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The molecular association of the carbamic esters

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C O N T E N T S

HISTORICAL INTRODUCTION

- (a) The bivalency of hydrogen.
- (b) The hydrogen bond.
- (c) The N-H-O bond.

T H E S I S.

- (a) The molecular association of the carbamic esters.
- (b) Experimental details.
- (c) Graphs (FIGS. I to VI)

HISTORICAL

(a) The bivalency of hydrogen

The view that hydrogen could link together two other atoms, and was thus, in effect, bivalent was first put forward in 1912 by Moore and Winmill (J.C.S. 1912, 1635) to account for the large increase in strength of the alkylammonium hydroxides in passing from the tri-alkyl to the tetra-alkyl compounds. They suggested that the alkyl groups formed strong links with the nitrogen atom, while the hydrogen atom formed a weaker link with the nitrogen, and had residual affinity with which it could attract the hydroxyl group, thus tending to prevent ionisation.

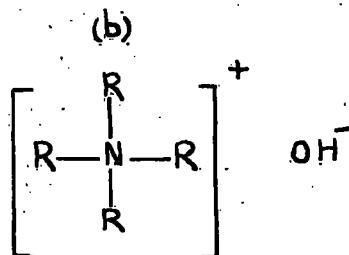
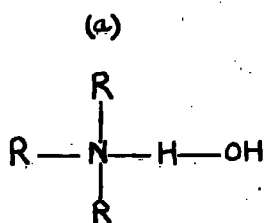
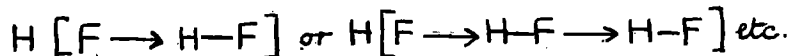


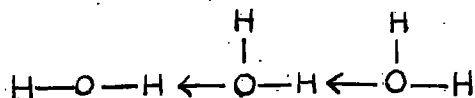
Diagram (a) shows the type of hydrogen bond they envisaged between the nitrogen and oxygen atoms. The tetra alkyl compounds are, however, completely dissociated because such a bond is impossible in (b).

The realisation that hydrogen can hold together two other atoms has been accepted only gradually during the last thirty.

years. The difficulty was that, at first, no explanation of its mechanism could be given. But nevertheless, the fact of its existence has had to be admitted. In 1927, Sidgwick (Electron Theory of Valency p.72) said there was strong evidence that hydrogen could form a valency group of four electrons - for example this would explain the behaviour of hydrofluoric acid and of water. Hydrofluoric acid is found to polymerise and even in the vapour state contains H_2F_2 molecules and higher polymers as well. Thus the formula for the acid must be



The physical properties of water are another argument in favour of bivalent hydrogen. Water polymerises and forms, especially at low temperatures, a triple polymer, the large molecular volume of which is responsible for the anomalous behaviour of water when cooled below $4^{\circ}C$. The high surface tension of water and its high boiling point (as compared with the alcohols for example) may also be attributed to the same cause. Sidgwick in the reference quoted above says there is no way of depicting a polymer of water with non-polar links except by supposing that the oxygen of one molecule forms a co-ordinate link with the hydrogen of another; thus



(b) The hydrogen bond

Some years later (see Organic Chemistry of nitrogen.

Sidgwick. Revised by Baker and Taylor p.XVI) Sidgwick's view that the hydrogen acted as an acceptor in a co-ordinate link had altered. He is now inclined to the view that this mechanism is not possible because it would necessitate two of the four shared electrons being in the second quantum group. But there they would not be held firmly enough to account for the stability of the link. This difficulty was first pointed out by Pauling (Proc. Nat. Acad. Sci., 1928, 359; J.A.C.S., 1931, 1367)

The difficulty was overcome by the application of wave mechanics - the theory of quantum mechanical resonance. Resonance, and resonance alone, gives a satisfactory explanation of co-ordinated or bivalent hydrogen. The conception of resonance is the most striking development in structural chemistry for seventy years (since the conception of a three dimensional structure put forward by van't Hoff in 1874). Physical science can now depict a possible, probable mechanism to explain the chemical facts which have so long been admitted.

For resonance to be possible, there must be several possible structures for the molecule, each with the positions of the atomic nuclei the same. Then, according to wave mechanics, the wave function associated with the true state of the molecule, is compounded of those associated with each possible structure, and in such proportions as to make the total energy of the system a minimum. If there are two possible

structures the true state of the molecule is neither one nor the other but somewhere between the two. The molecule will have to some extent the properties of each structure (although not necessarily to the same extent, because one form being slightly more stable may predominate). Resonance will occur whenever possible because the 'hybrid' so formed has a smaller energy content and therefore greater stability than either of the two possible structures. The latter are called the 'unreal' or 'extreme' forms. Substances with this type of structure will show tautomeric characteristics but it will never be possible to isolate two separate distinct isomers because the extreme forms do not really exist - they are only pictorial aids to help us to visualize the true state of the molecule.

In resonance, we can picture the hydrogen atom as being alternately bound to two other atoms, forming a 'resonance hybrid':



There are two essential conditions for the formation of such a hydrogen bond:

- (a) a suitably placed and suitably connected hydrogen 'acceptor' atom, and
- (b) a suitable electron 'donor' atom.

If these are both present in the same molecule then there

are two possibilities of hydrogen bond formation:

- (a) a hydrogen bond between neighbouring molecules,
- (b) a hydrogen bond within the molecule.

Whether a hydrogen bond can be formed within the molecule will depend on the relative position of the donor and acceptor atoms. The conditions which must be fulfilled (interatomic distance, valency direction etc.) before a hydrogen bond can result have been discussed by Hunter (Chem. and Ind., 1941, 32). If these conditions can be satisfied within the molecule, then intra-molecular hydrogen bonds will probably be formed. But where the atomic distance between the donor and acceptor atoms of the same molecule is too great (or other conditions unfavourable) then inter-molecular bonds between neighbouring molecules will be formed. This will result in molecular association and according to Hunter (Chem. and Ind. 1944 no. 17 p.155-7) this is by far the most common cause of molecular association, operating among many organic and inorganic compounds and also within the complex molecules which constitute a large proportion of living tissue - for example, protein molecules. According to Speakman (Journal of the Royal Society of Arts, Oct 26th 1945, p.604) a wool fibre consists of several layers "of linked peptide chains held together by hydrogen bonding and van der Waals forces".

Hirst, discussing the structure of cellulose (Chem. and Ind. March 9th 1946 p.110) says 'The general picture of

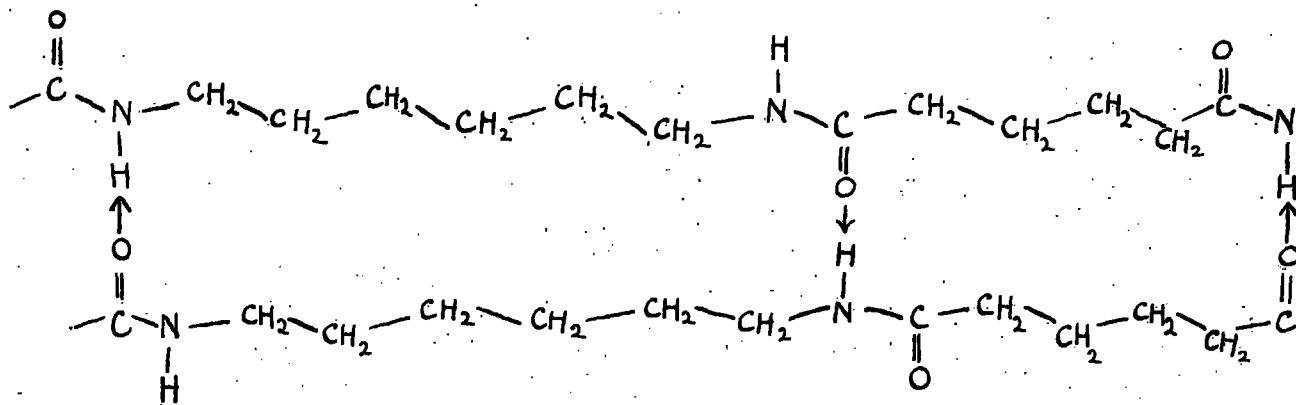
cellulose is a long straight unbranched chain with definite end groups. Models of this structure indicate more clearly the geometry of cellulose and raise the question of the forms of the six membered rings. It can be seen that cross-linkages between hydroxyl groups in parallel chains involving hydrogen bonds are possible, and may account for the slight reactivity of primary hydroxyl as compared with secondary hydroxyl groups.

(c) The N-H-O Bond

One of the most familiar types of hydrogen bond is that connecting two oxygen atoms (as in water, the alcohols, phenols, carboxylic acids). Fluorine can also form strong bonds with hydrogen, and recently there has been evidence that nitrogen and sulphur can do so [Hunter 'The Associating Effect of the Hydrogen Atom part VII (Journal of the Chem. Soc. 1941, 1) and part XI (Journal Chem. Soc. 1942, 638)] According to Sidgwick (Organic Chem. of Nitrogen: Revised by Baker and Taylor 1937, p.XV) the tendency of hydrogen attached to nitrogen to form a further link is small and confined almost to one group of compounds, the alkyl ammonium hydroxides (as first noted by Moore and Winmill in 1912). Sidgwick says the linkage of nitrogen to oxygen through hydrogen can no doubt occur to a small extent in other cases, as this presumably explains the association of the amides. But recently there has been evidence of several groups of compounds which have a hydrogen bond N-H-O structure; not only amides, but also

