A STUDY OF THE INFRA-RED ABSORPTION SPECTRA OF CERTAIN ORGANIC MOLECULES

I. CARBOXYLIC ACIDS
II. GLYCOLS AND GLYCOL DERIVATIVES
III. MOLECULES EXHIBITING KETO-ENOL TAUTOMERISM

BY

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THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY

SUPERVISION BY Walter Frederick Claussen

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

THE DEGREE OF Doctor of Philosophy in Chemistry.

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II - Introduction

The problem of molecular structure is one of fundamental importance in physical chemistry, and although the subject is primarily of theoretical interest, the results of this type of study are bound to have their reverberations in the field of applied chemistry as well.

The organic chemist has devised certain methods of determining molecular structure through the processes of synthesizing and degrading certain molecules. This method, although of fundamental importance, is limited to the determination of the configuration of an individual molecule, whose atoms are held together by ordinary chemical bonds whose strength are of the order of 100,000 calories. However, in order to study the structural phenomena involving bonds whose strength is of a smaller order of magnitude, the methods of the organic chemist fail, and new tools of research must be applied to attain a solution.

A field of investigation which has aided greatly in elucidating molecular structure has been spectroscopy. The study, in general, is based upon certain fundamentals developed through quantum mechanics, its primary assumption being that the energy of a given molecule can only assume certain discrete values, instead of a continuous range of values. The outcome of this is that the molecule can only absorb or transmit radiation of certain definite wave-lengths. The fields of molecular spectroscopy have been divided according to the wave-length of the radiation into three main classes, and their corresponding spectra include the ultra-violet spectrum, the near infra-red spectrum, and the far infra-red spectrum. Each spectrum is associated with a particular kind of change within the molecule.

This infra-red spectrum of a molecule is intimately connected up with the motions and modes of vibrations of molecules, and by knowing these, we can make some conclusions regarding the more intricate structure of the atoms comprising the molecule. This study is still in its early stage of development, and so the study is still a matter of correlating certain structures or functional groups in molecules with certain absorption spectra. When the functionally simple molecules have been thoroughly treated by this method, then it will be possible to go into the realm of more complicated and structurally-uncertain molecules to find out what is happening in these cases.

The work undertaken in the study herein summarized deals with the vibration spectrum of three classes of compounds. The first class includes carboxylic acids, both the mono- and the di-basic acids, the second class includes a series of glycols and glycol derivatives, and the third class includes some compounds known to undergo keto-enol tautomerism.

The object of the study of the acids was primarily to verify a certain prediction concerning a shift in wave-length due to change in mass in deuterium-substituted acids, and, in the case of the non-deuterated acids, the general work of wave-length assignment was carried on to various other homologues of the series.

The glycols were studied for the purpose of observing the role played by the hydrogen-bond in their high association. Another class of compounds related to these glycols is the ethoxy-alcohols, in which one of the hydroxyl groups of the glycol molecule is tied up in the form of an ether. A spectroscopic comparison of these two classes of compounds was thought to be worthwhile, from whence other physical properties could then be rationalized.

Since so much valuable information concerning hydrogen had already been found by means of infra-red spectroscopy, it was thought that some definite conclusions could be evinced concerning that class of molecules in which there was an active, mobile hydrogen. Therefore the study of keto-enol tautomerism was taken up.

III - Historical

Infra-red radiation was first studied in connection with absorption late in the last century. This line of research started in the region of the spectrum which was sensitive to a photographic plate. By this technique the absorption bands studied were only those of second and third harmonics of the fundamental absorption bands, and these were, therefore, necessarily very weak. As technique in the measuring of the intensity of radiation advanced, as knowledge increased in regard to the absorption of radiation by various kinds of prisms, and as better sources of radiation were discovered, more of the infra-red spectrum was capable of investigation. Now we are able to study even parts of the far infra-red spectrum.

Many molecules have been studied, and in particular, the vibration-rotation spectra of molecules containing hydrogen have been observed. A large part of the data verifying the concept of hydrogen bond formation has been due to infra-red spectroscopy.

The history of the hydrogen bond has been a short and an exciting one, and the applications of this bond in explaining various phenomena seem to be almost endless. This concept of bonding seems to have been in direct consequence to Lewis's theory concerning electron theory of valence (11), and Werner's theories concerning coordination compounds.

In 1920 Latimer and Rodebush (10) proposed a hydrogen bond to explain how the ionization of acids in certain solvents depended upon the basicity of that solvent. They advanced the proposition that the more basic solvent would have, structurally, an unshared pair of electrons which could be shared by the active hydrogen of the acid; or, in more conventional parlance, the basic solvent would act as the donor of electrons, while the active hydrogen of the acid would act as the acceptor of electrons. This point of view, which accepts as an hypothesis that hydrogen can assume a coordinate valence of two, was first thought unreasonable by certain workers (14,15), but now the experimental evidence has proven definitely that hydrogen can assume such a valence.

The experimental evidence pointing toward hydrogen bonding has been obtained through the study of the infra-red spectra of molecules, as well as through solubility measurements (22,24), heats of mixing (23), dielectric data (7), and cryoscopic data. The first workers (8,20) to utilize infra-red spectroscopy to study hydrogen bonding were handicapped, since their instrument could get only the first harmonic of the hydrogen vibration. However, more recent work has been done with a rock-salt prism spectrometer in our laboratory and elsewhere. Data on the fundamental hydrogen frequency has detected bonding between halogen acids and ether (4), bonding between chloroform and ether or acetone (4), as well as association of alcohols (1), amides, and oximes (3). Intra-molecular bonding, (i.e., bonding within the molecule,) has been described in molecules capable of forming a chelated ring (1,9,20).

The dimer formula for the carboxylic acids has been known for some time (16), and the spectra of these acids and their corresponding deuterium-substituted acids have been studied (2). However, this latter work was incomplete in that certain absorption peaks at a longer wave-length had been missed. The spectrum of the free hydroxyl of the acids was also observed, and it was noted that as the acid strength increased, the wave-length of absorption also increased.(21).

Formulas accounting for association of amides have been proposed (24), and the association present in these compounds may be compared to that of glycols and related compounds. Catechol, a di-hydroxy compound, has been studied (20), and its doublet structure has been rationalized by Pauling (13) in terms of orientation of the hydroxyl groups.

Formulas for molecules involving keto-enol tautomerism have been written, and tautomerism has been explained in terms of six-membered rings, hydrogen bonding, and resonance (18,19). Hilbert and others (8) studied dibenzoyl methane, acetyl acetone, and benzoyl acetone spectroscopically and found no band due to hydrogen bonding in the region of its first harmonic of the hydrogen vibration.

III - Theoretical.

According to concepts which have been developed through quantum mechanics, radiation is absorbed or emitted by a molecule in definite small packets or quanta, and the size of these quanta is related to the frequency of the radiation. Mathematically, the relation is

$$\Delta E = h\nu$$

where $\underline{\Delta E}$ is the change in energy in the molecule, $\underline{h}$ is Planck's constant, and $\underline{\nu}$ is the frequency of the radiation.

The spectrum is usually divided into divisions characterized by the energy of the radiation associated with the transition. Where large energy transitions of the order of a hundred thousand calories are involved in molecules, a high frequency of radiation in the visible or the ultra-violet region is associated with the change. These transitions involve the excitation of electrons. Changes in the vibrational energy of a molecule involve several thousand calories, and the radiation associated with it is in the near infra-red region, with wave-lengths varying from 1μ to about 25μ. Changes in the rotational energy involves only several hundred calories, and the corresponding radiation occurs in the far infra-red region, whose wave-lengths vary from about 25μ to as high as 500μ. With the vibrational absorption band, there is sometimes associated some fine structure, which is also attributed to the rotational phenomena, and which is therefore known as the vibrational-rotational spectrum.

Still another type of spectrum is known as the Raman spectrum, whose origin is in the scattering of radiation by molecules. This phenomenon also deals with the vibrations of molecules, but its sphere of applicability is somewhat different from that of the infra-red spectrum.

This naturally brings us to the question of selection rules, which define for us which type of vibration is active in the one spectrum and which is active in the other. This has been adequately treated elsewhere, and so only a brief statement will be given. A frequency is said to be active in the infra-red if in a given transition there is a net displacement of charge. On the other hand a frequency will be active in the Raman spectrum if there is a net change in polarizability for a given transition. The result of these selection rules is that quite frequently a frequency will be active in one spectrum and inactive in the other, and vice versa. In this way one seems to be the counterpart of the other, and both have been used by previous investigators in the study of molecular structure.

Infra-red spectroscopy is particularly valuable in the study of structure of organic molecules, because only the spectrum of the functional groups appear. All vibrations involving two carbon atoms are inactive because of the selection rules mentioned above. Infra-red spectroscopy gives us, in particular, the vibrational-rotational spectrum of the hydrogen atom attached to another atom, provided of course that there is a dipole moment associated with the bond. Since the hydrogen atom is so small, the remaining large part of the molecule has very little effect on the pure hydrogen vibration. Therefore the absorption peaks due to hydrogen all occur in a rather narrow region of the spectrum, and any small shifts in it are attributed to force constants (21), and inter-atomic distances. For this reason this method of research has been particularly valuable in elucidating certain problems connected with the hydrogen bond.

As stated previously, hydrogen bonds have been found to occur in a great variety of compounds. The question naturally arises as to which hydrogens are capable of forming these bonds. An empirical rule states that all hydrogens attached to nitrogen, oxygen, and fluorine fall in this group.(17). However, there are to be expected some exceptions. Ammonia and amines have not been found to be associated. Halogen acids, though not associated, have been found to form bonds with ethers, resulting in a type of compound which has been termed by organic chemists oxonium compounds. The hydrogen of chloroform has also been found to form bonds to various oxygen-containing molecules, while most other aliphatic hydrogens are inactive in this sense.

The nature of the hydrogen bond has been the subject of some controversy, and Rodebush (17) has shown that it is not a phenomenon of dipole interaction but rather a coordination of the hydrogen resulting in a more ionic character of the atom. Some workers (5) have attempted a quantum mechanical treatment of the hydrogen bond, but the results proved to be in not too close agreement with experiment. The bond must, however, have some ionic character and also some covalent character. In other words, a mathematical description of the hydrogen in the bonded state must include wave functions representing both ionic and covalent hydrogen.

The fundamental absorption peaks due to the dimers of carboxylic acids can be ascribed to modes of vibration arising from a quantum-mechanical treatment of the motions of the active hydrogen . As a result of dimer formation, each active hydrogen has two equilibrium positions, or two positions of minimum potential energy, in terms of the potential energy curve. Wave functions, both symmetric and antisymmetric, can be set up for each hydrogen, and combinations of these two wave functions will describe the vibration adequately. Let ψ_s and ψ_a refer to symmetric and antisymmetric wave functions respectively. Also let $\psi_s(1)$ and $\psi_s(2)$ refer to the symmetric vibrations of the first and the second hydrogens respectively. Then combinations of these wave functions result in the following four wave functions (Ψ) for the molecule:

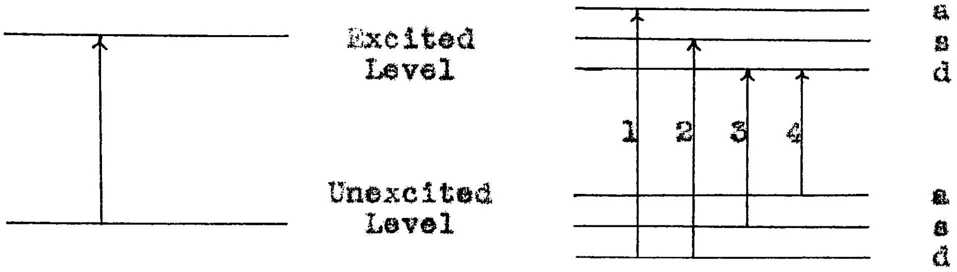
$$\Psi_s = \psi_s(1)\quad \psi_s(2)$$

$$\Psi_d = \psi_s(1)\quad \psi_a(2)$$

$$\Psi_d = \psi_a(1)\quad \psi_s(2)$$

$$\Psi_a = \psi_a(1)\quad \psi_a(2)$$

The subscripts, s, d, and a, refer to symmetric, degenerate, and antisymmetric wave functions respectively. The result on the energy levels of the vibrating hydrogen is that instead of two levels, one unexcited level and one excited level, each of these is split into three as follows:



Then, instead of one absorption band resulting from a single possible transition, the result should be four, as shown in the drawing. These four modes of vibration are:

Mode 1. Degenerate to antisymmetric levels.

Mode 2. Deganerate to symmetric levels.

Mode 3. Symmetric to degenerate levels.

Mode 4. Antisymmetric to degenerate levels.

All other possible transitions are inactive.

In the investigation of isotopic effect concerning hydrogen and deuterium, the prediction of wave lengths was made by the use of the well known expression for a harmonic oscillator,

$$\lambda = K\sqrt{\frac{M}{f}} \qquad (3)$$

where λ is the wave-length, M is the reduced mass of the system, f is the force constant, and K is a constant. The reduced mass is defined by the expression:

$$\frac{1}{M} = \frac{1}{m_1} - \frac{1}{m_2} \qquad (4)$$

where m_1 is the mass of one part of the vibrating system, and m_2 is the mass of the other. In the case of the acids, m_1 was taken to be the mass of the oxygen atom and m_2 was taken to be the mass of the hydrogen or the deuterium atom.

In going from the hydrogen acid to the deuterium acid, the spacing between the antisymmetric and the symmetric energy levels decreases exponentially as the mass increases. Therefore the difference between frequencies will also decrease, but it should, theoretically, still be possible to resolve them.

V - Experimental Procedure

A. Spectrometer and its application.

The spectrometer used was of a prism type built in this laboratory in 1936. (See figure 1 below, and figure 3, page 15. The foremost corner on the picture corresponds to the lower left-hand corner on the drawing of the optical system.)

The optical system is essentially that as shown in the figures. Two fore-mirrors were used to focus the beam on the slit whose width was approximately .01 millimeter. Another concave mirror reflected the resulting beam on the mirror-prism. The beam was then taken by means of another set of mirrors through another slit of width .01 millimeter to the thermocouple which measured the intensity of radiation. All of the mirrors were properly silvered to avoid as much absorption as possible.

