THESIS

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for the degree of

DOCTOR OF PHILOSOPHY,

by

CECIL LEEBURN WILSON, M. Sc.

THE PHYSICAL PROPERTIES OF MIXTURES

with special reference to

VISCOSITY.

with an additional paper

THE CONSTITUTION OF PHLOBATANNINS.

NOTE.

The results which are given in Part IV of this thesis have been published (Journal of the Chemical Society, 1934, 1360.) The results contained in the Additional Paper, Part V, have been published in a joint paper with Dr. A Russell and Dr. J. Todd of the Department of Chemistry of the University of Glasgow (Journal of the Chemical Society, 1934, 1940.) From this paper, a number of the figures attached to Part V have been obtained.

I wish to express my indebtedness to the Queen's University of Belfast for the award of a Musgrave Research Studentship during the sessions 1933-34 and 1934-35, which enabled me to carry out research through those two sessions at the University of Glasgow.

I also wish to express my thanks to Dr. R. Wright, Dr. A. Russell and Dr. J. Todd of the Department of Chemistry in the University of Glasgow, and to Professor A. W. Stewart and Dr. J. B. Parke of the Queen's University Chemical Department, for helpful advice, and for the interest which they showed in this work.

Chemical Department,
The Queen's University of Belfast.

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INTRODUCTION.

INTRODUCTION.

The property of viscosity is possessed by any fluid, and although the methods of investigation are widely different in each case, it may therefore be examined in either liquids or gases, or in solutions or mixtures, as long as only a single phase is present.

In this thesis, work is described on the viscosities of various types of mixtures; they are, briefly,

(1) solution mixtures, where various degrees of reaction may be expected between the substances in solution;

(2) mixtures of gases with vapours;

(3) emulsions, which, though strictly speaking not single phase liquid mixtures, are yet as a rule sufficiently homogeneous to permit of the measurement of viscosity.

Part I of this thesis contains the results obtained from the investigation of Solution Mixtures. At the same time, the densities, which have to be determined in order to calculate the viscosities, are included.

Part II consists of the investigation of the viscosities of mixtures of Gases with Vapours. As in the case of the solution mixtures, the mixtures are so chosen that various degrees of reaction may be expected between the two constituents of the mixtures.

Part III is an account of the examination of viscosity in Emulsions of Benzene and Water, with particular reference to the effect of the emulsifier on the property.

Arising out of the work described in Part III, an investigation of the Action of the Emulsifier in stabilising emulsions was carried out, and is contained in Part IV.

Additional Paper. This, Part V of this thesis, consists mainly of an account of the examination of the Absorption Spectra of Natural Tannins, Synthetic Phlobatannins, and related compounds.

Since, in some of the work carried out, the apparatus was specialised, it will be described in some detail in a special section where its nature warrants this.

PART I.

SOLUTION MIXTURES.

INTRODUCTION TO PART I.

When two liquids are mixed in varying proportions and a physical property-composition curve is plotted, it is found in general to be smooth and continuous, and to approximate to the Mixture Rule. In other words, it is approximately the average to be expected from calculation based on the extent of the physical property in each liquid separately.

However, in cases where combination, either definite or loose, is known to take place, between the two components of such a binary mixture, the property deviates to a considerable extent from the Mixture Rule, and frequently, when the formation of a compound is definite, the curve shows a sharp maximum or minimum.

Thus, Briscoe and his co-workers (1,2,3) show that where loose compounds are formed between such organic liquids as Chloroform and Ether (as evidenced by the heat of mixing) such properties as dielectric constant and depression of the freezing point do not obey the Mixture Rule, but show maxima and minima in the property-composition curves.

Again, notable exceptions are the cases of mixtures of mustard oils and amines (4,5) and of certain mixtures containing phenols (6,7).

Viscosity, where conditions render its determination possible, is a very suitable property to examine, in order to obtain evidence with regard to compound formation.

It has been used, for example, by Thorpe and Rodger(8) for mixtures such as Ether-Chloroform, where loose compound formation takes place.

Even more striking examples of its suitability are shown in the case of the Mustard Oil-Amine mixtures previously mentioned. These systems give sharp maxima in the viscosity-composition curves, which correspond with similar maxima in the freezing point curves, and indicate the formation of non-dissociated compounds.

Bramley, too, in his investigation of the binary mixtures containing phenol and substituted phenols (6,7) finds that where two substances react chemically forming an additive compound, the viscosity of a liquid mixture of these two substances should be higher than the calculated value, the maximum difference occurring with that mixture which contains the largest proportion of the compound. His results are, however, indecisive, which he traces to causes connected with dissociation and association of the constituents.

A number of other examples are quoted by Hatschek (9).

When, however, this method is applied to cases where definite compounds, capable of isolation, are formed, as in the case of the work of Kurnakow and his co-workers on the Mustard Oils (4,5), it is extremely difficult to investigate the property widely. This is because it is not possible, in general, to obtain a continuous series of liquid mixtures between two substances which form definite compounds, since, as in the case of Sulphuric Acid-Aniline, there is also a change in physical state.

In solution, however, this difficulty is avoided, and so the viscosities of a number of acid-amine solution mixtures have been investigated, in conjunction with solution mixtures where no compound can be formed.

Here we have not, however, an exact parallel to the case of the liquid mixtures; for the determination of the viscosities of a series of solution mixtures, since the solutes may very well be solid, shows in reality the effect of the solutes on the viscosity of the solvent, and cannot be considered a direct function of the constituents as in the case of a series of liquid pairs.

The conditions may be considered somewhat similar to those in gas-vapour mixtures, but where the effect of mixing is observed through its effect on the viscosity of the solvent.

VISCOSITY.

The viscosity of a fluid is that property to which is due the internal resistance offered to the motion of the fluid at any point with a velocity different from that of an immediately adjacent point. It determines the resistance to shear, that is, to slow stirring, or flow through a capillary.

The coefficient of viscosity, η , is the numerical value of the tangential force on unit area of either of two parallel planes at unit distance apart, when the space between these planes is filled with the fluid in question, and one of the planes is moving with unit velocity in its own plane relative to the other.

The fundamental unit of viscosity is 1 poise, which is equal to 100 centipoises.

When relative viscosities are to be determined, an Ostwald U-Tube Viscometer is suitable for the determinations. Poiseuille's Law (10) for viscosity may be written

$$\eta = \frac{\pi d^4 h \rho g t}{128 L v} - \frac{m \rho v}{8 \pi t L}$$

where η = Viscosity of liquid flowing through **capillary.**
d = Diameter of capillary.
h = Mean head of liquid.
ρ = Density of liquid.
g = Acceleration due to gravity.
v = Volume of liquid which flows in time t secs.
m = Constant.
L = Corrected length of capillary.

With relative viscosities, the elimination of the variation in pressure caused by the decreasing column of liquid is possible. In the Ostwald Viscometer (Fig. 1) a constant volume of liquid is used. The liquid is then drawn up into the left hand limb, above the mark A, and allowed to flow back, the time for the fall from A to B being noted. The flow may be considered to be caused by an average head, and all the constants may be combined to give the formula

$$\eta = K\rho t$$

By determining t, the time between the marks A and B for a liquid of known η and ρ, the viscosity of another liquid of density ρ' can be found from the equation

$$\eta' = \eta \frac{\rho' t'}{\rho t}$$

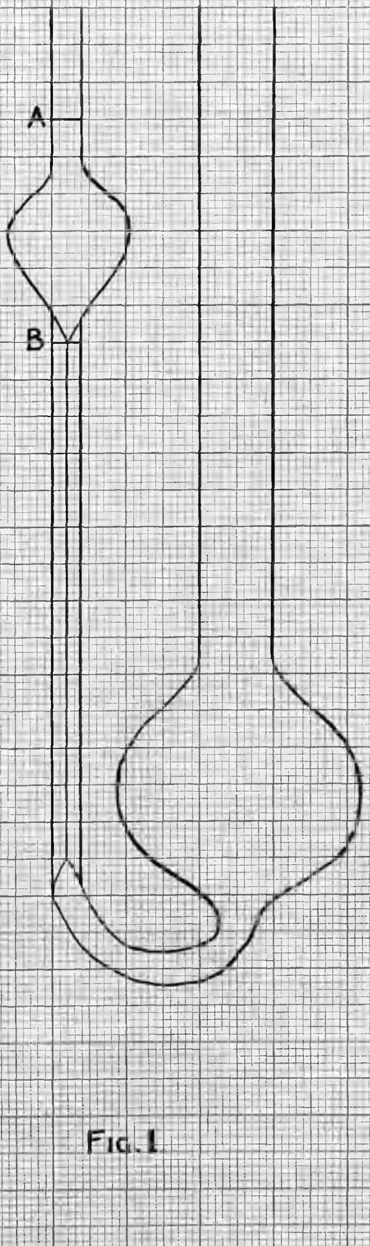


Fig. 1

EXPERIMENTAL.

Normal solutions of the substances were used, and the compositions of the mixtures were varied so that there was always 1 gramme equivalent per litre of dissolved substance.

Thus, as a specimen, we have the proportions used for the Hydrochloric Acid-Monomethylamine solution mixtures.

No. of soln.	% N/1 Monomethylamine	% N/1 Hydrochloric Acid
1	0	100
2	10	90
3	20	80
4	30	70
5	40	60
6	50	50
7	60	40
8	70	30
9	80	20
10	90	10
11	100	0

The viscometer was kept in a thermostat at 25° C., varying over not more than 0.1° C. After being allowed to reach the temperature of the thermostat, the time of flow of the solution was measured, the average of three determinations varying by not more than one second being taken. Since the viscometers used were special Ostwald U-Tube Viscometers, having a bulb capacity of about 15 cc., and so constructed that they gave a time of flow for water of about 400 seconds, this means a variation of less than 0.25%.

The substances used were chosen so as to give a range of strengths of both acids and bases. They were Hydrochloric Acid, Acetic Acid, Monomethylamine, Ammonia, Urea; and they were used in conjunction as follows:-

1. Hydrochloric Acid-Monomethylamine
2. Hydrochloric Acid-Ammonia
3. Hydrochloric Acid-Urea
4. Acetic Acid-Monomethylamine
5. Acetic Acid-Ammonia
6. Acetic Acid-Urea.

In order to show the difference in the case where no action between the two solutes is to be expected, the mixtures below were also examined:-

7. Hydrochloric Acid-Acetic Acid
8. Monomethylamine-Urea.

Finally, viscosities of two series of solutions in which one solute was present alone were measured, in order better to determine the effect due to interaction between the two solutes.

The two resulting viscosity curves were added together giving the effect of the sum of the two solutes independent of any interaction between them. The sum, when subtracted from the curve given by the mixed solutions, then shows the effect due to interaction between the solutes.

9. Monomethylamine-Water
10. Acetic Acid-Water.

Apart from one point, the preparation of the solutions, and the determinations of the viscosities and the densities, which were carried out in the normal way using a density bottle, requires no comment.

This one point was that the solutions, if allowed to sit for any length of time, changed considerably in strength, presumably due to loss by evaporation. This was particularly noticeable in the case of solutions which contained Monomethylamine as one of the constituents, and even in the preparation of the solution mixtures, if this was not carried out expeditiously, loss was to be expected.

It was found, finally, that it was necessary to carry out the preparation of the solution mixtures as quickly as possible, and as soon after the preparation of the original Monomethylamine solution as possible. The viscosities were then determined immediately on making up the solutions as mixtures.

RESULTS.

The most suitable form in which to present the results for the solution mixtures is in tabular and in graphical form, and both these methods are employed.

The table following gives the results for all the solution mixtures, and these are plotted as property-composition curves in Figs 2-7.

ρ = relative density: η = relative viscosity.

	% A		100	90	80	70	60	50	40	30	20	10	0
A	HCl	ρ	1.0173	1.0150	1.0127	1.0107	1.0086	1.0061	1.0033	0.99950	0.99613	0.99332	0.99012
B	CH_3NH_2	η	1.0542	1.0469	1.0413	1.0361	1.0290	1.0211	1.0400	1.0671	1.0843	1.0966	1.1015
A	HCl	ρ	1.0173	1.0150	1.01265	1.0112	1.0095	1.0077	1.0044	1.00135	0.99830	0.99502	0.99215
B	NH_3	η	1.0542	1.0430	1.0329	1.0173	1.00345	0.98775	0.99900	1.0063	1.0130	1.0169	1.0231
A	HCl	ρ	1.0173	1.0170	1.0169	1.0168	1.0167	1.01665	1.01645	1.0163	1.0162	1.0159	1.01575
B	$CO(NH_2)_2$	η	1.0542	1.0508	1.0497	1.0477	1.0454	1.0426	1.0441	1.0430	1.0399	1.0369	1.0338
A	HCl	ρ	1.0173	1.01625	1.01505	1.01425	1.0133	1.0125	1.0116	1.01055	1.0098	1.0090	1.0081
B	CH_3COOH	η	1.0542	1.0631	1.0697	1.07765	1.08525	1.0896	1.0953	1.1010	1.1061	1.11135	1.1157
A	CH_3COOH	ρ	1.0081	1.0079	1.0075	1.00715	1.00665	1.00635	1.00505	1.0020	0.99855	0.99535	0.99012
B	CH_3NH_2	η	1.1157	1.1178	1.12425	1.12705	1.12965	1.12835	1.12615	1.11695	1.11195	1.1071	1.1015
A	CH_3COOH	ρ	1.0081	1.00815	1.0084	1.00855	1.00860	1.00865	1.00565	1.00235	0.99900	0.99561	0.99215
B	NH_3	η	1.1157	1.11605	1.1187	1.1186	1.1160	1.11335	1.09555	1.07685	1.05855	1.03935	1.0231
A	CH_3COOH	ρ	1.0081	1.0090	1.00975	1.0101	1.0111	1.01205	1.0124	1.01335	1.01415	1.01495	1.01575
B	$CO(NH_2)_2$	η	1.1157	1.10915	1.1022	1.0930	1.0858	1.07825	1.0706	1.06405	1.05725	1.0475	1.03375
A	$CO(NH_2)_2$	ρ	1.01575	1.01285	1.0109	1.00895	1.00655	1.0043	1.0018	0.99892	0.99616	0.99280	0.99012
B	CH_3NH_2	η	1.03375	1.0397	1.0487	1.0557	1.0624	1.0695	1.0763	1.08175	1.0883	1.0949	1.1015
A	CH_3COOH	ρ	1.00817	1.0077	1.00672	1.00608	1.00530	1.00445	1.00375	1.00272	1.00167	1.00097	1.00000
B	H_2O	η	1.11515	1.10573	1.09668	1.08469	1.07150	1.06199	1.04870	1.03789	1.02195	1.01465	1.00000
A	CH_3NH_2	ρ	0.99016	0.99124	0.99256	0.99344	0.99436	0.99554	0.99632	0.99750	0.99825	0.99930	1.00000
B	H_2O	η	1.10188	1.08745	1.07539	1.06503	1.05673	1.04883	1.03943	1.03005	1.02023	1.01090	1.00000

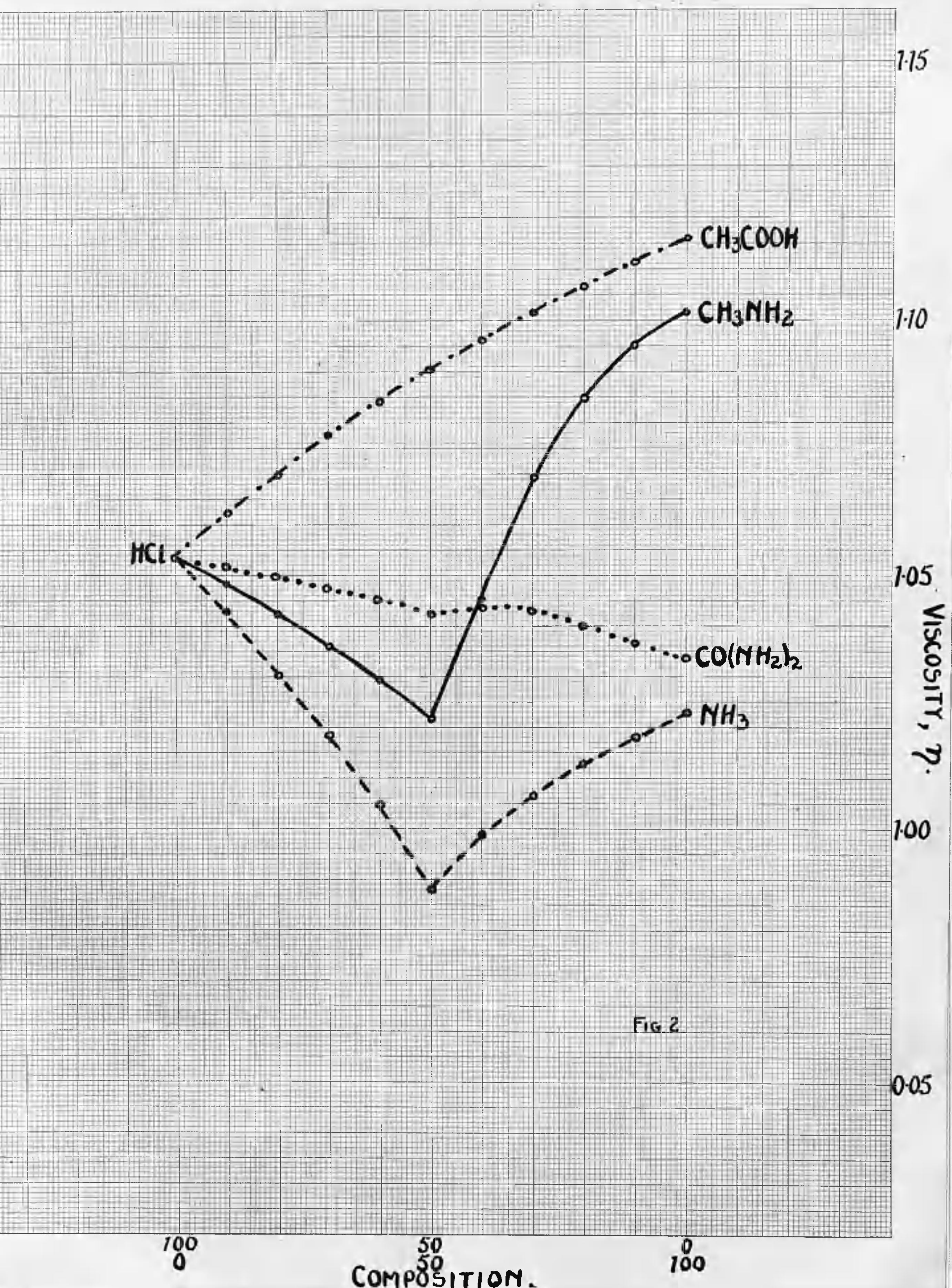

CH₃COOH
CH₃NH₂
HCl
CO(NH₂)₂
NH₃
1·15
1·10
1·05
1·00
0·05
VISCOSITY, η.
100
0
50
50
0
100
COMPOSITION.

FIG. 2

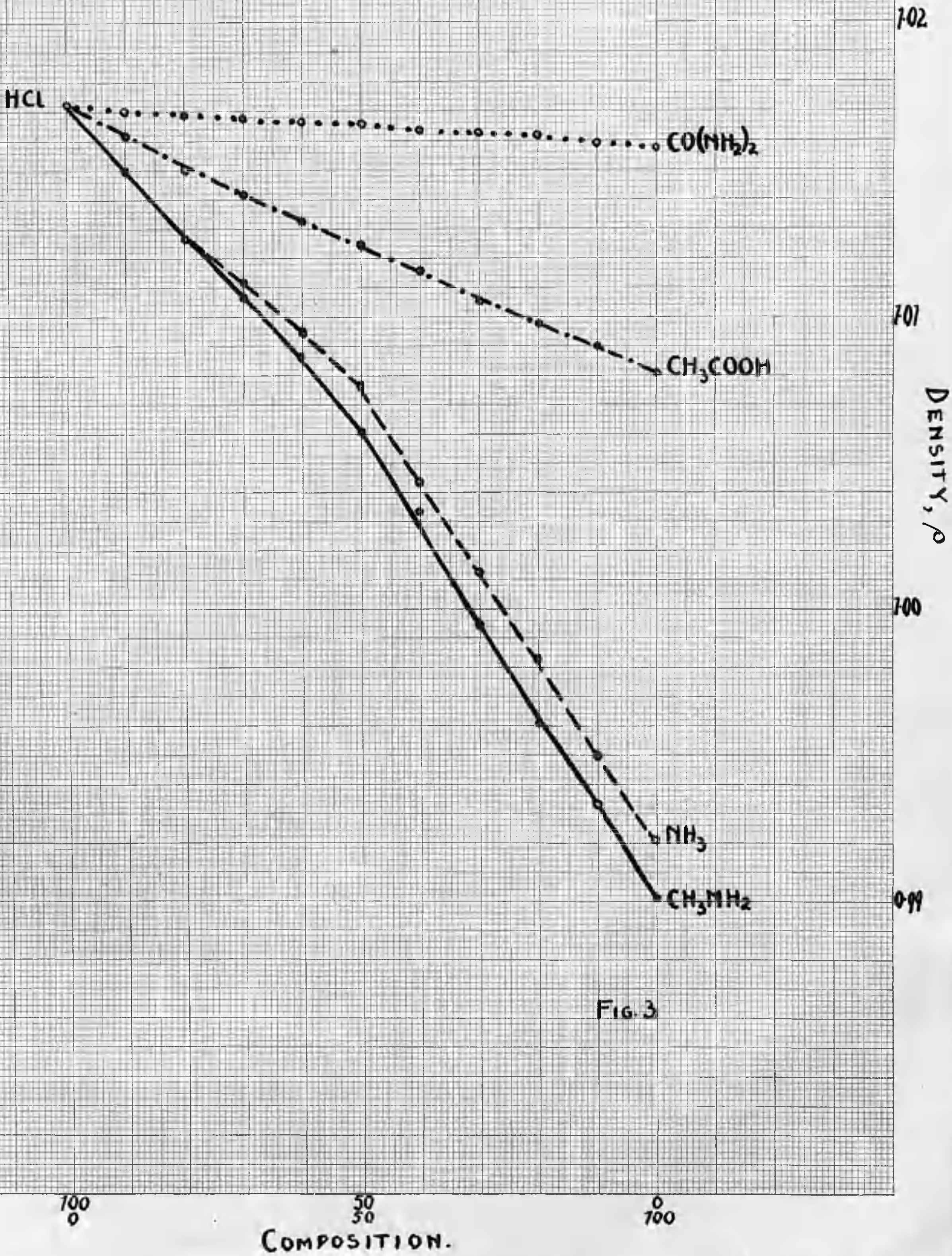

HCL
$CO(NH_2)_2$
CH_3COOH
NH_3
CH_3NH_2
1·02
1·01
1·00
0·99
DENSITY, ρ
100
0
50
50
0
100
COMPOSITION.

FIG. 3

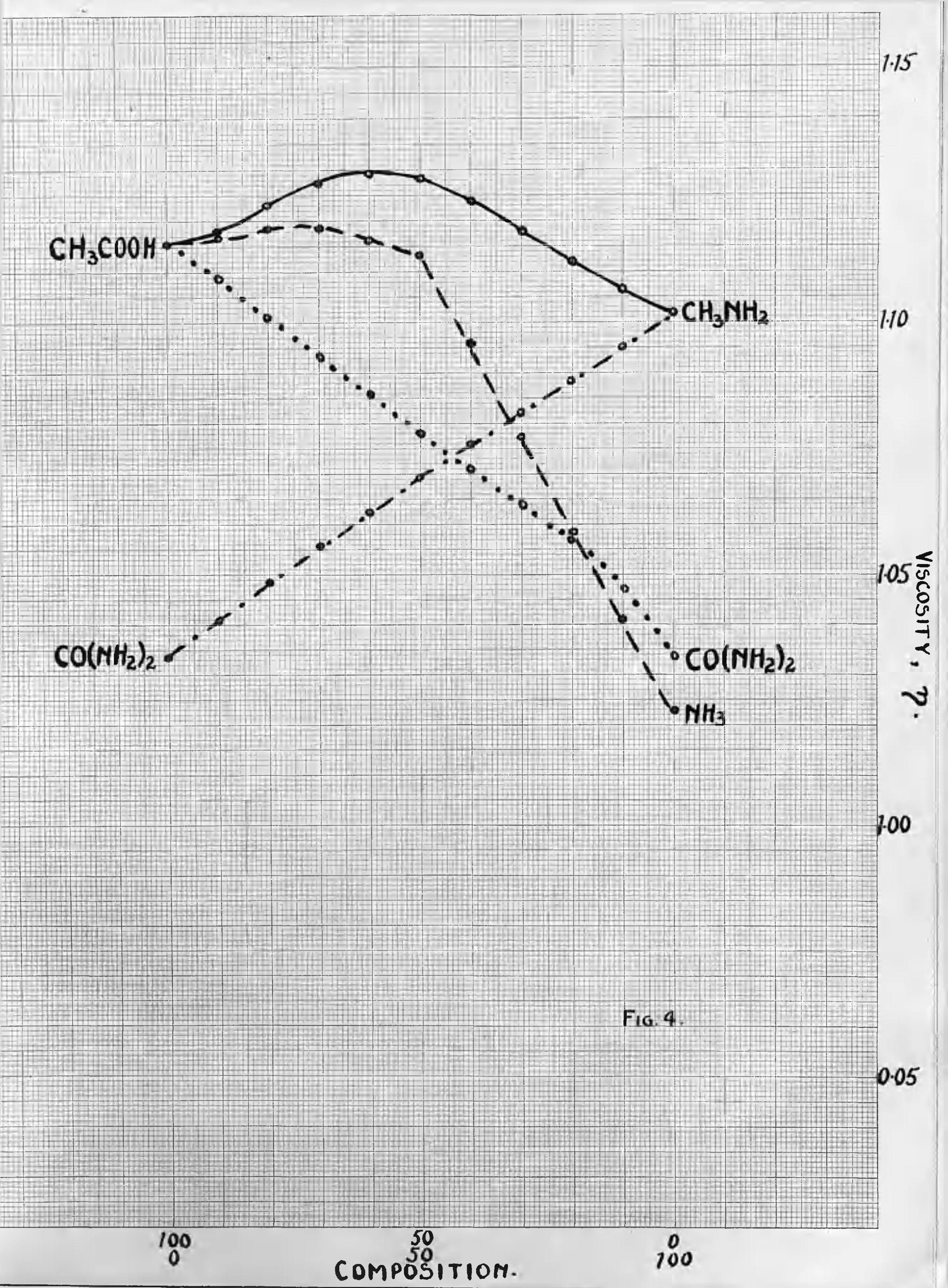

CH$_3$COOH
CH$_3$NH$_2$
CO(NH$_2$)$_2$
CO(NH$_2$)$_2$
NH$_3$
1·15
1·10
1·05
1·00
0·05
VISCOSITY, η.
100
0
50
50
0
100
COMPOSITION.