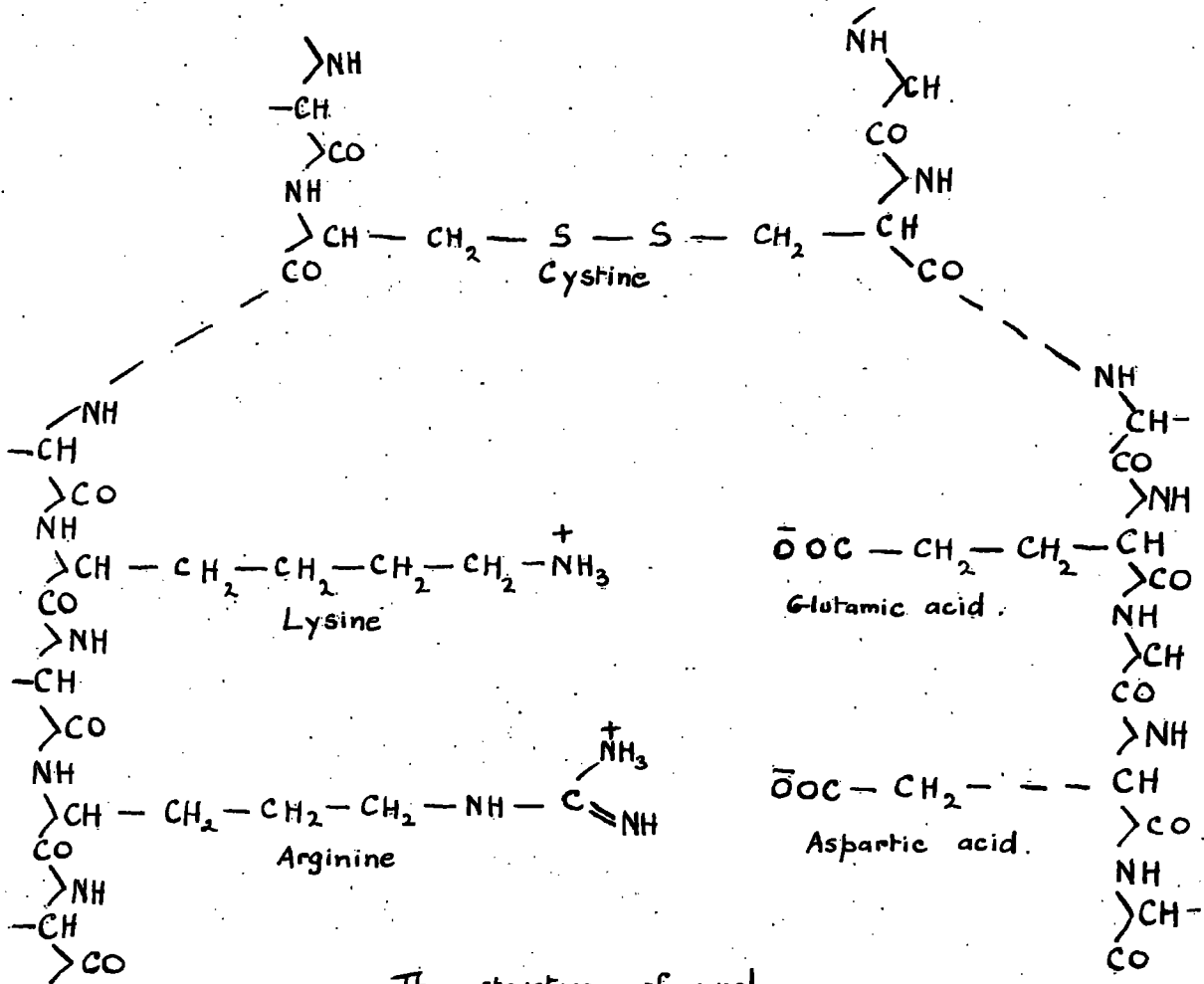
sulphonamides (Hunter, Journal Chem. Soc. 1937, 1114) and oximes (Sidgwick, Ann. Reports, 1934, 31, 41).

There are grounds too, for believing that the structure and strength of natural and synthetic protein fibres is due partly to N-H-O bonds. The ordinary type of nylon consists of long chains of $-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{NH}-(\text{CH}_2)_6-\text{NH}-$ groups. It is probable that adjacent chains are held together by hydrogen bonds so giving strength to the fibre (it is as strong as real silk). As can be seen from the diagram below, there is the possibility of N-H-O links at frequent intervals along the chains.



The structure of nylon.

Also, the hydrogen bonding mentioned by Speakman in connection with the structure of the wool fibre is probably an N-H-O linkage. He depicts the general features of the two-dimensional structure of ^{the} linked peptide chains ^{in wool} as shown below.



If, as he says, the more organised parts of the wool fibre consist of layers of these linked chains, there would be opportunities for N-H-O bonds between neighbouring chains, as can be seen.

The experimental work done during the last two years (1944-46) on the carbamic esters of which an account follows, gives strong evidence of the existence of hydrogen bonds consisting of N-H-O links in esters of the type R.NH.COO Et. such links existing sometimes between neighbouring molecules and sometimes within the molecule.

T H E S I S.

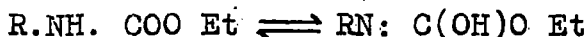
THE MOLECULAR ASSOCIATION OF THE CARBAMIC ESTERS.

THE MOLECULAR ASSOCIATION OF THE CARBAMIC ESTERS.

The N-H-O Bond.

The chemical properties of the carbamic esters R.NH.COO Et are a strong indication of molecular association in these compounds. The view is here put forward that the association is a resonance phenomenon due to hydrogen bonds.

Solubility considerations suggest a hydrogen bond structure - urethane, phenylurethane etc. being highly soluble in water and other donor solvents, but only sparingly soluble in benzene and other hydrocarbon solvents. The known tautomeric behaviour of the esters



can also be explained as a resonance effect.

An investigation was made into the molecular state of carbamic esters of the series R.NH. COO Et and R.NX. COO Et (where X = alkyl, aryl etc. groups) when in solution in benzene, to see whether they were uni-molecular or associated. The molecular weight measurements which have been made suggest that there is with the former series association of a hydrogen bond character - the latter series shows no association.

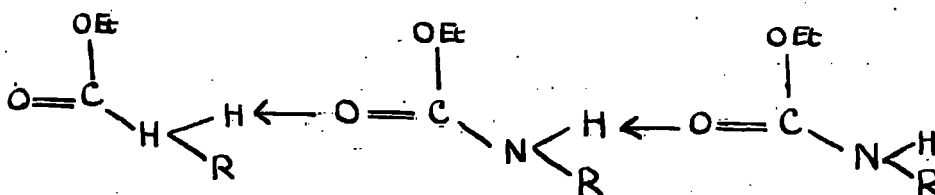
The measurements indicate clearly that the esters are of two distinct types. Those possessing an unsubstituted imino

hydrogen atom (R.NH. COO Et) are associated when in solution in benzene, whereas those in which the imino hydrogen is replaced (R.NX. COO Et) are uni-molecular.

The molecular weight determinations were made cryoscopically in benzene over a range of concentration and were calculated according to ideal solution laws. The degree of association (α) is expressed as the ratio of the molecular weight as determined experimentally, to the formula weight. By plotting α against concentration it will be seen that the curves fall into two distinct groups. The urethanes with a free imino hydrogen atom (nos. 1 to 7 FIG. I) give rise to fairly steep curves; those with no free imino hydrogen atom (nos. 8 to 12 FIG. I) give a flat or gently sloped curve in the region $\alpha=1$. A steep association-concentration curve is one in which α increases substantially with rising concentration, is taken to indicate association. A flat or gently sloped curve in the region $\alpha=1$ is interpreted as absence of association.

Since the concentrations are all over approximately the same range, and the range of molecular weights of the solutes not great, errors due to departure from ideal behaviour will be similar for each substance, and thus any errors due to basing the calculation of molecular weight (M) on ideal solution laws will be greatly minimised, if not obviated, by judging the relative positions and slopes of the curves.

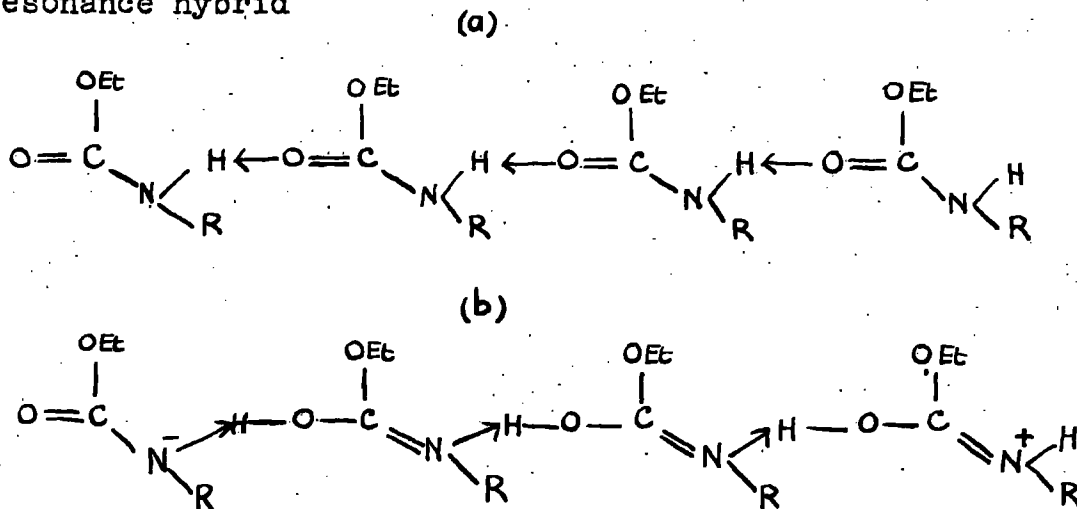
From the fact that the curves fall into two distinct groups, it is suggested that the association takes place through intermolecular hydrogen bonds between neighbouring molecules, in compounds of the R.NH.COO Et type. The imino hydrogen atom links the nitrogen atom of one molecule to the oxygen atom of a second molecule; that is, bonds of the N-H-O type, as depicted below, such bonds being a resonance phenomena



Some years ago this would have been explained by postulating that the hydrogen acted as the acceptor in a co-ordinate link N:H:O having four shared electrons. But as stated previously, this would necessitate two of these electrons being in the second quantum group, which means that they would not be held firmly enough to account for the stability of the link.