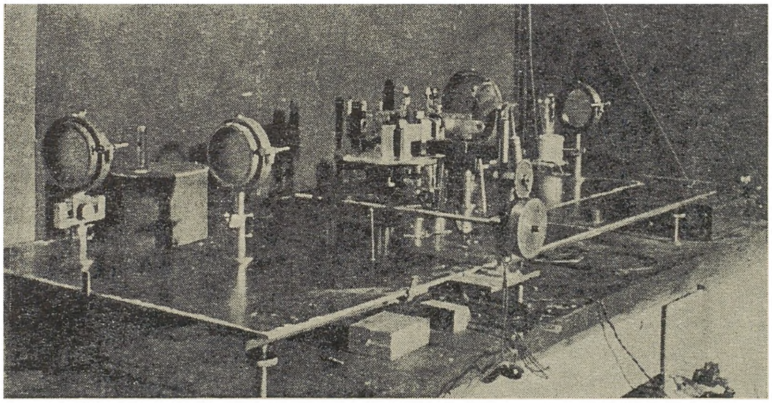


Figure 1. Spectrometer.

The prism used was of rock salt in order to overcome the great absorption found in a quartz prism which has been used by some other investigators (8). The prism and a reflecting

Figure 2.

Electrical Circuit for Nernst Glower.

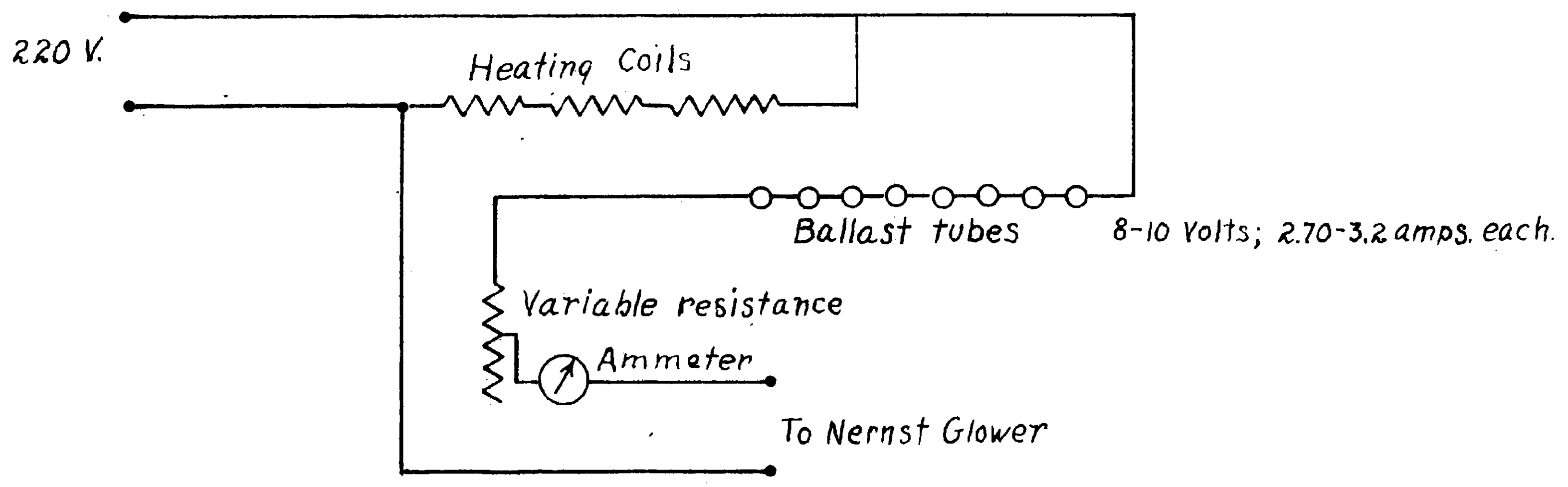
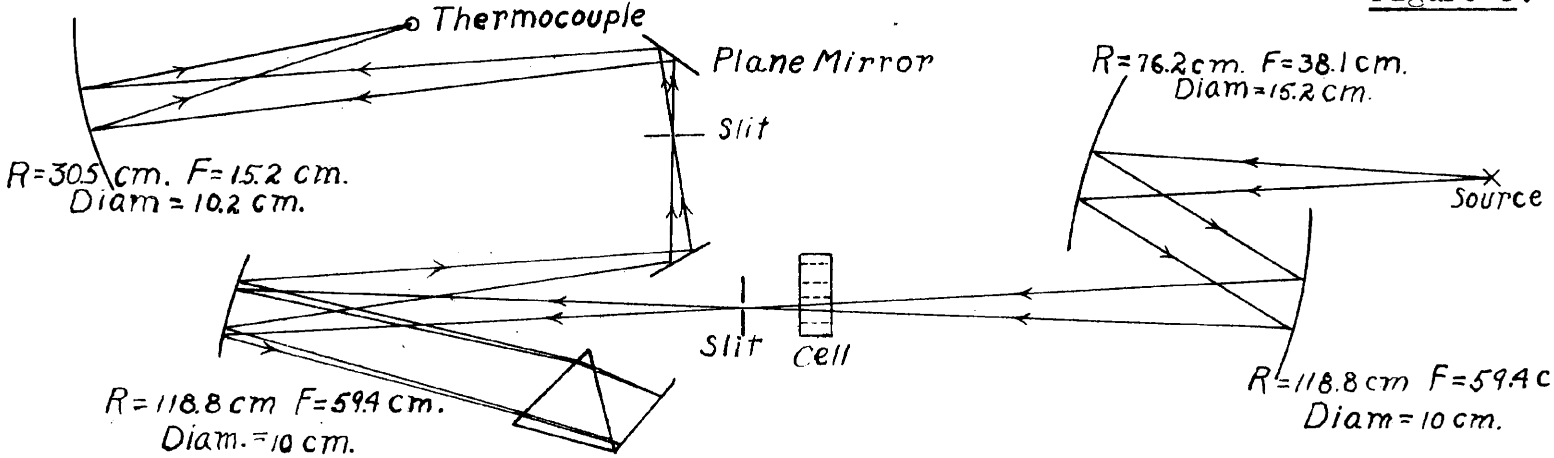


Figure 3.



Littrow-Wadsworth Mounting
Prism: 60° 6 cm. high. 7.5 cm. sides
Mirror: 6 X 8 x 1 cm.

The Optical System

Scale $\frac{1}{8}'' = 1''$

mirror were mounted on a rotating table which was connected to a numbered wheel. By turning this wheel, different portions of the spectrum could be observed. The wheel readings were calibrated to well-known absorption bands, and after each run, the wheel was recalibrated to the absorption peak at 2.673μ due to water vapor.

Great care was taken to supply constant source of radiation. A Nernst-glower was used for this purpose and a constant source of electric current was supplied to it by a suitable circuit. (See figure 2, page 15.) Ballast tubes were placed in series in order to maintain steady current, although small fluctuations over a period of hours still existed. A variable resistance in the circuit afforded the possibility of changing the current to the glower, thereby changing the intensity of radiation. From two to four tenths of an ampere were usually used.

The thermocouple was constructed of two alloys, bismuth-tin and bismuth-antimony. This junction of the two alloys was placed in evacuated system connected to a tube containing activated carbon. The latter was placed in a liquid-air trap so as to remove most of the residual gases of the system. In this way the greatest possible efficiency was obtained from the thermocouple.

The current from the thermocouple was taken directly to a HS high-voltage sensitivity galvanometer constructed by Leeds and Northrup. For some work the intensity of radiation was not great enough to get proper galvanometer deflections, and therefore an amplifying system had to be used. For this purpose an amplifying system known as the Moll-Relay (12) proved quite efficient.

A technique was employed whereby cells of different lengths could be readily placed in the spectrometer. Thus, the thickness and, of course, the concentration of the solution through which the radiation passed, could be varied. The cells are numbered on the graphs, and the corresponding lengths are given in Table 1.

Table 1.

Cell No.	Length (cm.)
1	10.18
2	5.070
3	2.532
4	1.262
5	.640
6	.325
7	.158

Beer's law was employed to study the effects of concentration upon the absorption spectrum. Mathematically, this law takes the form:

$$K = \frac{1}{C \times d} \log \frac{Io}{I}$$

Where Io is the transmission of radiation through pure solvent, measured as the deflection (in millimeters) by the galvanometer connected to the thermocouple; I is the transmission through solution; C is the concentration in moles per liter, and d is the length of the cell. It can be shown that the absorption due to the cell windows and the solvent cancels out in each case. Following from this, K would be defined as the molal absorption coefficient.

A difficulty arose, however, in its application. It was found that K was not a constant unless C x d was kept constant for the entire series of runs. The difficulty lies not in the law, which has been developed from sound optical principles, but rather in its application to our spectrometer. The fact that the resolving power of the instrument was not perfect would probably account for most of the deviations observed.

The spectra of all the substances studied were taken in carbon tetrachloride solution. This compound has proved the best solvent for this use although it has also several disadvantages.

The ideal solvent for use in infra-red spectroscopy should meet the following requirements: (1) It must be transparent to infra-red radiation. (2) It must be inert toward the solute. (3) It must be easily obtained in a high degree of purity and in large quantities. (4) It must afford a high solubility of the compound to be studied.

Carbon tetrachloride meets these requirements fairly well, and for the studies which were pursued, it was mostly satisfactory. In the region of the spectrum in which the investigation was carried out, carbon tetrachloride has very little absorption. However this solvent would fail in the regions of the spectrum where great absorption occured.

This solvent is inert toward most organic compounds, but with some compounds a reaction does take place. If no interaction took place between solvent and solute, then the spectrum of this solution should be the same as that of the compound in the vapor state. The slight shift of the spectrum of acetic acid in going from the solution to the vapor state (See figure 5, page), can be attributed to the small interaction between the solvent and the acid. This inertness of carbon tetrachloride is very probably carried over to the similar compounds studied in this investigation.

Some evidence has arisen recently in connection with compound formation between carbon tetrachloride and N-methyl acetamide. How far this phenomena goes with other compounds is a matter of further investigation. This in now being carried on in this laboratory and is as yet, therefore, unpublished.

The greatest difficulty, perhaps, arises in the purification of this solvent. Technical carbon tetrachloride is available in commercial quantities, but it has two impurities, water and chloroform, which are very hard to eliminate. The most practical device found in our laboratory to remove these was simple distillation. A six-foot distilling column, whose packing consisted of spirals of nichrome wire, removed most of the chloroform and water. The water remaining in the solvent is estimated to be less than .001 M., but the concentration of the chloroform is still problematical. An absorption band in the region of that of chloroform still remained, although it was considerably diminished after distillation. More work is being done on the problem at the present time by Mr. Maycock, and a publication of the results will probably be made within a few months. If chloroform is present to any concentration above .01 M., it is bound to cause some error in the spectrum, since chloroform does form hydrogen bonds with various oxygen-containing molecules (4).

Another disadvantage in using carbon tetrachloride as a solvent lies in the fact that very polar molecules are only slightly soluble in it. This difficulty thereby limits the number of compounds capable of being studied by ordinary technique. In the case of any solvent which might afford greater solubility, bonding between the solvent and solute would undoubtedly take place, thereby introducing a complicating factor in the resulting spectrum. This difficulty of solubility is therefore an inherent one, and can only be solved by improved technique with very dilute solutions.

B. Preparation and Purification of Compounds.

Certain of the compounds studied demanded special purification, and certain of these had to be first synthesized, a few of which had not been mentioned in the literature.

The deutero-acids were prepared by reactions of some acid derivative with deuterium oxide in one step. The heavy acetic acid was prepared by heating for several hours equimolar quantities of acetic anhydride and heavy water in a sealed tube. The benzoic acid resulted from an addition of an excess of heavy water to benzoyl chloride. After heating for several hours, the excess water and the by-product, hydrochloric acid, were pumped off. The deutero-propionic acid was prepared from the corresponding anhydride in a similar manner as was acetic acid.

Precaution was used to keep the deutero-acid away from the moisture of the atmosphere, since the exchange reaction to ordinary acetic acid would proceed readily in the presence of this moisture. The deutero-acid was dissolved in carbon tetrachloride, and the spectrum was taken. Subsequently, the same solution was allowed to come in contact with small amounts of light water. The exchange reaction which converted the heavy to the light acid was allowed to proceed for about two hours, after which the spectrum of the light and the heavy acids could not be due to impurities.

Almost all of the glycols were available either in large quantities for solvent use, as for example ethylene glycol, or were available in smaller quantities in the Preparation Stock Room of the Organic Division of the Chemistry Department. From the latter source were obtained trimethylene glycol, tetramethylene glycol, hexamethylene glycol, and pentamethylene glycol. Octadecamethylene glycol was specially prepared under the direction of Professor C. S. Marvel.

The pentamethylene glycol was prepared by the hydrolysis of pentamethylene dibromide in an alkaline water-alcohol solution. After refluxing for 48 hours, potassium carbonate was added to saturation and the layers were separated. The glycol containing layer was fractionally distilled.

Some physical constants of the glycols used are herewith listed.

Table 2.

Compound	Physical Constant
Ethylene glycol	B.P. 88° C/10mm.
Propylene glycol	B.P. 105° C/10mm.
Butylene glycol	B.P. 124° C/ 8mm.
Pentamethylene glycol	B.P. 104° C/ 4mm.
Hexamethylene glycol	M.P. 42° C.
Decamethylene glycol	M.P. 70° C.
Octadecamethylene glycol	M.P. 91° C.

The ethoxy-alcohols were all prepared in this laboratory, with the single exception of ethyl-cellosolve, which is available in commercial quantities.

3-Ethoxy-propanol-1 was synthesized from propylene cyanohydrin and sodium ethylate. One hundred and twenty five grams of the cyanohydrin was run slowly into 500 cc. absolute ethyl alcohol containing 46 g. of sodium. The mixture was refluxed for twelve hours, whereupon it was neutral to litmus. After removing the sodium chloride by filtration, the alcohol was distilled from the solution. The residue was fractionally distilled, yielding the product.

4-Ethoxy-n-butanol-1 was prepared from the mono-sodium salt of tetramethylene glycol and ethylene bromide. Ninety grams of the glycol was dissolved in 500 cc. dioxane, and to this, while refluxing, 25 g. of sodium was added. The sodium salt precipitated from the solution, but this did not seem to hinder the subsequent reaction. A slight excess of 125 g. of ethyl bromide was added, and the resulting mixture refluxed for forty-eight hours. Sodium bromide was separated from the solution by filtration, and the dioxane was removed by distillation. The remaining residue was fractionally distilled, yielding the final product.

