and variety as the Raoults Law curves for gases, in so far as that the polarization ofthe solute may increase, d decrease, or remain constant with increasing concentraion; the extropolation curves may exhibit positive, negative, or zero slopes (15). What is of particular importance is that the value obtained for the polarization at infinite dilution depends on what solvent is used.

The opportunity was taken in this research to determine the usefulness of the Yellow Springs Instrument Company Dielectric Constant Meter, Model 3A.

The dielectric constant meter is a device for measuring thechange in capacitance of an external capacitor by balancing it against a standard, arbitrarily calibrated, capacitor. The external capacitor is in the form of three parallel semie circular plates on a probe. The plates are mounted so as to permit rotation of the centre plate by means of a seven-position switch; in the first position the center plate is between the others, in the seventh position the middle plate no longer between the two other plates. The dielectric constant of a substance is then determined as the ratio of the differences of capacitance between two positions of the plates when the materials between the plates are that substance and air (theoretically it should be a vacuum). For example, the probe is inserted in a liquid and the instrument readings at positions seven and three are 400 and 200 respectively; when the probe is then taken out of the liquid the readings in air for the same positions are 200 and 150. The ratio of the differences, 200 : 50, gives a dielectric constant of four.

The density measurements were made using a ten-milliliter pyknometer calibrated with distilled water.

The procedure followed in each determination of the dielectric constant of a solution was as follows. While the instrumet was allowed to warm up (fifteen minutes), the solute and solvent were weighed out on an analytical balance, mixed in a 100-ml. beaker and then transfered to a large weighing bottle that was placed in a constant temperature bath. After allowing about fifteen minutes for the solution to come to t temperature ' a matter of almost five degrees, since room temperature was about 20° and and experimental temperature 25° C.) some of it was withdrawn, placed in the pyknometer, and its density determined. The capacitor probe was then placed in the solution in the bath and its capacitance value determined. After cleaning and drying the probe with alcohol and ether the capacitance value for air was determined.

The first step in this research was to determine the accuracy of the instrument; for this purpose the dipole moments of some substances which have become standards in the field were determined. The first compound so used was meta-dinitrabenzene with benzene as the non-polar solvent. From the data obtained the following calculation of the maximum possible error (M. P. E.) was made.

The basis ofthis calculation is the observation that the MPE that can be incurred in each capactance meter reading is ±0.4 units, i.e. the MPE of each capacitance value is 0.8 units since each value is based on two readings. The calculations below are based on the determination of the polarizations of solutions of meta-dinitrabenzene in benzene.

Capacitance with air	MPE
13.5*	5.92%

Cap. solution **	MPE	e + MP deviation	$\frac{e-1}{e+2}$ + MPE		P_1 & MP Dev.
36.2	2.21%	2.722±.221	.3646	7.95%	367 ± 29
38.9	2.06	2.837±.226	.3798	7.11	288 ± 27
40.9	1.96	3.017±.238	.4021	6.73	295 ± 20
48	1.67	3.603±.274	.4645	5.38	291 ± 16

*This is an average value of a number of determinations.
**This represents individual

The conclusions drawn from the runs made with meta-dinitrobenzene and pure nitrotoluene are that the largest source of error is the dielectric constant, i.e. the capacitance measurements. To obtain the least error in this measurement, without making the solutions so concentrated that the evaporation of solvent produces measurable concentration variations, it was decided that the best concentration range was from six to twelve mole-percent.

The MPE incurred in using a pyknometer for density measurements is usually of the order of one tenth percent and appears therefore to be a negligible factor in the total errors of this method of determination.

The increasing error as the dielectric constant decreases tends to justify an extrapolation curve that is weighted in favor of values obtained from solutions with higher dielectric constants.

Perhaps the most significant error in this kind of dipole moment determination is one that is only indirectly related to the experimental work; it is the error that may be incurred in drawing the extrapolation curve. Here a certain amount of judgement is needee. Apart from weighting the values of each point according to dielectric constants, the way in which the solution itself behaves may give a clue to the comparative value of any particular point. One clue to irregularity, and therefore perhaps to inaccuracy, is whether or not and how much crystallization takes place at the surface of a very oncentrated solution.