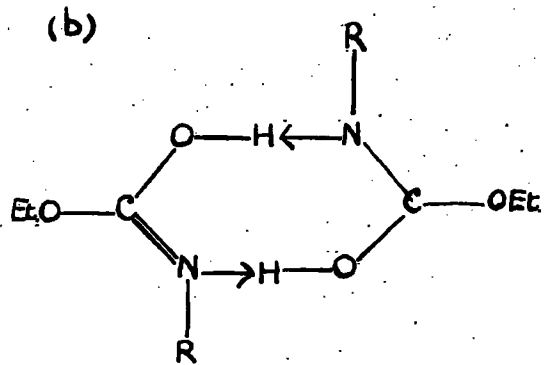
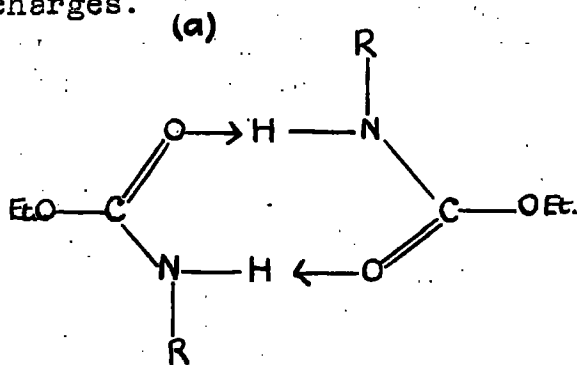
On the resonance theory the hydrogen is alternately linked to the nitrogen and oxygen atoms, this being possible because it does not necessitate any movement of the nucleus of the hydrogen atom, which is conveniently situated so as to be able to share electrons with either of the other two atoms. The

resonance may give rise to a linear polymer, as depicted below, in which (a) and (b) are the unperturbed forms of the resonance hybrid



Although the diagram shows how four molecules could link up, in fact no conclusion can be drawn from the shape of the association-concentration curves as to whether the polymer actually involves two, three or more molecules. The curves (nos. 1 to 7 FIG. I) show little or no falling off in slope with increasing concentration. This may indicate that in more concentrated solutions, association proceeds beyond the dimeric stage.

There is also, of course, the possibility of a cyclic structure for the polymer, having the unreal forms (a) and (b) shown below, neither of which involves any separation of charges.

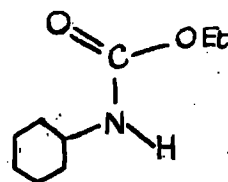


A cyclic structure involving more than two molecules is, of course, not excluded. X ray analysis of acetamide (Senti and Harker. J. American Chem. Soc. 1940, 62, 2008) has indicated the existence of a cyclic polymer of acetamide containing six molecules linked by N-H-O bonds. As yet not much work has been done on determination of structure by X ray diffraction, as it is a long process involving much mathematical calculation and expert interpretation. Apart from X ray analysis, some light might be thrown on the actual structure of the polymer by measurement of the di-pole moment of some of the R.NH.COO Et esters. A zero value of the di-pole moment would, for instance, lead to the inference that the cyclic form of polymer is more likely than the linear form. The real structure of the polymer will, on the resonance theory be intermediate between the two unreal forms (a) and (b). This would account for the ability of the carbamic esters to react as if they possessed both the structure R.NH.COO Et and RN:C(OH)O Et, and also for the impossibility of separating the two forms, as neither has a real existence.

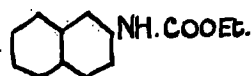
It will be noted that the compounds which showed association all had a hydrogen atom suitably placed to act as a link between neighbouring molecules, as is seen from an examination of their structural formulae.

FIG. I ASSOCIATED SUBSTANCES.

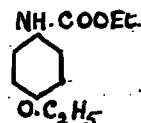
Curve 1. Phenylurethane



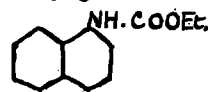
Curve 2. β naphthylurethane



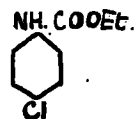
Curve 3. β -ethoxyphenylurethane



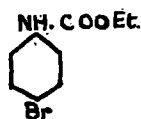
Curve 4. α naphthylurethane



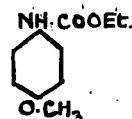
Curve 5. β -chlorophenylurethane



Curve 6. β -bromophenylurethane



Curve 7. β -methoxyphenylurethane



On the other hand, replacement of the imino hydrogen atom evidently prevents association, as the following compounds proved to be uni-molecular -

FIG. I NON-ASSOCIATED SUBSTANCES.

Curve 8.	Diphenylurethane	$\text{Ph}_2 \text{N.CO.OEt}$
Curve 9.	Phenylmethylurethane	$\text{Ph.N}(\text{CH}_3) \text{COO Et}$
Curve 10.	Phenylethylurethane	$\text{Ph.N}(\text{C}_2\text{H}_5) \text{COO Et}$
Curve 11.	N-diethylurethane	$(\text{C}_2\text{H}_5)_2 \text{N.CO.OEt}$
Curve 12.	Piperidylurethane	$\text{C}_5\text{H}_{10} \cdot \text{N.CO.OEt}$

THE ASSOCIATION OF ORTHO-SUBSTITUTED PHENYLURETHANES.

Further evidence for the hydrogen bond structure of the carbamic esters was obtained from an examination of the molecular state (in solution in benzene) of a series of *o*-substituted phenylurethanes as compared with the *p*-substituted compounds. The association concentration curves again fell into two distinct groups (see FIG. 2). The following compounds all of which had a substituent in the para position had steep association-concentration curves:-

- FIG. 2 Curve 1. *p*-ethoxyphenylurethane
 Curve 2. *p*-methoxyphenylurethane
 Curve 3. *p*-chlorophenylurethane
 Curve 4. *p*-tolylurethane.

Curves 9 and 10 which are for *p*-carbethoxyphenylurethylane and *p*-carbethoxyphenylurethane are not, strictly, comparable with the others because the molecular weights of these two substances were determined in naphthalene as they were not sufficiently soluble in benzene.

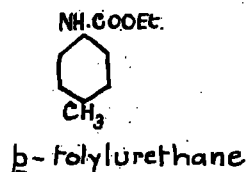
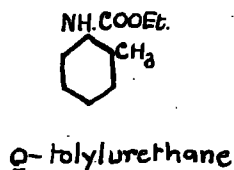
The compounds with ortho substituents had curves that were less steeply sloped, but which were not flat. That is, they showed some degree of association, but not as much as the para substituted compounds, although they all had an imino hydrogen atom capable of bringing about a hydrogen bond linkage. The compounds which showed this intermediate measure of

association were

- FIG. 2 Curve 5 *o*-tolylurethane
 Curve 6 *o*-ethylphenylurethane
 Curve 7 2:5 dichlorophenylurethane
 Curve 8 2:4 dimethylphenylurethane.

The difference between the two groups is brought out very clearly by a comparison of the corresponding isomers *p*-tolylurethane and *o*-tolylurethane which are plotted separately on FIG 3 (nos. 1 and 2 respectively).

It is suggested that the reduced association shown by the compounds with an ortho group is due to steric interference - the position of the ortho substituent, near the imino hydrogen atom, tending to make it difficult for a neighbouring molecule to get near the imino hydrogen so as to link up with it.



A substituent in the para position is too far away from the imino hydrogen atom to cause any interference, and hydrogen bond formation can take place freely between neighbouring molecules by means of N-H-O links.

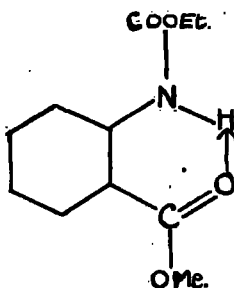
With a view to further examination of this question of steric interference with the imino hydrogen by substituents

in the same molecule; a further type of ortho substituted urethane was prepared and examined. In these the ortho substituent contained a suitable donor atom expected to be capable of bringing about chelate ring formation.

e.g. ortho-carbomethoxyphenylurethane



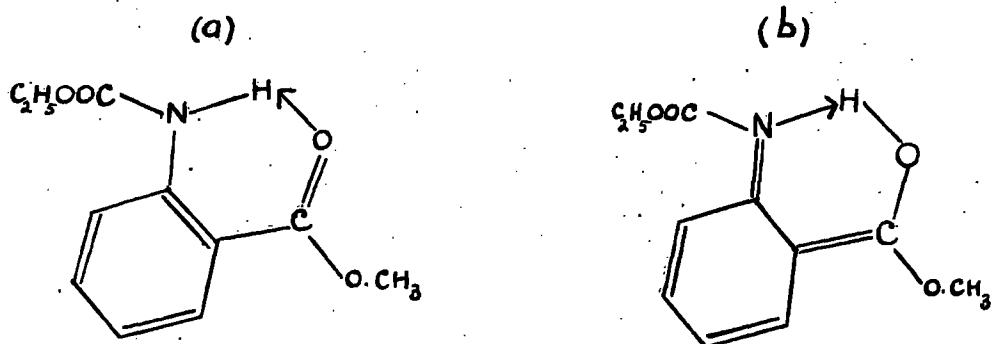
Here it is possible that an oxygen atom in the Coome group can act as a donor and perhaps form a hydrogen bond within the molecule as depicted below, owing to its close proximity to the imino hydrogen.



It is to be expected that this would happen, rather than the imino hydrogen atom being engaged by the oxygen atom of a neighbouring molecule. If such intra-molecular association does occur, inter-molecular association will be reduced or prevented. Three compounds of this type were prepared and their molecular state in benzene determined.

Their association-concentration curves were almost flat (FIG. 4 nos. 1, 2, 3) showing that, in fact, there was practically no association (the curve for diphenyl-urethane is shown for comparison). The curve for *o*-carbomethoxyphenylurethane was almost flat in the $\alpha=1$ position, thus supporting the

suggestion that chelate ring formation does take place, to the exclusion of hydrogen bonds between neighbouring molecules. It is therefore probable that *o*-carbmethoxyphenylurethane exists as a resonance hybrid having the two extreme forms (a) and (b)



The other compounds with an oxygen donor atom in the ortho substituent also show very little association and probably form chelate rings in a similar way: they were *p*-monobromo-*ortho*-carbmethoxyphenylurethane and *o*-carbmethoxyphenylurethane (Fig. IV no. 2+3)

For interest, and as a check on the accuracy of the association-concentration curves, the figures obtained for phenylurethane were compared with those obtained by v. Auwers (Zeit. physikal Chem. 1893, 12, 712)

von Auwers' figures for phenylurethane in benzene.

gm. benzene	gm. Ph.NH.CO O Et	M. W.
15.00	0.0710	155
	0.1534	161
	0.5292	170
	0.7876	183
	1.0978	193

From these figures the concentration and association were calculated, and the curve plotted on FIG. 5. *no. I. Auwers's* first two readings with very dilute solutions are not in line with his other points. Omitting his first two points, a line through the last three is parallel to the curve for phenylurethane obtained during the present work in 1944, but the latter occupies a higher position on the diagram. The slope of the two curves being the same indicates good agreement in the rate at which association increases with rise in concentration. The constant vertical displacement of *v. Auwers's* curve below the other one = 0.9; that is, his values for α differ by a constant figure of 0.9 over the range of values $\alpha = 1.0$ to $\alpha = 1.2$ approximately. This difference of 0.9 in 1.1 is about 8%, large enough to warrant speculation as to the cause of the difference. Perhaps the following factors might account for it:

- (a) perhaps the benzene used by von Auwers was not as pure as that obtainable to-day.
- (b) perhaps he used a different value for the constant k in calculating his molecular weights from the formula

$$M = \frac{100 k x}{\Delta W}$$

where

- x = weight of solute
- W = " " solvent
- Δ = depression of freezing point
- k = cryoscopic constant for benzene
which is nowadays taken as 51.2

It was found on reference to the literature (Zeit physikal Chem. 1893, 12, 712) that von Auwers had used the value $k = 49$. So his values for M and α were re-calculated to see what they would be using $k = 51.2$, and the association-concentration curve was re-drawn [FIG. 6 no. I]. It corresponds more closely than the previous curve [FIG. 5 no. I] with the figures obtained for phenylurethane in 1944 [FIG. 5 no. II and FIG. 6 no. II].