5-Ethoxy-n-pentanol-1 was prepared by treating pentamethylene dibromide with an equimolar quantity of sodium ethylate, and subsequently hydrolyzing the mono-bromide compound. One hundred and twenty-five grams of pentamethylene dibromide was dissolved in 200 cc. absolute ethyl alcohol. An equimolar quantity of sodium was dissolved in 400 cc. absolute alcohol, and the resulting solution was slowly added to the solution of pentamethylene dibromide. The mixture was refluxed for twenty four hours, after which several hundred cubic centimeters of alcohol were distilled from it to decrease the large volume of solution. The precipitated sodium bromide was separated by filtration.

Fifty grams of sodium hydroxide and 200 cc. of water were added, and the mixture was refluxed for twenty-four hours. The product was extracted with ether and fractionally distilled.

The observed boiling points for the ethoxy-alcohols used are herewith listed.

Table 3.

Compound	Physical constant
Ethyl cellosolve	B.P. 132° C.
3-Ethoxy-propanol-1	B.P. 158-159° C.
4-Ethoxy-butanol-1	B.P. 181° C.
5-Ethoxy-pentanol-1	B.P. 75-80° C./4 mm.

The compounds, dibenzoyl methane, benzil, and diphenyl methane, were purified by crystallization from alcohol and their melting points were checked with those in the literature.

The azo-compounds were prepared by the well known coupling reaction of diazonium compounds, and the melting points of the products were also checked with those in the literature.

The melting points observed for these compounds are as follows:

Table 4.

Compound	Physical constant
Dibenzoyl methane	M.P. 77° C.
Benzil	M.P. 95° C.
Diphenyl methane	M.P. 26° C.
3-Phenylazo-4-hydroxy-azobenzene	M.P. 123° C.
1-Phenylazo-naphthol-2	M.P. 131° C.

4-Hydroxy-azobenzene	M.P.	155°C.
2-Hydroxy-5 -methyl-azobenzene	M.P.	106°C.
4-Hydroxy-3-methyl-azobenzene	M.P.	128°C.

VI - Experimental Results.

A. Carboxylic Acids.

Both mono-basic and di-basic acids were studied, but, as stated previously, the study of the latter was impeded by their very slight solubility in carbon tetrachloride.

The mono-basic acids studied were benzoic acid, acetic acid, and propionic acid. The active hydrogen of these acids was substituted with deuterium to determine which part of the spectrum was due directly to the hydrogen or, in turn, to the deuterium. This data is given if figures 4 - 8, and, for the sake of convenience, the essential data is tabulated in Table 5.

Table 5.

Compound	Absorption Peaks					
	Ordinary acid				Deutero-acid	
Acetic acid	3.31μ	3.39μ	3.71μ	3.78μ	4.42μ	4.87μ
Propionic acid	3.22μ	3.36μ	3.79μ	3.87μ	4.40μ	4.85μ
Benzoic acid	3.29μ	3.45μ	3.74μ	3.91μ	4.49μ	4.87μ.

The dibasic-acids studied were only two, diethyl malonic acid and azelaic acid. The resulting data is in figure 9.

B. Glycols and glycol Derivatives

The spectra of eight glycols were determined, all in carbon tetrachloride, of course, and in saturated solutions. The exact solubility of these compounds was not accurately determined, but it is of the order of .001 M., judging from the amount of absorption observed. The essential data on these compounds is found in the form of graphs in figures 10 and 11, and also in Table 6.

Table 6.

Compound	Free OH	Bonded OH
Ethylene glycol	2.76μ	----
Propylene glycol	2.76μ	2.80μ
1,1 Diphenyl-propylene glycol	----	2.79μ
Butylene glycol	2.76μ	2.89μ
Pentamethylene glycol	2.76μ	2.84μ
Hexamethylene glycol	2.76μ	2.87μ
Decamethylene glycol	2.76μ	2.83μ
Octadecamethylene glycol	2.76μ	----

A series of compounds was studied, in which one of the hydroxyl groups of certain glycols was substituted by an ethoxy group. This data is found in figures 12-14, and for the sake of unity in comparing them, in Table 7.

Table 7.

Compound	Free OH	Intra-molecular bond	Inter-molecular bond
2-Ethoxy-ethanol-1	2.77μ	----	2.87μ
3-Ethoxy-n-propanol-1	2.75μ	2.82μ	2.85μ
4-Etholyl-n-butanol-1	2.75μ	2.89μ	2.91μ
5-Ethoxy-n-pentanol-1	2.75μ	2.87μ	2.90μ

C. Moleculea exhibiting keto-enol tautomerism.

The compounds in this group failed to give definite absorption peaks, but instead they displayed rather broad absorption bands.

The name of the compound studied with the corresponding figure number of the absorption curve is as follows:

Dibenzoyl methane	Figure	15
3-Phenylazo-4-hydroxy-azobenzene	"	16
1-Phenylazo-naphthol-2	"	16
4-Hydroxy-azobenzene	"	16
2-Hydroxy-5-methyl-azobenzene	"	17
4-Hydroxy-3-methyl-azobenzene	"	17

Figure 4.

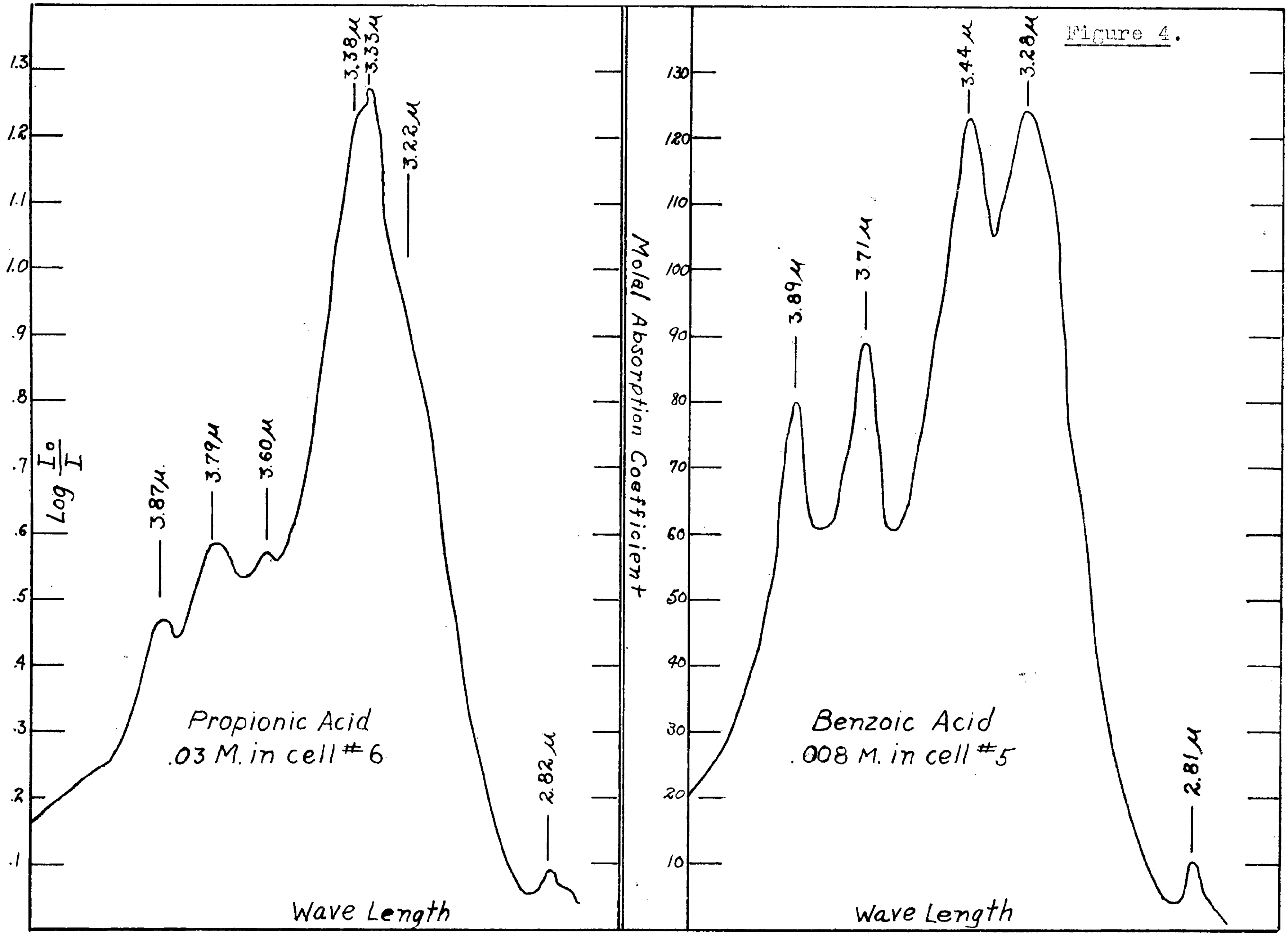
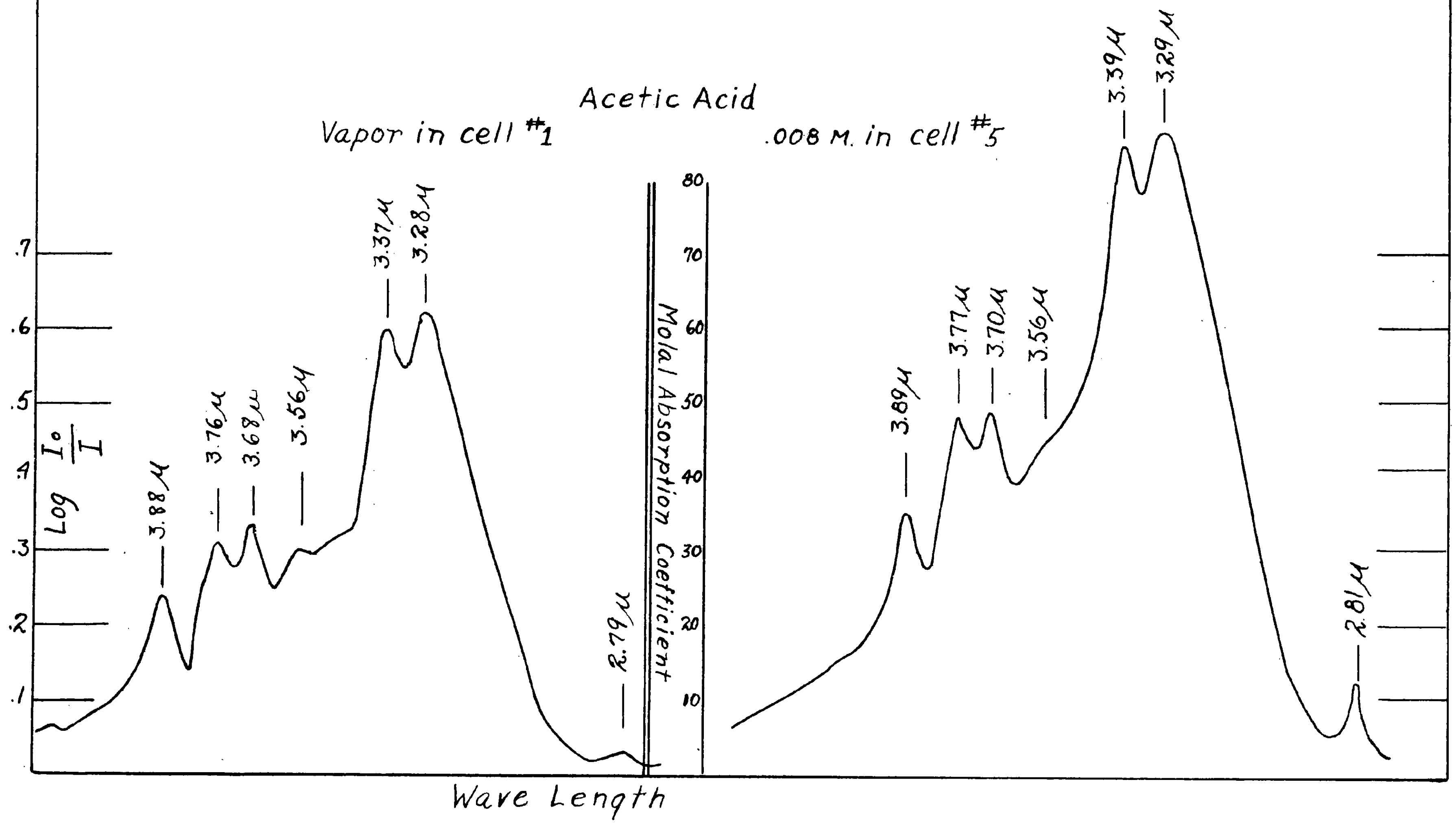

Log $\frac{I_0}{I}$
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
3.87μ
3.79μ
3.60μ
3.38μ
3.33μ
3.22μ
2.82μ
Propionic Acid
.03 M. in cell #6
Wave Length
Molal Absorption Coefficient
130
120
110
100
90
80
70
60
50
40
30
20
10
3.89μ
3.71μ
3.44μ
3.28μ
2.81μ
Benzoic Acid
.008 M. in cell #5
Wave Length

Figure 5.