To give some idea of how extrapolation affects the results of these determinations the percent change in the dipole moment caused by a 10 cc. increase in the extrapolated polarization value have been calculated. The results are as follows

Extrapolated Polarization* P_T	Percent Increase in μ for P_T + 10cc
289.5	1.97
445	1.31
375	1.29
55	22 .2
91.4	9.3

* These are the balues read off the graphs and used to calculate the dipole moments.

I. The first determination was made with metadinitrobenzene, using benzene as the solvent.

The solute had been recrystalized from carbon tetrachloride, the solvent was C. P.-Grade reagent.

The choice of solvent was made because of the wide use of benzene as the non-polar solvent for benzene derivatives. Using solutions in which the constituents are of a similar nature reduces the chances for complicatiions due to interaction.

The results of this determination were far from satisfactory, but nevertheless served to shed light on what difficulties were involved.

The error calculation (see above), when compared to the extrapolation curve, shows that the value for the polarization in the least concentrated solution is far out of the range of the other values, for which the error-ranges overlap at least fifty percent. The extrapolation curve was therefore drawn with the latter three points weighted in order of magnitude of the dielectric constant.

The dipole moment was found to be 3.50 ± .07 an error of 7.5% of the accepted value of 3.76 debye units (16).

II. It was decided to make a determintion of the dipole moment of para-nitrotoluene at the same concentration range as was used in the first determination, but to use a less volatile solvent than benzene.

The solvent used in this determination was dioxane. The liquid reagent which contained an anti-oxidant stabilizer, and possibly some moisture, was purified in three steps. It was first treated with a saturated potassium hydroxide solution, then dried with sodium metal, and finally distilled over sodium ribbon. The purity was assumed sufficient when the dielectric constant of the liquid checked within 0.5 percent of the value given in the literature. The constant for water is twenty-nine times as great, and any moisture would have shown up as a value greater than that of dioxene.

The polarization value obtained from the least concentrated solution was again too far out of the orbit of the other values, and was not considered in the estrapolation curve. The percent error in this determination was only one fifth as great as that of the previous determination and tends to point to the advisability of using less volatile solvents when an open apparatus is employed, as is the case in these experiments.

The dipole moment for para nitrotoluene was found to be 4.46 ± .04. The error is 1.5 percent of the accepted value of 4.40 debye units. (16)

III. In order to determine whether greater accuracy could be obtained by using more concentrated solutions and also to find out whether or not the preferable solvent would produce any serious complications when used in conjunction with a heterocyclic compound, a run was made with benzatriazole (C.P. reagent.)

The concentrations of the solutions used were between six and twelve mole percent, the previous determinations having been made in the one to six percent range. The dioxene's low volatility is here shown to permit the use of very concentrated solutions in an open apparatus without any apparent concentration change.

The results of using a less volatile solvent and higher concentrations was a lowering of the error to less than one percent and all the polarization values fell within six cc's of the extrapolation curve, whereas in the other determinations one of the points had deviated by 75 and 35 cc's.

The error in the dipole moment found, 4.10 ± .07, was 0.75 percent of the accepted value of 4.07 debye units. (8)

IV. The dipole moment of indole was determined in both dioxane and benzene, using solutions in the contration range of from seven to eleven mole percent.

The polarization values, judging from their plots on the extrapolation curve, appear to be of the same order of precision as those of the benzotriazole determination.

The effects of solvation and association are evident in the different slopes for the two solvents. The greater divergence with benzene as the solvent is probably due to its greater volatility. In both solutions the two constituents have certain things in common; among these is the fact that the indole molecule has the benzene ring as well as the heterocyclic nature which appears also in the dioxene molecule.