EXPERIMENTAL.

METHODS OF PREPARATION.

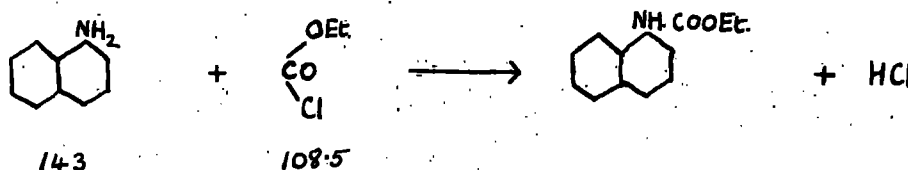
The urethanes were prepared by treating chloroformic ester with the appropriate base, in most cases an aromatic one. Two standard methods were used

- (a) treating one molecule of the base, dissolved in pyridine, with one molecule of ethyl chloroformate, the pyridine taking up the hydrochloric acid formed
- (b) by treating two molecules of the base with one of ethyl chloroformate, omitting the pyridine - the extra molecule of the base taking up the hydrochloric acid formed.

A typical example of (a) was the preparation of α -naphthylurethane

Method

14.3 gm. of α -naphthylamine was powdered and dissolved in 50 cc. pyridine. 11 gm. ethyl chloroformate was added dropwise, with cooling, in fume cupboard. The flask was heated for half an hour on a water bath, and then cooled.



The urethane was precipitated by adding the mixture slowly to dilute hydrochloric acid, in a beaker, and scratching well. The precipitate was filtered off and washed well with a large quantity of water to remove any hydrochloride formed (α naphthylamine hydrochloride is only 3% soluble in water). The precipitate was then dried, dissolved in alcohol and precipitated by addition of water (very slowly) and scratching. It was then filtered and dried.

The following compounds were prepared by the above method, only differing in the methods of re-crystallisation:-

phenylurethane, *o*-tolylurethane, α and β naphthylurethane, *p*-ethoxyphenylurethane, phenylmethylurethane, phenylethylurethane, *p*-tolylurethane, *p*-chlorophanylurethane, *p*-bromophenylurethane, *p*-methoxyphenylurethane, 2:5 dichlorophenylurethane, and 2:4 dimethylphenylurethane.

Method (b) was used in preparing diphenylurethane, *o*-ethylphenylurethane, *o*-carbmethoxyphenylurethane, *p*-carbethoxyphenylurethane and *p*-carbethoxyphenylurethylane.

A Typical Method (b)

Preparation of di-phenylurethane.

Two attempts were made to prepare diphenylurethane by method (a), adding ethyl chloroformate to diphenylamine dissolved in pyridine (commercial) but only crystals of unchanged diphenylamine were obtained (M.P. 54°). Commercial pyridine contains about 10% water which it was thought might

be more likely to react with the chloroformic ester than the rather inactive diphenylamine, so a third attempt was made using pyridine that had been dried over calcium chloride. The preparation was again unsuccessful.

Next 1 mol. of chloroformic ester (10.9 gm) was added slowly to 2 mols. (33.8 gm) of solid diphenylamine in a flask, with stirring. No heat was evolved. The flask was heated on a water bath. The solid matter melted to a brown liquid. After about twenty minutes, a whitish solid formed in the flask, suspended in the brown liquid. The flask was heated and stirred for another half hour. On cooling the contents of the flask became a solid mass.

About 20 ccs. benzene was added and the flask heated on water bath. It was stirred to break up the hard mass, so that any diphenylurethane would dissolve in the benzene (in which the hydrochloride is insoluble). The mixture was filtered, and the filtrate allowed to evaporate slowly. The crystals formed were dissolved in a small amount of slightly warmed alcohol, filtered, and the filtrate was allowed to cool. On standing for several days crystals were deposited of melting point 74°C (Beilstein gives 72°C for diphenylurethane)

Details are given of the preparation of the following new substances

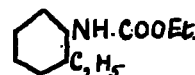
o-ethylphenylurethane, *p*-carbethoxyphenylurethane,

p-carbethoxyphenylurethane, monobromocarbethoxy-

phenylurethane 2:5 dichlorophenylurethane.

Preparation of o-ethylphenylurethane.

This was first tried in pyridine but only a very oily solid could be obtained. It was then tried using two molecules of the base o-ethylaniline to one mol. of ethyl chloroformate but a slight variation of procedure from the normal was used. Instead of adding the chloroformic ester directly to the base, the latter was suspended in 50 ccs. of water in a wide-mouth glass stoppered bottle. The ester was added dropwise with vigorous shaking which was continued until the smell of the ester had disappeared. The o-ethylphenylurethane formed as an oily substance which on cooling and scratching turned more solid. A little dilute hydrochloric acid was added to remove any excess base. The soft solid was filtered off and recrystallised in aqueous alcohol. It had a melting point of 43-5°C. The molecular weight determined cryoscopically ranged from 187.7 to 202.4 (theoretical M.W. = 193



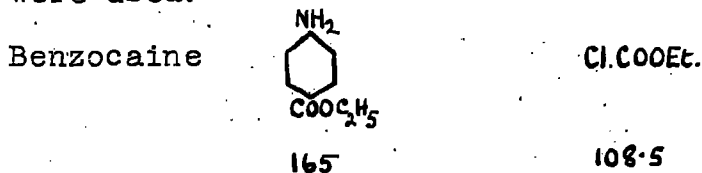
A second preparation of this yielded a specimen of melting point 38°

Calculation for $C_6H_4C_2H_5 \cdot NH.CO.OEt.$ N = 7.25%

By analysis of the specimen M.Pt. 38° N = 7.36%

Preparation of p-carbethoxyphenylurethane.

Two molecules of benzocaine to one of chloroformic ester were used.



$$2 \times 165 = 330 \quad 330 : 108.5 = 3\frac{1}{3} : 1 \text{ approx.}$$

Method. Some benzocaine was powdered and 16.7 gm were weighed. 5 gm ethyl chloroformate were added and mixture heated under a reflux for half an hour - it did not liquefy. It was left for several days. The solid was broken up, added to a beaker of distilled water and heated almost to boiling point with constant stirring - it did not dissolve. Mixture was filtered, and the pinkish white residue allowed to dry. The solid was dissolved in warmed alcohol cooled and filtered. On addition of water and scratching a white solid was precipitated. It was filtered and dried.

Melting point = 129°C. It was insoluble in benzene.

Calculation for C ₆ H ₄ COO Et. NH. COO Et	N = 5.91%
By analysis " " "	N = 5.85%

Formula weight = 237

By cryoscopic method M.W. = 229 to 285

Preparation of p-carbethoxyphenylurethane.

Three parts benzocaine to one part methylchloroformate were used. Benzocaine was powdered and 15 gm weighed, 5 gm

methyl chloroformate were added slowly - the flask being allowed to cool at intervals. The flask was heated in a waterbath under a reflux for $\frac{1}{2}$ hour. The white solid formed was ground up and heated in water. It did not dissolve. It was cooled, filtered and allowed to dry. It was re-crystallised in aqueous alcohol. It was only very slightly soluble in benzene.

Melting point = $151-2^{\circ}\text{C}$

Calculation for $\text{C}_6\text{H}_4 \text{ COO Et NH COO Me}$ N = 6.28%

By analysis N = 6.2%

Formula weight = 223

By cryoscopic method M.W. = 219 to 264

Preparation of ^{ortho}monobromocarbmethoxyphenylurethane.

o-carbmethoxyphenylurethane was prepared by adding one molecule of ethyl chloroformate to two molecules of methyl anthranilate. The o-carbmethoxyphenylurethane was dissolved in glacial acetic acid (about 1.6 gm of the former in 10 ccs. of acid). Bromine vapour was aspirated slowly through this solution, until the bromine was no longer decolourised. The solution was poured into a large volume of water and a whitish solid was precipitated. It was filtered, dried and then re-crystallised in pure alcohol in which it was sparingly soluble.

Melting point 94°C

Calculation for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N Br}$ Br = 26.5% N = 4.65%

By analysis Br. = 26.2% N = 4.55%

Formula weight = 302

By cryoscopic method M.W = 293.6 up to 312.1

Preparation of 2:5 dichlorophenylurethane.

This was first tried by the pyridine method, but was not successful. The preparation was repeated using two molecules of 2:5 dichloroaniline and one molecule of chloroformic ester, without pyridine.

10.9 gm of ethyl chloroformate were added to 32.4 gm of the dichloroaniline, slowly. Slight heating on a waterbath was given. The solid formed was extracted by adding about 20 ccs of benzene to the flask and heating slightly. On cooling the liquid was filtered into an evaporating basin. The benzene was allowed to evaporate slightly. The solid formed was re-crystallised in alcohol, being precipitated by adding a few drops of water. A white crystalline solid was obtained.

Melting Point 53-4° C

Calculation for $C_6H_3Cl_2NHCOOEt$.