Acetic Acid
Vapor in cell #1
.008 M. in cell #5
Log $\frac{I_0}{I}$
.1
.2
.3
.4
.5
.6
.7
3.88μ
3.76μ
3.68μ
3.56μ
3.37μ
3.28μ
2.79μ
Molal Absorption Coefficient
10
20
30
40
50
60
70
80
3.89μ
3.77μ
3.70μ
3.56μ
3.39μ
3.29μ
2.81μ
Wave Length

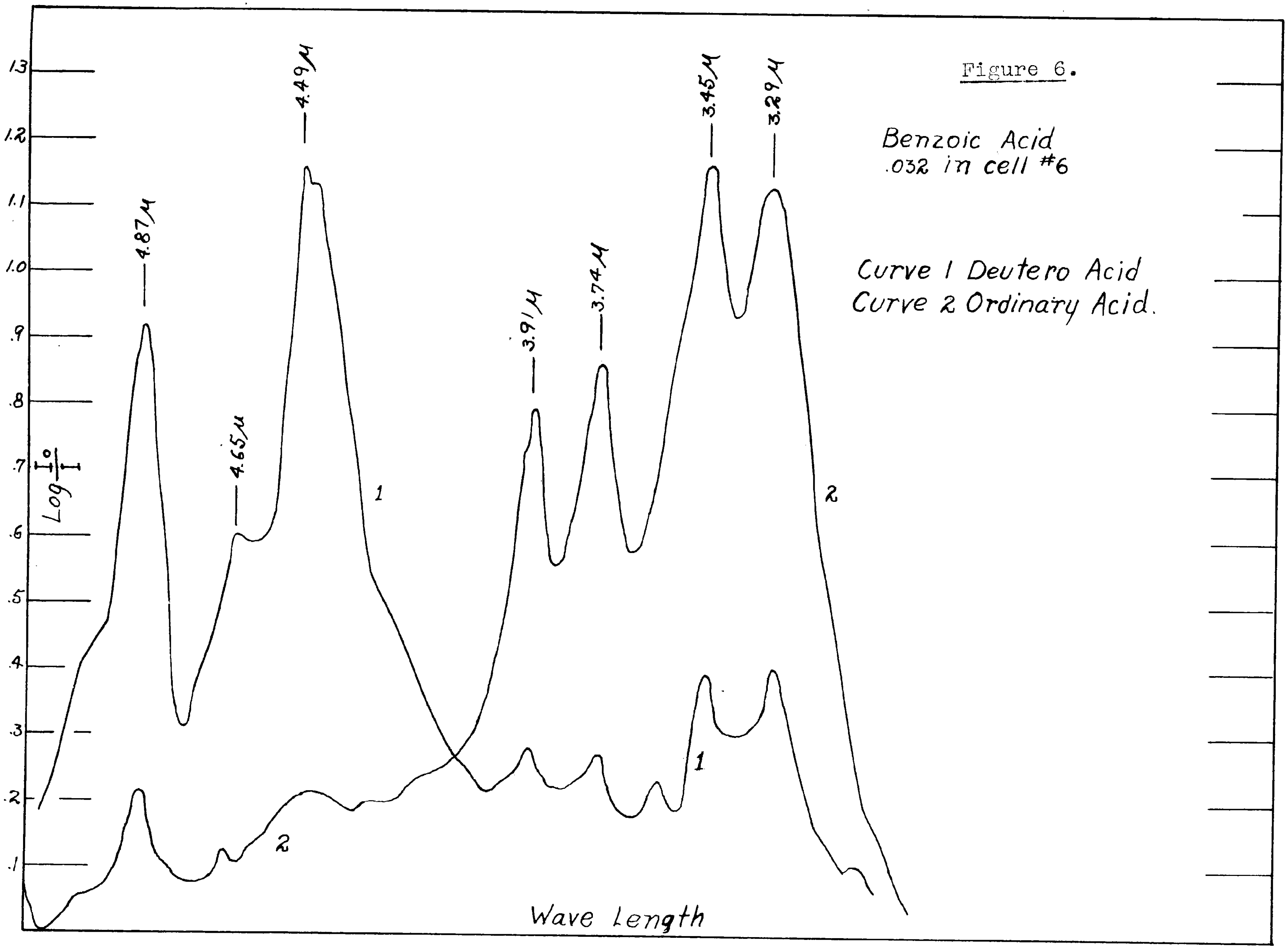


Figure 6.

Benzoic Acid
.032 in cell #6

Curve 1 Deutero Acid
Curve 2 Ordinary Acid.

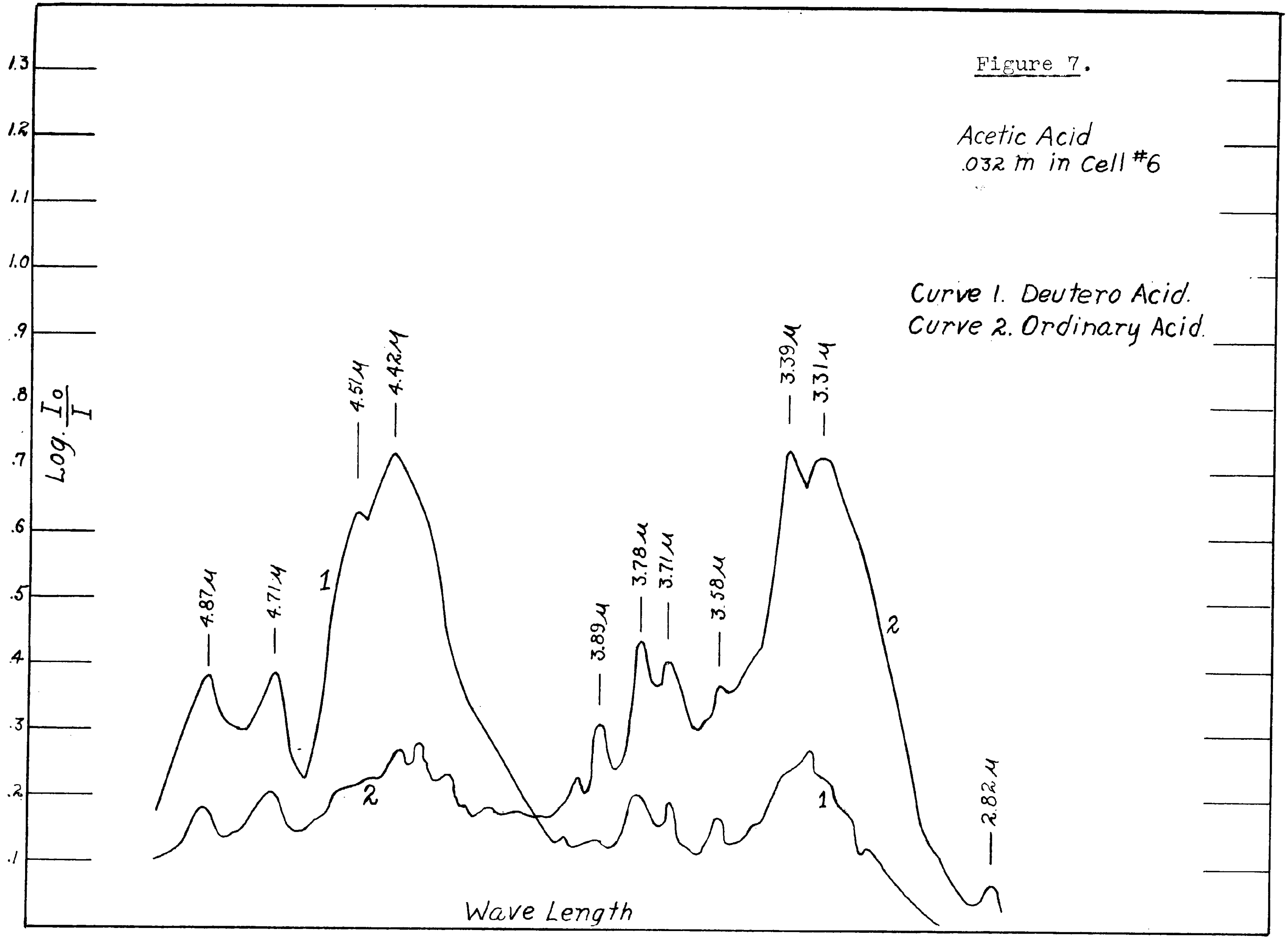


Figure 7.

Acetic Acid
.032 m in Cell #6
Curve 1. Deutero Acid.
Curve 2. Ordinary Acid.
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
Log. Io/I
Wave Length
4.87μ
4.71μ
4.51μ
4.42μ
3.89μ
3.78μ
3.71μ
3.58μ
3.39μ
3.31μ
2.82μ
1
2
2
1

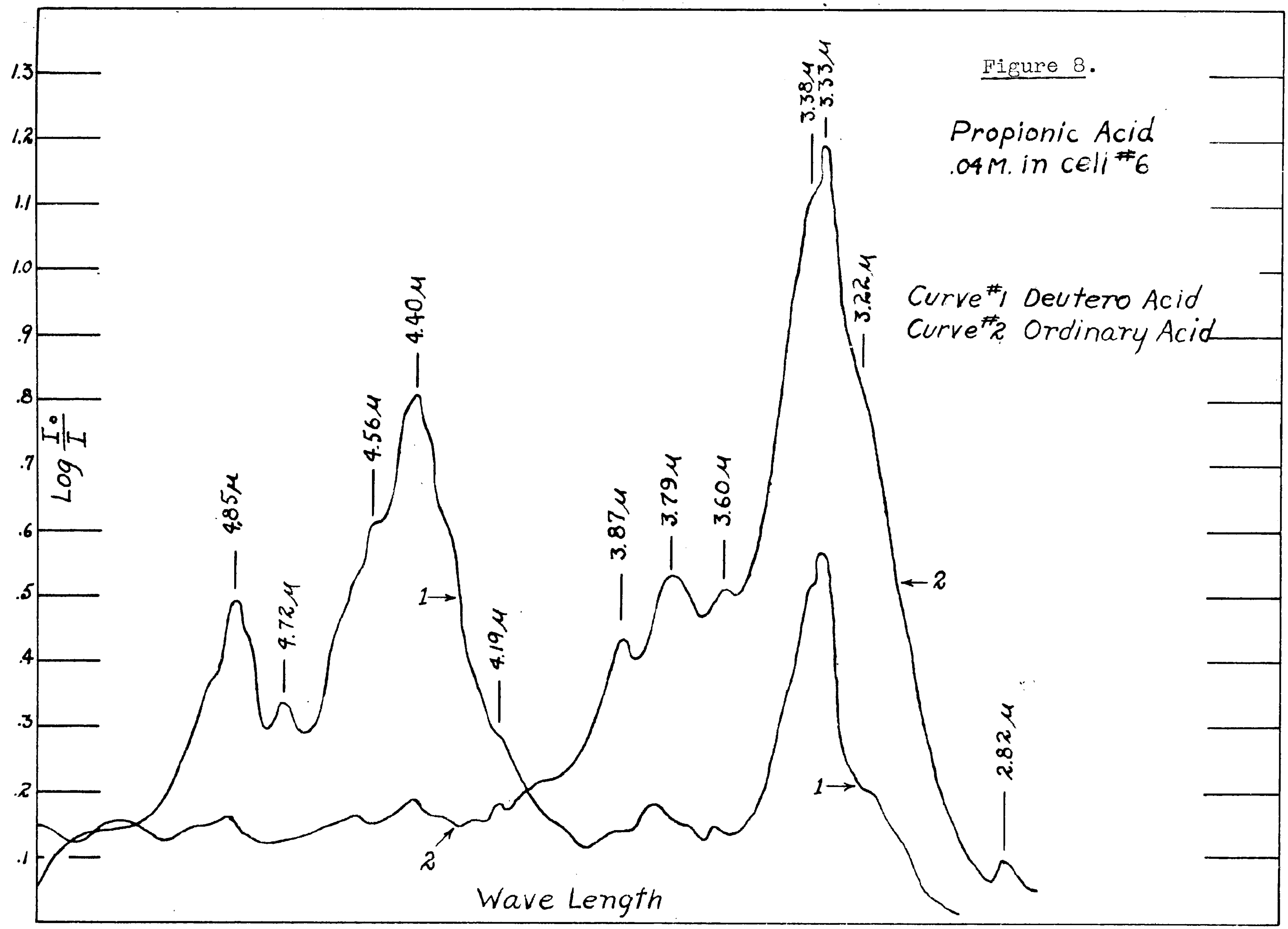


Figure 8.

Propionic Acid
.04 M. in cell #6

Curve #1 Deutero Acid
Curve #2 Ordinary Acid

Figure 9.

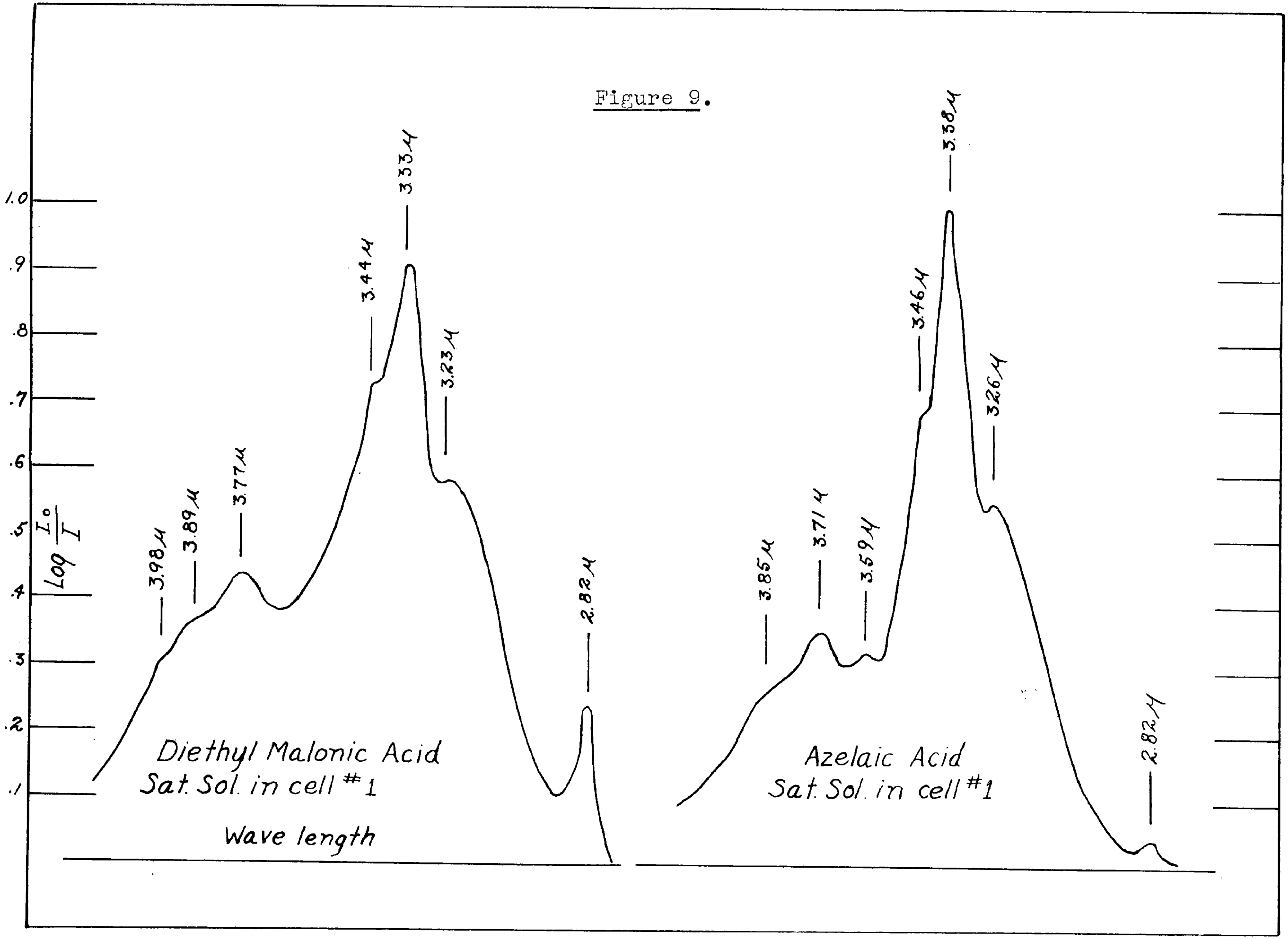

1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
Log $\frac{I_o}{I}$
3.98μ
3.89μ
3.77μ
3.44μ
3.33μ
3.23μ
2.82μ
Diethyl Malonic Acid
Sat. Sol. in cell #1
Wave length
3.85μ
3.71μ
3.59μ
3.46μ
3.58μ
3.26μ
2.82μ
Azelaic Acid
Sat. Sol. in cell #1

Figure 10.