FIG. 4.

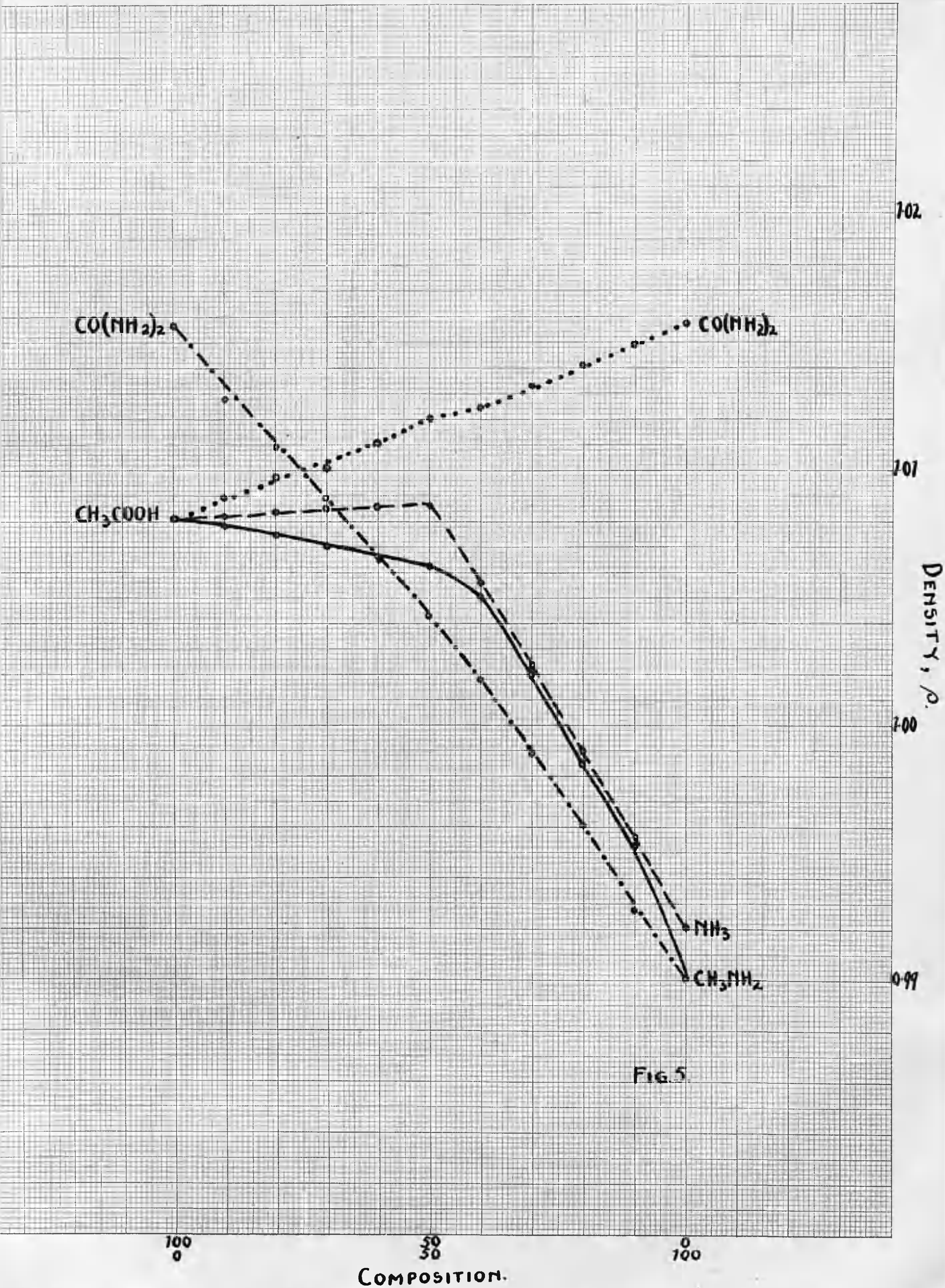

CO(NH2)2
CO(NH2)2
CH3COOH
NH3
CH3NH2
1·02
1·01
1·00
0·99
DENSITY, ρ.
100
0
50
50
0
100
COMPOSITION.

FIG. 5.

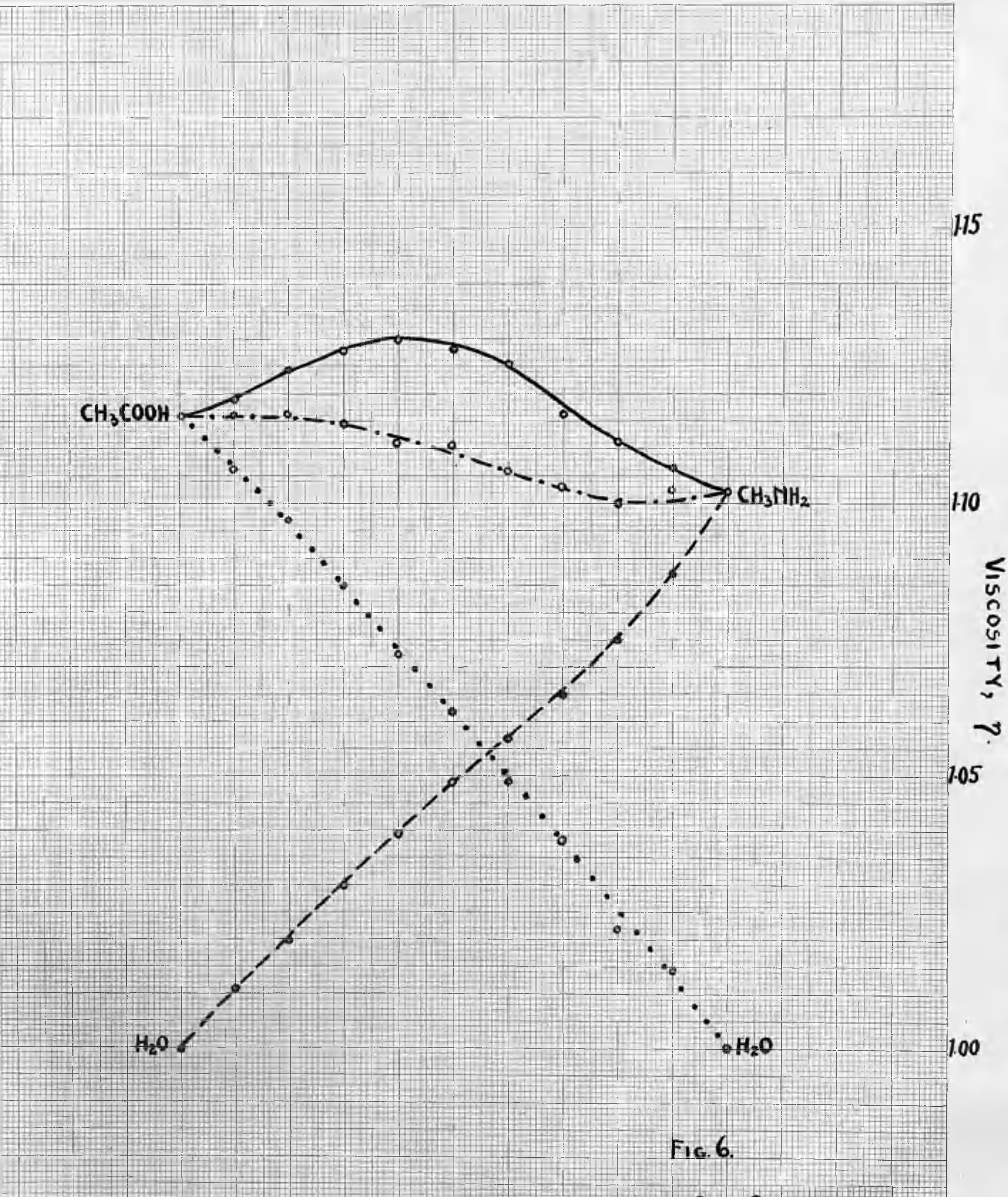

CH₃COOH
CH₃NH₂
H₂O
H₂O
1·15
1·10
1·05
1·00
VISCOSITY, η.
100
0
50
50
0
100
COMPOSITION.
-·-·- SUM CURVE.

FIG. 6.

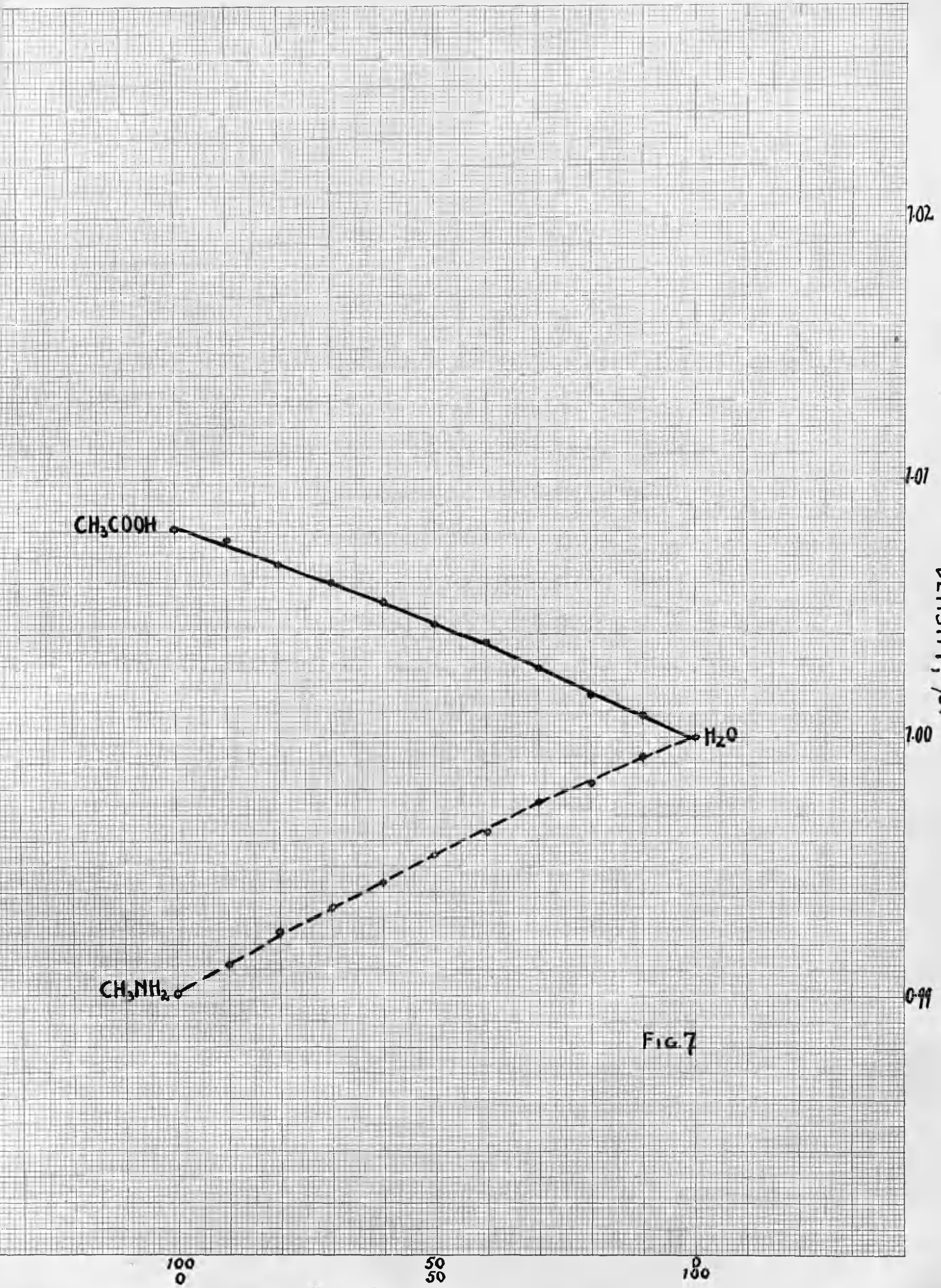

CH_3COOH
CH_3NH_2
H_2O
1·02
1·01
1·00
0·99
Density, ρ.
100
0
50
50
0
100
Composition.

Fig. 7

DISCUSSION.

While the results obtained in this investigation may be summarised quite briefly, several points of interest are raised which merit further discussion.

In consideration of the results, the first point to be noted is that the stronger the acid or base concerned, the sharper the break in the curve. Thus the curve for Hydrochloric Acid-Monomethylamine (Fig. 2) shows a much sharper break than that for Acetic Acid-Monomethylamine (Fig. 4) or for Hydrochloric Acid-Urea (Fig. 2).

This may definitely be attributed to the fact that in the former case the salt formed will be considerably less hydrolysed than will those formed in the case of the two latter mixtures.

In all cases where the formation of a compound is likely, the break can be seen distinctly in the curve, with the exception of the case of Acetic Acid-Urea (Fig. 4); but here the existence of a compound is much more doubtful than in the case of the other acid-base mixtures.

Surprisingly, too, in this case a more definite break is found in the density-composition curve than in the viscosity-composition curve. In general, the viscosity-composition curves seem to be much more suitable for demonstrating the effect than do the density-composition curves. In other words, the viscosity shows itself to be a more constitutive property than the density.

Since both of the curves Acetic Acid-Water and Monomethylamine-Water are almost straight lines, it follows that their sum will almost be a straight line also. (Fig.6). The difference curve will therefore be nearly identical with the Acetic Acid-Monomethylamine curve, if the end points of the former curve are lowered to the same level. Since the two curves appear alike, it follows that the deviation of the acid-amine curve is probably due to compound formation.

It will be seen that, with the exception of the Acetic Acid-Monomethylamine curve (Fig. 4) the break corresponds to the 50% mark, and so to the point where full compound formation might be expected. The endeavour to eliminate the effect of the solvent in this particular case throws no light on the peculiar behaviour of the Acetic Acid-Monomethylamine solution. It might, although without much basis for the theory, be attributed to association, for, though normally Acetic Acid appears to exhibit slight dissociation in aqueous solution, the presence of the Monomethylamine and the hydrolysis of the salt formed may have the effect of causing the acid to associate. This, however, is very hypothetical, and would necessitate verification by methods other than viscosity measurements, if, indeed, it would be capable of verification.

Even more interesting is the fact that, while the density curves all break upwards, the viscosity curves as a whole may be divided into two main classes, those which break upwards, and those which break downwards.

When arranged with this difference in mind, we have the two following groups of mixtures:-

Break up.	Break down.
Acetic Acid-Monomethylamine Acetic Acid-Ammonia	Hydrochloric Acid-Monomethylamine Hydrochloric Acid-Ammonia Hydrochloric Acid-Urea.

While on a cursory examination of this grouping it may appear that this is merely due to the different effect of two different acids, this may on further consideration be tentatively explained as follows.

In all the substances examined, Hydrochloric Acid may be expected to exhibit by far the greatest degree of ionisation in solution. Again, as mentioned above, Bramley (7) stated that where addition compounds are formed, a value higher than the calculated value is obtained in the property-composition curve, and further evidence supporting this theory is discussed by Hatschek(11).

May it not, then, be the case that, where addition compounds are formed, we have a maximum shown, that is, in the second group of mixtures? On the other hand, where a minimum is shown, the compound formed may be the result of a purely ionic reaction, as is to be expected, for example, in the case of Hydrochloric Acid-Monomethylamine.

Finally, it may be noted that, in general, where there is a considerable difference between the strengths of the two compounds in a mixture, the side on which the stronger one is in excess gives a straighter curve than that on which the weaker occurs.

In other words, one of the viscosity-composition curves may be considered as consisting of two viscosity-composition curves, that for acid and salt, and that for base and salt. Then if the acid is the stronger of the two, the curve for acid-salt will be straighter than that for base-salt.

If this property is general, and the selection of compounds dealt with here is representative enough to suggest that this is the case, this would appear to be a possible method for determining the relative strengths of acids and bases, albeit the determination would be only approximate.

CONCLUSION.

The viscosities and densities of a number of mixtures of Normal solutions of acids and bases have been determined.

Certain well defined relationships have been observed and discussed, the most obvious one being a sharp break in the property-composition curve at the 50% mark when the formation of non-hydrolysed compounds is to be expected.

In other words, where the formation of a compound takes place, this corresponds with a maximum or minimum value on the property-composition curve. The breaks disappear or are modified when hydrolysis is likely.

The viscosity-composition curves in particular would appear to indicate fully the conditions, complex or otherwise, in such a system.

PART II.

GAS-VAPOUR MIXTURES.

INTRODUCTION TO PART II.

The coefficient of viscosity, η, for a fluid has elsewhere in this work been fully defined (p. 6). It will be sufficient to state briefly that it is the force per square centimetre which gives a layer a velocity relative to a second layer which is numerically equal to the distance between them. In a liquid, the main factor affecting viscosity is the cohesion between the molecules. In a gas, the viscosity can be shown theoretically to be due to the kinetic motion of the molecules.

A gas flowing over a surface can be considered as consisting of a series of planes. These planes are slipping over each other, the velocity of a plane being a linear function of its distance from the surface. If we assume that the plane next to the surface over which the gas flows is retarded infinitely, while that one which is unit distance from the surface has unit velocity, then the friction, or tangential force, on unit area between any two contiguous planes is the coefficient of viscosity, η.

Since the velocity of the planes is so small compared with the motion of the molecules comprising the gas that it can be considered as having no effect on the motion of the molecules, we can see that the molecules passing from any plane to that immediately above will tend to retard it, while those passing from a plane to that immediately below will tend to speed up the slower plane. This motion of the molecules will be the cause of the internal friction between the layers, and the expression for the viscosity of a gas may be calculated directly from the basis of the kinetic motion of the molecules.

The average distance between any two consecutive layers of molecules in the gas is equal to the mean free path of the molecule, L. At a distance, x, from the surface over which the gas is flowing, the velocities of two adjacent layers are

$$x + L/2 \qquad \text{and} \qquad x - L/2.$$

The numbers of molecules passing from one layer to the other per unit area

$$= \quad 1/6\ (N.G)$$

where G = the kinetic velocity of the molecules
N = the number of molecules per unit volume.

Since the molecules pass in both directions, the nett loss in momentum of the faster layer

$$= 1/6\left[NmG(x + L/2)\right] - \left[1/6\ NmG(x - L/2)\right]$$

$$= 1/6\ NmGL.$$

The nett gain in momentum of the slower layer is similarily

$$1/6\ NmGL.$$

So that the total change in relative momentum per unit area per unit time is

$$1/3\ NmGL,$$

which is the expression for the viscosity, η, of a gas.

This formula can be written

$$\eta = 1/3 \rho GL.$$

We can see from this formula that if the pressure is changed there should be no change in the viscosity, for N is increased and L decreased to the same extent, while m and G are unchanged. That this is so within wide limits when the viscosity is measured by means of oscillating discs has been shown by Meyer (12), and later more conclusively by Maxwell(13,14), but it has been pointed out by Rankine(15) that when measured by flow through a capillary in apparatus similar to that used in the present work, low pressures have a decided effect on the times of flow, and hence on the apparent viscosity of a gas.

The effect of increase of temperature can be seen from the formula to be an increase in viscosity, a fact which is found experimentally(12).

The theoretical considerations above can easily be extended to include mixtures of gases.

At first sight it would appear that, since η is independent of the pressure, the viscosity of a mixture of two gases should be the sum of the viscosities of the constituent gases. But further consideration shows that this is not the case.

If equal volumes, v, of two gases at the same temperature are mixed, G and m for each gas remains unchanged. If these equal volumes are compressed, so that the resulting volume is also v, then N, the number of molecules per unit volume is unchanged for each type of molecule. L, however, has been reduced for each type of molecule, on account of the presence of molecules of the other type; so that the viscosity for each of the gases is reduced, and so the total viscosity of the mixture,

$$1/3\ NmGL\ ,$$

is less than the sum of the viscosities of the constituent gases,

$$1/3\ Nm_1GL_1 + 1/3\ Nm_2GL_2\ .$$

If the mean free path for each of the gases were exactly halved by the above process of mixing, the viscosity of the mixed gases would be the mean of the two viscosities of the constituent gases. In other words, the resultant viscosity would be that calculated from the Mixture Rule. Owing, however, to the difference in size and kinetic velocity of the two types of molecules, the exact halving of the mean free paths does not occur, and, as a consequence, the Mixture Rule is not obeyed.

The effect of the difference of molecular diameter on the mean free path in gas mixtures may be more easily followed if we consider the result of mixing equal volumes of two gases of different molecular weights at the same pressure and temperature. The resulting volume is then the sum of the volumes of the constituent gases. Under these conditions, N is halved for each gas, so that in order to obey the Mixture Rule, the mean free path, L, should be unchanged. Since, in the mixture, we have the same total number of molecules per unit volume as in the constituent gases, it follows that for the molecules of the gas of less molecular weight, the mean free path will be reduced, since the position originally occupied by 50% of these molecules is now held by larger molecules. In the same way, the mean free path of the larger molecules is increased to the same extent.

If we suppose x to be the change in length of the mean free path, the decrease in viscosity due to this cause for the gas of small molecules will be

$$1/3 \; (N/2.m_1 G_1 x)$$

and similarly the increase in viscosity for the gas of larger molecules will be

$$1/3\ (\ N/2.m_2G_2x\ ).$$

The total deviation in viscosity from that calculated from the Mixture Rule will therefore be

$$1/3\ \left[\ N/2.x\ (\ m_2G_2 - m_1G_1\ )\right].$$

If we now suppose the two gases to have the same molecular weight, M, the deviation in viscosity becomes

$$1/3\ \left[N/2.x\ (\ MG_2 - MG_1\ )\right].$$

At the same temperature, however, all gas molecules have the same value for kinetic energy,

$$\tfrac{1}{2}mG^2.$$

If the molecular weights of the two gases are the same then

$$\tfrac{1}{2}MG_1^2 = \tfrac{1}{2}MG_2^2$$

$$\therefore \qquad G_1 = G_2$$

and so the deviation from the calculated viscosity becomes

$$1/3\ \left[N/2.x\ (\ MG - MG\ )\right]$$

$$= \text{Zero.}$$

It would therefore appear that gases of the same molecular weight should obey the Mixture Rule with respect to viscosity.

While it is probable that the different velocities of constituent molecules in gas mixtures will affect the mean free path for the mixture, it must be remembered that gases of the same molecular weight will also have the same molecular velocity, and so the reasoning above is not affected.

INTRODUCTION TO EXPERIMENTAL.

(a) EXAMINATION OF LITERATURE.

In consideration of the theoretical proof of the behaviour of gas mixtures with respect to viscosity, an examination of records of gas mixtures in the literature was instituted, to see if the proof was borne out in practice.

It was found that, in general, gas mixtures of two gases of equal or nearly equal molecular weight obeyed the Mixture Rule, while in the case of mixtures where there was a large difference in the molecular weights of the constituent gases, the deviation was great.

Trautz and Melster(16) have examined binary mixtures of Nitrogen-Oxygen (28:32), Carbon Monoxide-Oxygen (28-32), Ethylene-Oxygen (28:32), Nitrogen-Ethylene (28:28), Carbon Monoxide-Ethylene (28:28), and Nitrogen-Carbon Monoxide (28:28), and have found that they give viscosity composition curves which are practically straight lines.

For Air-Ethylene (29 approx.:28) and Oxygen-Nitrogen (32:28), Landolt and Börnstein record values(17) which give practically straight line curves.

For Carbon Dioxide-Propane (44:44), Nitrous Oxide-Propane (44:44), Carbon Dioxide-Nitrous Oxide (44:44), Trautz and Kunz(18) give values which give almost straight line graphs.

Jung and Schmick(19) have found almost straight line viscosity-composition curves for Methane-Ammonia (16:17), Sulphur Dioxide+Carbon Dioxide (64:44), Sulphuretted Hydrogen-Air (34:29 approx.), Hydrogen Chloride-Air (36.5:29 approx.), Hydrogen Chloride-Carbon Dioxide (36.4:44) and Ammonia-Air (17:29 approx.)

On the other hand, mixtures of gases with Hydrogen always show a decided deviation from the values calculated from the Mixture Rule. In no case cited above does the ratio of the molecular weights reach the ratio 2:1. But with Hydrogen as one of the constituents of the mixture, ratios much greater than this are to be obtained, and so we find that the values given by Thomsen(20) for Carbon Dioxide-Hydrogen (44:2), Ammonia-Hydrogen (17:2), and Ethylene-Hydrogen (28:2) when plotted give curves which deviate markedly from the straight.

Similarly with mixtures of the inert gases and Hydrogen, the results given by Trautz and Ludewigs(21) for Argon-Hydrogen (40:2), by Nasini and Rossi(22) for

Helium-Neon (4:20) and Helium-Krypton (4:83), and by Gille(23) for Hydrogen-Helium (2:4) all deviate from the Mixture Rule markedly.

The difference between the two classes may be gathered from the two figures plotted from the results of Trautz and Kunz (Fig. 8) and from those of Trautz and Ludewigs, Nasini and Rossi and Gille (Fig. 9).