Cl = 30.3%

By analysis

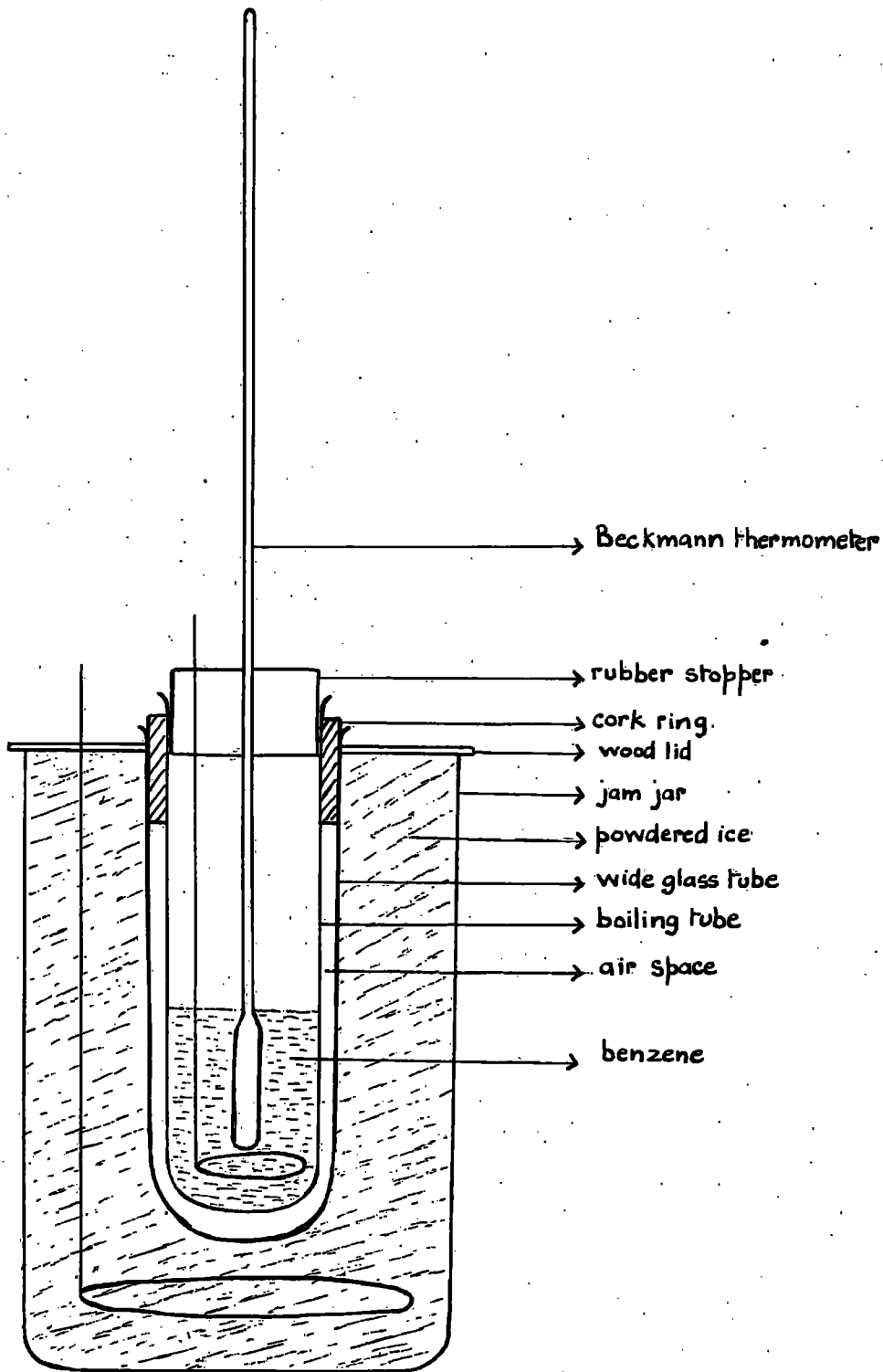
Cl = 30.3%

Formula weight = 234

By cryoscopic method M.W. = 238.4 up to 253.6

Method of determination of molecular weights.

Molecular weights were determined by the Beckmann cryoscopic method. The apparatus was fitted up as shown.



Sufficient benzene was used to cover the bulb of the thermometer; it was A.R. quality as supplied by B.D. Houses. The boiling tube contained a nickel stirrer. The solute, whose melting point, if known, had been checked with that recorded in Beilstein, was dried in a vacuum desiccator for several days before use. The boiling tube, fitted with a cork to prevent evaporation of benzene as far as possible, was weighed empty and then with the benzene.

The tube was then fitted with the Beckmann thermometer and placed in the cooling jacket. It was stirred slowly to maintain a steady rate of cooling, and a reasonably constant amount of supercooling each time. The freezing point of the pure benzene was determined. Then a small amount of the solid, taken from a weighed watch glass, was introduced, and stirred until it dissolved. The new freezing point was determined. In each case two determinations of the freezing point were made, and repeated if not in good agreement (i.e. if the difference was more than .005 or .006°C). When the benzene began to solidify the rate of stirring was quickened somewhat to keep the mixture at a uniform temperature. The highest steady temperature was recorded, the thermometer scale being viewed through magnifying lenses. The determination was repeated four or five times with solutions of increasing strength. It was usually found advantageous for readings after the first three, where the depression of the freezing

point was becoming greater, to speed up the cooling of the benzene by adding salt to the powdered ice - otherwise the supercooling took an unduly long time.

The amount of solvent lost from the tube by evaporation during the course of the experiment had been shown in previous work with the Beckmann apparatus to be too small to have any appreciable effect on the results; also the loss would be roughly the same in each determination. Thus it was neglected.

The molecular weight of the solute was calculated from the formula

$$M = \frac{100 k x}{\Delta W}$$

where k = cryoscopic constant = 51,2 for benzene.

x = wt. in gm. of solute

Δ = depression of the freezing point

W = wt. in gm. of solvent.

Determination of melting points.

The compound was dried in a desiccator, and then a small amount introduced into a capillary tube. This was attached to a thermometer in a liquid paraffin bath, heated slowly and the melting point noted. In the majority of cases it was found to be slightly higher than that recorded in Beilstein.

<u>Compound.</u>	<u>Melting Point.</u>	<u>Recorded M.P.</u>
Phenylurethane	51-2°	52°
o-tolylurethane	46-8°	46°
α-naphthylurethane	78-9°	79°
β-naphthylurethane	73-4°	69° and 73°
p-ethoxyphenylurethane	95°	94°
diphenylurethane	74°	72°
p-tolylurethane	53°	52°
p-chlorophenylurethane	70°	68°
p-bromophenylurethane	82°	81° and 84-85°
p-methoxyphenylurethane	67°	63-4°
2:4 dimethylphenylurethane	61°	58°
o-carbmethoxyphenylurethane	66-7°	62°
o-carbmethoxyphenylurethane	61-2°	61°
p-ethoxyphenylurethane	95°	94°
piperidyl urethane	B.P. 211°	211°

	<u>Boiling Point.</u>	<u>Recorded B.P.</u>
phenylmethylethane	242-5°	243-4°
phenylethylethane	228-31°	130° at 14 mms. pressure
N-diethylethane	170°	169-172°
<u>New compounds.</u>		
o-ethylphenylethane	42-5°	
2:5 dichlorophenylethane	53-4°	
p-monobromo ^{ortho} carbomethoxy-phenylethane	94°	
p-carbomethoxyphenylethane	129°	
p-carbomethoxyphenylethane	151-2°	

Analysis of preparations.

This was considered necessary only in the case of new compounds. The analysis figures are given on pages 24-28.

Data calculated from experimental readings.

In the following tables

M is the molecular weight calculated from ideal solution laws according to the formula previously given.

α is the degree of association i.e. the ratio of M to the formula weight, the latter being given in brackets.

All concentrations are expressed in gm. mols. $\times 10^2$ per 100 gm. of solution.

<u>FIG I</u>	Conc.	M.	α
Phenylurethane (165) Curve 1	0.8352	170.0	1.03
	1.885	183.9	1.114
	2.849	196.3	1.19
	3.732	204.9	1.242
	4.795	218.1	1.322
β naphthylurethane (215) Curve 2	2.901	262.3	1.22
	4.395	290.2	1.35
	6.162	321.8	1.497
	7.925	354.4	1.648
p -ethoxyphenylurethane (209) Curve 3.	.8535	212.8	1.018
	1.223	216.2	1.035
	1.72*	227.0	1.086

* limit of solubility.

FIG. I (Contd.)

	Conc.	M	α
α naphthylurethane (215) Curve 4	1.295	221.9	1.032
	2.018	236.0	1.097
	3.504	258.4	1.203
	.7432	223.6	1.04
β -chlorophenylurethane (199.5) Curve 5	1.856	229.1	1.148
	2.727	239.7	1.201
	3.779	253.2	1.269
	5.005	269.0	1.348
β -bromophenylurethane (244) Curve 6	1.092	271.7	1.114
	1.808	282.6	1.158
	2.700	292.1	1.197
	3.715	310.3	1.272
	4.948	334.9	1.372
β -methoxyphenylurethane (195) Curve 7	0.7211	201.2	1.031
	1.633	213.8	1.096
	2.679	232.4	1.192
	3.656	247.6	1.270
	5.220	273.1	1.401

FIG. I (Contd.)

	Conc.	M.	α
diphenylurethane (241) Curve 8	1.299	235.1	.9754
	2.307	233.7	.9699
	3.531	236.0	.9792
	4.805	237.3	.9849
	5.937	239.5	.9938
phenylmethylurethane (179) Curve 9	2.465	166.6	.9307
	2.995	168.7	.9423
	3.815	171.5	.9581
	4.538	174.0	.9718
phenylethylurethane (193) Curve 10	1.084	171.6	.8888
	2.118	171.4	.8880
	3.356	172.5	.8935
	4.732	174.0	.9014
N-diethylurethane (145) Curve 11	1.739	143.7	.9893
	2.875	143.5	.9890
	5.209	142.4	.9805
	8.178	143.0	.9847
	9.215	143.4	.9877

FIG I (Contd.)

	Conc.	M	α
Piperidylurethane (157) Curve 12	2.285	153.8	.9780
	3.409	153.4	.9755
	4.641	152.4	.9693
	6.113	152.9	.9725
	8.266	152.4	.9693

The figures for curves 11 and 12 were very kindly supplied by Mr. Reynolds B.Sc.