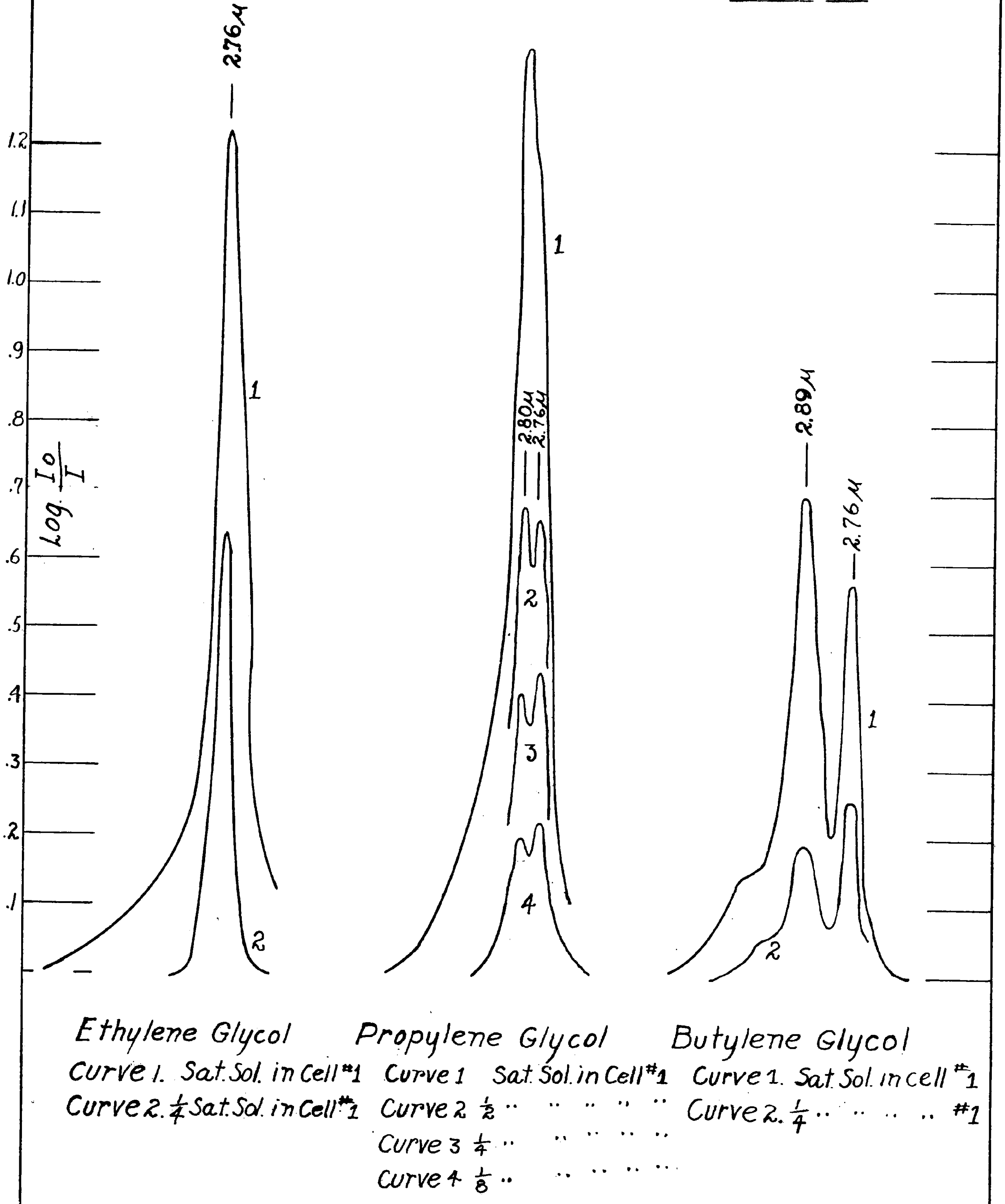
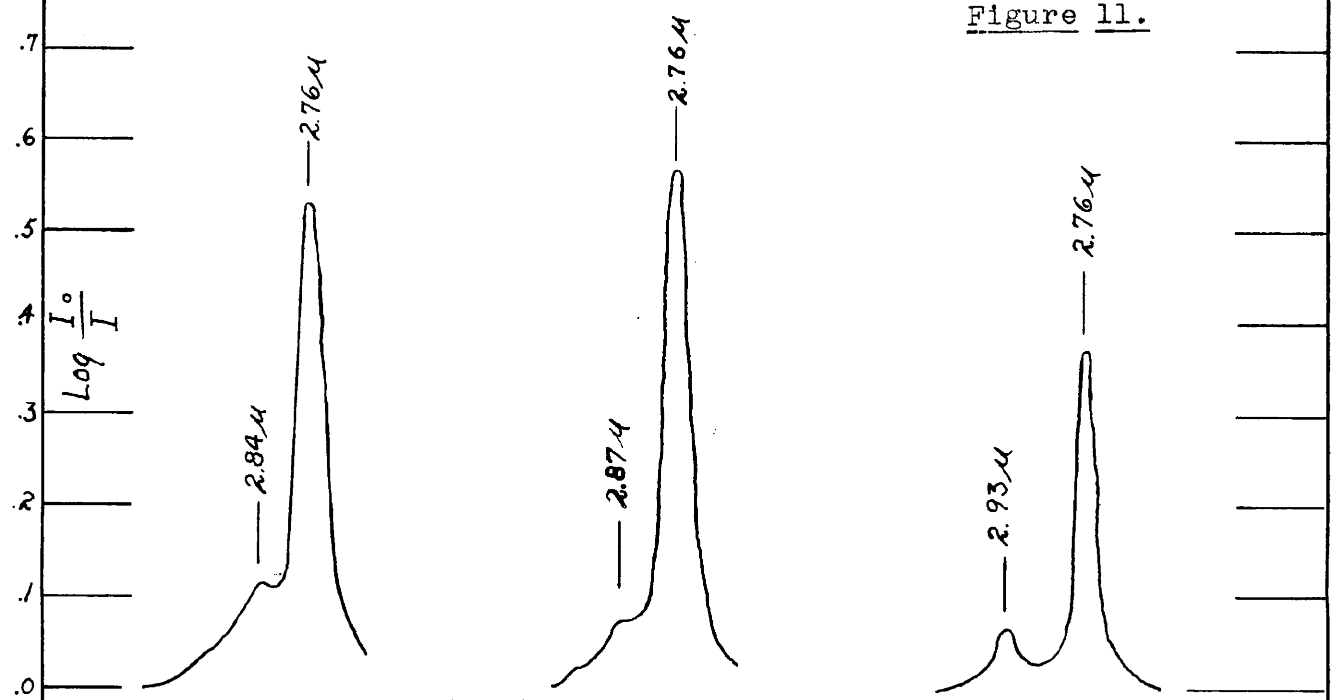

2.76μ
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
Log $\frac{I_o}{I}$
1
2
1
2.80μ
2.76μ
2
3
4
2.89μ
2.76μ
1
2
Ethylene Glycol
Curve 1. Sat. Sol. in Cell #1
Curve 2. ¼ Sat. Sol. in Cell #1
Propylene Glycol
Curve 1 Sat. Sol. in Cell #1
Curve 2 ½ " " " " "
Curve 3 ¼ " " " " "
Curve 4 ⅛ " " " " "
Butylene Glycol
Curve 1. Sat. Sol. in cell #1
Curve 2. ¼ " " " " #1

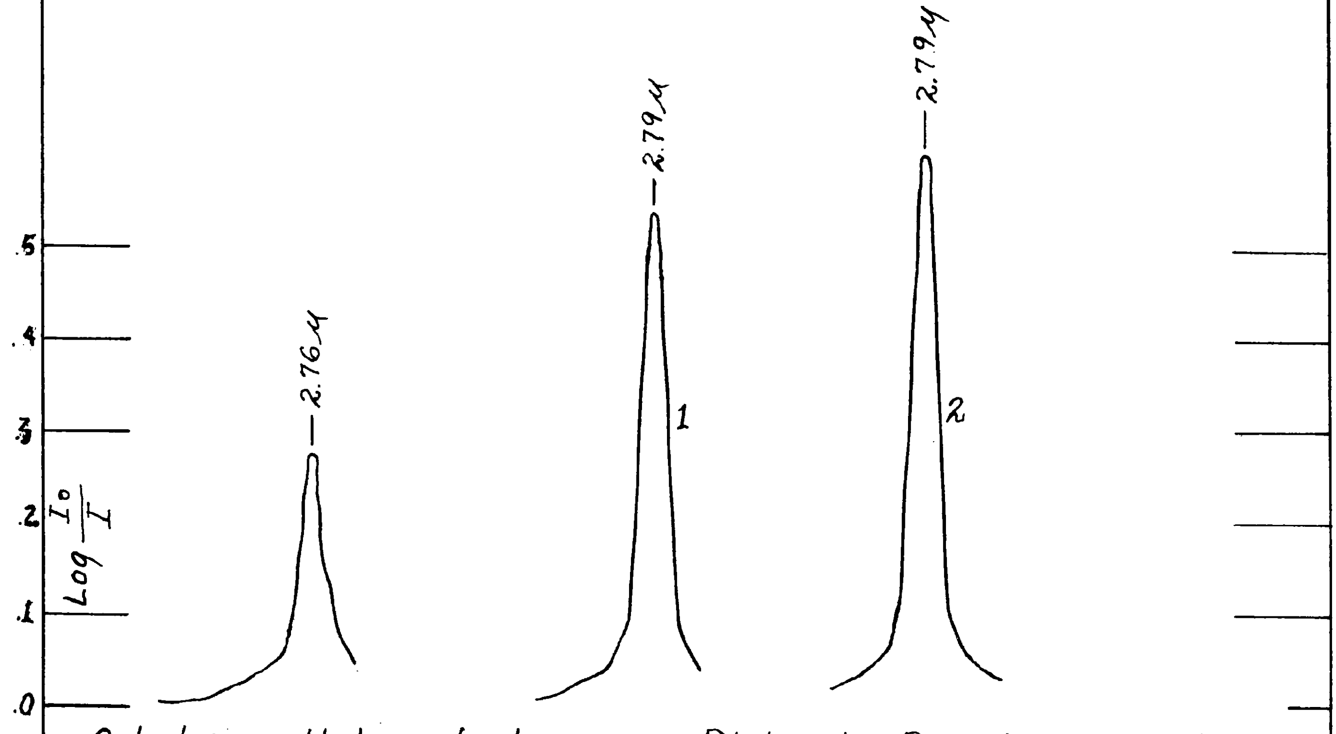
Figure 11.