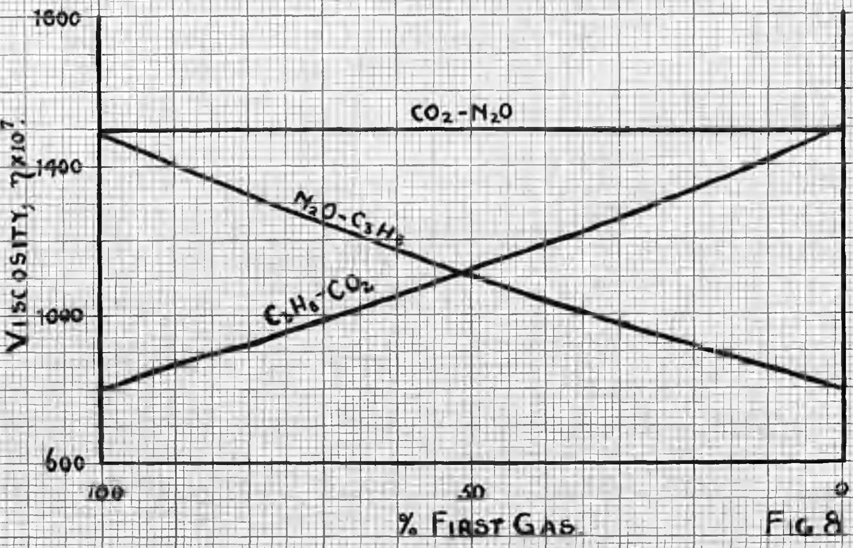

1600
1400
1000
600
Viscosity, $\eta \times 10^7$
CO_2-N_2O
N_2O-C_3H_8
C_3H_8-CO_2
100
50
0
% First Gas

Fig 8

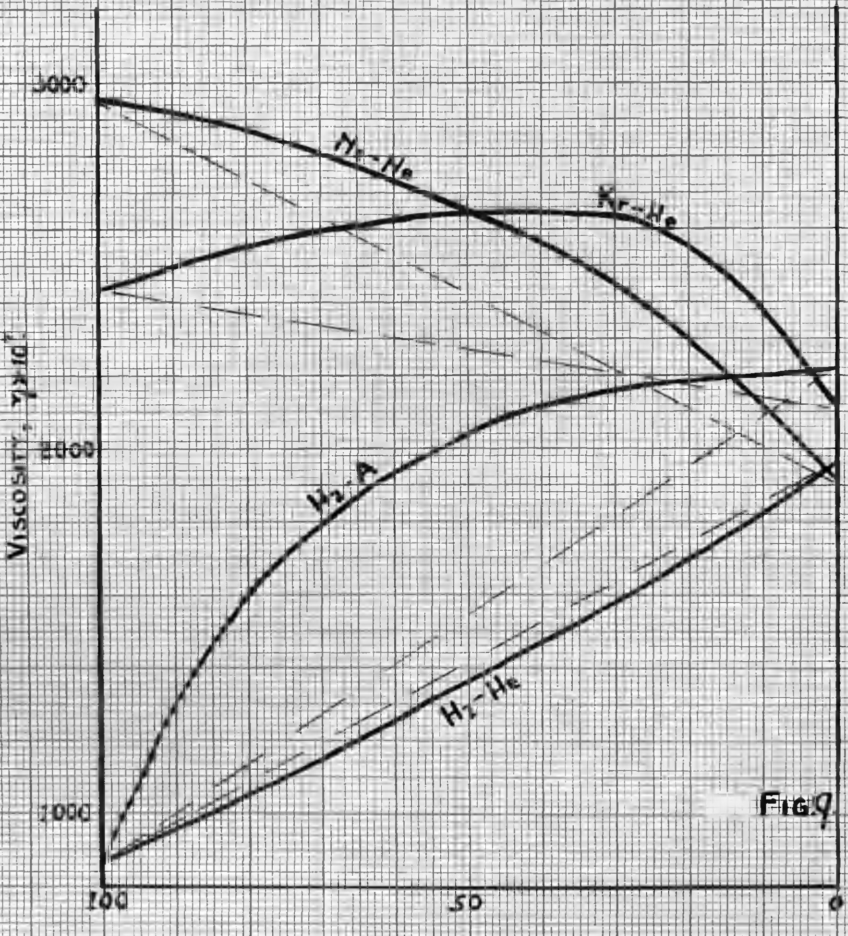

3000
2000
1000
Viscosity, $\eta \times 10^7$
Ne-He
Kr-He
H_2-A
H_2-He
100
50
0
% First Gas.

Fig. 9

(b) OUTLINE OF WORK.

Since a brief consideration of the problem will show that if there is an attraction between the molecules of the two mixed gases, there will be in all probability a very definite effect on the concordance of the viscosities with the Mixture Rule, this possibility of attraction was now examined.

It is, of course, extremely unlikely that there will be any attraction in the case of the gases quoted in the investigation illustrated by Fig. 9 above. But in other cases it is not so easy to specify when such an attraction exists. The best line of approach was therefore considered to be an examination, not of mixed gases, but rather of a mixture of a gas with a vapour. This is considered perfectly in order, for according to Meyer(24) vapours in most respects obey the laws of viscosity in the same way as gases.

If then, such mixtures, in which there is known to be a great attraction, while the molecular weights are in or about the same, are examined, it was thought that something could be learned regarding the part which attraction plays in the causation of deviation of the viscosity from the Mixture Rule, by comparison with such curves as those in Fig. 9, where no attraction is to be expected.

(i) Ammonia - Water Vapour.

A suitable mixture is that of Ammonia-Water Vapour, where the ratio of the molecular weights is 17:18, and the attraction is known to be appreciable, since this may be deduced from the results of Macfarlane and Wright(25), which show that very soluble gases show great attraction for the vapours of the liquids in which they are soluble.

This mixture was therefore investigated with regard to the change in viscosity with composition.

The results were somewhat unsatisfactory, owing to the fact that the Rankine Viscometer, as mentioned above (p.19), is unsuitable for work at low pressures, and at higher pressures only mixtures very rich in Ammonia could be obtained. All attempts to vary the composition by temperature control or otherwise failed to give any greater increase in the variation of the composition of the mixture.

(ii) Hydrogen Chloride - Methyl Alcohol Vapour.

Since there is an extremely strong attraction between Hydrochloric Acid Gas and Methyl Alcohol vapour(25), it would appear on first sight that this mixture is even more suitable than the previous one, the difference in molecular weights (36.5:32) being very little greater than before.

It was found on further investigation, however, that the variation in composition which could be obtained was extremely small. This was found to be due to the fact that an azeotropic mixture was formed in the same way as is found with Hydrogen Chloride-Water(26). The vapour pressure of Methyl Alcohol at 20°C. is 88.7 mm.(27), and the vapour pressures of the mixtures decreased from the pressure on the Methyl Alcohol side, and from atmospheric pressure on the Hydrogen Chloride side to reach a minimum. The consequence of this was that the vapour pressures of solutions of the gas in Methyl Alcohol were in many cases very low, whereas an essential for obtaining a large range of compositions for the mixture was a high vapour pressure.

(iii) Ammonia - Methyl Alcohol Vapour.

The next mixture investigated was Ammonia-Methyl Alcohol Vapour. This showed a fairly large attraction between the two constituents, although the difference in the molecular weights is somewhat greater (32:17).

Again the variations in composition were very small, but by using a variation of temperature control, a number a number of mixtures varying in composition over a small range were obtained.

(iv) Other Gases - Methyl Alcohol Vapour.

Since, however, the methods so far used showed that it was useless to hope for full curves for a range of gas-vapour mixtures, a number of gas-vapour mixtures with Methyl Alcohol Vapour as one constituent were examined. These were obtained by saturating the gas at a fixed temperature and pressure, and the compositions of the mixtures thus obtained enabled an idea of the deviation from the Mixture Rule to be obtained.

The results seem to show that both the amount of attraction between the constituents, and the ratio of their molecular weights play a considerable part in determining the deviation of the viscosity-composition from the Mixture Rule.

(v) Gases - Ether Vapour.

In order to extend the scope of this work, an attempt was made to carry out a similar investigation, substituting Ether Vapour for Methyl Alcohol Vapour. Ether was used because it was thought that, owing to its higher vapour pressure, a wider range of mixtures could be examined, or at least, mixtures containing a higher percentage of vapour.

However, this was abandoned on finding that, probably because the temperature control was insufficient to maintain the constant proportions of gas:vapour, consonant readings for the times of flow could not be obtained with mixtures which were prepared under similar conditions.

* * *

APPARATUS AND METHODS.

(a) VISCOMETERS.

The Rankine Apparatus for the determination of the viscosity of a gas depends in essence on a method of determining the time of flow of a gas under pressure through a very fine capillary.

The original apparatus, as used by Rankine(15), was of the type shown in Fig. 10. It consisted of a long narrow capillary, of diameter about 0.25 mm., joined at each end to a length of quill tubing with an internal diameter of about 3.5 mm. Two marks were etched at equal distances from the ends on the wide tubing. The capillary and the other limb were each about 45 to 50 cm. long, and the etched marks were 30 cm. apart. Two taps at either end of the apparatus enabled it to be filled with gas. A pellet of mercury was introduced into the wide arm, and the apparatus filled with the gas whose viscosity was required. It was necessary to have the wide tubing of such a diameter that the mercury pellet remained whole in it.

The whole apparatus was mounted on a wooden support which swivelled on a stand, so that the flow of the mercury pellet was started by reversing the support. A plumbline was attached to the stand to ensure that the apparatus was vertical.

The time of fall of the pellet of mercury between the two marks was noted, the direction of fall being the same for each observation, and the points of time where the top of the pellet of mercury passed the marks being those used for the observations.

The viscosity could then be calculated from the formula

$$\eta = \frac{\pi . p . r^4 . t}{8l . v}$$

where r = radius of capillary
p = difference in pressure on the two sides of the mercury
l = length of capillary
v = volume swept out by mercury
t = time of fall.

Rankine states that, while suitable for measuring viscosities at high and ordinary pressures, the apparatus was unsuited to determinations at low pressures.

It was found in this work that from pressures of about 150 mm. downwards, the fall of the mercury became very jerky, and in some cases the mercury even reversed its direction, and flowed up the tube if it was inclined at an angle of about 45°. There was also great risk of the pellet breaking up at low pressures, particles of it flying into the capillary.

Several modifications of the Rankine apparatus were used, which enabled the same pellet of mercury to be retained in a pocket provided while the apparatus was being filled with different gases, thus allowing the viscosity to be taken as proportional to the time of flow. The precaution also obviated any risk of the mercury coming into contact with tap grease, and so fouling the inside of the viscometer.

The apparatus was then calibrated against a standard, the viscosities of other gases and mixtures being found by simple proportion.

In one of the modifications (Fig. 12) the portion, A, of the apparatus was made entirely of the wide tubing, so that the length of capillary tubing, B, when fitted into place, was held tightly between the ends of A. The ends of both A and B were ground to make the joint tighter. Two tightly fitting pieces of rubber tubing were then drawn over the joints, and sealed thoroughly with Seccotine in order to make the joints airtight. Tests showed that, while not completely airtight, the pressure only rose a few mm. from 100 mm. in a few hours. The apparatus was easily taken apart for cleaning by soaking the joints with warm water. After re-sealing, it had, of course, to be re-calibrated against the standard.

A special modification (Fig. 14) was used for the Gas-Ether Vapour mixtures.

Since the possibility of ether vapour attacking the small amount of vaseline which greased the taps was great, the taps were completely replaced by metal valves as shown in Fig. 15.

The plungers of these valves were led into a seating of lead, and when screwed tight formed a seal which appeared, on testing, to be airtight, even at low pressures.

The valves were Seccotined on to the two side arms of the viscometer, $A\ A'$, which were both placed at an angle, which left room for a mercury pocket at each end of the viscometer. This proved a very satisfactory arrangement.

The details of the other modifications of the Rankine Apparatus may be gathered from the diagrams (Figs. 10-13).

Fig. 10.

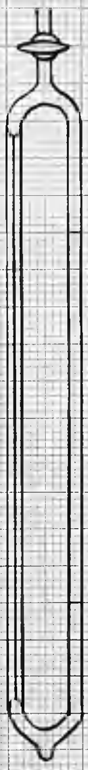


Fig. 11.

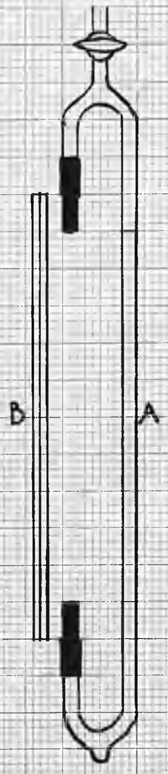


Fig. 12.

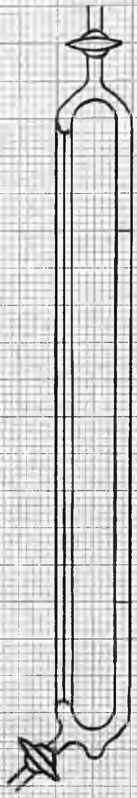


Fig. 13.

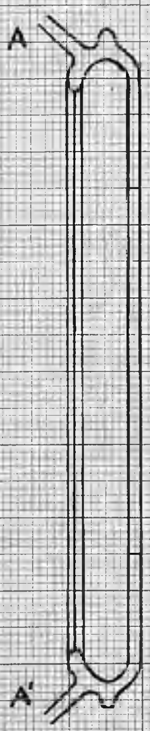
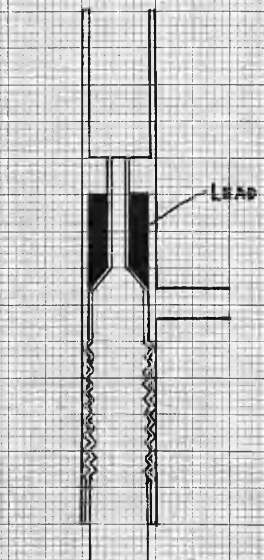


Fig. 14



(Enlarged)

Fig. 15.

(b) FILLING OF VISCOMETER.

The viscometer was filled by the following method, suitably modified for the different modifications of the Rankine Viscometer.

The mixture was set running slowly through the by-pass AB, (Fig. 18) and was then diverted through the viscometer. After the mixture had been passed through for some time, C was closed, and the apparatus evacuated through a filter pump. Tap B was then closed and C opened. After the head of the mixture was sufficient to overcome the back pressure caused by turning off the pump, that is, when it was considerably more than atmospheric, tap B was opened, and the mixture allowed to pass for some time longer. This was repeated for several times before finally closing off the viscometer taps at ordinary pressure.

Excess gas was retained by a trap.

This trap, which was used throughout this work where a soluble gas was being handled, warrants a special description.

It is recommended(28) for the absorption of water-soluble, noxious gases, and acts very efficiently for this purpose.

The gases are led into the chamber, A, (Fig. 20) in which a stream of water flows downwards into the large bottle, B. The level of the water in the bottle is maintained at a constant by the suction of a pump through the bent tube, C, and serves as well to act as a seal, to prevent the escape of the gas. The gas chamber must be of a sufficient capacity to prevent sucking back, a diameter of about 3 cm. and a length of about 25 cm. being satisfactory.

The apparatus for mixtures containing Ether Vapour was similar to that for the Methyl Alcohol Vapour mixtures, but all possible rubber connections were replaced by sealed glass joints, since ether is soluble in rubber. The viscometer used was, of course, the modification with the special metal valves (Figs. 14, 15).

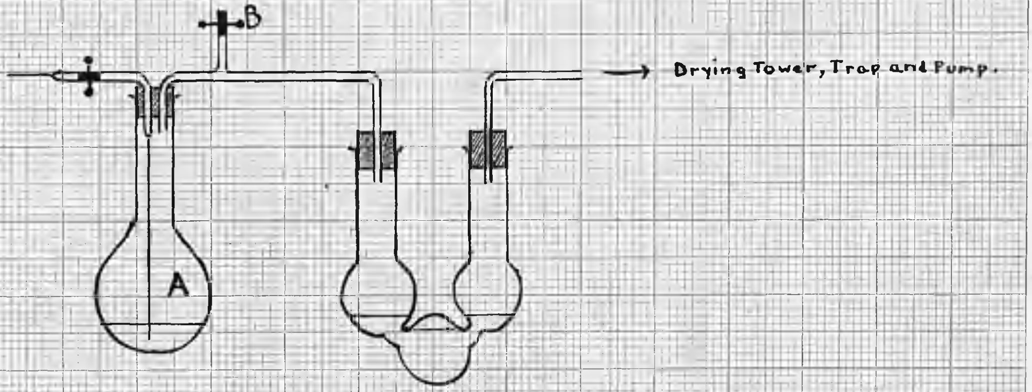


FIG. 16.

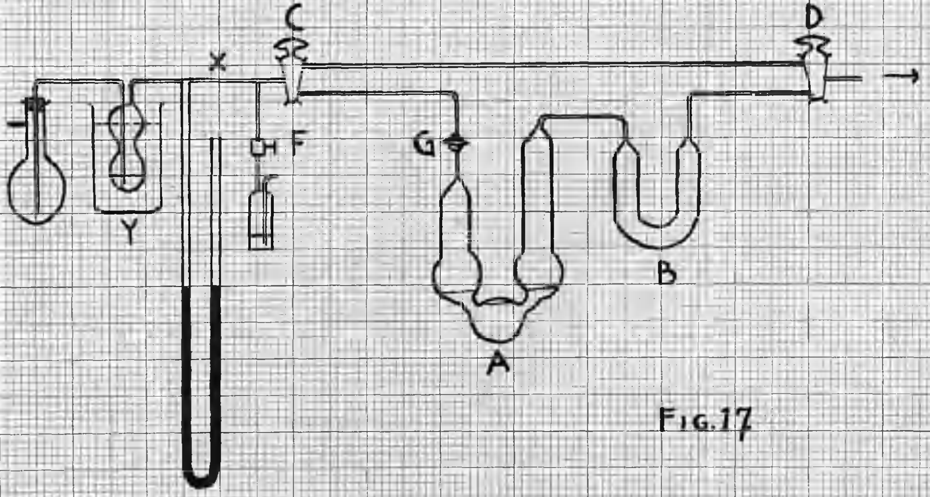


FIG. 17

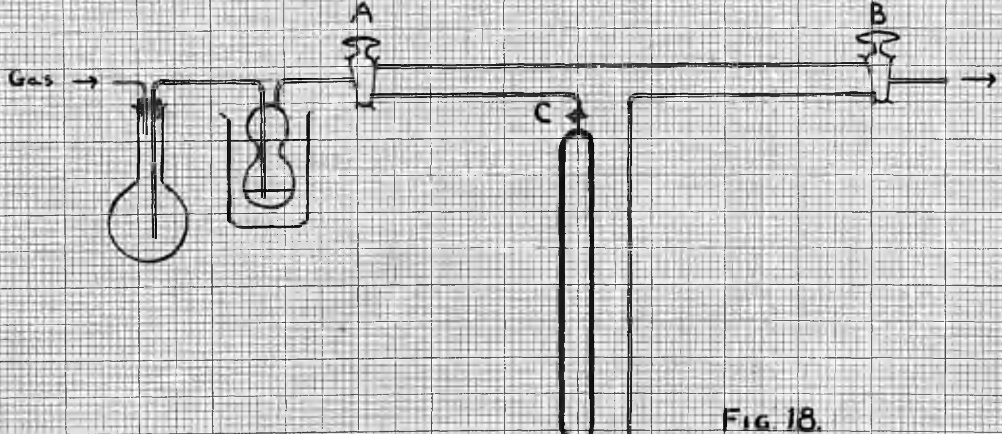


FIG. 18.

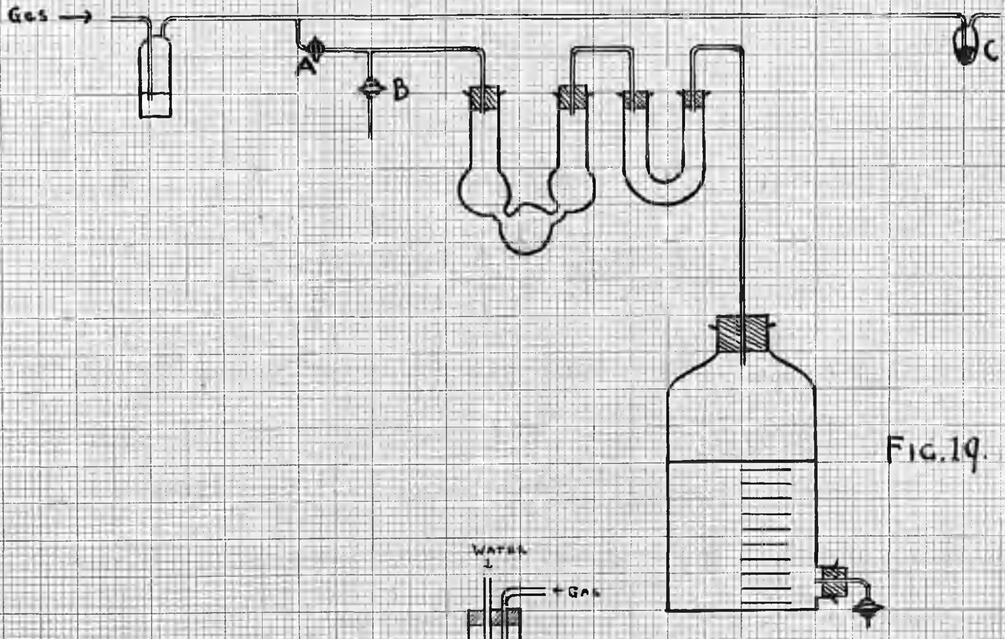


Fig. 19.

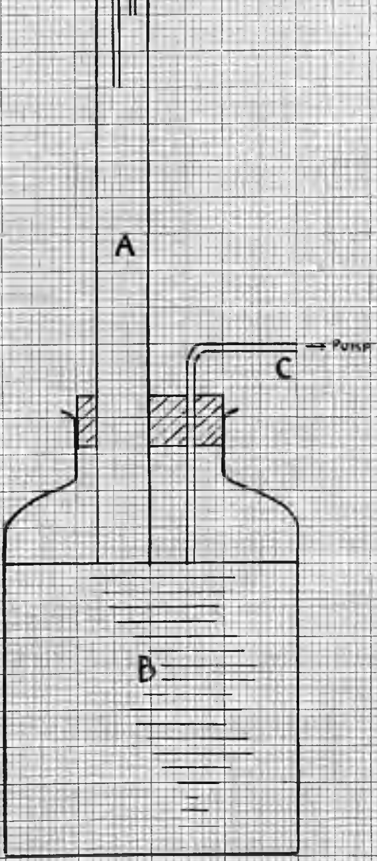


Fig. 20.

(e) METHODS OF ESTIMATING MIXTURES.

(i) Ammonia-Water Vapour.

In devising a method for the estimation of the composition of these mixtures, the main difficulty to contend with was the fact that efficient drying agents, such as concentrated Sulphuric Acid, also absorb Ammonia. It will be seen, conversely, that if, in any method which seeks to estimate the Ammonia and Water Vapour separately by weight, a drying agent which will not trap all the water is used, an error will creep in which will be doubled, as loss in percentage of Water Vapour will also be gain in percentage of Ammonia.

Experiments were made to determine the efficiency of Lime and Potassium Hydroxide as drying agents for the purpose.

Lime was found to be very inefficient, and while Potassium Hydroxide was somewhat more efficient, it was not nearly accurate for the purpose in view.

The mixture was therefore estimated by drawing a stream of air slowly through a solution of Ammonia in Water (Fig. 16), by which method a constant mixture of gas-vapour was carried over. This was passed into 5N Hydrochloric Acid standardised by means of Iceland Spar(29), which trapped the Ammonia. The amount of this was found by the addition of a known amount of standard alkali, and back titration. The amount of Ammonia-Water Vapour was found by the difference in weight of the flask A, before and after the experiment. From the results, the proportion of Ammonia to Water Vapour could be determined. The leak, B, was employed to allow the apparatus to fill slowly with air after a determination, so that the acid should not be sucked back when the pump was turned off.

The percentage composition was altered by changing the strength of the Ammonia solution used. Since the amount of loss in the solution was very small, there was a negligible change in composition during work on it.

(ii) Ammonia-Methyl Alcohol Vapour.

The apparatus is shown in Fig. 17. The trap, A, contains 10 cc. 5N Sulphuric Acid and a few drops of indicator (Methyl Red). The trap B, contains concentrated Sulphuric Acid to trap the Water Vapour which may come over from A. Both traps are weighed and then fitted into place, and connection is made through the by-pass CD.

The Ammonia is run till it is certain that the solution, E, is thoroughly saturated at the temperature of the bath (which must be below room temperature, to prevent the alcohol vapour from depositing on the walls of the viscometer while the viscosity is being measured.)

The pump is run all the time to maintain a steady stream of air from the metal leak, F, and to keep the pressure, as shown by the manometer, as near atmospheric as possible.

The tap, G, is then opened, C and D reversed, care being taken that the bubbling through A is not so rapid as to push any of the liquid into B. The flow of gas is run until the acid in A is near the neutral point. G is closed first, C and D quickly reversed, and the Ammonia Cylinder shut off. The apparatus is then disconnected at X, and a stream of air run through the apparatus for a short time to restore the air atmosphere inside the traps before reweighing. The percentage Ammonia is then calculated as before by the difference in weight, and titration of the standard acid.

This method appeared to give very satisfactory results, although it was discovered later that they were probably a little low in Ammonia content, as compared with the results obtained by another method for the mixture at 15°C. (p.43). However, any error was probably constant for the apparatus, since concordant results were obtained. The compositions were varied by changes in the temperature of the bath, Y, but it was found that this had a disappointingly small effect. The temperature range was from 17°C. to -10°C. It was impossible to carry the temperature much higher than this, since the Methyl Alcohol vapour would probably have condensed out on the walls of the viscometer when the viscosity determinations were being made, at 20°C.

(iii) Gas-Methyl Alcohol Vapour.

As a result of the small variation found with any one gas-vapour mixture, the viscosities of mixtures of various gases with Methyl Alcohol vapour were determined. All viscosity determinations were made, as before, at 20°C, and the solutions from which the mixtures were obtained were kept at 15°C. The gases used were such as to give as large a range as possible in the attraction between the gas and the vapour, being Air, Hydrogen Chloride, Sulphur Dioxide and Carbon Dioxide.

Determinations of the times of flow at 75 mm. pressure were also made (to correspond to the determination for Methyl Alcohol Vapour itself). Great trouble was experienced with the viscometer during these determinations, the tendency of the pellet of mercury to shoot out of control, or to break up without warning being very great. As a consequence, the viscometer was frequently put out of order by blocking of the capillary, necessitating frequent cleaning.

The apparatus for estimation of the mixtures is as shown in Fig. 19. The gas is passed under pressure into a bubbler containing Methyl Alcohol and maintained at 15°C., and is kept running through the weighed bubblers by means of an aspirator. The tap, A, regulates the amount taken by the aspirator, and the tap, B, is an air leak to prevent sucking back.

A mercury bubbler, C, is placed on an outlet branch, allowing the solution to become saturated before passing the mixture through the aspirated branch. The gas flow is regulated to keep this bubbling continuously, thus maintaining a sufficient pressure throughout the apparatus.

For Hydrogen Chloride-Methyl Alcohol vapour, the U-tubes contained (i) standard Sodium Hydroxide and Methyl Red, (ii) concentrated Sulphuric Acid, and the percentage composition was found by weighing and by allowing the hydroxide to become completely neutralised.

The same absorbents were used for Carbon Dioxide-

Methyl Alcohol Vapour.

For Ammonia-Methyl Alcohol Vapour the absorbents were standard Sulphuric Acid and Concentrated Sulphuric Acid.

For Sulphur Dioxide-Methyl Alcohol Vapour the indicator in the first bubbler was bleached, so that an indirect method of titration had to be used.

The mixture was passed through standard Sodium Hyrdoxide and then through concentrated Sulphuric Acid. The tube containing the alkali, which trapped all the Sulphur Dioxide, was then washed out into a dish, excess Barium Chloride added, precipitating the Sulphur Dioxide and liberating Hydrochloric Acid. The excess alkali was then back titrated with standard Hydrochloric Acid, using Methyl Orange.

For Air-Methyl Alcohol Vapour, the percentage composition was calculated from the vapour pressure of Methyl Alcohol, since no method of estimating the mixture accurately could be devised.

Since Landolt and Börnstein(30) only record the vapour pressure at 10°C. and 20°C., the vapour pressure was taken as half the logarithmic sum of these, at 15°C., 72.5 mm. The percentage composition was then taken as being the ratio of the partial pressures.