FIG II

	Conc.	M	α
<i>p</i> -ethoxyphenylurethane (209) Curve 1	.8535	212.8	1.018
	1.223	216.2	1.035
	1.72	227.0	1.086
<i>p</i> -methoxyphenylurethane (195) Curve 2.	0.7211	201.2	1.031
	1.633	213.8	1.096
	2.679	232.4	1.192
	3.656	247.6	1.270
	5.220	273.1	1.401
<i>p</i> -chlorophenylurethane (199.5) Curve 3	1.856	229.1	1.148
	2.727	239.7	1.201
	3.779	253.2	1.269
	5.005	269.0	1.348

FIG. II (Contd.)	Conc.	M	α
p-tolylurethane (179) Curve 4	.7158	187.2	1.046
	1.559	195.4	1.091
	3.005	215.8	1.205
	4.766	237.4	1.326
o-tolylurethane (179) Curve 5	1.124	176.8	.988
	1.592	181.1	1.012
	2.077	185.9	1.039
	3.037	191.1	1.068
	3.689	195.4	1.091
o-ethylphenylurethane (193) Curve 6	.7784	187.7	.9725
	1.400	190.6	.9877
	2.057	196.2	1.016
	2.883	202.4	1.048
2:5 dichlorophenylurethane (234) Curve 7	.9815	238.4	1.019
	1.872	239.0	1.021
	2.694	240.7	1.029
	3.615	245.2	1.048
	4.776	253.6	1.083
2:4 dimethylphenylurethane (193) Curve 8	1.821	201.0	1.041
	2.502	205.8	1.066
	3.354	211.0	1.093
	4.503	219.4	1.137

FIG. II (Contd.)

	Conc.	M	α
<u>p</u> -carbethoxyphenylurethane (223) Curve 9	0.780	219	0.981
	2.669	242.5	1.086
	3.451*	264	1.184

* limit of solubility

<u>p</u> -carbethoxyphenylurethane (237) Curve 10	0.695	229	0.966
	1.867	249	1.050
	3.279	265	1.116
	4.260	275	1.158
	5.256	285	1.203

The readings for curves 9 and 10 above were obtained in solution in naphthalene (as the compounds were not soluble in benzene) by Mr. Reynolds B.Sc.

FIG. III

	Conc.	M	α
<u>p</u> -tolylurethane (179) Curve 1	.7158	187.2	1.046
	1.559	195.4	1.091
	3.005	215.8	1.205
	4.766	237.4	1.326
<u>o</u> -tolylurethane (179) Curve 2	1.124	176.8	.988
	1.592	181.1	1.012
	2.077	185.9	1.039
	3.037	191.1	1.068
	3.689	195.4	1.091

FIG. IV

	Conc.	M.	α
<u>o</u> -carbmethoxyphenylurethane (223) Curve 1	1.765	221.2	.9919
	2.797	222.1	.9961
	3.614	222.9	.9997
	4.407	223.9	1.004
	5.343	225.2	1.010
<u>o</u> -carbmethoxyphenylurethane (209) Curve 2	.8997	211.9	1.014
	1.696	207.1	.991
	2.657	208.7	.9988
	3.514	208.4	.9977
	4.771	215.3	1.0300
<u>p</u> -monobromo ^{ortho} carbmethoxyphenylurethane Curve 3 (302)	0.9245	293.6	.9723
	1.727	294.9	.9766
	2.563	302.4	1.000
	3.374	309.0	1.023
	4.103	312.1	1.034

FIG V

Values of conc. and α were calculated from Von Auwers' figures for phenylurethane (Zeit. physikal chem. 1893, 12, 712)

Conc.	M	α	α^*
·2856	155	·9393	·9815
·6137	161	·9757	1·020
2·065	170	1·030	1·076
3·023	183	1·109	1·159
4·133	193	1·169	1·222

Values for M are those given by Von Auwers, calculated by him using $k = 49$.

α^* These are the corrected values for α using $k = 51.2$

Experimental Readings

<u>Phenylurethane.</u>		Wt. Benzene gm. (W)	Wt. solute gm. (x)	Freezing Point		Average	Δ
Solution	1	14.72	0	5.288	5.286	5.287	-
"	2	15.62	0.2183	4.865	4.866	4.866	.421
"	3	14.72	.4725	4.391	4.395	4.393	.894
"	4	14.72	.7265	4.000	4.000	4.000	1.287
"	5	14.72	.9655	3.650	3.648	3.649	1.638
"	6	15.62	1.3424	3.265	3.271		
					3.269	3.270	2.017

o-tolylurethane.

Solution	1	16.799	0	5.325	5.324	5.324	--
"	2	"	.1706	5.025	5.022	5.023	.301
"	3	"	.3452	4.731	4.727	4.729	.595
"	4	"	.4926	4.496	4.495	4.495	.829
"	5	"	.6488	4.262	4.258	4.260	1.064
"	6	"	.9660	3.784	3.783	3.783	1.541
"	7	"	1.1879	3.468	3.471	3.470	1.854

<u>β naphthylurethane</u>		Wt. Benzene gm. (W)	Wt. solute gm. (x)	Freezing Point		Average	Δ
Solution 1		14.28	o	4.293	4.303		
				4.298		4.300	-
2	"		.5145	3.543	3.558		
				3.554		3.556	.744
3	"		.9500	3.005	3.00	3.002	1.298
4	"		1.4895	2.458	2.450	2.459	1.841
5	"		2.1795	1.871	1.871	1.871	2.429
6	"		2.9315	1.335	1.334	1.334	2.966

p-ethoxyphenylurethane

Solution 1		13.689	o	5.291	5.290	5.290	--
2	"		.2486	4.856	4.851	4.853	.437
3	"		.3590	4.667	4.671	4.669	.621
4	"		.5104 [*]	4.448	4.451	4.449	.841

* limit of solubility

<u>α-naphthylurethane</u>		Wt. Benzene gm.	Wt. solute gm.	Freezing Point ^{°C}		Average	Δ
Solution 1		14.47	o	5.285	5.282	5.283	-
2	"		.0550	5.203	5.206	5.205	.078
3	"		.2350	4.911	4.911	4.911	.372
4	"		.4146	4.622	4.621	4.622	.661
5	"		.6566	4.298	4.299	4.299	.984
6	"		1.1785	3.670	3.670	3.670	1.613

p-chlorophenylurethane

		Wt. Benzene gm.	Wt. solute gm.	Freezing Point °C		Average	A
Solution	1	14.24	o	4.421	4.424	4.423	-
"	2	"	.2402	4.031	4.035	4.033	.390
	3	"	.5479	3.563	3.563	3.563	.860
	4	"	.8193	3.194	3.194	3.194	1.229
	5	"	1.1608	2.774	2.774	2.774	1.649
	6	"	1.5802	2.308	2.313	2.311	2.112

p-bromophenylurethane

Solution	1	14.95	o	4.422	4.424	4.423	-
"	2	"	.4095	3.906	3.907	3.907	.516
	3	"	.6900	3.585	3.588	3.587	.836
	4	"	1.0535	3.184	3.189	3.187	1.236
	5	"	1.4900	2.778	2.779	2.779	1.644
	6	"	2.0520	2.313	2.325		
		"		2.323		2.324	2.099

p-methoxyphenylurethane

Solution	1	14.62	o	4.402	4.407	4.405	-
	2	"	.2085	4.045	4.039	4.042	.363
	3	"	.4810	3.617	3.616	3.617	.788
	4	"	.8055	3.193	3.188	3.191	1.214
	5	"	1.1215	2.817	2.819	2.818	1.587
	6	"	1.6555	2.279	2.282	2.281	2.124

<u>Diphenylurethane</u>		Wt. Benzene gm.	Wt. solute gm.	Freezing Point		Average	Δ
Solution	1	14.72	0	5.452	5.453	5.453	-
"	2	"	.4758	4.748	4.750	4.749	.704
"	3	"	.8661	4.163	4.165	4.164	1.289
"	4	"	1.3686	3.434	3.436	3.435	2.018
"	5	"	1.9284	2.630	2.623	2.627	2.826
"	6	"	2.4581	1.883	-	1.883	3.570

Phenylmethylurethane

Solution	1	13.91	-	4.260	4.264	4.262	-
"	2	"	1.2303	1.660	-	1.660	2.602
"	3	16.78	1.2303	2.074	2.074	2.074	2.188
"	4	21.71	1.2303	2.540	2.544	2.542	1.720
"	5	26.64	1.2303	2.845	2.842	2.844	1.418

Phenylethylurethane

Solution	1	13.52	-	5.520	5.516	5.518	-
"	2	"	.2890	4.879	4.881	4.880	0.638
"	3	"	.5766	4.246	4.243	4.244	1.274
"	4	"	.9365	3.464	3.460	3.462	2.056
"	5	"	1.3592	2.562	2.558	2.560	2.958

<u>o-ethylphenylurethane</u>	Wt. Benzene gm.	Wt. solute gm.	Freezing Point		Average	Δ
Solution 1	11.84	-	5.798	5.801	5.779	-
" 2	"	.1806	5.380	5.388	5.382	.416
" 3	"	.3289	5.048	5.056	5.055	.746
" 4	"	.4896	4.722	4.717	4.720	1.079
" 5	"	.6979	4.299	4.316	4.306	
				4.309	4.308	1.491
<u>p-tolylurethane</u>						
Solution 1	14.599	-	5.468	5.466	5.467	-
" 2	"	.1895	5.112	5.113	5.112	0.355
" 3	"	.4192	4.718	4.712	4.715	0.752
" 4	"	.8302	4.117	4.120	4.118	1.349
" 5	"	1.3624	3.456	3.455	3.455	2.012
<u>2:5 dichlorophenylurethane</u>						
Solution 1	12.46	-	4.388	4.394		
				4.396	4.395	-
" 2	"	.2930	3.890		3.890	0.505
" 3	"	.5705	3.417	3.411	3.414	0.981
" 4	"	.8383	2.963	2.964	2.964	1.431
" 5	"	1.1510	2.455	2.464		
				2.467	2.466	1.929
" 6	"	1.5677	1.851	1.856	1.854	2.541