It seems reasonable to assume that theerror in this determination is of the same order as that in the benzotriazole run, ±0.75 percent. The values for the dipole moment of indole are found to be

0.98 ± .04 debye units in dioxene

1.65 ± .07 debye units in benzene

The difference due to extrapolation is so large due to the relatively small polarization. No attempt was made to calculate the moment in the vapor phase. (See 13)

Physical Constants for compounds used

Compound	Molecular Weight	Density (19)(20)	Dielectric Constant (17)	Molar Refraction (14)	Molar* Polarization
Meta-dinitrobenzene	168.11			39.3 (18)	
para nitrotolvene	137.13			37.4	
benzotriazole	119.12			32.3	
indole	117.14			35.4	
benzene	78.11	$.8724^{z}$	2.270		26.63*
dioxene	88.10	$1.028^{25°}$	2.280		26.65

(*Calculated from dielectric constant)

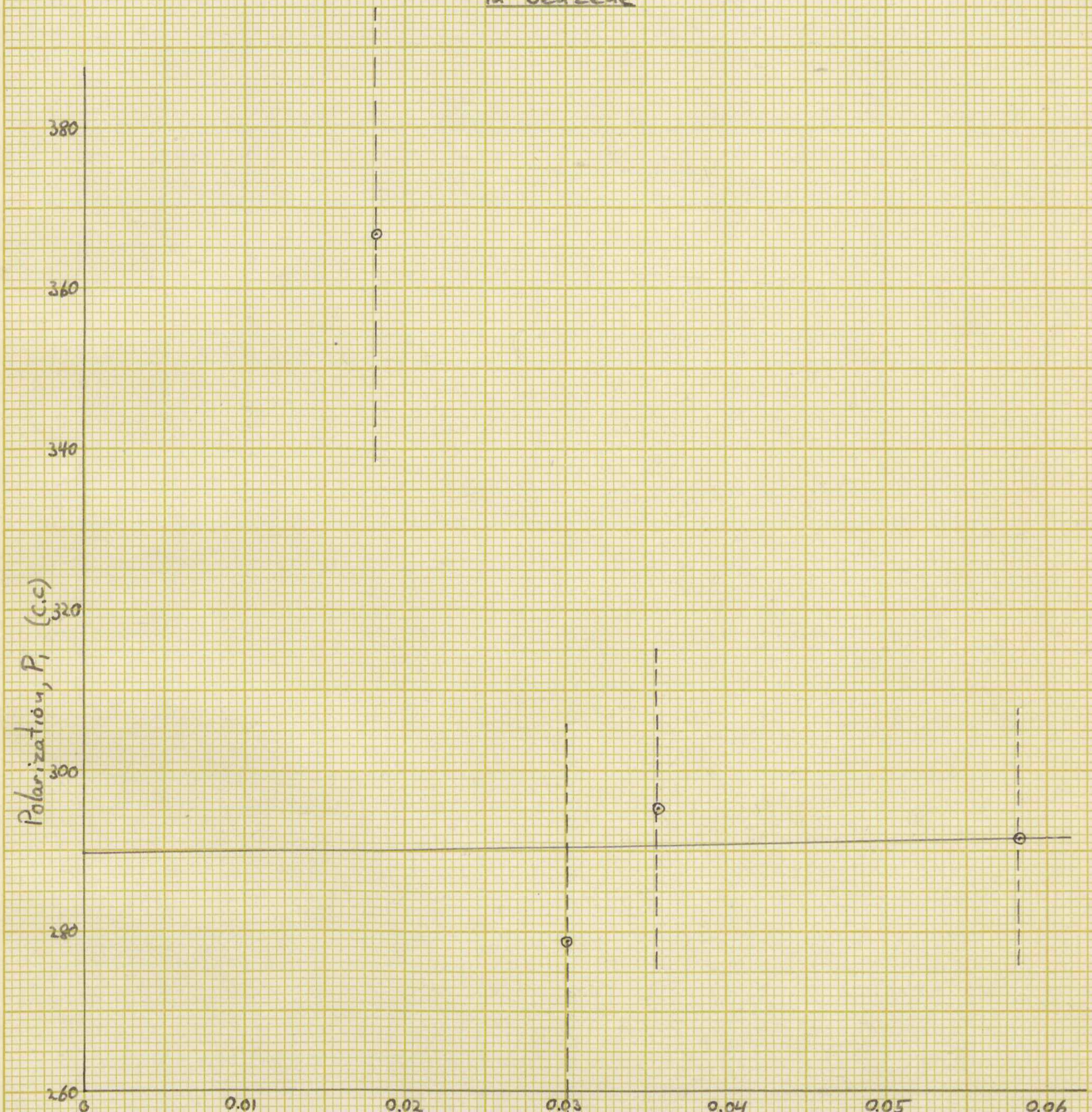
Data and Calculations

	Wt. Solute	Wt. Solvent	x_1	x_2	d1,2	e1,2	P1,2	P2x2
(1)	3.0000g	75.000g	.01825	.9817	.879	2.7218	32.836	26.143
	5	75	.03004	.9700	.884	2.8370	34.201	25.831
	6	75	.03584	.9642	.899	3.0172	36.253	25.677
	10	75	.05833	.9417	.919	3.6025	42.056	25.077
2)	1	46.5	.0136	.9864	1.0315	2.6540	30.584	25.284
	1.5	46.5	.0203	.9798	1.0332	2.9338	33.798	25.115