On account of the range of gases used, the percentage composition is expressed as molecular percentage instead of ordinary percentage by weight, in order to bring the various gases under as similar conditions as possible.

RESULTS.

(a) AMMONIA - WATER VAPOUR.

The times of flow for Ammonia, and for the Ammonia-Water Vapour mixtures were determined at 150 mm. pressure, on account of the fact that the lower of the two mixtures examined had a vapour pressure in this region at room temperature. A small variation in pressure had no appreciable effect on the time of flow.

There was a noticeable amount of slip in the fall of the pellet of mercury, and a consequent jerkiness in its motion, which led to inconsistencies in the times of flow. This was due, in part at least, to the reduced pressure within the viscometer. The inconsistencies were, however, surprisingly small.

All times of flow are the average of three determinations, varying by less than 1%.

The temperature at which the times of flow were observed was 20°C., maintained in a constant temperature room which was regulated by means of an electrically controlled heater.

Mixture No.	% Ammonia	Time of flow(secs.)
1	94.1	94.1
2	96.7	102.9

In the literature(31) the viscosity of Ammonia is given as $\eta_{20^\circ} \times 10^7 = 1080$, and that for Water Vapour is given as $\eta_{20^\circ} \times 10^7 = 975$.

Using the value for Ammonia as a basis of calculation, the results become as follows:-

% Ammonia	$\eta_{20^\circ} \times 10^7$	
	Observed	Calculated.
100.0	1080	---
96.7	1005	1076.6
94.1	854	1073.8
0.0	975	---

(b) AMMONIA - METHYL ALCOHOL VAPOUR.

The estimation of these mixtures gave the following results:-

Mixture No.	Temperature	% Ammonia
1	17	86.9
2	11	87.8
3	5	88.53
4	0	89.5
5	-5	90.36
6	-10	90.95

As can be seen, the Ammonia content of the mixtures only varied over about 4%. The graph plotted from these results (Fig. 21) enables the composition of a mixture, at any temperature over the range, to be determined.

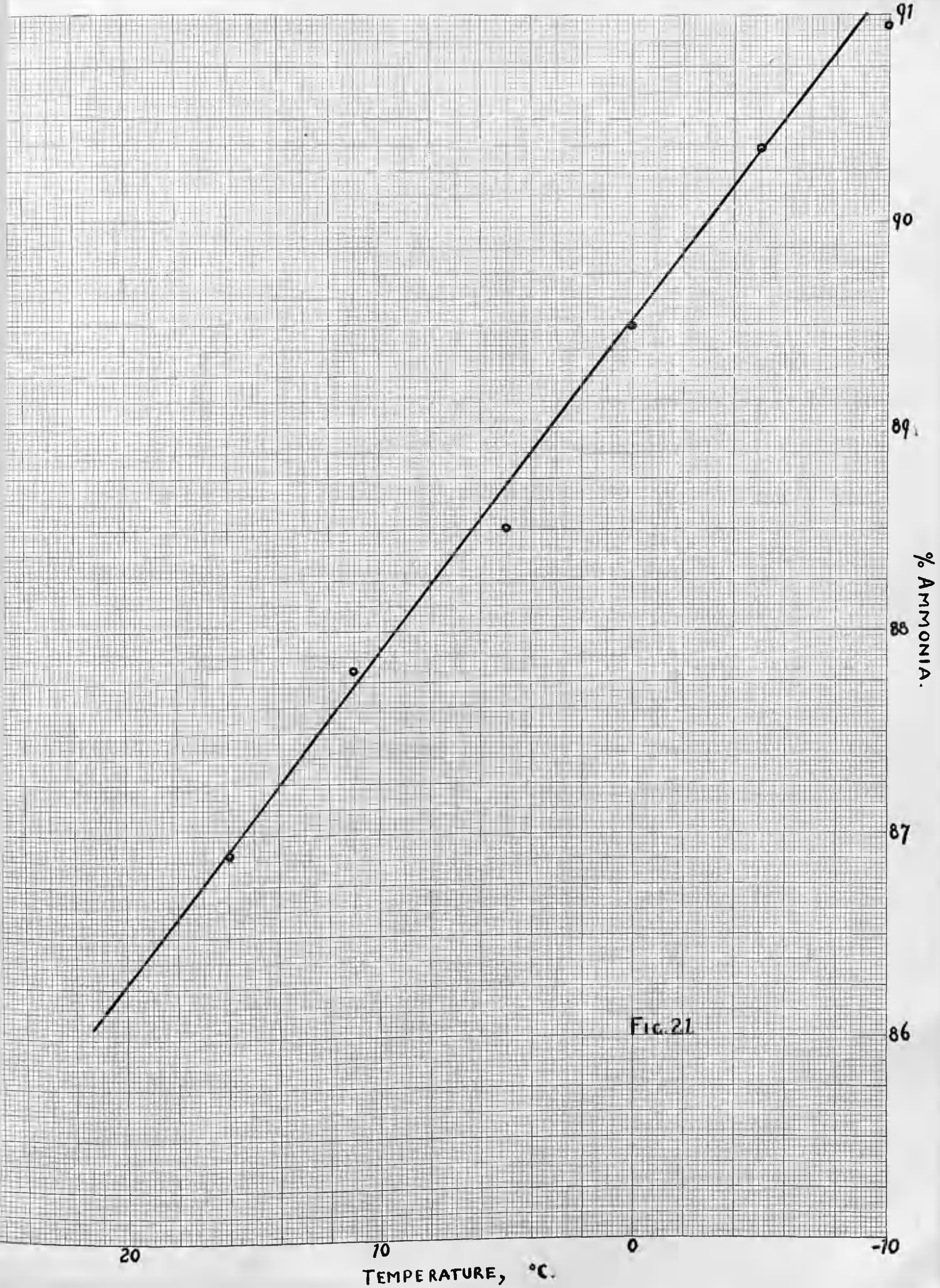


FIG. 21

For the viscosities, air was taken to be the standard, the time of flow for dry air being 313.9 secs. The results were all reduced to the standard of Air = 100.

Mixture No.	Temp.	% Ammonia	Time	η (Air = 100)	
				Obs.	Calc.
1	18.5	86.5	157.8	50.310	51.67
2	16	86.9	158.6	50.565	51.69
3	14	87.2	159.6	50.884	51.71
4	7.5	88.3	160.1	50.960	51.77
5	Pure NH_3	100	164.4	52.414	---

An exhaustive search of the literature showed that the viscosity of Methyl Alcohol Vapour over a range of temperatures had evidently not been determined, the only viscosity measurement available being that at 66.8°C.(31).

It is probable that the value obtained here, determined at 75 mm. pressure, is only approximate, and, as is shown by the determinations for other gases later, there seems to be no regular relation between the viscosities at low and atmospheric pressures, when measured by the Rankine Viscometer.

Time for air	324.7 secs.
Time for Methyl Alcohol Vapour	152.26 secs.
Viscosity (Air = 100)	46.903

(c) GASES - METHYL ALCOHOL VAPOUR.

The full series of determinations for all these gas-vapour mixtures is given in the following table for easy comparison.

Gas or Mixture	Pressure	Time (secs.)	Time for Air	η (Air = 100)	% CH_3OH, 15°C.	η, Calc.	Deviation
Air	Atmos.	265.1	265.1	100	----		
CH_3OH	88 mm.	152.25	324.7	46.903	100		
Air-CH_3OH	Atmos.	247.2	265.1	93.550	9.5	94.956	1.406
Air-CH_3OH	88 mm.	243.1					
NH_3	Atmos.	127.5	243.25	52.414	----		
NH_3	88 mm.	124.6					
NH_3-CH_3OH	Atmos.	158.7	243.25	50.724	6.4	52.062	1.338
NH_3-CH_3OH	88 mm.	155.4					
CO_2	Atmos	225.25	283.3	79.517	----		
CO_2	88 mm.	223.0					
CO_2CH_3OH	Atmos	215.6	283.3	76.103	9.2	76.518	0.415
CO_2-CH_3OH	88 mm.	213.4					
SO_2	Atmos.	181.8	268.4	67.735	----		
SO_2	88 mm.	180.0					
SO_2-CH_3OH	Atmos.	183.6	268.4	68.405	5.8	66.529	1.876
SO_2-CH_3OH	88 mm.	180.2					
HCl	Atmos.	233.1	297.7	78.300	----		
HCl	88 mm.	229.4					
HCl-CH_3OH	Atmos.	307.8	315.2	97.398	2.2	71.397	26.001
HCl-CH_3OH	88 mm.	300.2					

The very small percentage of vapour is a direct result of the solubility of the gas in the liquid whose vapour is being used. The vapour pressure of the liquid is lowered by the dissolved gas, so that the partial pressure of the vapour and its percentage afe correspondingly decreased. The effects of this phenomenon are evident throughout this research.

(d) GAS - ETHER VAPOUR.

As mentioned earlier, this part of the work was finally abandoned, owing to the impossibility of getting constant times of flow for the mixtures.

The results below will show the variation, and although the investigation was extended to the whole range of gases previously examined, in the hope that with smaller percentage mixtures more constant readings would be obtained, it will be seen that the variation was too great for any reliance to be placed on the results.

Mixture	Times of flow (secs.)
Air-Ether Vapour	162.4, 165.5, 169.1
Ammonia-Ether Vapour	131.8, 135.8, 137.5
Sulphur Dioxide-Ether Vapour	179.5, 166.5, 170.1
Carbon Dioxide-Ether Vapour	160.9, 153.2, 154.1
Hydrogen Chloride-Ether Vapour	208.6, 202.8, 207.7

DISCUSSION.

The main fact which emerges on examination of the results obtained in these viscosity determinations is that the ratio of the molecular weights is not the only factor which affects the deviation of the viscosity-composition in such mixtures from the Mixture Rule.

If we first examine the viscosities of the Ammonia-Water Vapour mixtures, where there is a ratio between the molecular weights of 17:18, we see, even from the few mixtures examined, that without a doubt they are different in character from the Nitrogen-Ammonia mixtures and others quoted in the Introduction. In the latter gas mixtures, of course, it is difficult to find any other factor which might affect the viscosity, and so it is not surprising to find that the curves they give are practically straight line graphs.

On the other hand, this is definitely not the case with Ammonia-Water Vapour. Quite a large deviation is to be found, and this leads us to look for some other factor. The attraction between Ammonia and Water Vapour, which may very possibly be the sign of the formation of a loose molecular compound, seems to be the most likely factor in producing the deviation.

When we pass on to a consideration of the Ammonia-Methyl Alcohol Vapour mixtures, we are again struck by the large deviation from the Mixture Rule. But the deviation here is less than in the previous case, though the molecular weight difference is greater. This fact substantiates the view that the molecular weight ratio is not the only factor producing deviation, and that the attraction has to be taken into account.

This view is still further borne out when we consider the various other Gas-Methyl Alcohol Vapour mixtures. Here we see that in the case of Hydrogen Chloride-Methyl Alcohol Vapour, where the difference in molecular weights is not very great (35.5:32), but the attraction is extremely great, the deviation is also very great. Conversely, in the case of Carbon-Dioxide-Methyl Alcohol Vapour, where the difference between the molecular weights is much greater (44:32), but the attraction is much smaller, the deviation is very small.

The relation between deviation and the two properties of attraction and molecular weight ratio is approximately, but somewhat strikingly demonstrated by comparing the deviations with these properties, as in the following table.

Gas	Mol. Wt.	Deviation	$\frac{\text{Mol. Wt.}}{CH_3OH}$	Attraction	M.A
Air	29	1.406	0.9	----	----
CO_2	44	0.415	1.4	0.71	0.99
NH_3	17	1.338	0.5	4.17	2.08
SO_2	64	1.876	2.0	1.40	2.8
HCl	35.5	26.001	1.1	26.0	28.6

It will be seen from this that there is quite an appreciable similarity between the relation M×A, where M is the molecular weight ratio and A is the attraction given by Macfarlane and Wright$^{(25)}$, and the deviation. As said before, this method must of necessity be very approximate, but it would nevertheless appear to show that there is a very strong basis for the belief that the two main factors affecting the viscosity-composition relation, each of which is capable of causing deviation from the Mixture Rule, are ratio of molecular weights, and attraction between the constituents of the mixture, the latter of which may, in some of the cases examined above, and almost certainly does in the case of the Hydrogen Chloride-Methyl Alcohol Vapour, amount to a loose kind of molecular compound formation.

It would also appear from the results obtained in this investigation, that of the two properties that of the attraction between the gas-vapour is capable of having the most powerful effect.

CONCLUSION.

Experimental results show that viscosities of gas-vapour mixtures often show a deviation in the viscosity-composition values from those calculated from the Mixture Rule. While in gas mixtures the deviations noted would appear to be due to difference in the molecular weights of the constituents, in gas-vapour mixtures a second factor, the attraction, or possibly the formation of loose molecular compounds between the constituents also enters in, and would appear to have a greater effect accordingly than has the molecular weight ratio on the deviations.

This is shown approximately in the case of mixtures of several gases with Methyl Alcohol Vapour, which proved to be the most suitable for this investigation of those mixtures examined.

PART III.

VISCOSITIES OF EMULSIONS.

INTRODUCTION TO PART III.

An emulsion(32) is generally considered to be a system containing two liquid phases, one of which is dispersed as globules in the other. The liquid phase which is broken up into globules is known as the disperse phase, while the other is known as the continuous phase. The two liquids must be almost, or quite immiscible.

For two liquids, say water and an oil, two types of emulsion are theoretically possible, one where the oil is dispersed in the water, and one where water is dispersed in the oil. It is found that when two pure liquids such as Benzene and Water are agitated together, an emulsion is produced temporarily, but as soon as the emulsion is allowed to stand at rest, the disperse phase coalesces, and the emulsion becomes two distinct layers of liquid again. Besides the two liquids, a third substance known as an emulsifier is necessary to produce other than very dilute lasting emulsions. On the nature of this emulsifier, which may vary greatly, it is found that the type of the emulsion depends, that is, whether it will be oil-in-water or water-in-oil in type. The two theoretical types do not in general exist for any two liquids with any one emulsifier.

Sodium Oleate, a soap which is water soluble and colloidal, is an excellent emulsifier for emulsions of Benzene-in-Water. On the other hand, Magnesium Oleate, which is practically insoluble in water, promotes Benzene-Water emulsions of the water-in-oil type. Finely divided solids of many different kinds, such as Carbon, Lime, the basic sulphates of Copper or Iron, may also act efficiently as emulsifiers, the type depending on the emulsifier.

Emulsions will break down immediately if the emulsifier is destroyed. For example, if an acid, or any sodium salt, is added to an emulsion in which a soap is the emulsifier, the emulsion cracks. Alcohol, or any liquid which dissolves both phases breaks an emulsion.

ACTION OF EMULSIFIER.

Harkins, Davies and Clark(33) concluded that the type of emulsion promoted by an oleate is very closely connected with the number of oleate radicles which it contains, and that the stability of emulsion globules appeared to be brought about by the orientation of molecules of emulsifier at the surface between the globules and the continuous phase. According to their theory, the molecules of emulsifier orient themselves so that the polar groups are in the water phase, and the non-polar groups are in the oil phase. If the emulsifier is a monovalent metallic oleate, the surface of the globules is thus curved to form an oil-in-water emulsion. If it is a divalent oleate, the globules are made of the water phase. This theory obviously cannot be applied to solid emulsifiers. It has been criticised by Stamm(34) on the grounds that it is only justifiable if the emulsifier molecules are packed together, and Stamm's work would seem to show that this is not the case.

Finkle, Draper and Hildebrand(35) attempt to explain the action of solid emulsifiers such as Carbon, by saying that if the emulsifier is wet by one liquid more than the other in an emulsion, it will be drawn more largely into that liquid. If, then, sufficient particles are present to cover the liquid-liquid interface completely, the tendency to contract should cause it to bend in such a way as to become concave to the more poorly wetting liquid, thus making it the disperse phase. This theory, however, can only be applied to solid emulsifiers.

The action of the emulsifier has been suggested by Harkins and Zollmann[36] to be due to the lowering of the interfacial tension between say Benzene and Water to a very great extent, as is found with the Sodium Oleate. This theory, like the two previous ones, does not seem to have a general application.

PHASE VOLUME THEORY.

Emulsions prepared by shaking generally cream after standing for a short time. The globules tend to pack as closely as possible, giving a sharp boundary between the cream and the continuous phase which is thus left free.

Emulsions which contain more than about 74% by volume of the disperse phase do not cream, even after long standing.

Now it can be shown mathematically that in a collection of closely packed spheres of uniform size, whatever that size may be, the volume of the spheres is 74.048% of the total volume of the mass. Consideration of this fact led Ostwald[37,38] to formulate the Phase Volume Theory of emulsions, which postulates that an emulsion of one liquid in another is only possible if the volume concentration of the disperse phase is less than 74%. But Pickering(39) has prepared very concentrated emulsions, containing 99% of disperse phase by volume. Pickering pointed out that in an emulsion the spheres are not uniform, and that therefore there is no reason why the volume of the disperse phase should have any fixed value.

While Ostwald's theory, in the form put forward by him, is untenable, more recently Parke(40) has shown that on homogenisation, a process which consists in forcing an emulsion through a very fine jet, and thus breaking up the globules to a uniform size, an emulsion containing more than 74% by volume of disperse phase will break, giving rise to a new emulsion containing approximately 74% of disperse phase. In this resultant emulsion, which is very stable, the globules are found on examination to be of almost uniform size.

VISCOSITY OF EMULSIONS.

Very little work has been done on the quantitative determination of viscosity in emulsions. Viscosity is known to increase rapidly with increase of the volume of the disperse phase(41).

Hatschek(42) has deduced the formula

$$\eta = \frac{\sqrt[3]{A}}{\sqrt{A} - 1}$$

where A is the ratio $\frac{\text{Total volume of emulsion}}{\text{Volume of disperse phase}}$.

This formula is said only to hold when the amount of disperse phase is greater than 50%. It is to be criticised, however, on several grounds. It suggests that an emulsion on homogenisation would have the same viscosity, since there is no factor involving the radius of the spheres. But homogenisation very greatly(43) increases the viscosity, at least, when the amount of emulsifier is large. Neither is there a term in Hatschek's formula for the amount of emulsifier.

Joshi claims that the concentration of the emulsifier appears to have no effect on the viscosity of the emulsion(44). The work described here shows this statement to be inaccurate.

That this was so was first noticed by Parke(45) in his investigations on the relation between viscosity and the volume of disperse phase. It was in order to determine quantitatively the amount of change in the viscosity that this work was first undertaken.

EMULSION TYPE.

When experimenting in order to investigate the action of the emulsifier, after data had been obtained for the viscosity changes, an important phenomenon was noticed, a reversal in type dissimilar to any yet reported in the literature, which led to the investigations described in Part IV of this thesis.

In general, one emulsifier will only stabilise one type of emulsion. It has been found, however,(46) that by the addition of electrolytes or emulsifiers which promote the opposite type of emulsion, the type can be reversed. The amount which it is necessary to add depends on the amount of emulsifier present, and the amount of disperse phase.

In reversals of the above kind, it is useful to be able to determine the point where the emulsion changes over. There are three recognised methods of determining the type of an emulsion, all three dependent on the different properties of the two phases.

1. Indicator Method. This makes use of the difference in solvent power of the two phases. If an oil-soluble, water-insoluble dye is sprinkled on the surface of the emulsion, it will gradually spread through the emulsion if the oil is the continuous phase, but if water is the continuous phase, the dye is confined to those globules with which it comes directly in contact.

2. Drop Dilution Method. If some of the contin-

uous phase of an emulsion is added to it, the emulsion will become more dilute, but if the disperse phase is added, it can be seen moving through the emulsion, bounded by the continuous phase.

3. Electrical Conductance Method. This is the most reliable and most delicate test. An oil-in-water emulsion will show an electrical conductance, particularly when the continuous phase contains small quantities of electrolyte, as when Sodium Oleate is the emulsifier. On the other hand, a water-in-oil emulsion will not conduct electricity.

APPARATUS.

(a) VISCOMETERS.

The Viscometers used to determine the viscosities of the emulsions investigated were a set of four Standard Ostwald U-Tube Viscometers (Fig. 22), made according to the specifications laid down by the British Engineering Standards Association(47). These viscometers are such that, within a degree of accuracy of 0.5%, and above the minimum viscosity for which the instrument is designed, a single calibration is sufficient to give the constant of the Viscometer.

The Viscometers were calibrated by means of air-free distilled water, 40% sucrose solution, 60% sucrose solution and castor oil. All viscosities were determined in a thermostat regulated to 20°C. The dry clean viscometer was placed in the thermostat and filled to the marks from a bottle of the liquid which had been allowed to come to 20°C. by immersion in the thermostat for a period varying from ten minutes to half an hour, according to the viscosity. The liquid was allowed to sit for a short time longer in the viscometer to permit currents in it to settle, and the time of flow was then

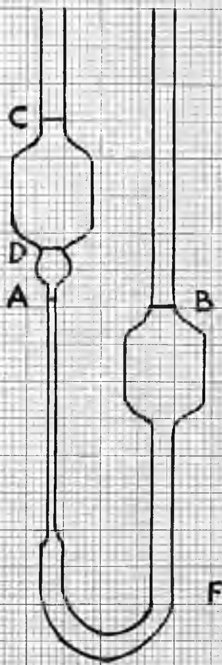


FIG. 22.

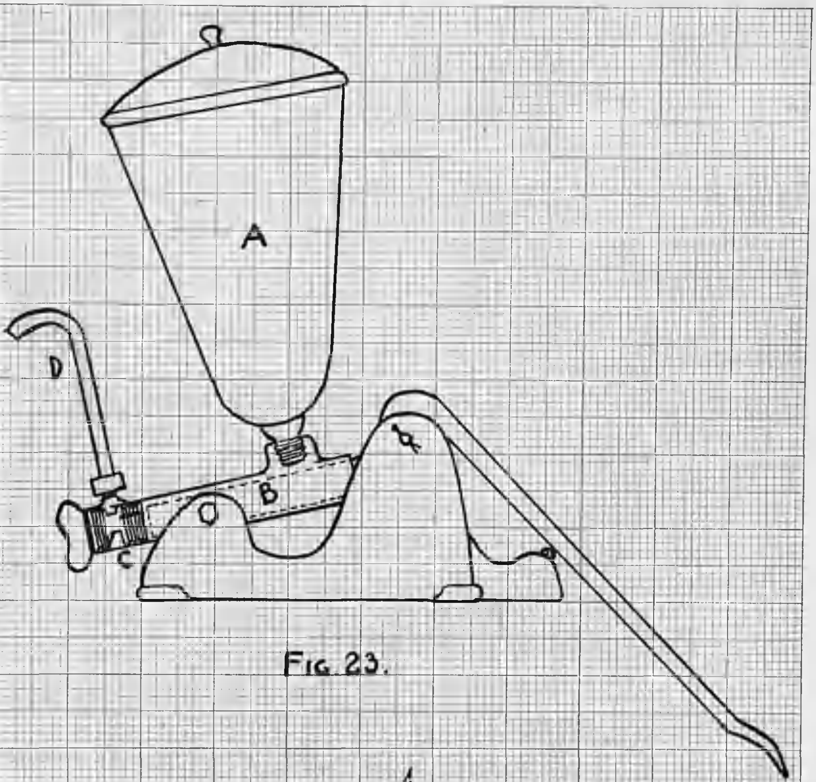


FIG. 23.

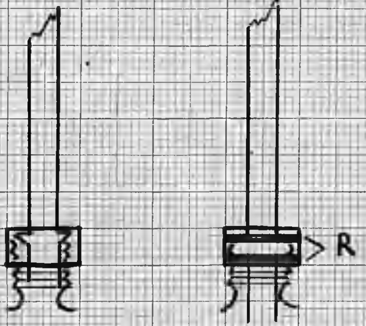


FIG. 24.

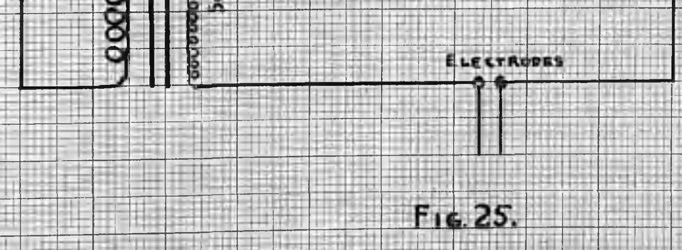


FIG. 25.

determined. Each reading is the average of three times of flow varying less than 1%, as laid down in the regulations. The constants for the viscometers were then determined through the formula

$$\eta = K\rho t$$

Viscometer Number	Liquid	Viscosity	Time	K
1	Water	1.0087	106.90	0.00945
2	Sucrose ρ1.17336	6.106	88.88	0.05850
3	Sucrose ρ1.28342	55.74	147.93	0.29359
4	Castor Oil		4027.1 (3) 174.4 (4)	6.594

(b) HOMOGENISER.

The homogeniser used throughout was a Pentecrème Hand Homogeniser (Fig. 23).

The emulsion to be homogenised is placed in the container, A, and is forced by the strokes of the piston, B, through the extremely fine apertures in the screw, C, out through the delivery tube, D.

The homogeniser could be taken apart easily for the purpose of cleaning, and all parts were readily accessible for this except the delivery tube, D. Since it was found that the action of Oleic Acid and Sodium Hydroxide on the metal formed traces of a blue compound, which was presumably Copper Oleate, formed from Copper Hydroxide, when allowed to remain in contact with the metal for any length of time, the delivery tube, as being the most likely part to be attacked in this way, was replaced by a glass delivery tube (Fig. 24). This delivery tube was seated as the original tube had been, but as it was impossible to screw it down tightly, it was packed in the seating by means of two small cork rings, R, and formed a reasonably tight joint.

(c) ELECTRIC TYPE DETERMINATOR.

The apparatus used for the Electrical Conductance method of type determination (p. 61) was similar to that used by Parke(48), with the substitution of headphones for the Loudspeaker (Fig. 25.)

Normally a faint note is heard in the headphones, but when the electrodes are immersed in a conducting medium, the note becomes very loud.

For the same reason as in the case of the homogeniser, copper electrodes could not be used, and platinum electrodes sealed into glass tubes were employed instead.

EXPERIMENTAL.

(a) VISCOSITY DETERMINATIONS.

As has been shown in the introduction, it was noticed that if the amount of emulsifier in a Benzene-Water-Sodium Oleate emulsion were varied, the viscosity varied markedly, and the first investigation undertaken was in connection with this phenomenon (p. 59).

Since the relation of about 74% disperse phase and 26% continuous phase by volume is, according to the Ostwald Phase Volume Theory, and the later work of Parke, the most suitable proportion to use, this proportion was maintained in the emulsions examined.

The emulsions were, of course, all oil-in-water emulsions.