<u>2:4 dimethylphenyl- lurethane</u>		Wt. Benzene gm.	Wt. solute gm.	Freezing Point		Average	Δ
Solution	1	12.35	-	4.399	4.400	4.400	-
"	2	"	.2345	3.915	3.915	3.915	0.485
"	3	"	.4499	3.471	3.473	3.472	0.928
"	4	"	.6270	3.134	3.139	3.137	1.263
"	5	"	.8550	2.719	2.721	2.720	1.680
"	6	"	1.1760	2.177	2.178	2.178	2.222

o-carbomethoxyphenyl-
lurethane

Solution	1	12.23	-	5.093	5.090	5.092	-
"	2	"	.501	4.140	4.148	4.144	0.948
"	3	"	.813	3.562	3.557	3.560	1.532
"	4	"	1.072	3.080	3.078	3.079	2.013
"	5	"	1.332	2.598	2.603	2.601	2.491
"	6	13.55	1.654	2.011	2.025	2.018	3.074

o-carbomethoxyphenyl-
lurethylane

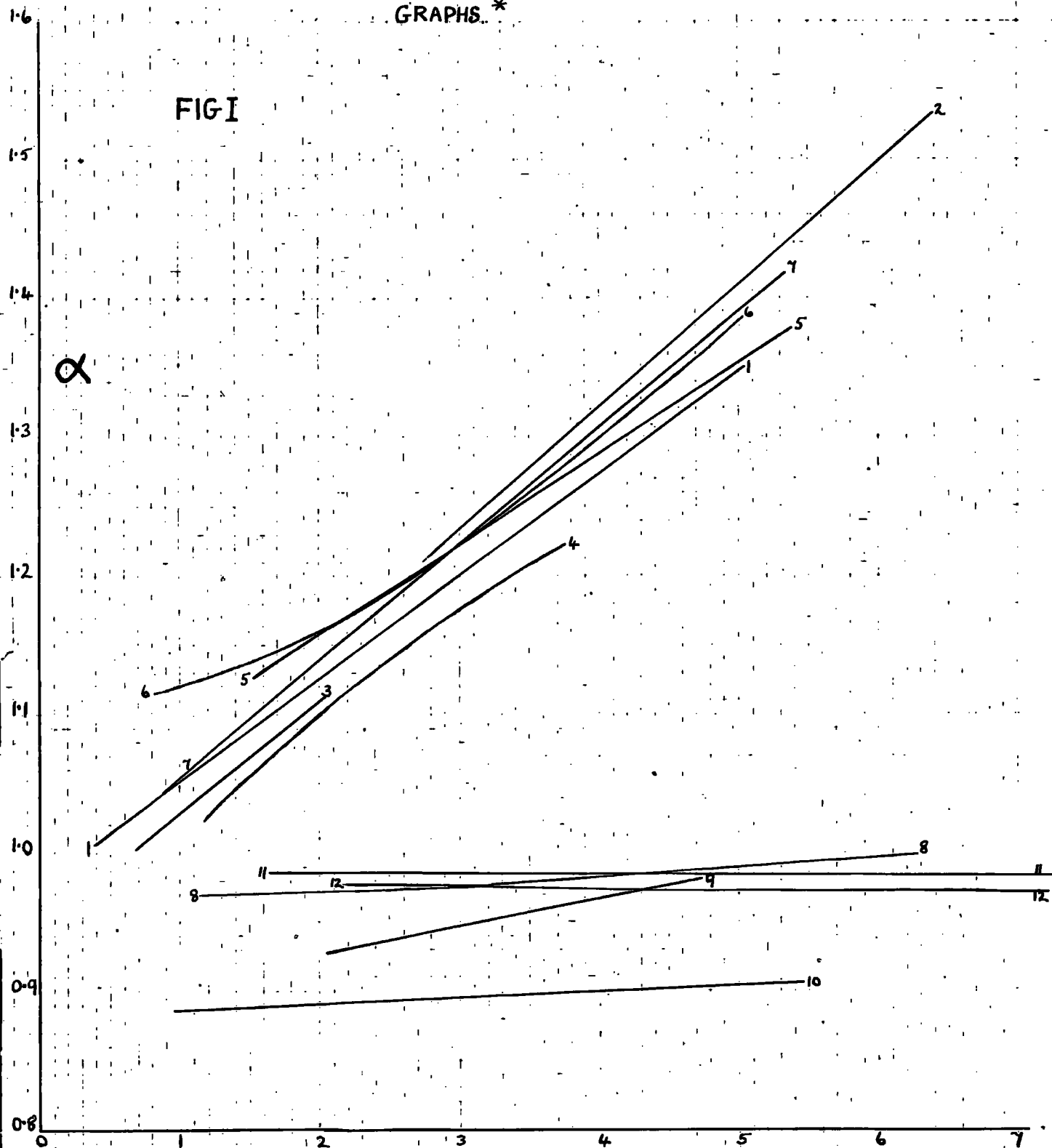
Solution	1	14.58	-	4.189	4.193	4.191	-
	2	"	.2794	3.728	3.728	3.728	.463
	3	"	.5360	3.282	3.282	3.282	.909
	4	"	.8570	2.747	2.750	2.749	1.442
	5	"	1.1545	2.247	2.243	2.245	1.946
	6	"	1.6150	1.553	1.558	1.556	2.635

<u>p-^{ortho}monobromocarb- methoxyphenylurethane</u>		Wt. Benzene	Wt. solute	Freezing Point		Average	Δ
Solution	1	14.24	-	5.838	5.840	5.839	-
"	2	"	.4091	5.333	5.341		
				5.336		5.338	.501
"	3	"	.7831	4.881	4.886	4.884	.955
"	4	"	1.1935	4.418	4.420	4.419	1.420
"	5	"	1.6155	3.958	3.959	3.959	1.880
"	6	"	2.0135	3.520	3.518	3.519	2.320

GRAPHS *

FIG I

α



CONCENTRATION in gm. mols. $\times 10^2$ per 100 gm. of solution.

* See pages 34-41 for key to names of compounds.