	2	46.5	.0269	.9731	1.0349	3.1830	36.393	24.943
	2.5	46.5	.0333	.9667	1.0365	3.4300	38.741	24.779
3)	6	50	.08152	.9185	1.0463	4.8140	48.481	24.481
	7	50	.09382	.9062	1.0490	5.3527	51.361	24.152
	8	50	.1058	.9842	1.0500	5.7633	53.402	23.833
	8.5	50	.1117	.8883	1.0566	6.0652	54.423	23.676
	9	50	.1175	.8825	1.0565	6.0386	54.534	23.521
)	D6	50	.08277	.9172	1.0370	2.9058	33.9057	24.446
	7	50	.09527	.9047	1.0407	3.0580	35.5277	24.113
	7.5	50	.1014	.8986	1.0363	3.1304	36.4864	23.950
	8	50	.1074	.8926	1.0388	3.1594	37.5211	23.791
)	B6	50	.07409	.9260	.8985	2.7273	32.945	24.659
	6.5	50	.07977	.9202	.8986	2.7724	33.573	24.505
	7	50	.08538	.9146	.8984	2.7738	33.686	24.356
	8	50	.09640	.9036	.9023	2.8468	34.571	24.063
	9	50	.0172	.8928	.9045	2.9549	35.893	23.775

Data and Calculations (continued)

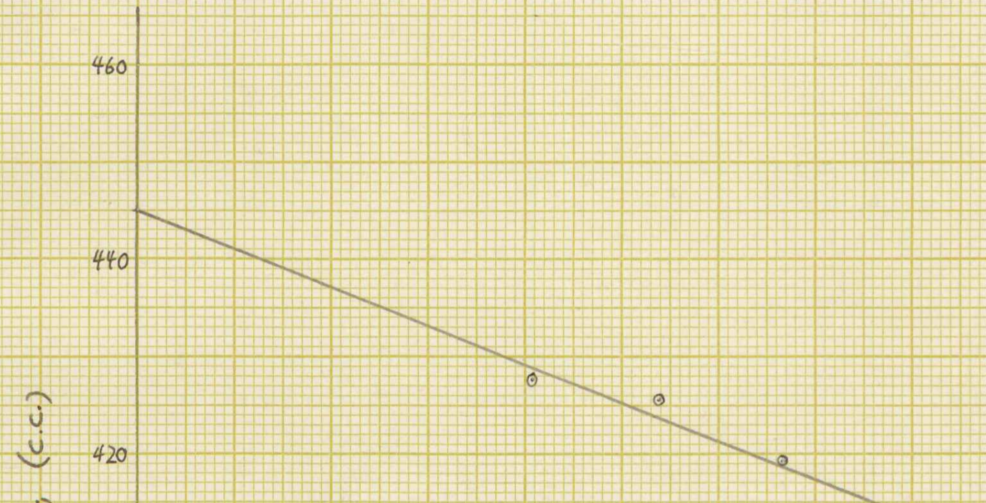
Pl xl	Pl	P_T	μ
6.693	366.7		
8.37	278.6		
10.576	295.1		
16.979			
16.979	291.2	289.5	3.50 ± .07
5.300	389.7		
8.683	427.7		
11.450	425.7		
13.962	419.3	445	4.46 ± .04
24.001	294.4		
27.209	290.0		
29.569	279.5		
30.747	275.3		
31.012	263.9	375	4.10 ± .05
9.4590	114.3		
11.414	119.8		
12.536	123.6		
13.731	127.9	55	0.98 ± .04
8.2851	111.8		
9 .0683	113.7		
9.3301	109.3		
10.508	109.0		
12.118	113.0	91.4	1.65 ± .07