They were prepared by adding the constituents in the order Water, Benzene, Oleic Acid, the equivalent amount of Sodium Hydroxide. In all cases, as much uniformity as possible was maintained in the preparation of the emulsions. Emulsification was produced by means of intermittent hand shaking, as recommended by Briggs(49), with an endeavour to make the amount of shaking identical for each emulsion. The emulsions were then allowed to stand for several days before the viscosities were determined, for Parke(45) has found that the viscosities of both freshly prepared and freshly homogenised emulsions changes for the first few days, until they reach a constant figure for any emulsion about the fourth day.

Series A_1 was composed as follows:-

No.	Oleic Acid Grs.	NaOH, N/1 Ccs.	Water Ccs.	Benzene Ccs.	Na Oleate Grs./200Ccs.
1	0.2319	0.83	51.18	148	0.25
2	0.4638	1.64	50.36	148	0.50
3	0.6957	2.46	49.54	148	0.75
4	0.9277	3.28	48.72	148	1.00
5	1.1595	4.10	47.90	148	1.25
6	1.3914	4.92	47.08	148	1.50
7	1.6233	5.74	46.26	148	1.75
8	1.8552	6.56	45.44	148	2.00
9	2.0971	7.38	44.62	148	2.25
10	2.3190	8.20	43.80	148	2.50
11	2.5509	9.02	42.98	148	2.75
12	2.7828	9.84	42.16	148	3.00
13	3.0147	10.66	41.34	148	3.25
14	3.2466	11.48	40.52	148	3.50
15	3.4785	12.30	39.70	148	3.75
16	3.7104	13.12	38.88	148	4.00
17	3.9423	13.94	38.06	148	4.25
18	4.1742	14.76	37.24	148	4.50
19	4.4061	15.58	36.42	148	4.75
20	4.6380	16.40	35.60	148	5.00

It was noticed in this series when made up, that there was a large amount of creaming, decreasing from No.1 to No. 20, in which the amount was comparatively small.

Before the determination of the viscosities, the bottle containing an emulsion was immersed in the thermostat for half an hour. It was then turned end over end slowly five times, to eliminate the effects of creaming. It will easily be understood that the viscosities had to be determined as soon as possible after the emulsion had been placed in the viscometer, in order that creaming should have as little effect as possible.

The viscosities for this series are tabulated below. Times, T, are given in seconds. Viscosities, η, are given in centipoises.

Number	Viscometer	T	ρ	η
1	3	147.8	0.9048	39.261
2	3	127.9	0.9098	34.163
3	3	160.2	0.9124	42.887
4	3	175.4	0.9137	47.051
5	3	191.9	0.9150	51.573
6	3	222.4	0.9164	59.835
7	3	279.1	0.9177	75.197
8	3	252.4	0.9190	68.104
9	3	451.5	0.9203	120.20
10	3	410.5	0.9217	111.07
11	3	497.9	0.9233	134.97
12	3	579.3	0.9243	157.05
13	3	645.4	0.9257	175.40
14	3	702.9	0.9270	191.29
15	3	537.8	0.9283	146.57
16	3	616.5	0.9296	168.26
17	3	635.3	0.9309	173.62
18	3	654.2	0.9323	179.55
19	3	702.0	0.9336	192.40
20	3	782.5	0.9354	214.89

As can be seen from these results, the curve of Viscosity plotted against Weight of Emulsifier (Fig. 26), while very similar in the general increase in viscosity to the curves found by Parke and Graham(41) for their viscosity-disperse phase concentration values, yet has a num-

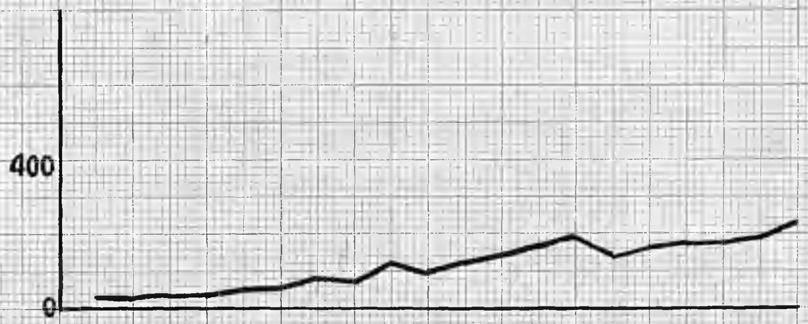


Fig. 26.

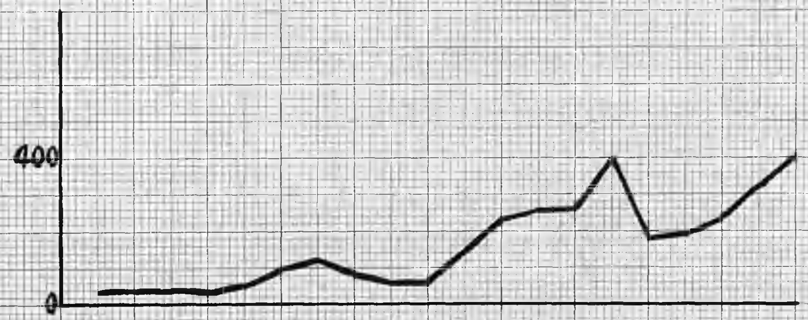


Fig. 27

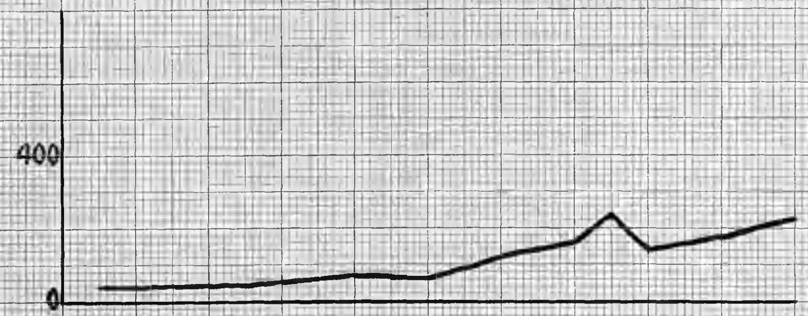


Fig. 28

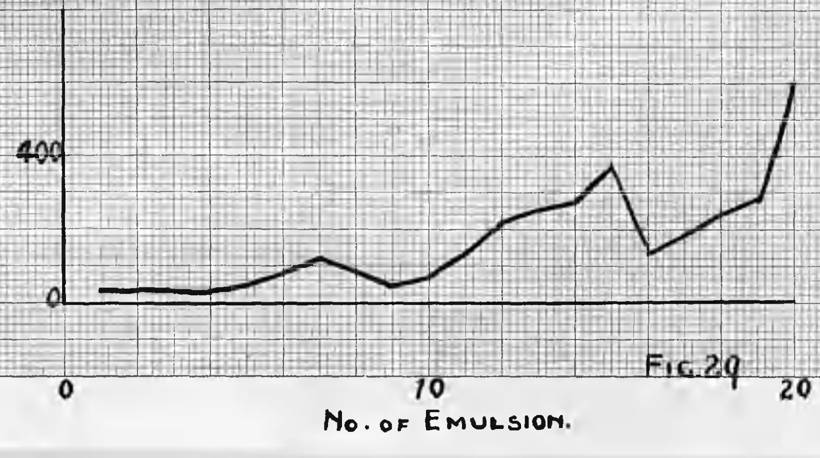


Fig. 29

ber of very marked irregularities for which it was very difficult to account at this stage. The problem was left over for the moment, and the emulsions homogenised.

By homogenisation, the character of the emulsions was changed somewhat. They appeared much thicker, expecially in the higher members of the series, and there was no sign of creaming taking place, except in one or two of the first members of the series, where the tendency was very slight.

Each emulsion was passed through the homogeniser five times, as recommended by Parke(40), and after being allowed to sit for a few days, the viscosities were determined.

Number	Viscometer	T	η
1	3	200.1	53.15
2	3	139.3	37.20
3	3	137.4	36.81
4	3	157.3	42.18
5	3	193.2	51.89
6	3	242.4	65.22
7	3	284.1	76.54
8	3	330.1	89.07
9	3	467.8	126.40
10	3	560.9	151.75
11	3	918.4	248.93
12	4	54.7	333.30
13	4	85.9	524.45
14	4	183.1	1119.5
15	4	245.9	1505.3
16	4	315.4	1933.6
17	4	376.8	2313.0
18	4	913.3	5614.7

It will be seen by the curve plotted from these figures (Fig. 30) that, with the exception of one small

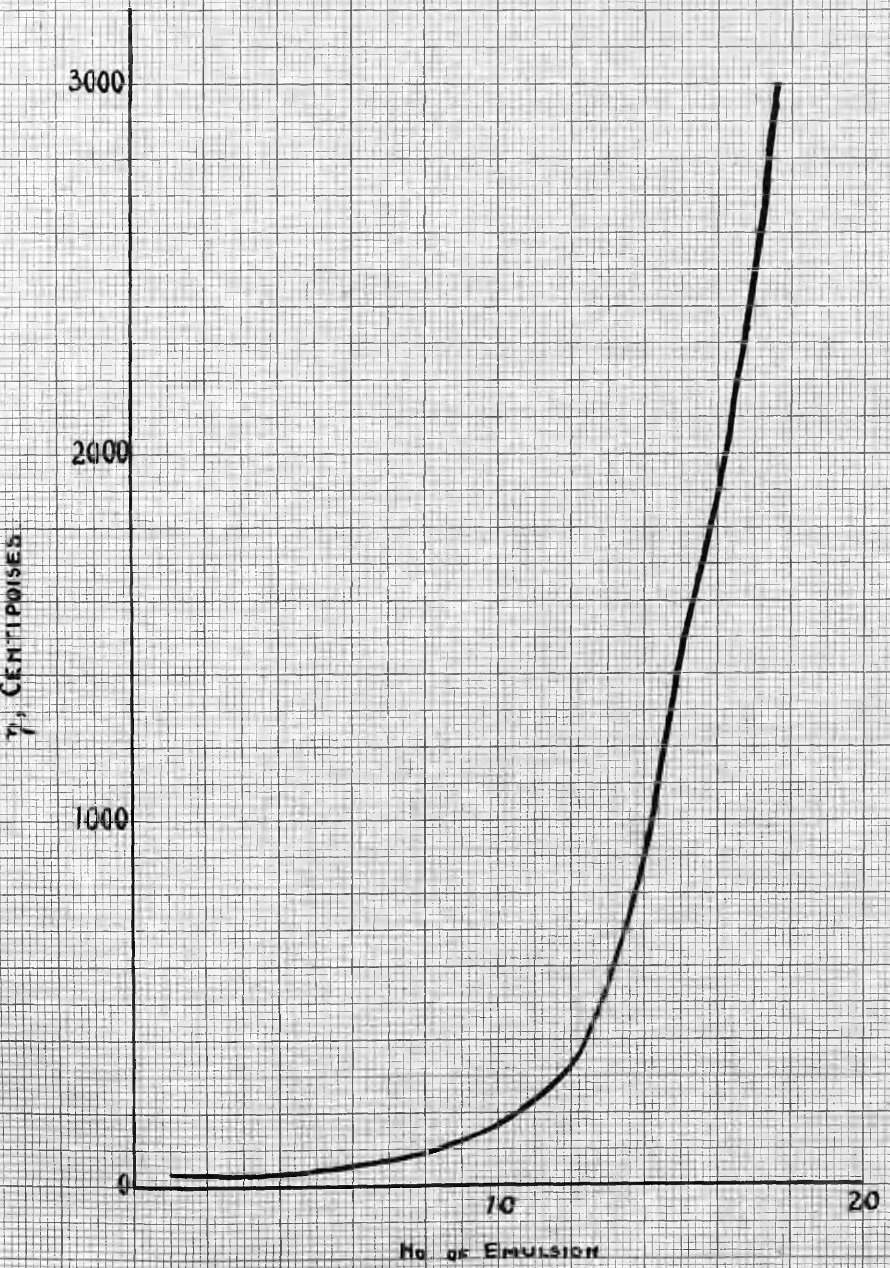


Fig. 30.

drop in the curve from No.1 to No.3, the curve is regular, and is very similar in type to those found by Parke and Graham for viscosity-disperse phase concentration. Nos. 19 and 20 were too viscous for determination, even in Viscometer No. 4.

In order to check up on the peculiar irregularities in the curve for the unhomogenised emulsions, a series, A_2, was made up with exactly the same proportions of constituents as Series A_1.

The viscosities were repeated with the same methods.

Number	T	η
1	139.7	37.11
2	150.4	40.18
3	150.4	40.29
4	137.9	36.99
5	176.9	59.82
6	376.2	101.23
7	477.6	128.68
8	290.2	80.11
9	259.5	70.11
10	223.2	60.39
11	537.6	145.72
12	885.1	240.19
13	968.6	263.23
14	959.6	261.17
15	1495.9	407.65
16	647.5	176.26
17	729.3	199.31
18	807.9	222.12
19	1204.4	330.10
20	1456.4	399.91

It will be seen by a comparison of these results and the curve obtained from them (Fig. 27) with those for Series A_1, that the irregularities occur in this series also, but at slightly different points in the curve.

Homogenisation, as the results below will show, gave the same smooth curve (Fig. 31) and almost exactly the same values for the viscosities as had been found in the homogenised Series A_1.

Number	T	η
1	187.6	49.82
2	138.6	37.02
3	138.0	34.82
4	156.4	41.95
5	190.1	51.07
6	241.3	64.92
7	284.0	76.52
8	333.3	89.93
9	463.5	125.2
10	555.1	150.2
11	911.2	274.0
12	54.0	329.1
13	85.8	524.8
14	183.6	1127.3
15	246.6	1509.7
16	312.4	1915.0
17	374.5	2298.6
18	910.0	5594.5

The series was repeated two further times, using exactly the same amounts of constituents, and, as far as possible, the same methods of making up. The results obtained, and the curves plotted from these (Figs. 28, 29), only serve to substantiate those above, obtained for Series A_1 and A_2.

In Fig. 32, the average of the results for the unhomogenised emulsions is plotted against the results for the homogenised emulsions, in order to bring out the difference between them.

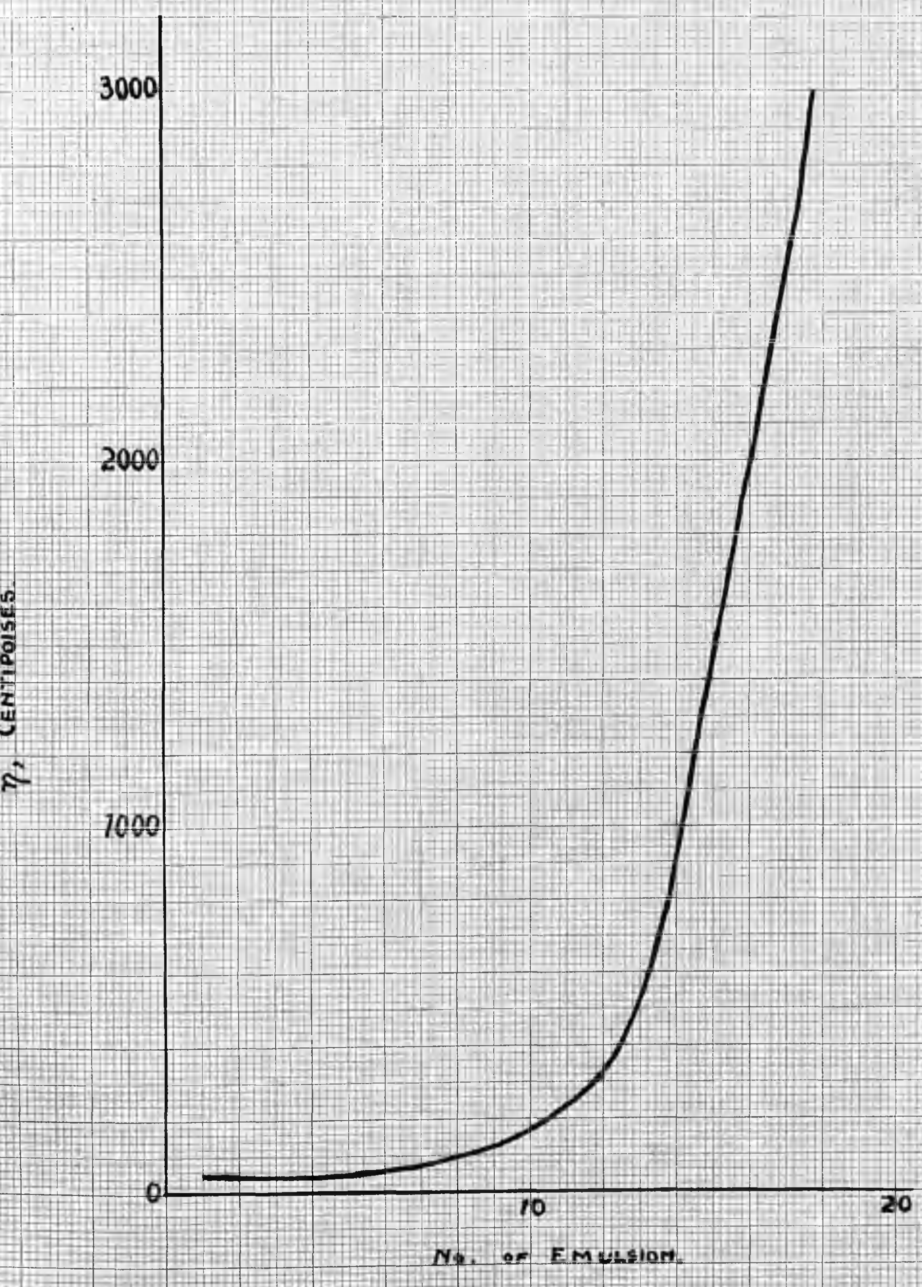


FIG. 31.

Unhomogenised.

Number	T for A	η for A	T for A	η for A
1	116.6	30.96	126.9	33.71
2	128.4	34.29	165.5	44.21
3	152.9	40.96	146.1	39.14
4	168.8	45.29	131.0	35.15
5	179.6	48.25	212.2	57.00
6	206.4	55.54	315.0	84.75
7	244.6	65.91	403.4	108.69
8	257.5	69.47	321.9	86.76
9	276.6	74.73	194.0	52.52
10	271.2	73.58	228.5	61.84
11	340.0	92.16	519.4	140.79
12	458.5	124.42	813.4	220.74
13	555.8	151.05	921.0	250.32
14	607.3	165.28	1039.6	282.94
15	857.7	233.74	1395.2	380.24
16	544.9	148.71	488.8	133.41
17	600.9	163.84	657.6	179.31
18	650.2	177.97	927.5	253.92
19	742.8	203.55	1014.9	278.19
20	795.2	218.37	1455.6	399.71

Homogenised.

Number	T for A	T for A	T for A
1	200.1	202.4	196.3
2	139.3	139.1	138.2
3	137.4	138.0	137.2
4	157.3	156.3	156.6
5	193.2	193.1	192.8
6	242.4	243.6	242.0
7	284.1	284.7	284.2
8	330.1	331.5	332.6
9	467.8	468.5	465.0
10	560.9	558.2	564.0
11	918.4	917.2	915.5
12	54.7	55.0	55.2
13	85.9	85.9	85.3
14	183.1	182.6	182.8
15	245.9	244.5	244.6
16	315.4	312.5	311.4
17	376.8	375.9	374.5
18	913.3	915.0	911.6

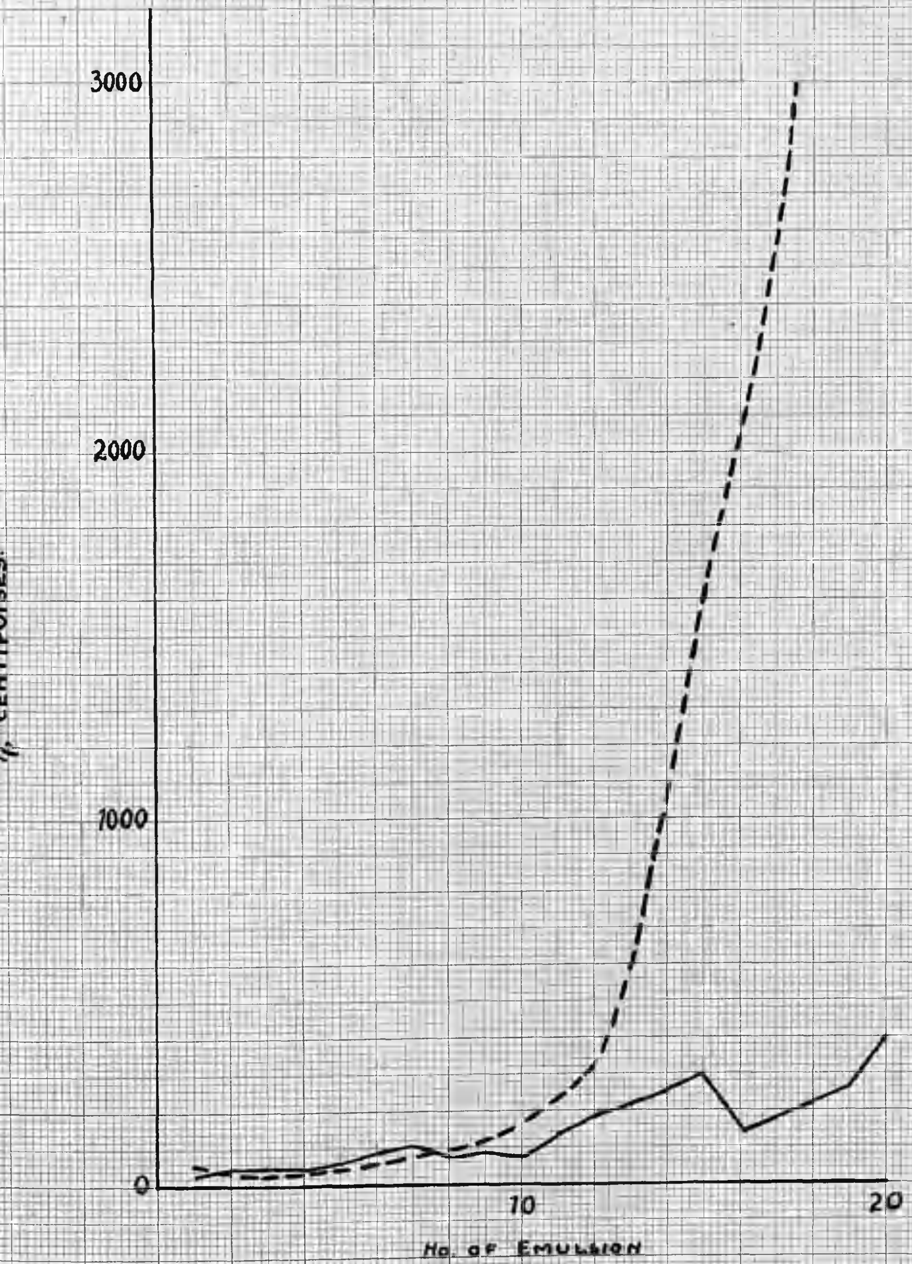


Fig. 32.

The unhomogenised series again gave irregular curves, always having the same general shape, but with the irregularities varying from curve to curve. The homogenised series gave practically identical results with those for series A_1.

These peculiar irregularities in the curve for the unhomogenised emulsions have since been confirmed by Parke and Larmour(45).

(b) MICROSCOPIC EXAMINATION.

In a search for some explanation of the phenomena observed, the series was examined under the microscope, using a dark ground illuminator. A very significant distribution was disclosed on this examination.

In No.1 (Plate I) of the unhomogenised series, the globules were found to be of varying dimensions, ranging, in some cases, from globules larger than the field of the microscope, to globules which were extremely small. There was also a relatively large amount of free continuous phase present, as was to be expected from the amount of creaming shown by the emulsion. Consequently, the globules were free to move, at the slightest disturbance, in all directions. The size of the globules decreased, as far as could be judged by the eye, fairly regularly throughout the series, and became more uniform with increased amount of emulsifier. The amount of free continuous phase also decreased, and consequently the globules became more closely packed.

An examination of Plate II, which is a photomicrograph of No.20 of the unhomogenised series, shows that the globules were, on the average, as small as the smallest globules in No.1, and were comparatively tightly packed.

No.1 of the homogenised series closely resembled No.20 of the unhomogenised series. The globules were perhaps slightly more tightly packed, and more uniform in size. Their average size was about the same.

In No.20 of the homogenised series, the globules were so small that they could not be distinguished under the microscope, and on dilution of the emulsion with water, (the continuous phase), they appeared only as points of light.

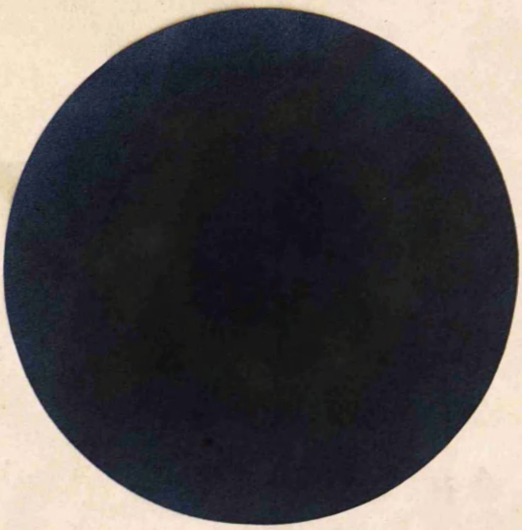


PLATE I.

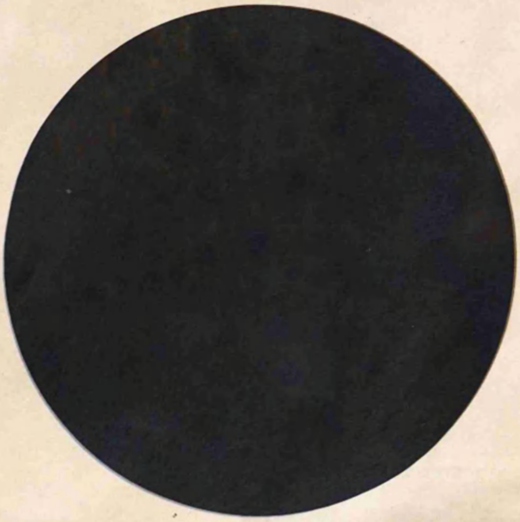


PLATE II.

DISCUSSION.

When we attempt to explain the irregularities in the viscosity curve of the unhomogenised series of emulsions, three factors are to be noted, each of which probably has some part in the production of the phenomenon. They are

(1) the varying sizes of the globules of disperse phase
(2) the large amount of free continuous phase
(3) the rapid and extensive creaming consequent on (1) and (2).

Factors (1) and (2) tend to create the effect of an unhomogeneous liquid, which will not, of course, give a constant viscosity. Factor (3), in a slightly different way, will also tend to produce the same effect.

That these three factors have at least some effect is borne out by the change produced by homogenisation. Homogenisation, in the first place, will tend to remove these irregularities. It will also serve to distribute the emulsifier more evenly throughout the emulsion than any hand or mechanical method of shaking is capable of doing, for it must be remembered that diffusion will not take place in the same way as in a homogeneous liquid.