FIG II

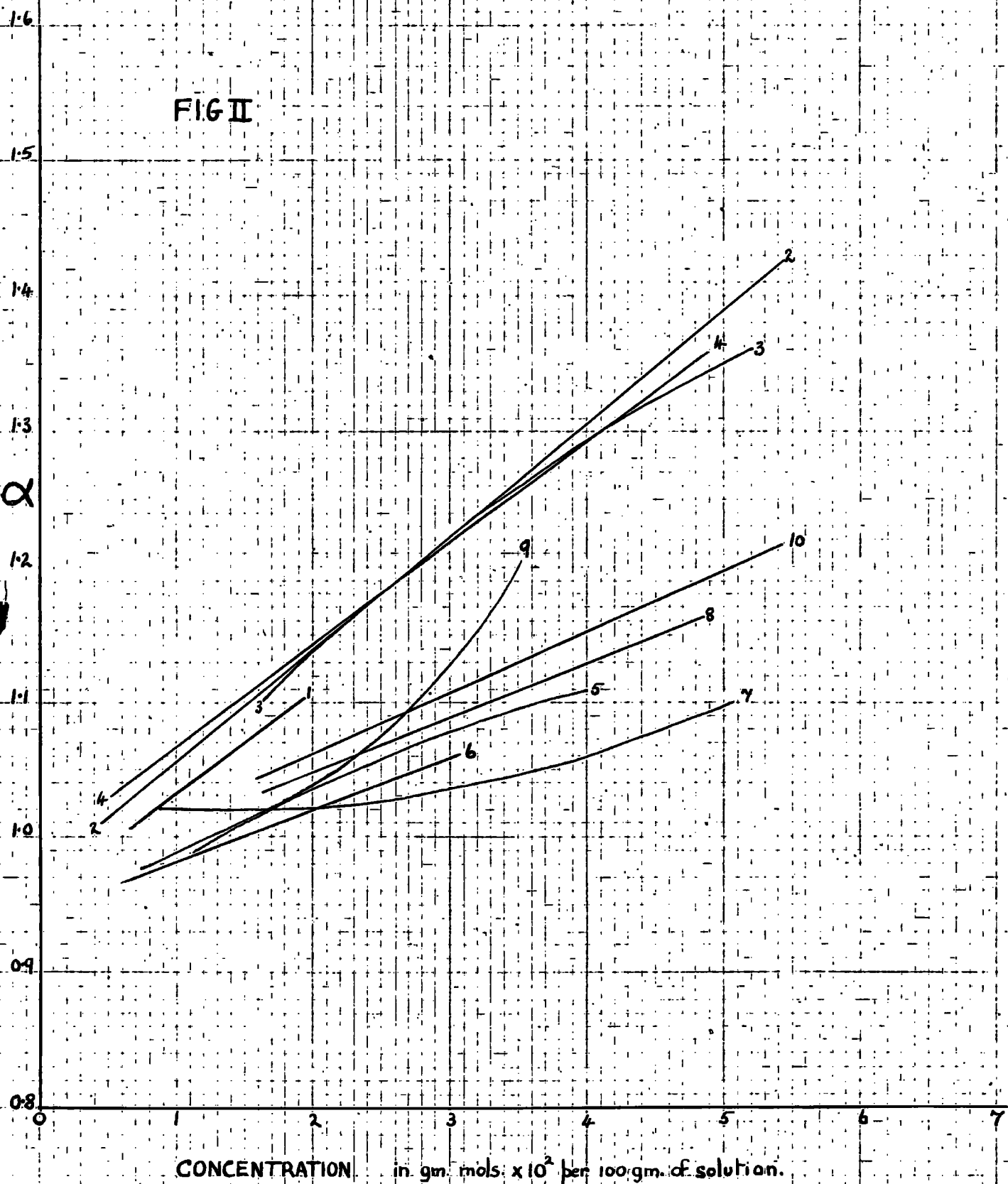


FIG III

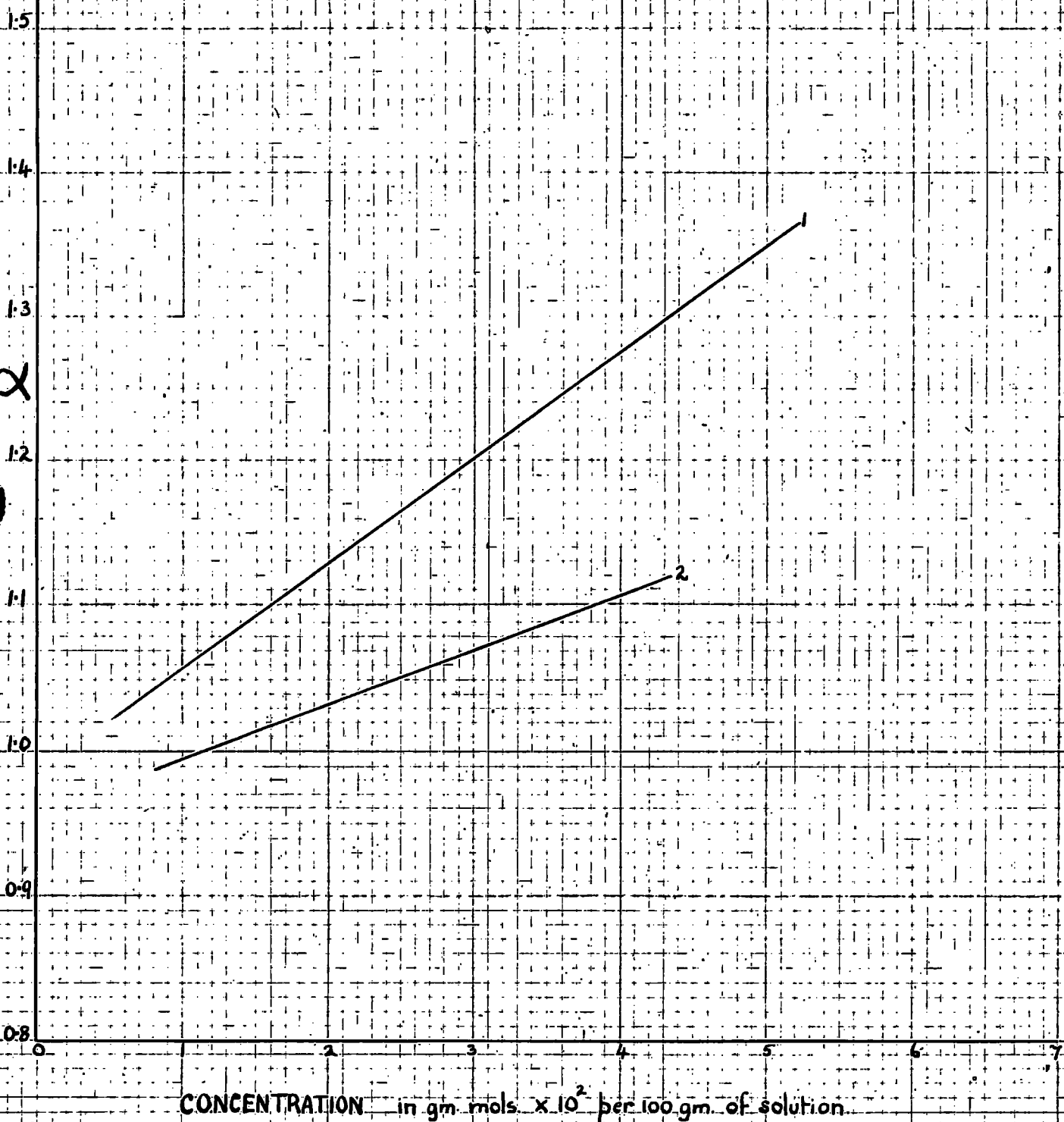


FIG IV

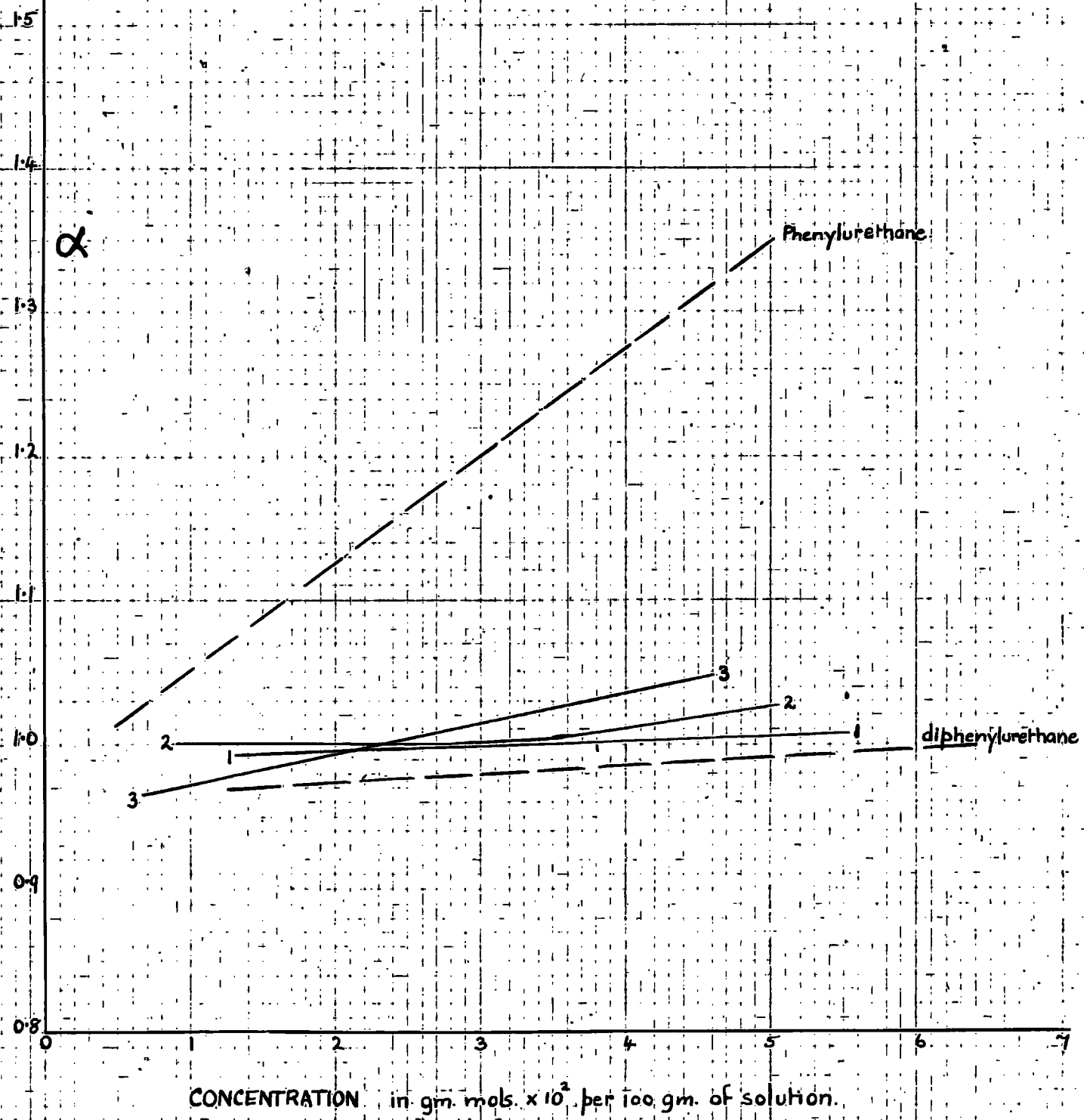


FIG. V

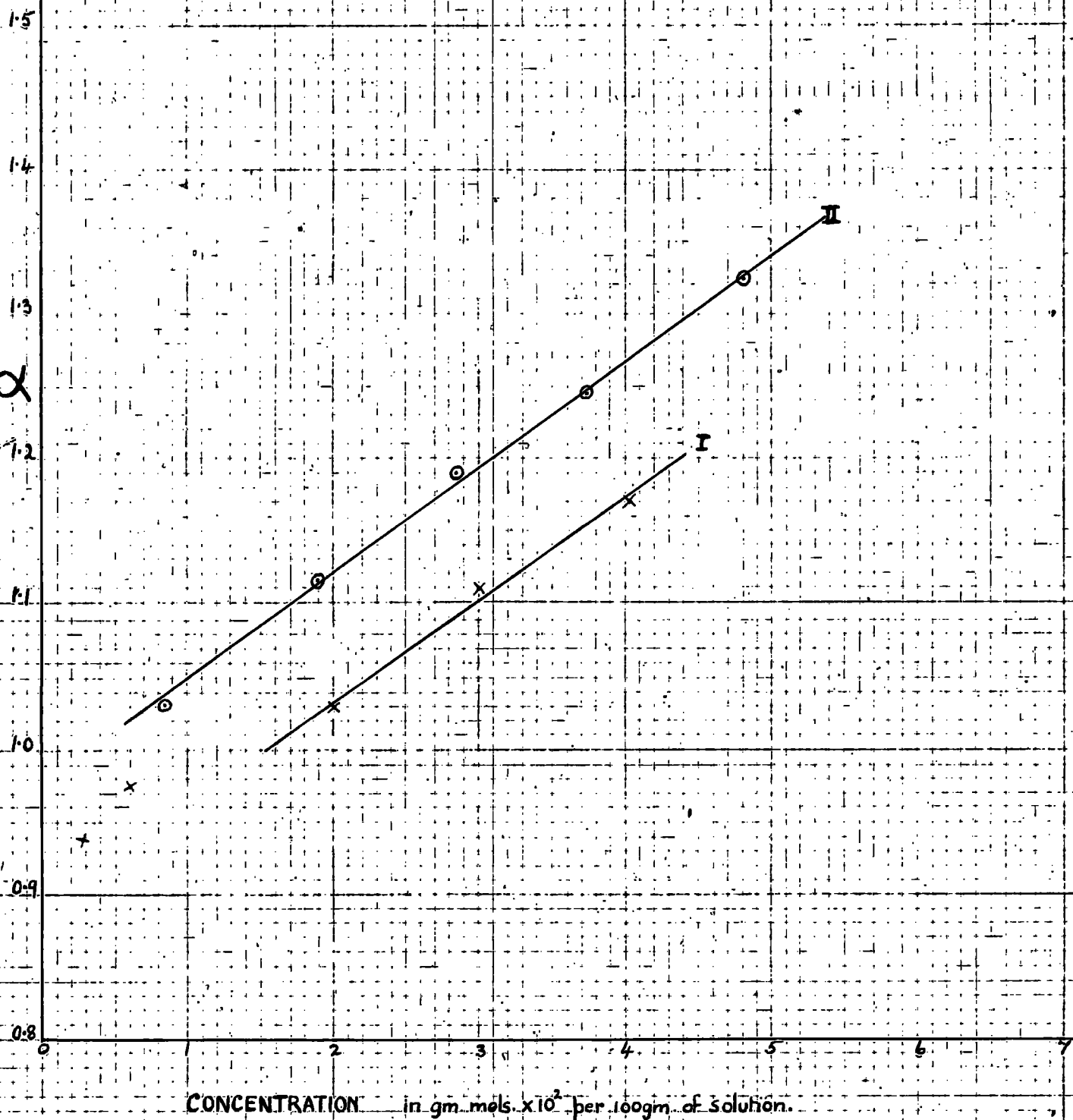


FIG VI