Penta methylene glycol
Sat. Sol. in cell #1

Hexa methylene glycol
Sat. Sol. in cell #1

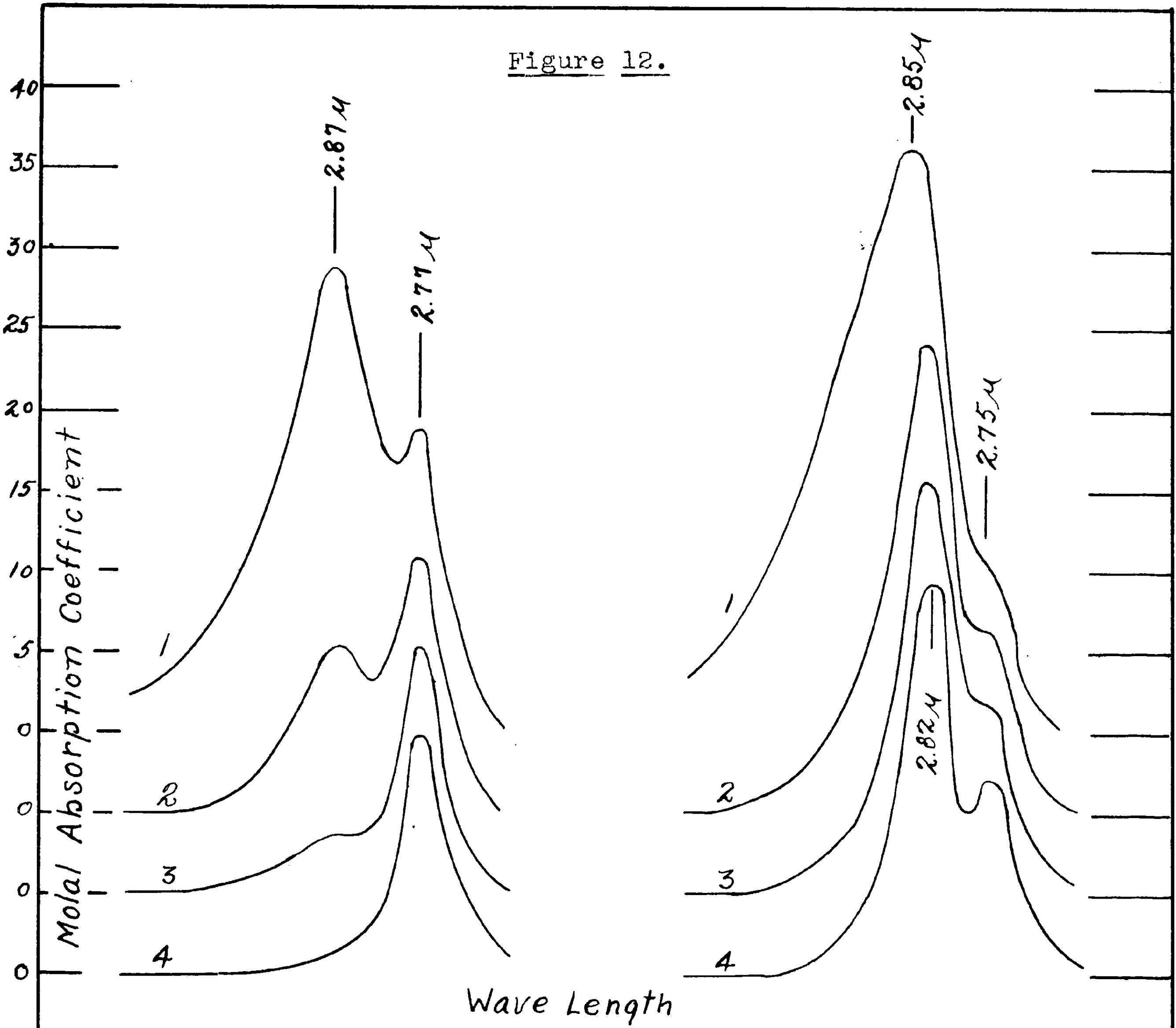
Decamethylene glycol
Sat. Sol. in cell #1



Octadecamethylene glycol
Sat. Sol. in Cell #1

Diphenyl Propylene glycol
Curve 1- .004 in cell #3
Curve 2- .001 in cell #1

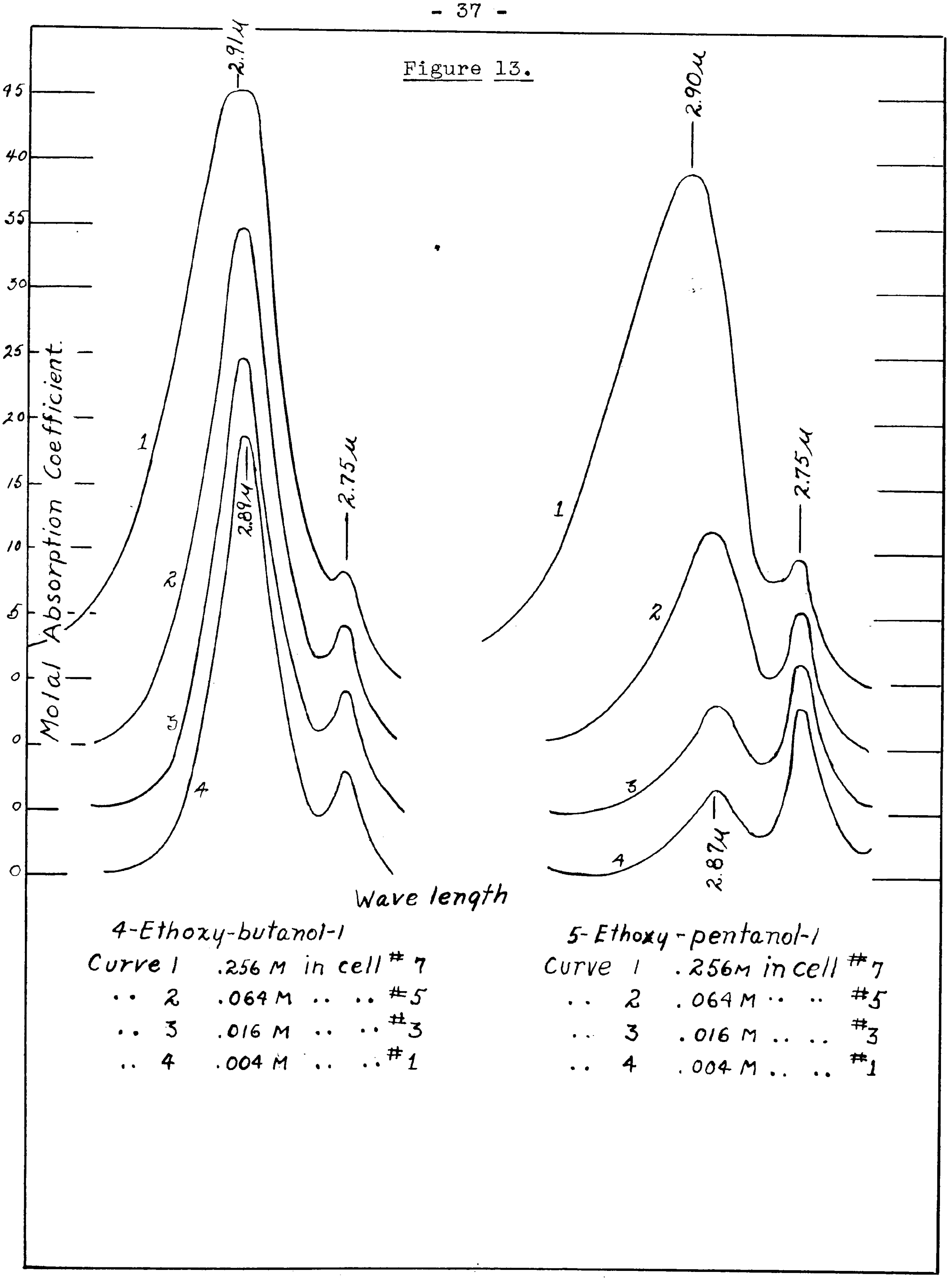
Figure 12.



2-Ethoxy-ethanol-1
Curve 1 .256 M. in cell #7
Curve 2 .064 M. in cell #5
Curve 3 .016 M. in cell #3
Curve 4 .004 M. in cell #1

3-Ethoxy-n-propanol-1
Curve 1 .256 M. in cell #7
Curve 2 .064 M. in cell #5
Curve 3 .016 M. in cell #3
Curve 4 .004 M. in cell #1

Figure 13.


2.91μ
2.90μ
2.89μ
2.75μ
2.75μ
2.87μ
45
40
35
30
25
20
15
10
5
0
0
0
0
Molal Absorption Coefficient.
1
2
3
4
1
2
3
4
Wave length
4-Ethoxy-butanol-1
Curve 1 .256 M in cell #7
.. 2 .064 M .. .. #5
.. 3 .016 M .. .. #3
.. 4 .004 M .. .. #1
5-Ethoxy-pentanol-1
Curve 1 .256M in cell #7
.. 2 .064 M .. .. #5
.. 3 .016 M .. .. #3
.. 4 .004 M .. .. #1

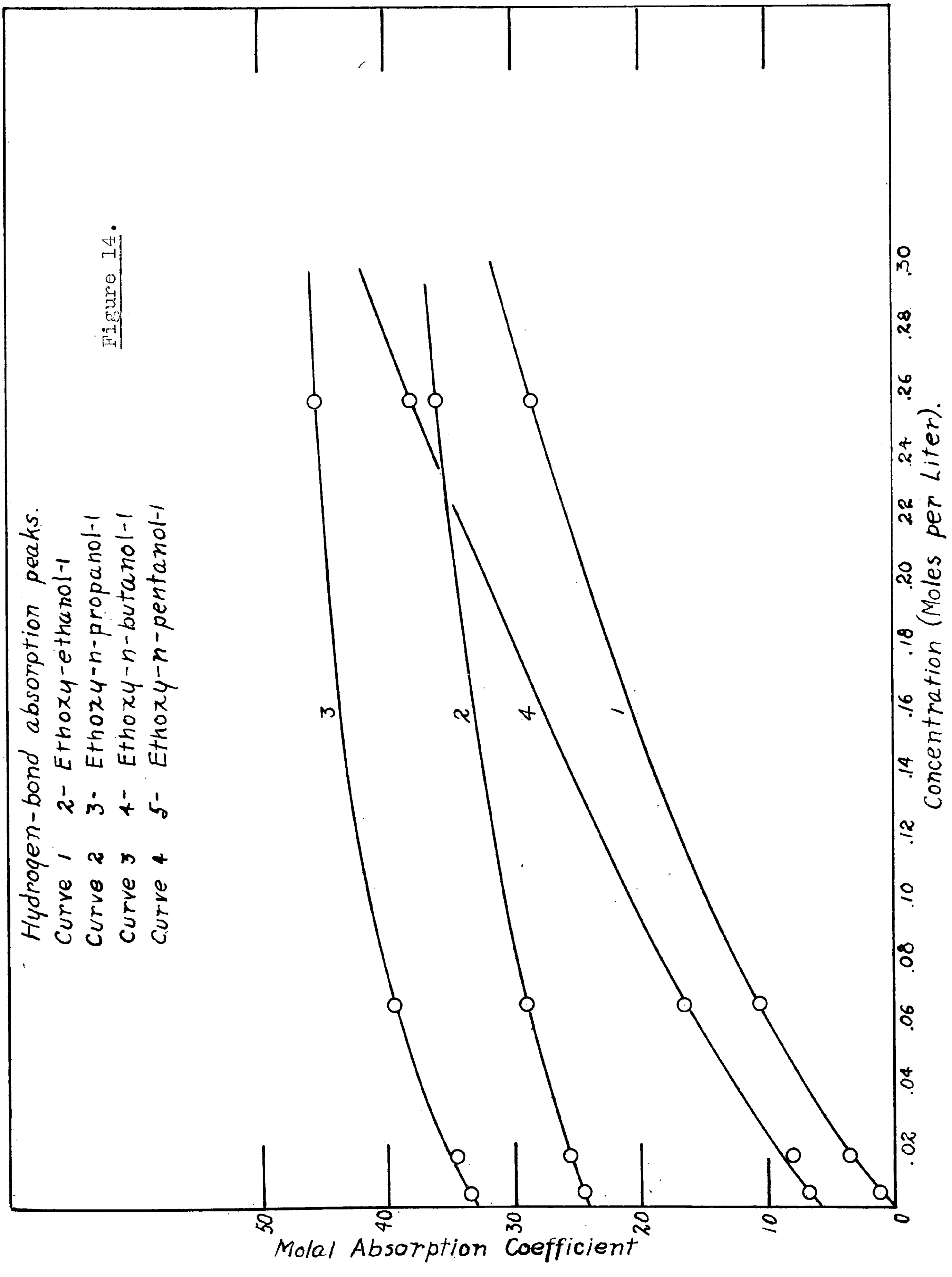


Figure 14.

Hydrogen-bond absorption peaks.
Curve 1 2- Ethoxy-ethanol-1
Curve 2 3- Ethoxy-n-propanol-1
Curve 3 4- Ethoxy-n-butanol-1
Curve 4 5- Ethoxy-n-pentanol-1
1
2
3
4
Molal Absorption Coefficient
0
10
20
30
40
50
Concentration (Moles per Liter).
.02
.04
.06
.08
.10
.12
.14
.16
.18
.20
.22
.24
.26
.28
.30

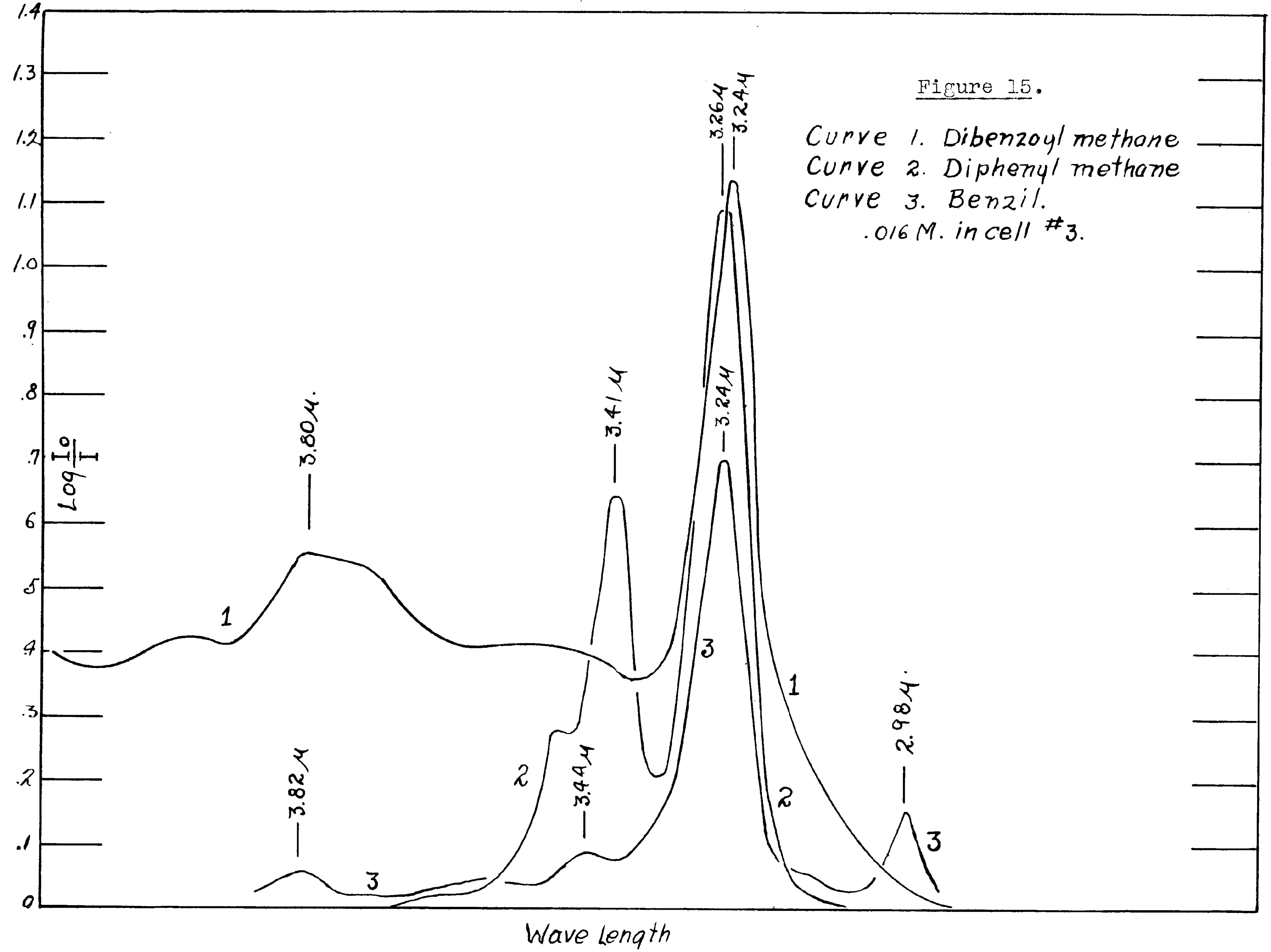


Figure 15.