The drop in viscosity noticeable in the beginning of the series of homogenised emulsions, which is the only outstanding irregularity in the curve, is perhaps due to the relatively small amount of emulsifier present, by reason of which the emulsions must be less stable than the higher members of the series.

This view is supported by the fact that the lower members of the series still tend to cream a little, indicating that there is insufficient emulsifier present to produce a stable emulsion which has the globules tightly packed.

The large increase in viscosity noticed throughout the higher members of the series is probably due in part to the very tight packing of the small globules, and the small amount of free continuous phase, which has a much smaller viscosity than the emulsion formed from it. Also, as there is probably excess emulsifier present in the higher members of the series, this excess, whether it goes into solution in the continuous phase, or coats the globules, will tend to increase the viscosity, though the first of these two factors, the packing of the globules, is more probably the one with the greater effect.

CONCLUSION.

While there is a general increase of viscosity in unhomogenised emulsions of the Benzene-Water-Sodium Oleate type, with increase in amount of emulsifier, the increase is very irregular. This irregularity is removed by means of homogenisation, which also in general ingreases the viscosity, and destroys the tendency to cream, particularly when there is more than a small amount of emulsifier present.

These results lead one to lay stress on the necessity for homogenisation of emulsions to standardise them, before any investigation is made of the physical properties, such as viscosity. It would appear that, unless the emulsions are homogenised, there can be no certainty of reproducing the same conditions in two emulsions of the same composition, no matter how much care is taken to maintain uniformity in their preparation.

PART IV.

ACTION OF EMULSIFIERS, AND TYPE REVERSAL.

INTRODUCTION TO PART IV.

Following on the work on the relation of Viscosity of Emulsions to the amount of Emulsifier present, it was decided to attempt to elucidate the action of the emulsifier.

It was found that a peculiar type of reversal could be obtained under certain conditions, and the problems raised by this were followed up. In this work, no one line of approach to the problem could be taken up to the neglect of others, and many of the lines of approach which appeared promising did not lead to any useful results.

The consequence of this is that the experimental work could not be described in a connected fashion, and so it is considered advisable to preface it by a brief description of the several lines which were tried.

INTRODUCTION TO EXPERIMENTAL.

The whole of the work arose from the consideration of the fact that it can be shown, by the action of phenol phthalein in soap solution, that a soap soluble in water, such as Sodium Oleate, is hydrolysed on the addition of water. From this it follows that, when an emulsion is formed with Sodium Oleate as emulsifier in Water-Benzene, the Oleate is hydrolysed just as it is in Water, and is presumably present as Sodium Hydroxide, Oleic Acid and Sodium Oleate, rather than as a simple substance.

From the consideration that the partition coefficient of Oleic Acid between Benzene and Water is about 500:1, it was thought possible that the hydrolysis was almost complete, and that therefore the state in such an emulsion would be in the main, Water with dissolved Sodium Hydroxide, and Benzene with dissolved Oleic Acid.

(a) NON-REACTING BINARY EMULSIFIERS.

It was thought possible, from the above considerations, that substances with a high molecular weight, like Oleic Acid, which were insoluble in Water, soluble in

Benzene, and unlike Oleic Acid, did not react with Sodium Hydroxide, might give emulsions in the system Benzene-Water-Sodium Hydroxide, if the small amount of Sodium Oleate which is probably present in an ordinary emulsion is not essential to the formation of an emulsion. Experiments in this line gave negative results.

(b) VARIATION OF ALKALI WITH STEARIC ACID.

The next line tried in the elucidation of the action of the emulsifier was to make up a series of emulsions, each containing a fixed amount of fatty acid, but with a varying amount of alkali, in order to see if the point where the acid and alkali are present in equimolecular amounts is the best emulsion of the series. It should be noticed that a theoretically neutral emulsion always gives an alkaline reaction.

Since the figures for the solubility of Stearic Acid in various organic liquids were available(50), and the same figures were not available for Oleic Acid, it was decided to use Stearic Acid in the first instance, so that, if the investigation was extended, liquids other than Benzene could be employed.

It was found, however, that the emulsions given with Stearic Acid were unsuitable.

(c) VARIATION OF ALKALI WITH OLEIC ACID.

For this reason, Oleic Acid was again used, and the amount of alkali was varied. An unexpected reversal of type was noticed in the series, at a point where there was a large excess of Oleic Acid over Sodium Hydroxide. On further examination, there proved to be really a double reversal.

(d) VARIATION OF FOUR CONSTITUENTS.

There are a number of factors which might cause this reversal.

(1) It might be caused by the extremely small amount of emulsifier present.

(2) It might at least be influenced by the fact that there is a great excess of Benzene over Water, when the amount of emulsifier is so small.

(3) It might be the result of the large excess of Oleic Acid.

Since, according to the theory, there are Water, Benzene, Oleic Acid and Sodium Hydroxide present, the obvious method of determining which factor is at work was to vary each of these constituents. Series E to L were designed for this purpose.

Apart from giving rough limits within which this reversal occurs, these variations in the constituents are not very informative. It was decided, therefore, that nothing further of value could be learned merely by varying the amounts of the constituents.

(e) VARIATION OF METHOD OF PREPARATION.

The method of making up the emulsion was investigated, and found to be effective when homogenisation did not take place.

(f) SURFACE TENSION AND TYPE CHANGE.

Attention was now turned towards the relation of surface tension to the type change.

It is known that soap lowers the surface tension of Water to a value very close to that for Benzene(51). In other words, the interfacial tension in an emulsion is very low. If the only effect of Sodium Oleate in an emulsion is to lower the interfacial tension, then any two immiscible liquids whose interfacial tension is very low should give stable emulsions.

Binary mixtures with low interfacial tension were examined.

(g) BINARY MIXTURES WITH LOW INTERFACIAL TENSION.

From the results obtained from (f) it would seem that the requisite conditions for the formation of an emulsion are

(1) Low interfacial tension

(2) A third substance, not soluble in both phases, to act as a coater of the globules.

An investigation of the action of various substances, when added to binary mixtures with low interfacial tension, was undertaken with respect to the second of these two conditions, but the results were indefinite.

(h) BENZENE-WATER WITH LOW INTERFACIAL TENSION.

Here the investigation in (g) was confined to Benzene-Water mixtures, in which the interfacial tension had been lowered by the addition of a small amount of soap solution. Here, also, the results could not be interpreted.

EXPERIMENTAL.

(a) NON-REACTING BINARY EMULSIFIERS.

For the purpose of testing the first theory, regarding substances with a high molecular weight which do not react with Sodium Hydroxide, higher alcohols were used, those available being Benzoyl Alcohol, $C_6H_5CH_2OH$, Phenyl Ethyl Alcohol, $C_6H_5CH_2CH_2OH$, and Octyl Alcohol, $C_8H_{17}OH$.

Systems were made up containing

(1) 50cc. Benzene, 40cc. Water, 10cc. N/10 Sodium Hydroxide (0.04 grs. Sodium Hydroxide.).

(2) 50cc. Benzene, 50cc. Water, the weight of alcohol equivalent to 0.04 grs. Sodium Hydroxide.

(3) 50cc. Benzene, 40cc. Water, 10cc. N/10 Sodium Hydroxide, the weight of alcohol equivalent to 0.04 grs. Sodium Hydroxide.

The third set of systems is, of course, the one which should correspond to the proper emulsion.

It was found that none of the series gave an emulsion which remained stable for a minute, and there seems to be no regular relation between the stabilities of the three series.

(b) VARIATION OF ALKALI WITH STEARIC ACID.

For this investigation, a solution of Stearic Acid in Benzene was made up, containing 56.8 grs. per litre of benzene. This solution is of such a strength that 50cc. of it are equivalent to 10cc. N/1 NaOH.

A series, Series B, was made up as follows:-

Number	Ccs. Water	Ccs NaOH, N/1	Ccs. Benzene Soln.
1	48	2	50
2	46	4	50
3	44	6	50
4	42	8	50
5	40	10	50
6	38	12	50
7	36	14	50
8	34	16	50
9	32	18	50
10	30	20	50

In this series, No.5 contains equivalent amounts of Sodium Hydroxide and Stearic Acid.

It was found that there was a grading of the emulsions up to No.6, from which point an increasing amount of hard curd was formed, the soap evidently being salted out by the excess of Sodium Hydroxide.

No.1 broke almost immediately. No.2 had a stability of about half an hour. Nos. 3 and 4 were very good liquid emulsions. No.5 was a very good thick emulsion, almost solid.

Since this series could not be homogenised on account of the curd, it was decided to abandon the work with Stearic Acid, and to return to the use of Oleic Acid.

(c) VARIATION OF ALKALI WITH OLEIC ACID.

In the first Series made up with Oleic Acid, Series C, the ratio 70:30 for disperse phase:continuous phase was used, as it was just possible that the use of the 50:50 ratio in the case of the Stearic Acid had had some effect on the amount of curd present.

A solution of Oleic Acid in Benzene was made up having 20.1685 grs. per litre. 70Ccs. of this solntion are equivalent to 5cc. N/1 Sodium Hydroxide.

Series C.

Number	Ccs. Water	Ccs NaOH, N/1	Ccs Benzene Soln.
1	29	1	70
2	28	2	70
3	27	3	70
4	26	4	70
5	25	5	70
6	24	6	70
7	23	7	70
8	22	8	70
9	21	9	70
10	20	10	70

Here again, No.5 is the one containing equivalent amounts of acid and alkali.

Nos. 2-10 seemed to be ordinary emulsions. From No.5 upwards, there was an increase in the amount of creaming, and so in the amount of free aqueous phase.

But No.1 of the series, when tested both by the drop dilution method, and electrically, proved to be a Water-in-Oil emulsion, which had been deduced by the fact that it creamed to the bottom.

Nos. 2-10, when tested for type, proved to be normal Oil-in-Water emulsions.

The viscosities of the series were determined after homogenisation, and although the graph obtained from them (Fig. 33) is not very informative, as the emulsions seem to give very irregular viscosities in the earlier part of the series (which is to be expected on the approach to a change of type), the graph would seem to show that the point of greatest viscosity is not at the theoretically neutral point, but rather lower in the series.

The viscosity of No.1 was not determined, as it was of a different type, and also because it creamed much too quickly for an accurate determination.

Number	Time	Viscosity
2	676.5	184.7
3	572.4	156.3
4	680.9	185.9
5	259.6	70.9
6	220.0	60.1
7	208.1	56.8
8	199.4	54.5
9	180.5	49.3
10	166.5	45.5

It was obvious that there must be some point of reversal between No.1 and No.2, and so, to determine where this took place, a mixture of 70ccs. Benzene solution and 29ccs. Water was taken, and titrated at intervals of 0.1cc. with N/1 Sodium Hydroxide, with testing between

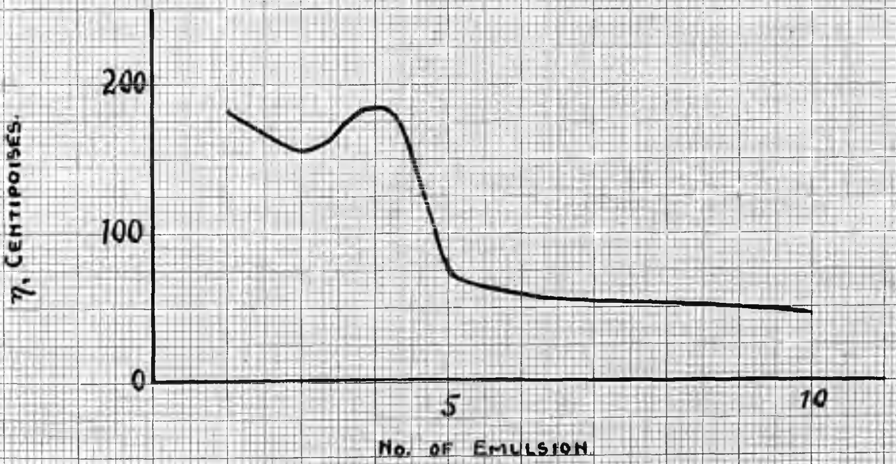

η, Centipoises.
200
100
0
5
10
No. of Emulsion

Fig. 33

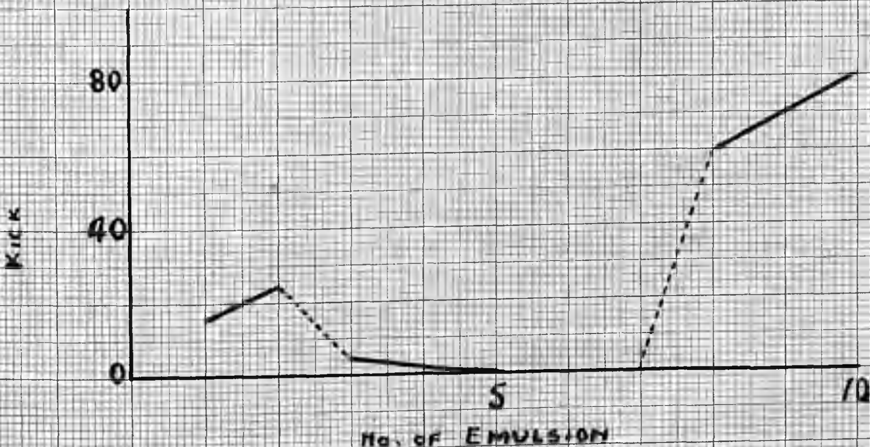

Kick
80
40
0
5
10
No. of Emulsion

Fig 34.

each titration for type. The first two additions gave very unstable emulsions, but even after a stable emulsion had been formed, no Water-in-Oil emulsion was formed, even up to the addition of 2ccs. N/1 Sodium Hydroxide.

It would seem that something similar to the inoculation of colloids with electrolytes was taking place.

Series D was made up, covering the region from no Sodium Hydroxide to 2ccs. N/1 Sodium Hydroxide.

Series D.

Number	Ccs. Water	Ccs. NaOH, N/10	Ccs. Benzene Soln.
1	28	2	70
2	26	4	70
3	24	6	70
4	22	8	70
5	20	10	70
6	18	12	70
7	16	14	70
8	14	16	70
9	12	18	70
10	10	20	70

On shaking, Nos. 1, 8, 9 and 10 gave fairly stable Oil-in-Water emulsions. The others would not give definite or stable emulsions.

The series was therefore homogenised, and the types were as follows:-

1. Oil-in-Water
2. Oil-in-Water, with a large amount of free Benzene.

3, 4, 5, 6, 7, Water-in-Oil.

8, 9, 10, Oil-in-Water, stable.

The comparative conductances of this series were measured by means of the kick on a milliammeter, when a current was passed through them.

With 5-lamp resistance (about 50 volts.)

No.	1	2	3	4	5	6	7	8	9	10
Kick	1.7	2.4	---	---	---	---	---	6.0	7.0	8.0

With no resistance (250 volts.)

No.	1	2	3	4	5	6	7	8	9	10
Kick	15.0	24.0	4.0	1.0	---	---	----	60	70	80

This confirms the fact that Nos. 1, 2, 8, 9 and 10 are Oil-in-Water emulsions. As will be seen from the graph (Fig. 34) the portions of the curve pertaining to these emulsions are probably part of one smooth curve, and the conductivity increases regularly, as is to be expected, with increase in amount of Sodium Hydroxide.

The two breaks in the graph coincide with changes of type, as is generally the case in physical measurements of emulsions where type change occurs.

The fact that a small conductivity occurs in Nos. 3 and 4 would indicate that they are probably dual in type, while Nos. 5, 6 and 7 are almost entirely of the Water-in-Oil type. The occurrence of dual emulsions near the lower break, and not near the upper one can be accounted for by the less amount of neutral emulsifier present, which consequently gives a reduced stability, and a greater tendency to inversion.

(d) VARIATION OF THE FOUR CONSTITUENTS.

In the following series, E to L, the proportions of all four constituents in turn were varied.

Series E consisted of 50:50 Benzene:Water emulsions, with graded amounts of emulsifier from 5ccs. N/1 Sodium Hydroxide dropping by 0.5cc. to 0.5cc., and from 5ccs. N/10 Sodium Hydroxide, dropping by 0.5cc. to 1cc. N/10, with equivalent amounts of Oleic Acid in each case. In all cases, stable Oil-in-Water emulsions were formed on homogenisation.

Series F was as follows:-

Number	Ccs. Water	Ccs. NaOH,N/1	Ccs Benzene	Ccs Oleic Acid,N/1
1	49.5	0.5	45	5
2	49.0	1.0	45	5
3	48.5	1.5	45	5
4	48.0	2.0	45	5
5	47.5	2.5	45	5
6	47.0	3.0	45	5
7	46.5	3.5	45	5
8	46.0	4.0	45	5
9	45.5	4.5	45	5
10	45.0	5.0	45	5

In this case, No.10 is the theoretically neutral emulsion, and the variation in constituents follows the same principle as in Series D, except that in this case we have a 50:50 instead of a 30:70 Water:Benzene emulsion.

When homogenised, all the emulsions were of the Oil-in-Water type, so that an inversion, if it occurs, would be below No.1.

Series G was designed to cover this region.

Number	Ccs. Water	Ccs. NaOH, N/10	Ccs. Benzene	Ccs. Oleic Acid, N/1
1	49.5	0.5	45	5
2	49.0	1.0	45	5
3	48.5	1.5	45	5
4	48.0	2.0	45	5
5	47.5	2.5	45	5
6	47.0	3.0	45	5
7	46.5	3.5	45	5
8	46.0	4.0	45	5
9	45.5	4.5	45	5
10	45.0	5.0	45	5

When homogenised, all of these were stable Oil-in-Water emulsions, though before homogenisation, a number of the lower members were very unstable.

It would appear from this that a 50:50 Water:Benzene emulsion series will not show the inversion point at all. The next step was to find at what point in the range from 50:50 to 30:70 the inversion can occur.

Series H covered the region from 70% Benzene to 30% Benzene, and contained 5ccs. N/1 Oleic Acid, and 6ccs. N/10 Sodium Hydroxide, which amounts are those present at the inversion point in Series D.

On homogenisation, the first three, containing respectively 70, 66 and 62% of Benzene, turned type to Water-in-Oil emulsions. The rest were Oil-in-Water emulsions.

Series I, which contained a constant concentration of Oleic Acid per amount of Benzene, 5ccs. N/1 per 70ccs.

Benzene, and a constant concentration of Sodium Hydroxide per amount of Water, 6ccs. N/10 per 30ccs. Water, and which varied in phase proportions from 30:70 to 70:30 Benzene:Water, gave no additional positive results, the only emulsion showing inversion being the 70:30 Benzene: Water one, which corresponds to No.3 of Series D, and No.1 of Series H.

Series J retained the 70:30 ratio of the Benzene: Water, and varied the ratio of Oleic Acid to Sodium Hydroxide, this being a series similar in principle to Series D.

Number	Ccs. Water	Ccs. NaOH,N/10	Ccs.Benzene	Ccs.Oleic Acid,N/1
1	25	5	69	1
2	25	5	68	2
3	25	5	67	3
4	25	5	66	4
5	25	5	65	5
6	25	5	64	6
7	25	5	63	7
8	25	5	62	8
9	25	5	61	9
10	25	5	60	10

On homogenisation, Nos. 1 and 2 were Oil-in-Water emulsions, Nos. 3 and 4 seemed to be dual in type, but with free Benzene on top, and definitely tending towards the Water-in-Oil type. The rest were Water-in-Oil emulsions.

Series L was also similar in principle.

Number	Ccs. Water	Ccs. NaOH,N/10	Ccs.Benzene	Ccs. Oleic Acid,N/1
1	20	10	65	5
2	20	10	64	6
3	20	10	63	7
4	20	10	62	8
5	20	10	61	9
6	20	10	60	10
7	20	10	59	11
8	20	10	58	12
9	20	10	57	13
10	20	10	56	14

The first of these was Oil-in-Water, the rest were Water-in-Oil emulsions.

It was further noted in dealing with these series, that gentle continuous shaking tends to give Water-in-Oil emulsions, while vigorous intermittent shaking gives Oil-in-Water emulsions, which are reversed on homogenisation, if the necessary amounts of Oleic Acid and Sodium Hydroxide are present.

(e) VARIATION OF METHOD OF PREPARATION.

In order to determine if the method of making up the emulsion had any effect on the type, other than the variation produced by different shaking, an emulsion, starting from 30ccs. Benzene and 30ccs. Water, and containing 5ccs. N/1 Oleic Acid and 6ccs. N/10 Sodium Hydroxide, was made up, and it was found that, on addition of Benzene in 5cc. lots, with shaking, the Oil-in-Water type persisted all through. Change in type occurred when the final 70:30 emulsion was homogenised.

(f) SURFACE TENSION AND TYPE CHANGE.

The interfacial tension of Phenol-Water is 0.34 (20°C.), of Aniline-Water is 5.2 (25°C.), and of Methyl Alcohol-Carbon Disulphide is 0.16 (20°C.), as compared with 73-74 for the surface tension of water(52).

Following on the reasoning already stated, these binary mixtures were examined, and found to give emulsions, which were, however, not very stable, breaking down over night.

From this it follows that the action of the emulsifier comprises more than the lowering of the interfacial tension. Deducing from the abnormal reversal, it is possible that part of the function of the emulsifier is to coat the globules, and that in these emulsions where the abnormal type occurs, there is not enough emulsifier proper to act thus, while being sufficient to lower the interfacial tension sufficiently to allow an emulsion to be formed. The Oleic Acid may then act as a coater for the globules, keeping them apart once they are formed following on the lowered interfacial tension.

It was found that Phenol-Water and Aniline-Water gave good emulsions on addition of a little Oleic Acid, while Methyl Alcohol-Carbon Disulphide separated almost as quickly with Oleic Acid as without. This would seem to indicate that the coater must not be soluble in both phases.

(g) BINARY MIXTURES WITH LOW INTERFACIAL TENSION.

A number of substances, soluble only in one phase, were added to Phenol-Water and Aniline-Water, to see if any clue could be obtained as to the type of substance necessary to coat the globules, and thus form an emulsion.

It was found that no definite results could be arrived at, for the substances which gave good results in the case of the Phenol-Water did not always do so with the Aniline-Water, and there seemed to be no guiding principle throughout.

This great variation was somewhat to be expected, for the effect of adding a third substance on the interfacial tension is not yet known, and in some cases there is also a possibility of compounds being formed.

(h) BENZENE-WATER WITH LOW INTERFACIAL TENSION.

Emulsions were made up containing 70% Benzene, 29% Water, and 1% N/10 Soap solution. They only formed after continuous shaking, in other words, they were in a somewhat unstable condition, and might almost be regarded as systems in which there was low interfacial tension, but hardly sufficient material to coat the globules.

Various substances were added to these emulsions, to see the effect on the stability of the emulsions, and to see if there was any effect on the type, as it was thought possible that the phase in which the emulsifier was soluble might have some effect on the type of emulsion formed.

As will be seen from the examples appended, the results here were also irreconcilable with any apparent order.

Substance added	Effect
Oleic Acid	Dual type.
Stearic Acid	Less effect than Oleic Acid.
Palmitic Acid	Ditto.
Sucrose solution	Broke emulsion.
Urea	Lessened stability.
Phenol	Broke emulsion.
Aniline	No discernable effect.

DISCUSSION.

The problem raised by the entirely unexpected reversal in type noticed on the addition of excess Oleic Acid to a Benzene-Water-Sodium Oleate emulsion would appear to be of a particularly complicated nature. This is suggested from the start by the double reversal in Series D.

In first considering the type of emulsions formed when the constituents are extensively varied, as in the Series D to L, we see that, in general, a large excess of Oleic Acid produces, with small amounts of Sodium Oleate, on homogenisation, a Water-in-Oil emulsion, when there is a certain excess of Benzene over Water. The lowest percentage of Benzene where this type of emulsion was noted was 62% The type also appears to be more influenced by the variation of the amount of Sodium Oleate, than by variation in the amount of Oleic Acid.

In discussing the cause of these phenomena, there are at least two agents to be taken into consideration. The first of these is the marked lowering of the surface tension of water by the addition of soap, and the second is the presence of the large excess of Oleic Acid. This Oleic Acid, deducing from the Partition Coefficient, must be almost entirely in the Benzene, or continuous phase. It is thought that the action of this may be somewhat similar to that taking place in a Benzene-Water-Magnesium Oleate emulsion, in which, since the solubility of Magnesium Oleate in Water is 0.23 grs. per litre, the greater part of the emulsifier is contained in the Benzene phase. Here also a Water-in-Oil emulsion is formed, and the Benzene is the continuous phase.

The action of an emulsifier such as Sodium Oleate-Oleic Acid may be taken to have at least two separate and definite functions,

(1) to lower the interfacial tension

(2) to render the globules, once formed, stable, presumably by some form of coating, through adsorption to the interface between the Benzene and Water.

The reversing action of Oleic Acid can in no way be considered to be an electrolytic inversion of the type cited by Clayton(46), on account of the low solubility of Oleic Acid in Water. Also, since Oleic Acid itself does not emulsify Benzene:Water, it cannot be considered as an emulsifier of the opposite type, giving inversion when present in excess.

The theory above serves to explain the reversed emulsions, but it does not explain why there should be two emulsions of normal type in Series D before the reversed emulsions. Nor has anything come to light in the investigations above which will serve to throw light on this.

As can be seen by the account of the above investigations, a number of interesting problems are opened up, which should repay further study. Also, some of the investigations could not be continued with, on account of lack of data. The determination of these would be useful.

A number of these points are minor, but three of the more important are appended here.

Useful work could be done in connection with the effect of the addition of substances to binary mixtures, such as Phenol-Water, on the interfacial tension, and the possibility of compounds being formed.

It would also be interesting to investigate the relation of emulsion type to the preponderance of emulsifier in one or other phase, following up the theory set out above. From this work, it would seem extremely likely that this has a fundamental effect.

Perhaps most important, however, would be the examination of the exact partition of the emulsifier in the two phases, close to the point of reversal. There seems to be no doubt that the emulsifier used so much, Sodium Oleate, is largely hydrolysed, and it would appear that this factor is extremely important in the production of the phenomena described.

CONCLUSION.

In general, the use of a simple emulsifier with a pure oil and Water will, under all conditions, give the same type of emulsion, e.g., Sodium Oleate with Benzene-Water always gives Oil-in-Water emulsions, no matter in what proportions the Benzene and Water are present; and similarly, Magnesium Oleate gives emulsions of the reverse type.

Further, it has always been held that in order to reverse the type of an emulsion, it was necessary to add an appreciable amount of a new substance, which either has in itself, or will produce by its action on the emulsifier, an opposite emulsifying effect, e.g., addition of Magnesium Chloride or Magnesium Oleate to a Benzene-Water-Sodium Oleate emulsion will eventually change the type when there is a greater equivalent of Magnesium than of Sodium present.