Polarization of meta dinitro benzene in benzene

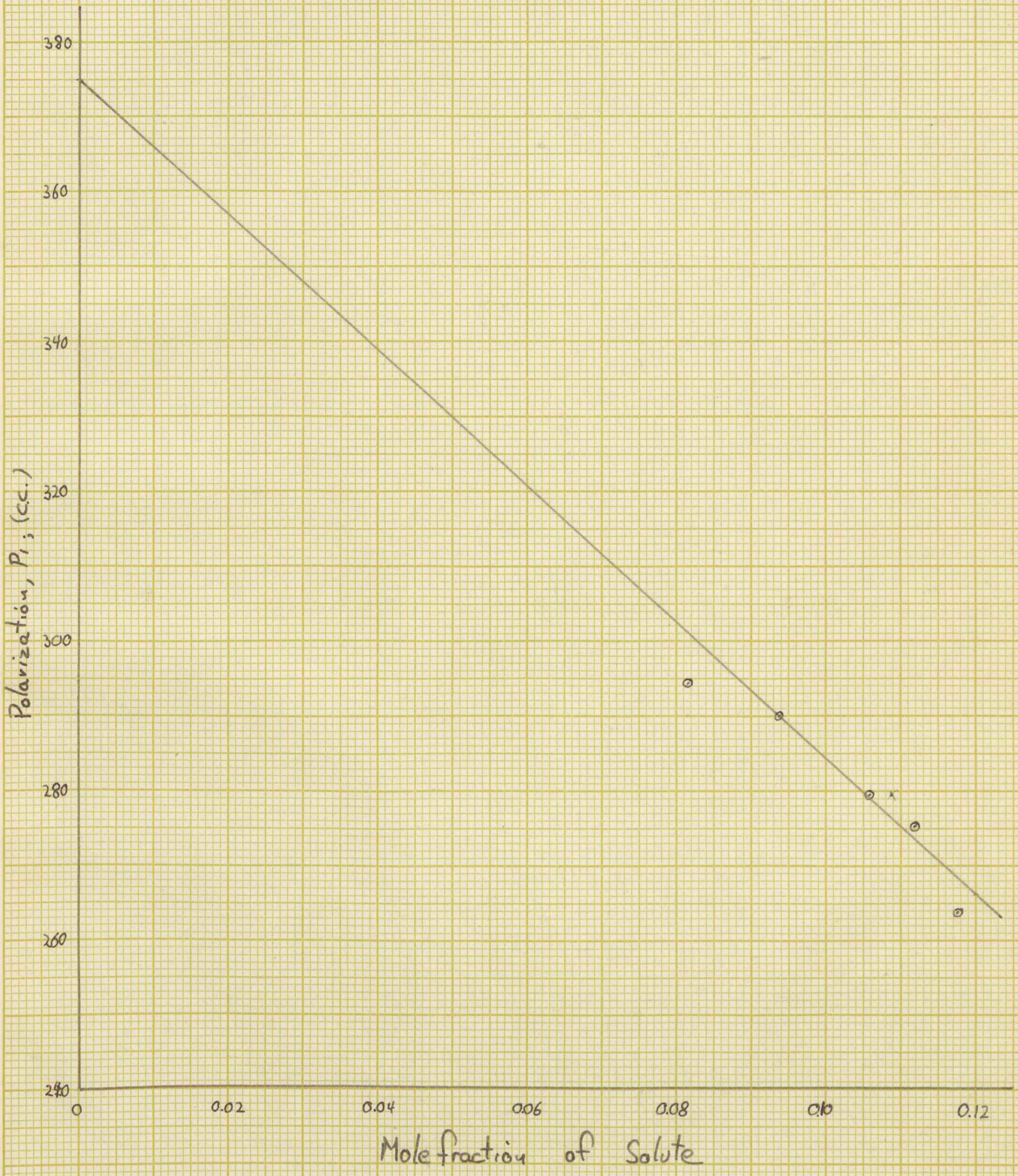


Vertical Lines represent M.P.E. calculations

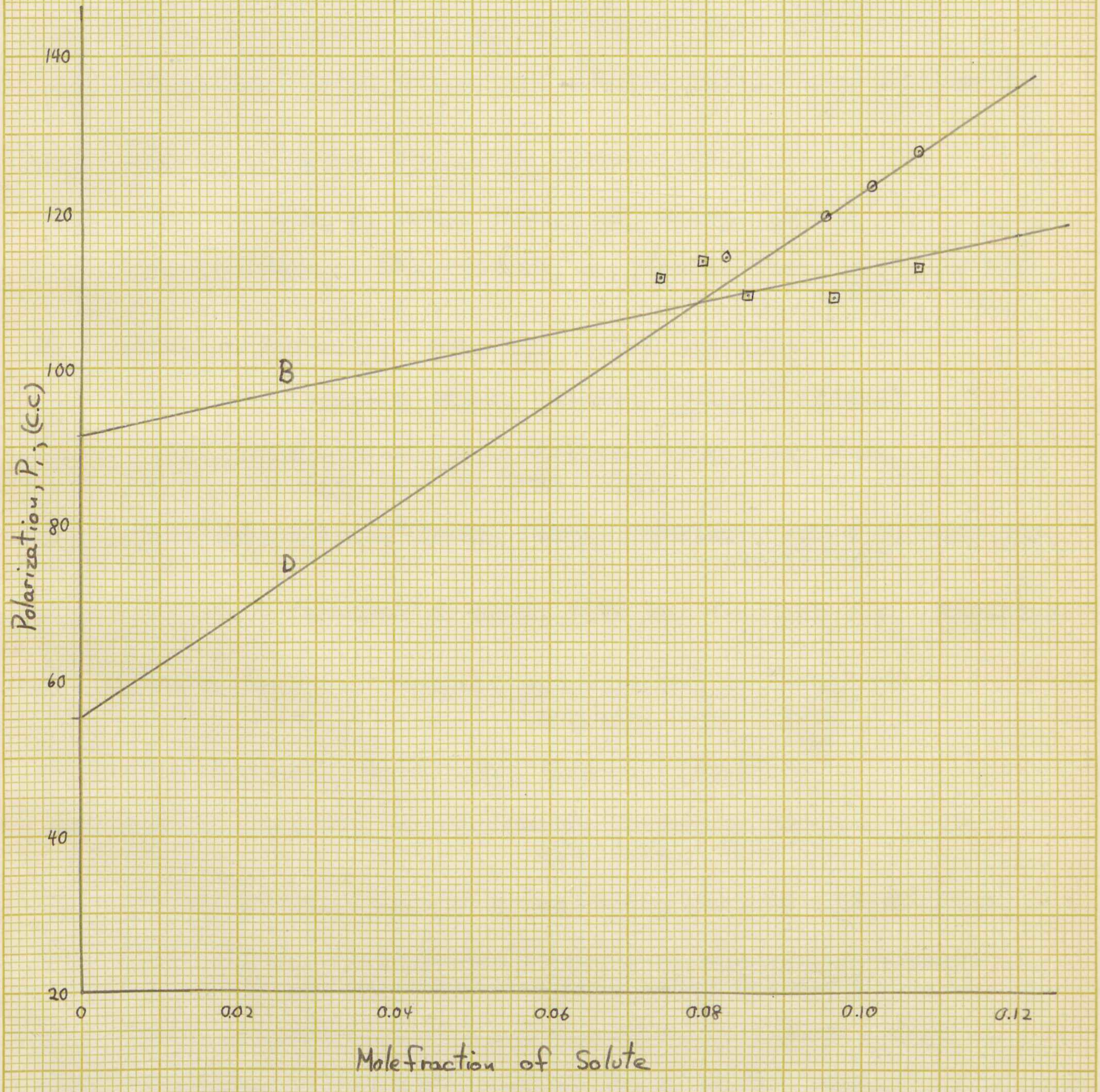
Polarization of para-nitrotoluene in dioxane



Polarization of benzotriazole in dioxane



Polarization of indole
in benzene (B) and dioxane (D)



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