Curve 1. Dibenzoyl methane
Curve 2. Diphenyl methane
Curve 3. Benzil.
.016 M. in cell #3.

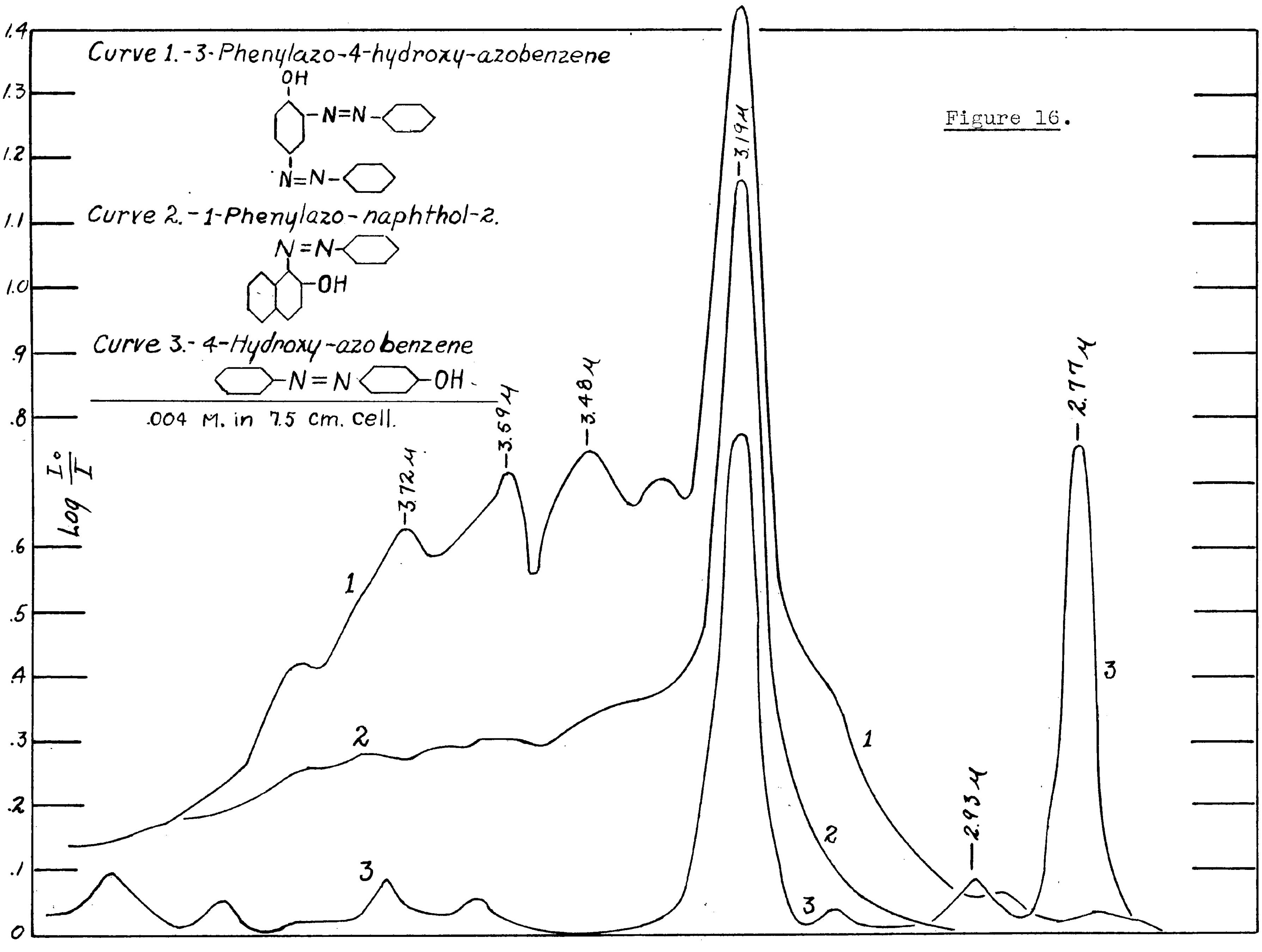


Figure 16.

Curve 1.-3-Phenylazo-4-hydroxy-azobenzene
OH
N=N
N=N
Curve 2.-1-Phenylazo-naphthol-2.
N=N
OH
Curve 3.- 4-Hydroxy-azobenzene
N=N
OH
.004 M. in 7.5 cm. cell.
Log $\frac{I_0}{I}$
1.4
1.3
1.2
1.1
1.0
.9
.8
.6
.5
.4
.3
.2
.1
0
3.72μ
3.59μ
3.48μ
3.19μ
2.93μ
2.77μ
1
2
3
1
2
3
3

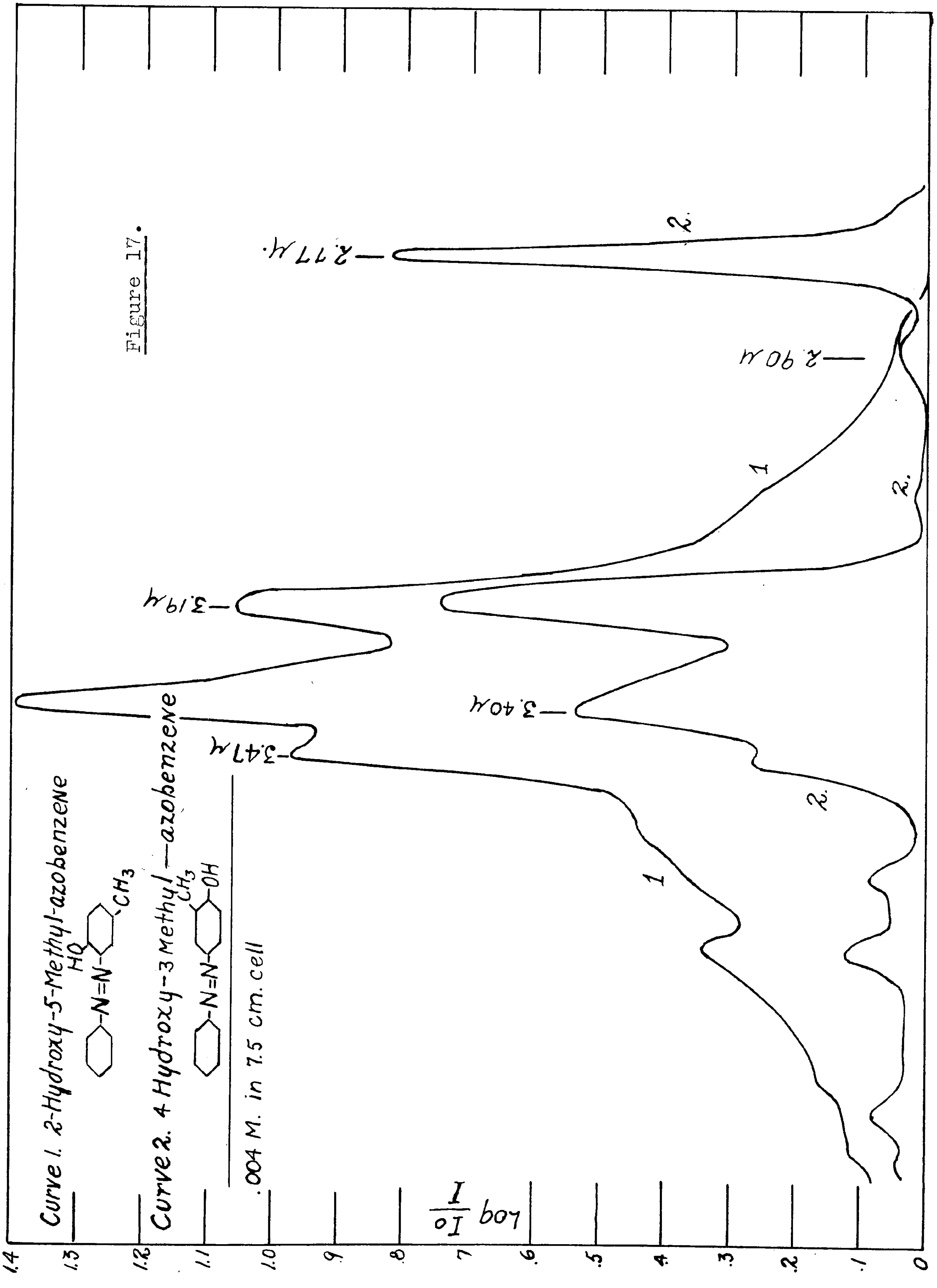


Figure 17.

Curve 1. 2-Hydroxy-5-Methyl-azobenzene
Curve 2. 4 Hydroxy-3 methyl-azobenzene
HO
-N=N-
CH3
OH
.004 M. in 7.5 cm. cell
log I0/I
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
3.41μ
3.40μ
3.19μ
2.90μ
2.77μ
1
2.

VII - Discussion of Results

A. Carboxylic Acids.

The carboxylic acids exhibit a rather complicated absorption spectrum in comparison to simple hydroxy compounds such as alcohols. The clue to this intricate structure lies, probably, in the fact that the mono-basic acids are, to a very large extent, associated in the form of dimers, while, in the case of dibasic acids, they are capable of forming large polymers (9).

The simplest of the acids, from the point of view of its spectrum, seems benzoic acid. If a solution of the spectrum of this acid can be obtained, then, perhaps, we might also obtain solutions for the still more complex spectra of some of the other acids.

After we have proven that there are four possible active frequencies (See page 12-13), it becomes a simple task to assign them correctly. Transitions 1 and 2 involve the greatest energy change and therefore will involve radiation of the shorter wave-length, while the remaining two transitions will involve radiation of the longer wave-length. The assignment of wave-length to a mode of vibration in the case of the mono-basic acids investigated is, therefore, as shown in Table 8. It might be mentioned that difficulty was encountered in ascertaining the exact wave-length for Mode 1 in acetic and propionic acids, since the absorption due to carbon-hydrogen vibration comes very close to it.

In order to show conclusively that the absorption so assigned above is due to the active hydrogen of the acid, the deuterium-substituted acid was studied. There should be, thereby, a disappearance of the original hydrogen absorption with a reappearance of the deuterium absorption at a longer wave-length (See page 13.) Using formulas (3) and (4), page 13, the deutero-wave-lengths were calculated, using the mean of each doublet as the original wave-length, and the following table gives the calculated and the observed values.

Table 8.

Compound	Mode 1	Mode 2	Average (calc.)	Deutero (calc.)	Deutero (obs.)
Benzoic acid	3.29μ	3.45μ	3.37μ	4.62μ	4.49μ
Acetic acid	3.31μ	3.39μ	3.35μ	4.60μ	4.42μ
Propionic acid	3.30μ	3.38μ	3.34μ	4.57μ	4.40μ
	Mode 3	Mode 4			
Benzoic acid	3.74μ	3.91μ	3.83μ	5.26μ	4.87μ
Acetic acid	3.71μ	3.78μ	3.75μ	5.15μ	4.87μ
Propionic acid	3.60μ	3.79μ	3.70μ	5.08μ	4.85μ

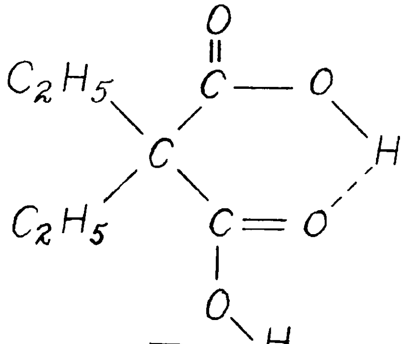
Although the calculated and the observed values are somewhat different, the order of magnitude is correct, and a more perfect solution can only be obtained by overcoming some of the previously made assumptions. The assumptions entertained by the use of formula (3) in this problem are (1) that the vibrations are strictly harmonic, and (2) that the force constant does remain constant in going from ordinary acid to deuterium-substituted acid. The difficulty involved in the use of formula (4) is correctly selecting the masses of the two vibrating compounds. For some modes of vibration the effective mass of the remaining part of the molecule, $\underline{m_1}$, might be greater, and for some modes the mass might be less. In this case, the assumption of a lower effective mass would result in a more accurate prediction of wave-length for the deutero-compound.

It would be a difficult task to attempt an assignment to the remaining observed absorption peaks, and for the present one can only say that they are probably due either to combination frequencies, to overtone frequencies, or, more probably, to both. This conclusion is reached by the observation that, while benzoic acid, which contains only aromatic hydrogens, has a comparatively simple spectrum, acetic and propionic acids, which contain aliphatic hydrogens, have characteristically modified spectra.

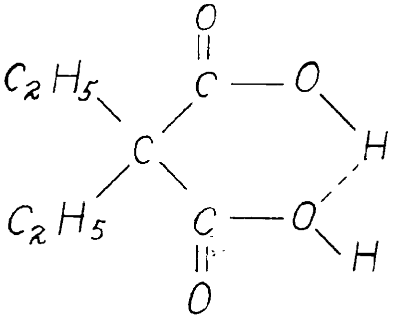
Conclusions with regard to the structure of di-basic acids become even more complex, and the effects of small impurities become more pronounced with these less soluble compounds. Some evidence has been found that the absorption due to water bonded to acids occurs in the region of 3.4μ, but confirmation is still needed. However, the trend seems to be toward greater absorption due to carbon-hydrogen vibration, which absorption tends to blot out part of the probable doublet structure due to the active hydrogens. One positive result can be obtained by a comparison of the 2.82μ absorption peak of diethyl malonic acid and azelaic acid. Since less absorption is observed in the latter, the natural conclusion is that it has less of the unassociated or unbonded acid than has diethyl malonic acid. This outcome is not hard to rationalize when one considers the respective structures of the two molecules. Diethyl malonic acid is a very short-chained dibasic acid, while azelaic acid is a rather long-chained acid, having nine carbon atoms. This fact offers azelaic acid the possibility

Figure 18.