In this investigation, two reversals of type have been observed under conditions which more nearly approach those obtaining with the use of a simple emulsifier, since it is a case where the equilibrium of a hydrolysed salt is changed.

A theory has been formed, based on experimental data gathered in the investigation, which explains one of the reversals. Lines of research are suggested which might lead towards the solution of the second reversal.

As in Part III of this thesis, the need for homogenisation of emulsions for standardisation is emphasised.

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PART V.

Additional Paper.

THE CONSTITUTION OF PHLOBATANNINS.

INTRODUCTION TO PART V.

The tannins are distributed very widely throughout the vegetable kingdom, and are chiefly important for their power to precipitate proteins, and convert animal hides into leather.

The classification of this large group of substances was unsatisfactory for a very long time, but that due to Freudenberg is now generally accepted. He(1) recognised recognised two main groups of tannins, according to their behaviour on treatment with mineral acids, namely, the hydrolysable tannins, and the non-hydrolysable tannins. Members of the first group are characterised by possession of the depside linkage, -CO-O-, and suffer fusion at this part of the molecule during hydrolysis. The second group of tannins, on the other hand, yield characteristic red, water-insoluble products on treatment with warm dilute mineral acid.

The first group of tannins is further divided into three sub-groups, according to the products of hydrolysis, namely:- (1) Gallotannins, (2) Ellagitannins, (3) Caffetannins.

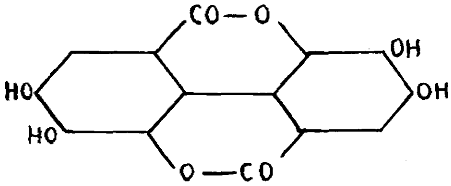
(1) The Gallotannins have been fairly fully investigated by Fischer, who found that the products of hydrolysis were Gallic Acid and Glucose. He studied in particular that tannin obtained from Chinese Galls, and assigned to it the structure of a penta-(m-Digalloyl)-glucose, with the formula

$$C_6H_7O_6\left[C_6H_2(OH)_3.CO.OC_6H_2(OH)_2CO\right]_5$$

m-Digalloyl residue.

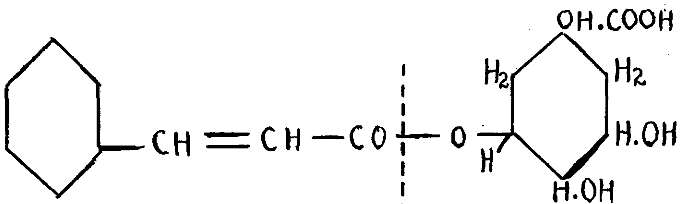
or $C_{76}H_{52}O_{46}$.

(2) The Ellagitannins are characterised by the production on acid hydrolysis of Ellagic Acid, a diphenyl derivative produced through the condensation of two molecules of Gallic Acid, and having the structure



Apart from this fact, little is known of this group.

(3) The Caffetannins, obtained from coffee berries, yield Caffeic Acid, Quinic Acid, and a residue, the nature of which is unknown. They are thus considered to be derivatives of Chlorogenic Acid, which has the formula

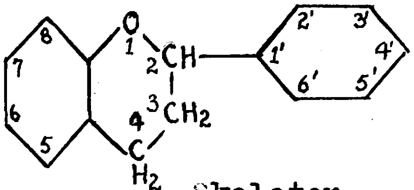


Caffeic Acid residue | Quinin Acid residue and yields Caffeic Acid and Quinic Acid through rupture of the depside bond.

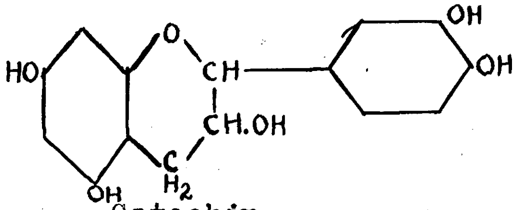
The second main group of tannins, as has been mentioned above, are not hydrolysed with acids, but give characteristic red products, called Phlobaphenes, from which the name Phlobatannins is derived for this group of substances. It is with this group of Phlobatannins that the work to be described is concerned.

Phlobatannins have been the subject of numerous researches over a long period of time, but progress in the elucidation of their constitution has been decidedly slow, and most of the proposals which have been made have been highly speculative. The only suggestion which need be mentioned was due to Freudenberg, who put forward the theory that Phlobatannins should be considered to be polymerised forms of Catechins. He based this hypothesis on certain resemblances in properties between tannins and Catechin, although it was recognised that Catechin is definitely not a tannin.

In order to explain the great variety of the natural Phlobatannins, it was necessary to assume the existence of a number of Catechins, but, so far as is known, only one Catechin, 3:4:7:3':4'-pentahydroxyflavan, is known to occur in nature.



Skeleton

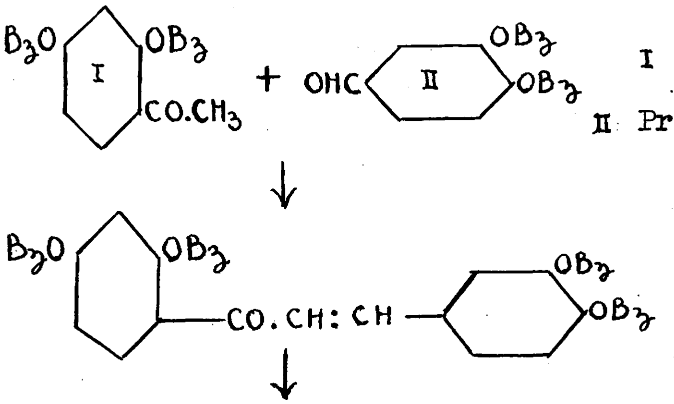


Catechin

Recognising this objection to the above scheme of formulating the Phlobatannins, Russell(2) thought that they might possibly be related to 4-hydroxyflavan, instead of to 3-hydroxyflavan (Catechin) as above. So he attempted to prepare a series of hydroxylated 4-hydroxyflavans.

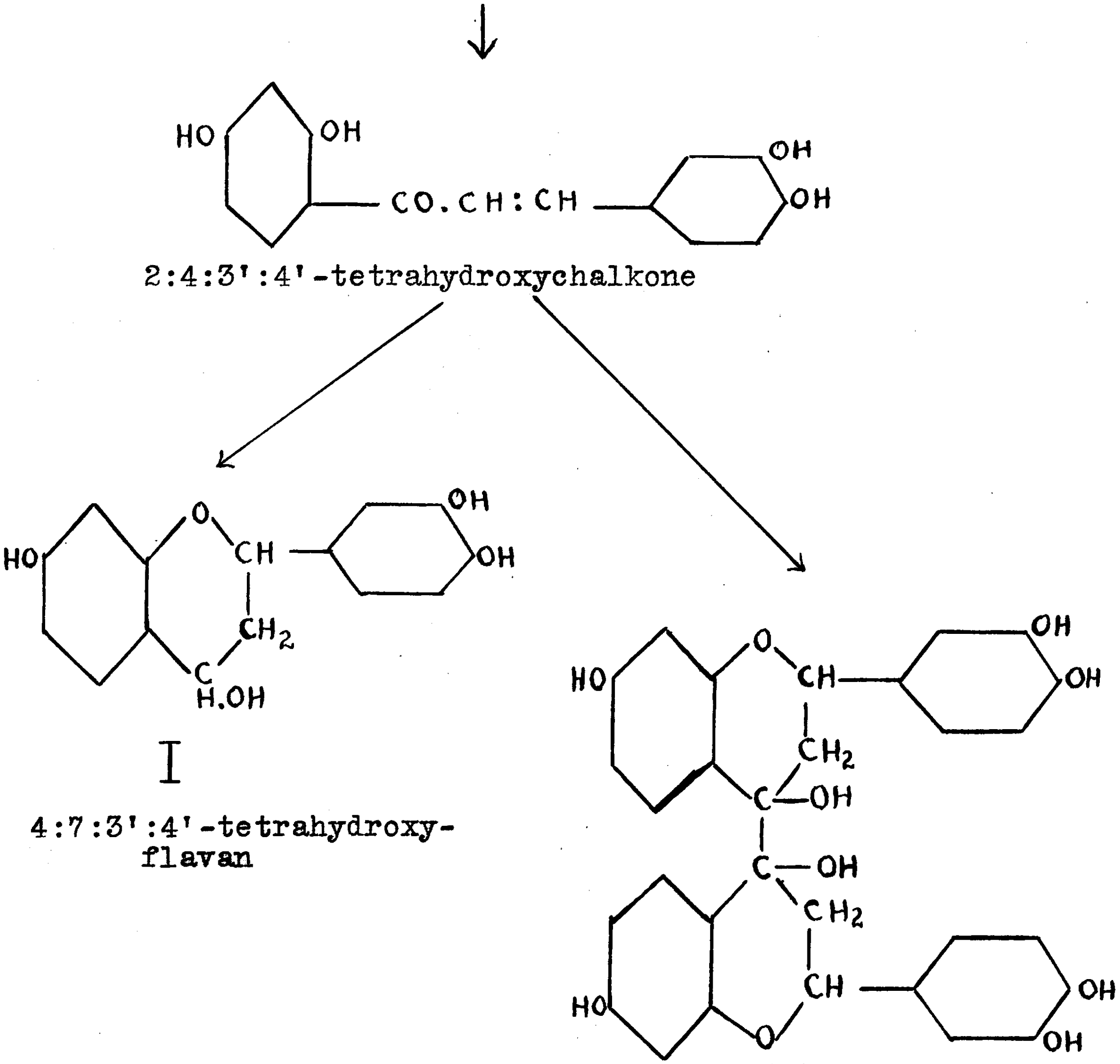
It was found that reduction by means of Zinc dust and alcoholic Acetic Acid of the polyhydroxy chalkones, which contained one of the hydroxyl groups in the 2-position, yielded substances which could not be distinguished qualitatively from natural Phlobatannins, and which were capable of converting prepared sheepskin into leather.

The process followed in the initial experiment is shown schematically, as follows:-



I Resacetophenone Dibenzoate.
II Protocatechualdehyde Dibenzoate.

2:4:3':4'-tetrabenzoyloxychalkone



2:4:3':4'-tetrahydroxychalkone

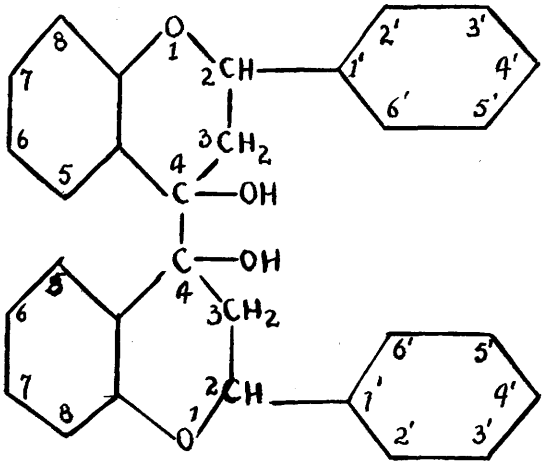
I

4:7:3':4'-tetrahydroxyflavan

II

bis-(7:3':4'-trihydroxy)flavpinacol

It will be seen that an alternative formulation of the end product is provided, but, in a subsequent paper(3), Russell and Todd produced conclusive evidence in favour of the pinacol structure, II. The same authors studied a number of such polyhydroxychalkone reduction products, and concluded that Phlobatannins are polyhydroxyphenolic derivatives of a parent substance, which they have called Flavpinacol, of the following formula:-



Incidentally, they express the view that natural Hemlock Tannin is a flavpinacol,(4) having as essential skeleton the structure of bis-(7:8:3':4':-tetrahydroxy)-flavpinacol, and is probably identical with the latter substance.

These Phlobatannins are amorphous substances, and are mainly characterised by means of a whole range of qualitative tests. On account of the nature of such substances, analyses, molecular weights and melting point determinations could not be employed in a close comparison of synthetic and natural products, and it was suggested by Dr. Russell that comparative physicochemical measurements, which were at least partly quantitative, should be used as a basis for comparison.

EXPERIMENTAL.

(a) MOLECULAR WEIGHTS FROM VISCOSITY MEASUREMENTS.

The first line of research was an attempted comparison of molecular weights by viscosity measurements, along lines similar to those indicated by Staudinger(5) for complex aliphatic compounds.

According to Staudinger, highly polymerised synthetic products, and natural substances like rubber and cellulose form macromol disperse solutions containing isolated fibre molecules, whose chain length can be determined by the formula

$$\eta\ \text{sp.(equiv.)} = K_m . M$$

where K_m is a characteristic constant varying for each of the known hydrocarbon series, and chain equivalent weight is the average weight per carbon atom. In Staudinger's determinations, K_m is of the order 10^{-4}.

The viscometer used in the present investigation was one of the set of Standard Ostwald U-Tube Viscometers used in the determination of emulsion viscosities described in Part III of this thesis (p.62 seq.). The solutions used were solutions in absolute alcohol, containing 0.1 gr. per 100 ccs.

The following results were obtained, each time of flow being the average of three determinations, varying by less than 1%.

	Time (Secs.)	Viscosity, η.
Alcohol	148.0	1.0985
bis-(7:8:3':4'-tetrahydroxy)-flavpinacol	147.0	1.0921
Hemlock Tannin	147.5	1.0958
Mimosa Tannin	147.5	1.0958
Methylated Hemlock Tannin	148.2	1.1010
Methylated Mimosa Tannin	148.8	1.1055

It was found impossible to interpret these results by any variation of Staudinger's formula, and it would seem from them that the relation between molecular weight and viscosity postulated by him does not hold for substances such as the Phlobatannins and Flavpinacols, which have complicated ring structure. This is somewhat borne out by the variation between the changes in viscosity caused by the methylation respectively of Hemlock and Mimosa Tannins.

(b) ABSORPTION SPECTRA.

Attention was now turned to Absorption Spectra, as being the most likely of all physicochemical methods to give suitable results, since they are in part quantitative. It is, of course, obvious that such data as extinction coefficients of bands could not be determined, since the purity of both natural and synthetic substances could not be relied on.

In addition to measuring the absorption spectra of some synthetic Flavpinacols and natural Phlobatannins, the data for the starting materials and intermediate products used in the syntheses were obtained. For the purpose of comparison, two types of tannin other than the Phlobatannins were also included in the scheme.

Apparatus.

The spectroscope used for these investigations was a Hilger Medium Quartz Spectrograph (E2). The spectra were obtained by the Hartley method, using a Baly Tube, and the solvent in all cases was Absolute Alcohol which showed no absorption above λ 2350.

The spectrograph scale was calibrated against a photograph of the iron arc, and the data obtained for the calibration curve (Fig. 1) is as follows:-

Scale reading	Actual Wavelength Å.U.
39	3776
38	3687
37	3590
36	3506
35	3414
34	3327
33	3233
32	3142
31	3050
30	2950
29	2859
28	2761
27	2668
26	2574.5
25	2470

The source of light used was the iron arc, giving twenty seconds exposure for each photograph.

In order to test the dispersion of the spectrograph, the curve for Benzene was determined, and four bands were noted at λ2410, λ2490, λ2560 and λ2610 (Fig. 2). Baly

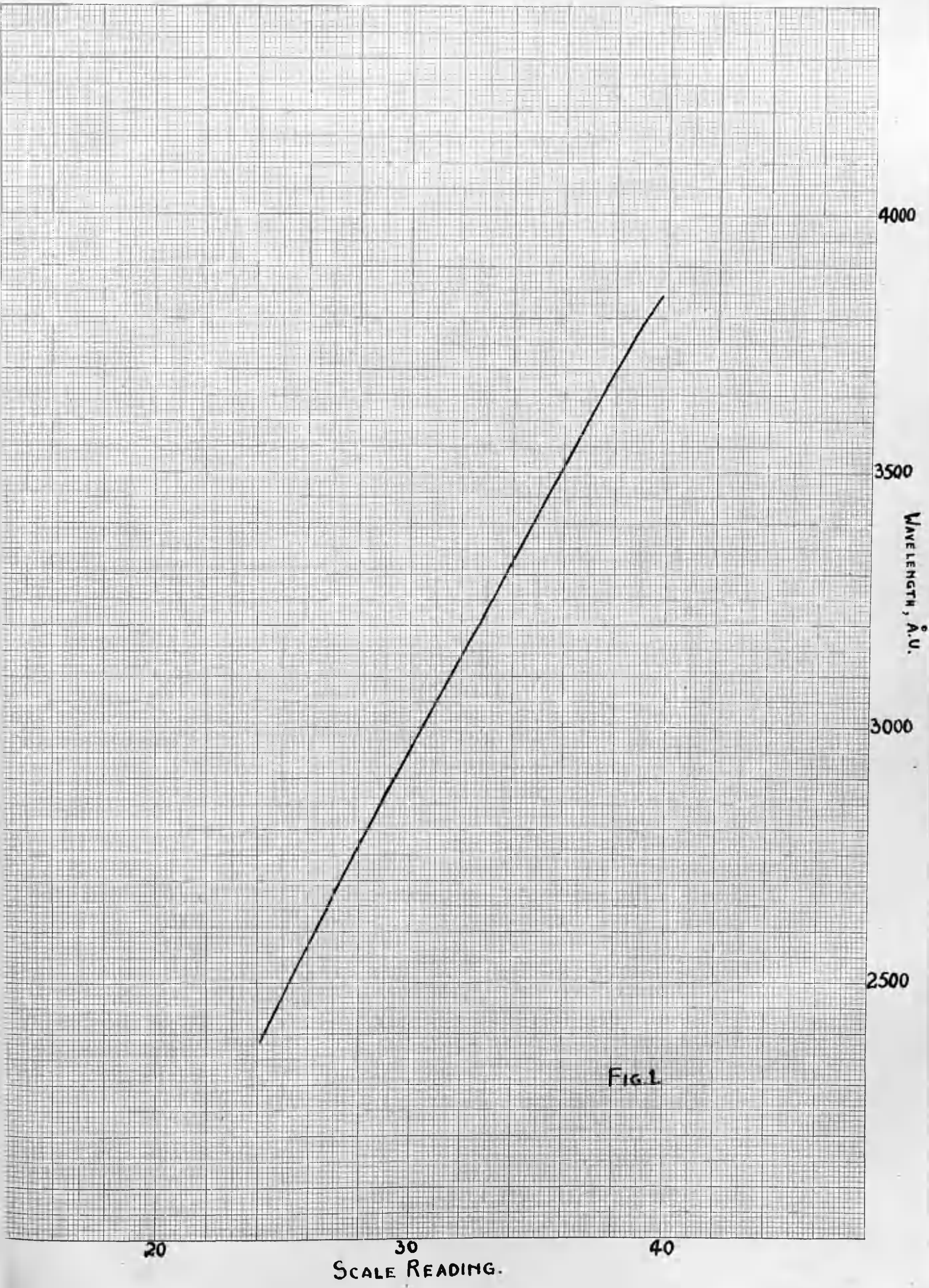


Fig. 1.

and Collie(6) record seven bands at λ2380.9, λ2433.1, λ2484.3, λ2554.3, λ 2611.0, λ2656.0, λ2684.6 (Fig. 3).

The general method of procedure in taking the photographs of the spectra was to begin with log. thickness 1.9, using a solution of 0.1 gr. per 100 ccs. The log. thickness was reduced by 0.1 for each photograph down to log. thickness 1.0. The solution was then diluted ten times, and the series repeated. This was repeated again with the solution diluted 100 times. In all cases these two dilutions were sufficient to take in the spectrum over the range of the plate.

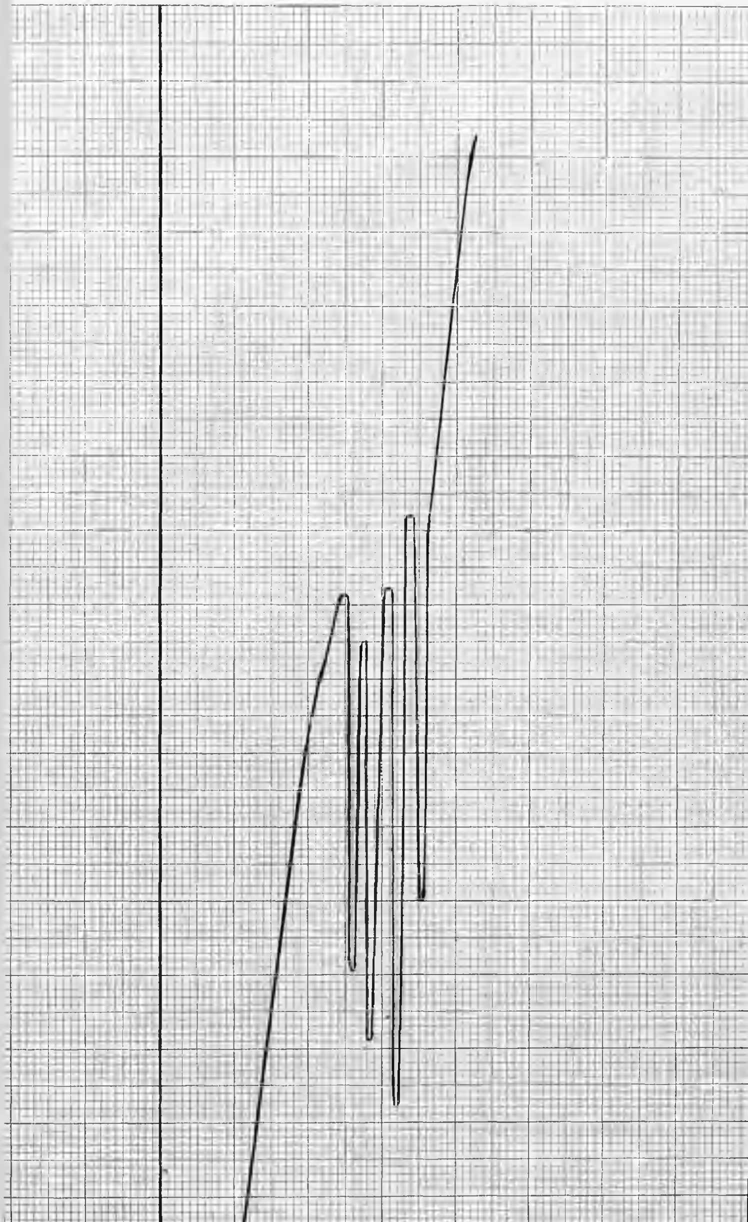

2100
2500
2900
Wavelength, Å.U.

FIG 2.

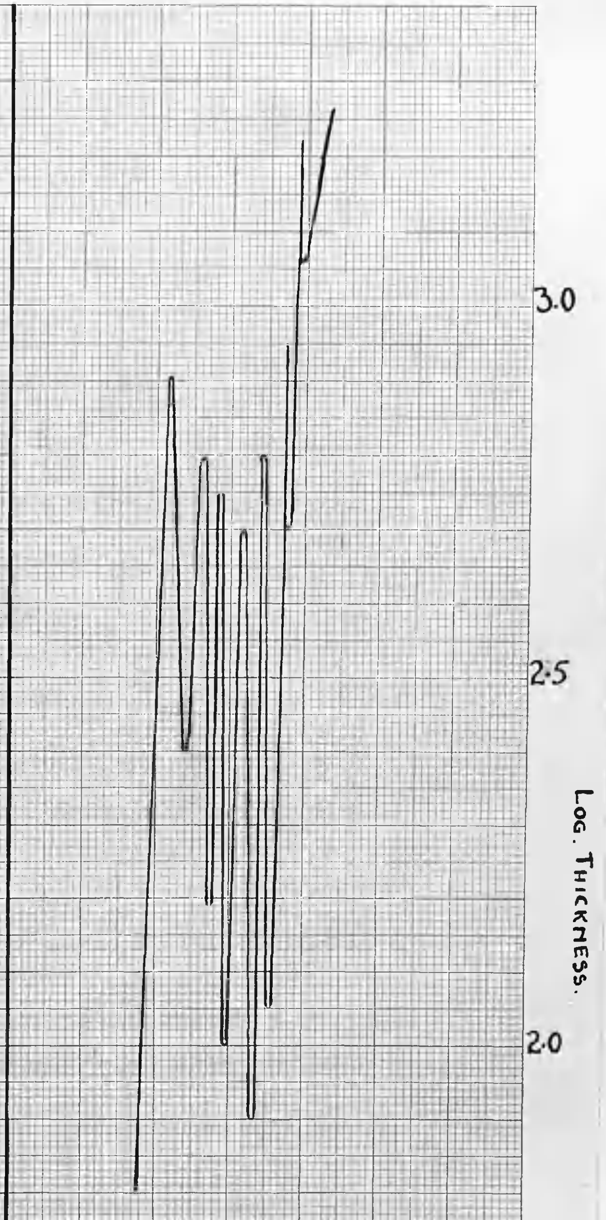
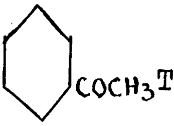

2100
2500
2900
3.0
2.5
2.0
1.5
Log. Thickness.

FIG 3.

Results.

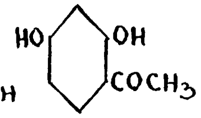
In the presentation of the results, they will be given in tabular form as far as possible, with compounds of the same type grouped together, before any detailed discussion of the individual curves is undertaken.

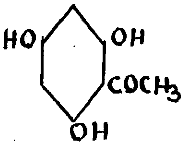
(a) Starting Materials.

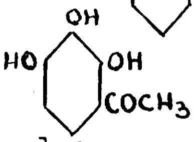
Acetophenone (Fig. 4) 

This showed general absorption, with a pronounced extension of the curve at λ2620-2880.

Baly and Collie(7) record a similar curve, showing an extension at λ2630-2900.

Hydroxy-ketones. Three hydroxy-ketones were examined, Resacetophenone, 

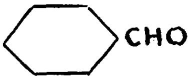
Phloracetophenone, 

and Gallacetophenone 

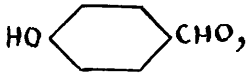
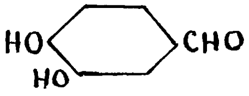
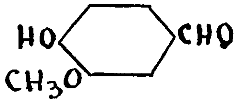
.

Each of them showed a very strong band, and an extension which may be a weak band.

	Band Head	Extension
Resacetophenone (Fig. 5)	2780	3000-3300
Phloracetophenone (Fig. 6)	2860	3200-3380
Gallacetophenone (Fig. 7)	2800	3200-3400

Benzaldehyde (Fig. 4) 

The absorption shown by this agrees with that recorded by Baly and Collie(7) being a small band with its head at λ2850.

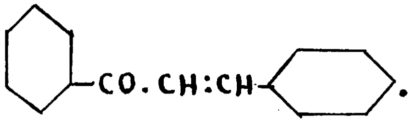
Hydroxy-aldehydes. Three of these compounds were examined, p-Hydroxybenzaldehyde, ,Proto-catechualdehyde, , and Vanillin .

The monohydroxyaldehyde shows an inflexion or weak band, and a strong band. The dihydroxyaldehyde and the hydroxymethoxyaldehyde both show two very similar bands, which in greater thicknesses of solution merge into one strong band.

	Inflexion	Band Head	Band Head
p-Hydroxybenzaldehyde (Fig.9)	2650	2880	----
Protocatechualdehyde (Fig.5)	----	2760	3120
Vanillin (Fig. 8)	----	2780	3120

For p-Hydroxybenzaldehyde, Tuck(8) records a band with its head at λ 2880-2890, and for Vanillin, Purvis(9) records two bands at λ 2776 and λ 3120.

(b) Intermediate Products.

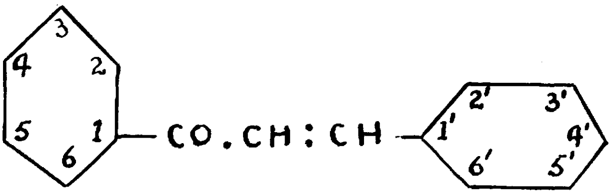
Chalkone. (Fig. 4) . This compound, which is also known as Benzylideneacetophenone, is formed by the condensation of Benzaldehyde and Acetophenone.

Its spectrum shows two bands, a weak one at λ 2880, and a stronger one at λ 3125, the two merging, in thicker solutions, into one broad band. Two records of the spectrum of Chalkone are found in the literature, one by Stobbe and Ebert(10), and one by Shibata and Nagai(11). The results obtained in this investigation agree fairly well with those given in the former reference, a broad band with its head at λ 2857, and an extension of the curve at λ 3100-3300. This is totally different from the curve given in the second reference, which gives one broad band with its head at λ 3300. The spectrum determination was repeated, using Chalkone which had been further recrystallised twice, but the results served only to verify those now given.

Polyhydroxychalkones. The hydroxylated chalkones submitted to examination were formed by the condensation of Resacetophenone, Phloracetophenone and Gallacetophenone successively with Protocatechualdehyde, and also with p-Hydroxybenzaldehyde. As typical of an intermediate series was also included that chalkone with Phloracetophenone as ketonic component, and Vanillin as aldehydic component, that is, 2:4:4'-trihydroxy-3'-methoxychalkone.

The three 3':4'-polyhydroxychalkones give rise to Flavpinacols which are qualitatively indistinguishable from natural Phlobatannins.

All of the polyhydroxychalkones gave three bands, one of which was a colour band, and an extension of the curve.



Skeleton of Chalkones.

	Fundamental Bands		Extension	Colour Band
2:4:3':4'-tetrahydroxy- (Fig.5)	2670	2900	3160-3380	3840
2:4:6:3':4'-pentahydroxy-(Fig.6)	2700	2880	3160-3300	3970
2:3:4:3':4'-pentahydroxy-(Fig.7)	2700	2890	3100-3500	3860
2:4:4'-trihyd.-3'-meth.- (Fig.8)	2670	2910	3120-3320	3840
2:4:4'-trihydroxy- (Fig.9)	2690	2810	3150-3400	3760
2:4:6:4'-tetrahydroxy- (Fig.10)	2700	2880	3100-3300	4570
2:3:4:4'-tetrahydroxy- (Fig.11)	2700	2880	3560	above 5000

The two bands which appear in the Ultma-Violet would appear to be fundamental bands.

Chalkone Reduction Product. $C_{30}H_{26}O_2$ (Fig. 4). At this point might be included the data for the reduction product obtained from Chalkone itself by the action of Zinc dust and dilute Alcoholic Acetic Acid. The selective absorption has disappeared almost entirely, but there are two small extensions of the curve, which may be weak bands, at λ2370-2500 and λ2730-2880.

(c) Synthetic Flavpinacols.

The spectra of the Flavpinacols show a close similarity to those given by the Chalkones in the Ultra-Violet, but the colour band is found to have disappeared,

Fig. 4.

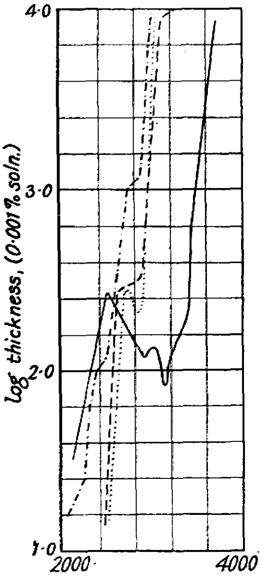


Fig. 5

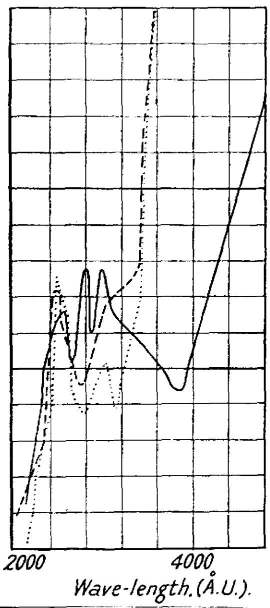


Fig. 6

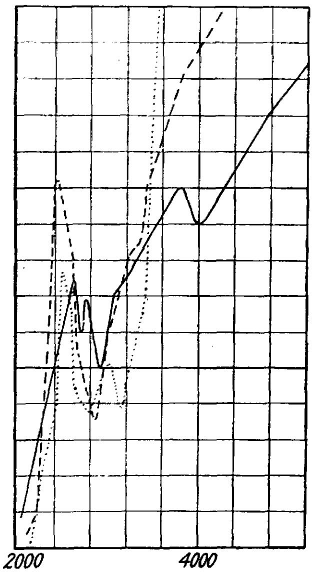


Fig. 7.

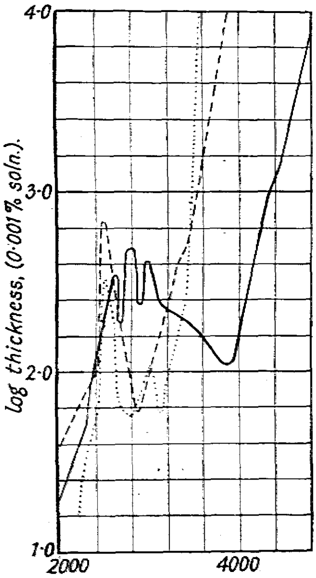


Fig. 8

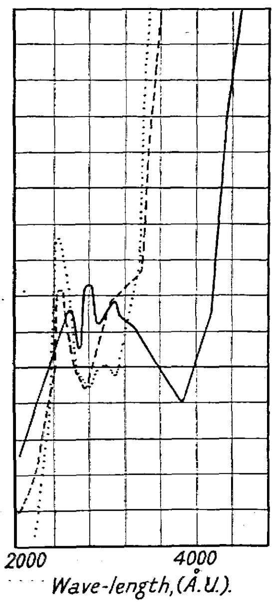


Fig. 9.

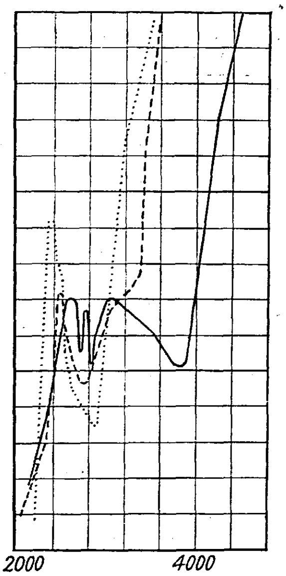


FIG. 4.

– – – – *Acetophenone.*
.... *Benzaldehyde.*
——— *Chalkone.*
–·–·–· *Bis-reduction product of chalkone.*

FIG. 5.

– – – – *Resacetophenone.*
.... *Protocatechualdehyde.*
——— 2 : 4 : 3′ : 4′-*Tetrahydroxychalkone.*

FIG. 6.

– – – *Phloracetophenone.* ..... *Protocatechualdehyde.* ——— 2 : 4 : 6 : 3′ : 4′-*Pentahydroxychalkone.*

FIG. 7.

– – – – *Gallacetophenone.*
.... *Protocatechualdehyde.*
——— 2 : 3 : 4 : 3′ : 4′-*Pentahydroxychalkone.*

FIG. 8.

– – – – *Resacetophenone.*
.... *Vanillin.*
——— 2 : 4 : 4′-*Trihydroxy*-3′-*methoxychalkone.*

FIG. 9.

– – – – *Resacetophenone.* .... p-*Hydroxybenzaldehyde.* ——— 2 : 4 : 4′-*Trihydroxychalkone.*

except in one instance, that of bis-(7:4'-dihydroxy)flavpinacol, which shows a band above λ5000, as well as an extension of the curve about λ3300.

3':4'-dihydroxypolyhydroxyflavpinacols.

	Band Head	Band Head
bis-(7:3':4'-trihydroxy)- (Fig.15)	2700	2850
bis-(5:7:3':4'-tetrahyd.)- (Fig.15)	2700	2880
bis-(7:8:3':4'-tetrahyd.)- (Fig.12)	2700	2890

4'-hydroxypolyhydroxyflavpinacols.

	Band Head	Band Head
bis-(7:4'-dihydroxy)- (Fig.16)	2690	2820
bis-(5:7:4'-trihydroxy)- (Fig.16)	2700	2890
bis-(7:8:4'-trihydroxy)- (Fig.16)	2690	2900

(d) Natural Phlobatannins.

If we now turn to an examination of the spectra of the natural Phlobatannins, we find a very close similarity to those of the Flavpinacols. Two natural Phlobatannins were investigated, Hemlock Tannin and Mimosa Tannin, as were also Methylated Hemlock and Mimosa Tannins.

Each of the four gave two bands, as follows:-

Natural Phlobatannins.

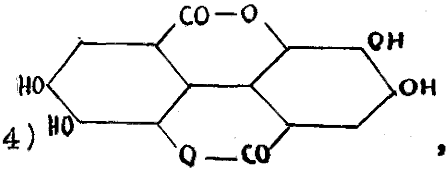
	Band Head	Band Head
Hemlock Tannin (Fig.12)	2710	2860
Mimosa Tannin (Fig.12)	2700	2860

Methylated Natural Phlobatannins.

	Band Head	Band Head
Methylated Hemlock Tannin (Fig.13)	2700	2800
Methylated Mimosa Tannin (Fig.13)	2700	2810

(e) Natural Tannins other than Phlobatannins.

To complete this investigation, the spectra of Ellagic Acid and Gallotannin, which contain the characteristic groupings of two other groups of tannins were also examined.

Ellagic Acid (Fig. 14) 

, gives three bands at λ2480, λ3140 and λ3680. That at λ2480 is probably the diphenyl band, which is given by Adam and Russell(12) at λ2461.

Gallotannin (Fig. 14). The absorption for this substance appears to be general, except for two extensions at λ2740-2920 and λ3300-3740, which may be weak bands.

Fig. 10.

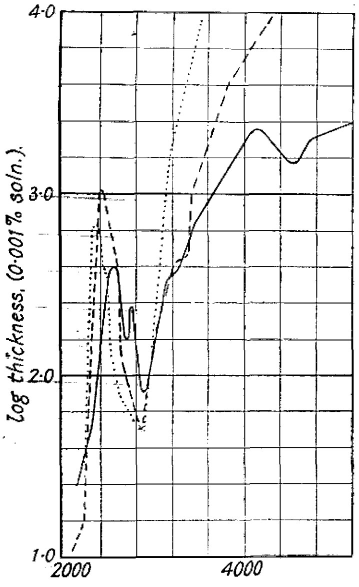


Fig. 11.

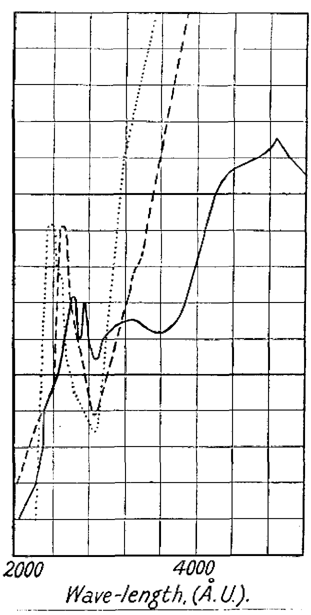


Fig. 12.

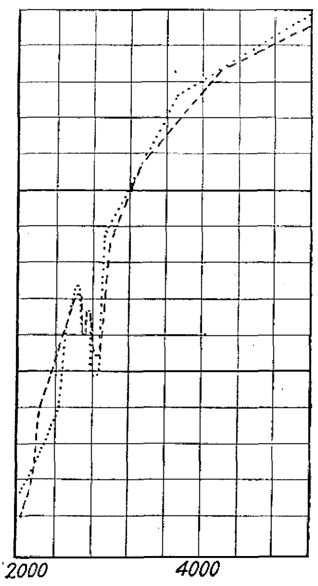


Fig. 13.

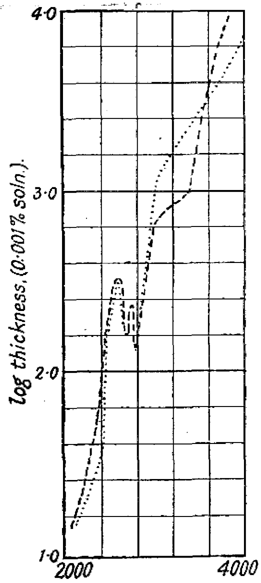


Fig. 14

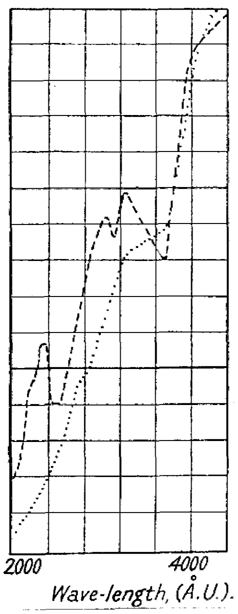


Fig. 15.

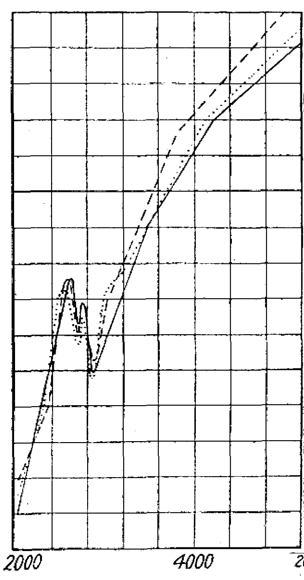


Fig. 16.

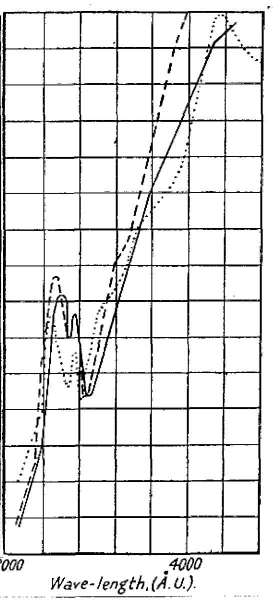


Fig. 10.

– – – – *Phloracetophenone.*
.... *p-Hydroxybenzaldehyde.*
——— 2 : 4 : 6 : 4′-*Tetrahydroxychalkone.*

Fig. 11.

– – – – *Gallacetophenone.*
.... *p-Hydroxybenzaldehyde.*
——— 2 : 3 : 4 : 4′-*Tetrahydroxychalkone.*

Fig. 12.

– – – – *Hemlock tannin.*
.... *Mimosa tannin.*

Fig. 13.

– – – – *Methylated hemlock tannin.*
.... *Methylated mimosa tannin.*

Fig. 14.

– – – – *Ellagic acid.*
.... *Gallotannin.*

Fig. 15.

– – – – *Bis*-(5 : 7 : 3′ : 4′-*tetrahydroxy*)*flavpinacol.*
——— *Bis*-(7 : 8 : 3′ : 4′-*tetrahydroxy*)*flavpinacol.*
.... *Bis*-(7 : 3′ : 4′-*trihydroxy*)*flavpinacol.*

Fig. 16.

– – – – *Bis*-(5 : 7 : 4′-*trihydroxy*)*flavpinacol.*
——— *Bis*-(7 : 8 : 4′-*trihydroxy*)*flavpinacol.*
.... *Bis*(-7 : 4′-*dihydroxy*)*flavpinacol.*

Discussion.

(a) Starting Materials.

When we come to consider the curves more particularly, we may first remark on the very marked effect of the introduction of the phenol groups into Acetophenone. That the band shown in each of the three hydroxyketones is the phenol band may be deduced, firstly from a comparison with the spectrum of Phenol itself, which shows a very similar strong band at λ2600-2800 (13), and secondly, from its continued appearance throughout the series. Also, the addition of the third hydroxyl group in Phloracetophenone and Gallacetophenone seems to have the effect of strengthening the band, and shifting the extension still further towards the higher wavelengths. The extension shown in the three spectra may very possibly be the extension of Acetophenone itself, pushed to a higher wavelength, from λ 2700 to λ3200-3300.

A similar type of change is to be noted when we come to the Hydroxyaldehydes.

When one hydroxyl group is present, e.g., in p-Hydroxybenzaldehyde, we find only the phenol band, with a very weak inflexion at λ 2650. The appearance of the head of the band suggests that further resolution would split it into two bands. The band here is stronger than in the case of the dihydroxyketone, probably because the phenol band is almost exactly superimposed on the Benzaldehyde band at λ 2850.

The addition of a second phenolic group to give Protocatechualdehyde serves to bear out the theory that the p-Hydroxybenzaldehyde band really consists of two bands, for here we get two clearly defined bands, which merge at greater thicknesses into one strong band. Here it would appear that the lower of the two, that at λ 2760, is the true phenolic band. The other, at λ 3130, may be the Benzaldehyde band, pushed so far towards to red as to enable it to be differentiated from the phenol band.

As is to be expected, the methylation of one of the hydroxyl groups in Protocatechualdehyde to give Vanillin does not alter the spectrum appreciably, the general shape and position of the bands being very similar in the two spectra.

(b) Intermediate Products.

In Chalkone, we have an evident visible colour band appearing for the first time in the series. The radical difference in the spectrum of Chalkone may be deduced from the radical changes which take place in the structure --- the destruction of the -CHO group, and the introduction of the double bond as a new centre of absorption. The "colour band" which appears first in Chalkone persists all through the Hydroxychalkones, and it is evidently to it that these compounds owe their strong and characteristic colour. The colour varies from bright yellow in Chalkone itself, to deep red-brown in the 2:3:4-trihydroxyhydroxychalkones. It is chiefly remarkable for its persistence, being usually visible, even on the second dilution.

The colours of the various chalkones in alcoholic solution are here tabulated against the positions of the colour band.

	Band Head	Colour
2:4:3':4'-tetrahydroxy-	3840	Bright yellow
2:4:6:3':4'-pentahydroxy-	3970	Orange Red
2:3:4:3':4'-pentahydroxy-	3860	Deep Red brown
2:4:4'-trihydroxy-3'-methoxy-	3840	Bright yellow
2:4:4'-trihydroxy-	3760	Pale yellow
2:4:6:4'-tetrahydroxy-	4570	Orange Red
2:3:4:4'-tetrahydroxy-	above 5000	Deep Red brown

These appear to grade in accordance with each other, with the exception of the 2:3:4:3':4'-pentahydroxychalkone, the colour of which would suggest that there is a band high in the red, beyond the limit of the spectrum examined, which terminated a little above λ5000.

Even more interesting in these compounds is the presence of the two bands which have been referred to as "fundamental bands", at roughly λ2700 and λ2880. It is suggested that both these bands are phenolic in origin, one of them originating from the hydroxybenzaldehyde residue in the chalkone, and the other from the hydroxyacetophenone residue. This view is borne out by their non-appearance in the spectrum of Chalkone itself, since the λ2880 band in Chalkone does not appear to be of the same type as that which appears in the Hydroxychalkones at that position. It is more probable that the band λ2880 in Chalkone is similar in origin to the extension in the various Hydroxychalkones, where it is merely forced by the phenolic bands towards the red end of the spectrum.

On the whole, the similarity between the spectra of the 3':4'-dihydroxypolyhydroxychalkones may be noticed, though the resemblance is not so marked in the other group, the 4'-hydroxypolyhydroxychalkones. Naturally, the spectrum given by 2:4:3':4'-tetrahydroxychalkone is very little different when one of the hydroxyl groups is methylated to give 2:4:4'-trihydroxy-3'-methoxychalkone.

The reduction product of Chalkone, which is colourless, gives only two small extensions (or weak bands), which agrees with the view that reduction destroys, or modifies very considerably, the centres of absorption.

(c) Synthetic Flavpinacols.

The last stage in the synthesis of the Flavpinacols, the reduction of the hydroxychalkones, again produces marked changes in the parts of the structure likely to affect absorption. The double bonds disappear, and the carbonyl group becomes $\begin{smallmatrix}\diagdown\\ -\\ \diagup\end{smallmatrix}$COH. One of the hydroxyl groups becomes an oxygen included in one of the rings by closure.

From this we see that a considerable difference is to be expected between the Flavpinacol spectra and those of the hydroxychalkones. We find that the colour band has disappeared entirely, with one exception, bis-(7:4':-dihydroxy)-flavpinacol, obtained from 2:4:4'-trihydroxychalkone, where there is a band above λ5000.

The extension has also disappeared, with an exception in the same case. This is capable of two interpretations. Firstly, that the reduction and condensation has shifted the colour band of the chalkones further towards the red end of the spectrum, and out of the region covered by the spectra examined, with this one exception. The second possible interpretation, and one which seems more likely, is that the band and extension are due to a trace of unreduced 2:4:4'-trihydroxychalkone in the case of the bis-(7:4'-dihydroxy)-flavpinacol, and that in general the reduction from chalkone to flavpinacol destroys all colour absorption.

It is, of course, to be noted that flavpinacols are reddish in colour, and give dark brown solutions, but it is thought that this is due to the presence of oxidation products, as they are light in colour when prepared, and darken on standing. Also, the colour has not the same persistence that is found in the colour of the chalkones on dilution. It may be mentioned here that the colour of the Phlobatannins shows the same phenomena as that of the Flavpinacols. However, the possibility of absorption in the red must not be lost sight of.

The outstanding feature in the spectra of the Flavpinacols is the persistence of the two "fundamental bands", and this lends support to the theory that they are phenolic in origin, since the hydroxyl groups would appear to be the only centres of absorption which have remained unchanged.

It may be speculated, though without a very strong basis for the theory, that the λ 2700 band is that due to the hydroxybenzaldehyde residue, and the other "fundamental band" that due to the hydroxyacetophenone residue, since the former of these bands is even less affected and variable than the latter, and this might be expected by the change in the hydroxyacetophenone residue through the course of the reduction, as compared with the less change in the hydroxybenzaldehyde residue.

(d) Natural Phlobatannins.

When compared with the spectra of the natural Phlobatannins and Methylated Phlobatannins, the spectra of the Flavpinacols show a remarkable similarity, not only in the position of the bands, but in their character. This similarity is only shown to be the more striking when we add to the comparison the spectra of the two substances characteristic of the two other groups of tannins.

(e) Natural Tannins other than Phlobatannins.

These last two substances, Ellagic Acid and Gallotannin extracted from oak galls, give spectra differing widely, not only from those of the Phlobatannins, but also from each other, and leave no room to doubt the wide difference in structure between the different groups of tannins.

Conclusion.

This investigation of the spectra of the natural Phlobatannins and synthetis Flavpinacols shows quite conclusively that Flavpinacols are identical in basic structure with Phlobatannins, and that the two are totally different from the other group of natural Tannins in structure, while having the same property of tanning leather.

The course of the synthesis of Flavpinacols has been closely followed by means of the examination of the spectra of the starting substances and intermediate products, and while it is not possible to deduce from the spectra whether the polyhydroxyflavan or the polyhydroxyflavpinacol is formed in the last stage of the synthesis, the other stages of the synthesis, as put forward, are borne out by the examination.

The essential difference in structure between the chalkones and flavpinacols is also shown, and the difference in colour between solutions of the two groups is, when considered in conjunction with the spectra, explained.

The course of the synthesis of a Flavpinacol, as followed by the spectra, may be summed up as follows:-

the hydroxychalkone spectrum is roughly the sum of the spectra of the hydroxyaldehyde and the hydroxyketone which form it, with the addition of a "colour band" in the visible region. On reduction, the colour group is destroyed, and ring closure takes place. The visible band disappears, giving reduction products showing spectra which are in every way indistinguishable from those of typical natural Phlobatannins.

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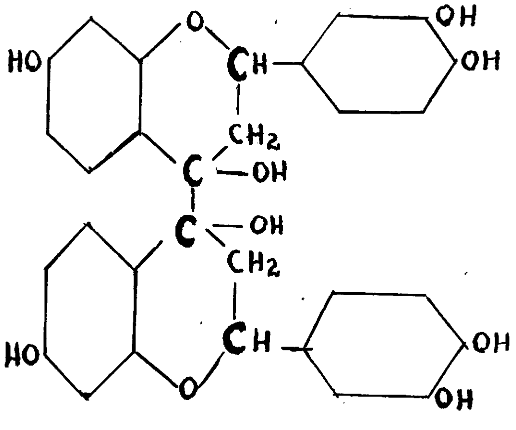
(3) OPTICAL ROTATION IN THE NATURAL PHLOBATANNINS.

While the investigation of the spectra of the tannins was in progress, the determination of the optical activity of solutions of the natural Phlobatannins was also undertaken.

As can be seen from the formula put forward for a typical Flavpinacol, there are four asymmetric Carbon atoms in it.



If, as has been indicated in the investigations of Phlobatannins, Flavpinacols and natural Phlobatannins are of the same basic structure, then it is quite possible that the natural compounds are optically active.

Owing to the dark red colour of the solutions given by the natural phlobatannins, the solutions had to be very weak, and red light, of λ6600 was used for the determinations.

The substances examined were Hemlock Tannin, Mimosa Tannin, Methylated Hemlock Tannin and Methylated Mimosa Tannin. The solutions were in absolute alcohol.

The polarimeter used was a Lippich triple field Polarimeter, made by Hilger, and a 20cm. polarimeter tube was employed. The half shadow angle was set at 2.

Each result is the average of three readings. All readings were made at 20°C. Zero reading, 90.80°.

Solution	Strength	Polarimeter Reading	$\frac{100 A_t}{l_t \cdot c_t} = [\alpha]^{6600}_{20^\circ}$
Hemlock	0.1%	90.750	-25°
Mimosa	0.25%	90.641	-31° 54'
Methylated Hemlock	0.5%	90.922	+12° 12'
Methylated Mimosa	0.25%	90.981	+36°.12'

Owing to the weak solutions which had to be employed, and their dense colour, these rotations are all subject to an experimental error of about ± 5°.

Apart from proving that natural Phlobatannins do show optical activity, these rotations do not throw any light on their constitution, and so they are given here without any further comment.

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PART V.

ADDITIONAL PAPER.

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