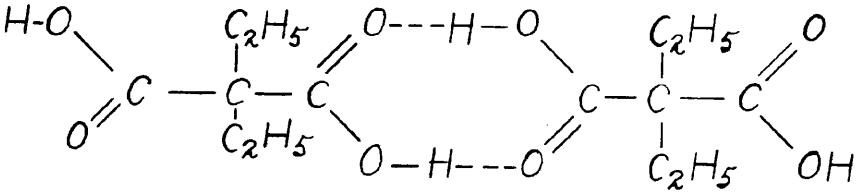
Molecular Structures.



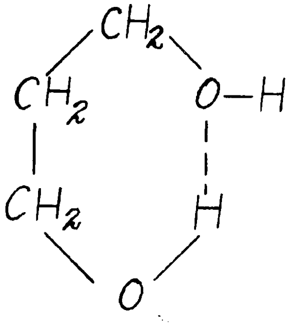
I



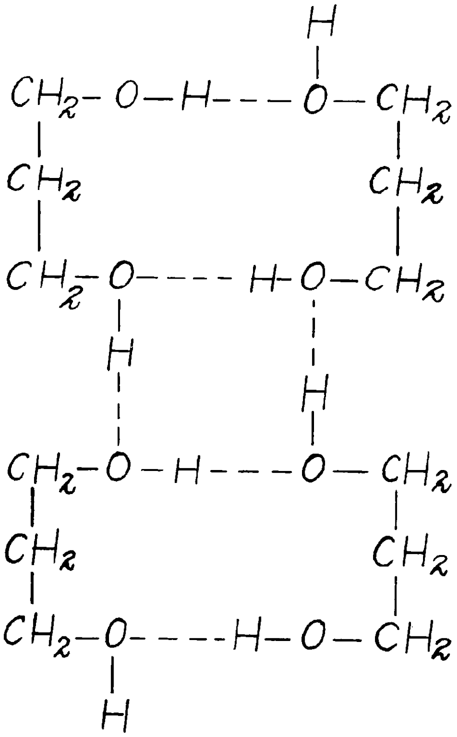
II



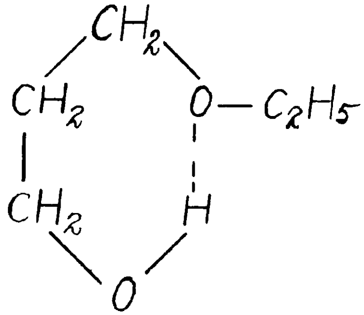
III



IV



VI



V

of forming a ring structure, with the carboxyl groups bonding much in the same way in which a dimer is formed in benzoic acid. Since this ring structure is a physical impossibility in the case of the malonic acid, more free carboxyl groups are the result, and a greater absorption for free OH is observed. Some ring structures might be possible in the case of diethyl malonic acid, (See figure 18, no. I,II, page 45), but these would result in an entirely different spectrum in comparison to that observed in the mono-basic acids. Any structures in the spectrum of malonic acid which are comparable to those of dibasic acid are probably due to dimer formation (See figure 18, no. III, page 45.) or perhaps long-chain polymer formations (9).

B. Glycols and Glycol Derivatives.

The glycols were studied in solutions of very low concentration, and therefore, it was assumed that very little association was taking place between molecules. All of these compounds had an absorption peak at 2.76μ, and this was attributed to the fundamental oxygen-hydrogen vibration. Alcohols in very dilute solutions have also been found to have similar absorption in this region.

The significant point about the glycols is the second peak, which appears at a slightly longer wave-length. The immediate thought on this observation is hydrogen bonding, since it also has a parallel in the alcohols. But in this very dilute solution, it probably is not bonding between molecules, but rather bonding within the molecule (see Figure 18, no. IV, page 45). This point of view immediately clears up the question why a second peak does not appear for the first and the last of this series of glycols. In ethylene glycol, bonding cannot take place because the atomic distances and the bond angles are not suitable for ring formation. Although the five-membered ring should be the one involving the least strain, the hydrogen atom is so small in comparison to the other atoms that the ring in ethylene glycol would virtually approach the character of a four-membered ring. In the case of octadecamethylene glycol, the hydroxyl groups are too far apart to have much effect on each other. Here one might compare the glycol to two separate alcohol molecules in a very dilute solution. Although they do come together and bond for a short period of time, they soon break by the force of collision with other molecules, with the result that most of the time they are in an unbonded state.

A peculiar behavior is to be noted in the case of 1,1-diphenylpropylene glycol. It has a single absorption peak at 2.79μ in contrast to the two peaks of propylene glycol. A possible explanation might be that both hydrogens are bonded intra-molecularly. A tertiary hydroxyl group may have greater bonding properties than a primary hydroxyl. Another explanation might be that there is an actual shift in the unbonded hydrogen. However, this is unlikely, since triphenyl carbinol has been found in this laboratory to have a fundamental absorption peak at 2.76μ. Another explanation might be that the compound was not actually a glycol, but some isomer of it.

In order to find out something about how the glycols were associated, some compounds were prepared in which one of the hydroxyls of some glycols was substituted by an ethoxy group. These compounds were completely miscible with carbon tetrachloride, indicating that they were not nearly as associated as were the glycols.

Due to the greater solubility of these ethoxy-compounds, it was possible to study the effect of concentration on the absorption spectrum. As higher concentrations were used, it was noted that a different type of a bonded absorption peak than that of the alcohols came into the picture. The first conclusion is that the other ether oxygen is playing some part in this act. It is also to be noted that, as in the shorter glycols, there was some hydrogen bonding even at the lowest concentrations.

It was thought profitable to plot the molal absorption coefficient of the hydrogen bond of the ethoxy-alcohols against concentration for the various ethoxy-alcohols to show more clearly what is happening in these compounds (See figure 14, page 38). It will be noticed that at higher concentrations, the absorption is approaching a more or less constant value, while at lower concentrations, considerable differences are present in the various compounds. By extrapolating to zero concentration, the resulting molal absorption coefficient should be that due only to intra-molecular bonding, since it is assumed that all association between molecules has ceased. Thus, 2-ethoxy-ethanol-1 shows evidence of no intra-molecular bonding. This is in agreement with steric considerations in the molecule. A five-membered ring, according to organic chemists, is a very stable affair, but, as stated previously, because the hydrogen atom is so small, what we really have is a pseudo-four-membered ring. 3-Ethoxy-propanol-1 was found to have for the molal absorption an extrapolated value of 24, while 4-ethoxy-n-butanol-1 and 5-ethoxy-n-pentanol-1 had values of 33 and 6 respectively. In the case of the propanol derivative, the pseudo-five-membered ring is possible; but the greatest bonding was found in the butanol derivative, where a pseudo-six-membered ring is possible. In the pentanol derivative, the extrapolated molal absorption coefficient dropped because of increased distance between the hydroxyl and the ether-oxygen groups.

But how does inter-molecular bonding take place, and to what extent does association occur? Copley has proposed a mechanism of association for amides, both un-substituted and substituted (24), and also for glycols, which mechanism would lead to dimers, in the case of alkyloxy-compounds, and polymers in the case of the glycols. (See figure 18, no. VI, page 45) If dimers are formed in the case of the glycols, there still remain in the structure two unbonded hydroxyl groups, which are capable of further bonding. In this way an unlimited number of molecules could join together to form a polymer of high molecular weight. On the other hand, if one of the hydroxyl groups in the glycol molecule is tied up in the form of an ether, the association would, according to mechanism, have to stop at the dimer stage. These dimers would still be soluble in carbon tetrachloride, and while the glycol polymers would be insoluble.

It might also be asked how much effect this ether oxygen has on the association as it becomes farther away in chain length from the hydroxy group. Of course the molecule must then become more and more like an ordinary alcohol molecule, with its increasing molecular weight making it less soluble in carbon tetrachloride. The effect of increased chain length is shown in the wave-length of the absorption due to the intra-molecular bond. In the compounds of longer chains, the wave length increases, indicating a weakening of the bond, a greater average distance between the two oxygen atoms, and in general, a type of bonding found between two alcohol molecules at high concentrations.

These speculations concerning dimer formation in the ethoxy-alcohols should be capable of more definite experimental proof, other than that given in terms of spectroscopy. Cryoscopic data and vapor pressure data might be used. Also the equilibrium constant for the association reaction might be studied to see in what order the reaction may be classed. Some rough calculations had been made using the equation

$$2A = A_2 .$$

Concentrations of the two forms present were calculated from the relative height of the absorption peaks of their infra-red spectrum. The results indicated a second order reaction for 2-ethoxy-ethanol-1 and 3-ethoxy-n-propanol-1, while considerable deviation from second order was noted in 5-ethoxy-n-pentanol-1. These results, therefore, seemed to qualitatively agree with the hypothesis that dimer formation was present, and that, as the distance between the oxygens increased, the resulting compound approaches that of an ordinary alcohol.

C. Molecules Exhibiting Keto-Enol Tautomerism.

Compounds containing keto-enol tautomerism which were studied spectroscopically with the hope of finding out what is happening in these molecules with respect to their active hydrogens.

In the case of dibenzoyl methane, (See figure 15, page 39), a diffuse absorption band was found beyond the 3.2 region, which absorption was not found in the case of the somewhat similar molecules, benzil and diphenyl methane. It was therefore concluded that this absorption was due in some way to the active hydrogens in dibenzoyl methane and not to some other structure in the molecule. On comparison of the enolic structure of this molecule with that of the dimer of benzoic acid, and on comparison of its absorption spectra with that of benzoic acid, a striking similarity is found in each case. Both molecules contain hydrogen bonds in a ring structure, and both spectra contain this absorption, although in the case of benzoic acid more definite peaks are observed.

Another class of compounds, although not strictly of the keto-enol type but very closely related to them, contains those molecules in which an active hydrogen is capable of migrating from an oxygen to a nitrogen atom. (See figures 16 and 17, page 40-41) This migration must be intimately connected with the possibility of intra-molecular hydrogen bonding. Upon analysing the absorption spectra of this class of molecules, it is found that they also have an unusual absorption in the region beyond 3.0μ. A contrast in spectrum is also to be noticed in the case of 4-hydroxy-azobenzene and 4-hydroxy-3-methyl-azobenzene. (See figure 16 and 17, page 40-41) A lack of absorption in the 3.5μ region and the presence of the free hydroxyl absorption band at 2.77μ coincides with the molecular structure where hydrogen bonding is a physical impossibility. This data, therefore, tends to confirm the idea that this diffuse absorption is due in some way to the migrating hydrogen atom.

It might also be pointed out that these compounds, aside from the possibility of hydrogen bonding, are known to exist in two tautomeric forms. If the hydrogen is attached to the nitrogen atom, resulting in a quinoid structure for the benzene nucleus, there should be some evidence of a nitrogen-hydrogen absorption peak. A small absorption peak has been found in the region of 2.9μ, which might very well be attributed to this vibration. This type of a bond has been found to have this absorption in other molecules.

Attempts to deuterate these molecules were unsuccessful, and for the time being the absolute solution to the problem can not be given. The actual assignment of the absorption peaks to particular modes of vibration would be a still more difficult task and for the present we await further information on the general structure of molecules.

VIII - Summary

The work here summarized seems to me like a single link in a long chain of events that which may ultimately explain structural phenomena more completely. Certain acids have been studied and certain modes of vibration have been assigned to particular absorption bonds. The shift in frequency due to mass effect has been observed and again verified through the substitution of hydrogen by deuterium.

The glycols were studied from the point of view of association and the ethoxy-alcohols aided in this study. Both were found to contain certain similar hydrogen bonds while at the same time certain dissimilarities were observed. A formula was found which could account for association in these compounds and which agreed with the observed data. Intra-molecular bonding was observed in the ethoxy-alcohols and glycols, which bonding, I believe, is the first to be observed within a molecule whose structure did not involve a chelated ring.

An anomalous behaviour was observed in the case of molecules exhibiting keto-enol tautomerism, and this can probably be ascribed to the active hydrogen present. However, no definite conclusions could be reached on the subject, and future work will probably decide the matter.

This research is of course not closed, and more data from infra-red spectroscopy and also probably from other sources will be necessary to carry the work to completion. Better technique with the less-soluble compounds will bring forth the desired information concerning such compounds as dibasic acids, hydroxy-acids, and poly-functional molecules in general. Improved technique with thin films of pure substance would also afford information concerning the state of these molecules in the highly associated form. An exact study of the infra-red spectrum of water bonded to an acid is still needed. A problem of stereo-chemistry might be developed in the ethoxy-alcohols. Changes in hydrogen bonding with the variation in size of other attached inactive groups in the molecule might be significant.

The question naturally arises in scientific work as to what is the practical value of the investigation. More frequently than not, a given piece of work is only one step closer to something of greater benefit. This work in infra-red spectroscopy might be applied to analysis of organic compounds or it may develop in such a way to aid technologically in the solution of an entirely different problem. It can only be said that theoretical work should not be demanded an immediate justification interms of dollars and cents, for, as experience has taught us, many of our modern conveniences due to science started as insignificant theoretical hobbies.

IX - Bibliography

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X - Vita

Walter Frederick Claussen was born in Rock Rapids, Iowa, on June 25, 1916. He attended grammar schools in Chicago and in DuPage County, Illinois. During the years 1929-1933, he was successively enrolled in the high schools of Bensenville, Elmhurst, and Geneseo, Illinois. In June 1933, he was awarded a County Scholarship to the University of Illinois, and he attended this university for his entire advanced education. After receiving the degree of Bachelor of Arts in 1936, he continued graduate study in physical chemistry and related subjects. At this time he received a research assistantship, made possible through the Rockefeller Foundation. Since 1937 he has held a teaching appointment in physical chemistry at the University. He is a member of Phi Eta Sigma, of Sigma Xi, and of the American Chemical Society.