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The density, refractive index, magnetic susceptibility and viscosity of five pure mono-hydric saturated alcohols and nine sets of binary mixtures made up from pairs of the five pure alcohols have been measured at ordinary temperatures, and property-composition curves have been constructed in each case. The results show that none of the mixtures are ideal. Deviations from the theoretical curve, constructed from values calculated from the simple mixture law, are shewn graphically for every property for every mixture examined, except in the case of density for the mixture n-iso butyl alcohols, when the deviation is so small as to appear almost negligible.

It is noticed that the properties viscosity and magnetic susceptibility give deviation values which are distinctly greater than those of density and refractive index. Of the alcohols used, the propyl alcohols with n butyl alcohol gave the greatest deviation values for density and refractivity, but these gave the lowest viscosity and magnetic susceptibility deviation values. The position of maximum deviation is similar in density and refractivity-composition curves. There is a general tendency throughout most of the property-deviation

curves, for the position of maximum deviation to shift gradually towards the larger percentage of n butyl alcohol, in mixtures of that alcohol with iso, normal propyl, iso butyl, and iso y methyl butyl alcohols respectively.

The results indicate that coordination occurs at least to some extent between n butyl alcohol and the other alcohols considered, on mixing. The magnetic susceptibility measurements yield interesting results in so far that they shew good agreement with molecular susceptibility values obtained from Pascal's atomic susceptibilities.

CONTENTS.

AN INVESTIGATION OF CERTAIN PHYSICAL PROPERTIES OF BINARY MIXTURES OF SOME ORGANIC LIQUIDS.

In this thesis is described an account of the examination of certain physical properties of binary mixtures of aliphatic monohydroxy alcohols, one in particular of these alcohols being a constant constituent of each mixture.

The objects of the investigation were as follows:-

I. To ascertain by the investigation of changes occasioned in the physical properties density, refractivity, viscosity, heat of mixing, magnetic susceptibility, what changes, physical or chemical, occur when the compounds are mixed. The changes sought included compound formation, (inter molecular coordinated), deassociation, association.

II. To ascertain whether magnetic measurements are likely to prove more suitable than others for indicating the changes which occur.

III. To examine the results with the view of obtaining an insight into the electronic and magnetic relationships of the molecules.

The liquids used were mixtures of n-butyl alcohol with iso propyl, normal propyl, iso butyl and γ methyl butyl alcohols respectively, and the density, refractivity, viscosity, and magnetic susceptibility of a complete series of mixtures were examined in each case. Heat of mixing measurements were made only in the case of n-butyl alcohol with iso-propyl alcohol. The heat change as shown by preliminary experiments proved to be too small and to vary so little in the various mixtures as to be useless for the present purpose, particularly as the accuracy of the method employed was in many cases not so great as the divergences observed.

Purification of materials.

The liquids used were A.R. n and iso-propyl, n and iso-butyl, and iso-γ-methyl butyl alcohols, purchased from the British Drug Houses Ltd. Each alcohol was dried by warming to about 60°C. with freshly dried potassium carbonate, and was quickly filtered through glass wool. The liquid was distilled using a Dufton fractionating column and the portion coming over at a steady temperature, as read from a standardised thermometer, was collected separately. Its density was determined and taken as a criterion of purity if in good agreement with values obtained by former workers.

In Table 1. are given the boiling points of the liquids, under atmospheric pressure at which they were collected (columns I and II) together with results of other investigators (columns III and IV).

In Tables (2-6) values obtained for density, refractive index, viscosity, magnetic susceptibility of the pure liquids (columns I), are compared with those of other investigators (columns II).

TABLE 1.

Liquid	I Boiling point °C.	II Atmospheric pressure (mm.)	III Boiling point °C.	IV Pressure (mm.)	Ref.
n-butyl alcohol	118·2	775			
	117·5-117·8	764			
	117·25-117·5	760	117·02	760	(1)
n-propyl "	96·4- 96·7	774	97·4	760	(2)
iso-propyl "	81·4 - 81·7	745	80·7-81·4	760	(3)
iso-butyl "	107·4-107·6	751	107·19-107·48	760	(4)
iso γ methyl butyl "	130·0-130·2	749	131·6	760	(2)

TABLE 2.

Liquid	Density		Ref.no.
	I $^{25}d_{25}$	II $^{0}d_{4}$	
n-butyl alcohol	0·80888	0·82393	(3)
	0·80841		
	0·80839		
	0·80827		
iso-propyl "	0·78343	0·81873	(3)
n-propyl "	0·80236	0·82135	
iso-butyl "	0·80041	0·80014-0 80032 ($^{25}d_{25}$)	(4)
iso methyl butyl "	0·81286	0·8110 ($^{25}d_{4}$)	(5)

TABLE 3.

Liquid	Refractive Index		Ref.no.
	I n^{25}_{D}	II n^{20}_{D}	
n-butyl alcohol	1·39747	1·39931	(6)
	1·39749		
iso-propyl "	1·37538	1·37757	(7)
n-propyl "	1·38343	1·38726 (n^{15}_{D})	(8)
iso-butyl "	1·39387	1·39750 (n^{15}_{D})	(9)
iso γ methyl butyl "	1·40781	1·4107 (n^{10}_{D})	(10)

TABLE 4.

Liquid	Viscosity		Ref.no
	I. η 25	II.	
n-butyl alcohol	0·025628	0·028016 η 21·83	(11)
	0·025750		
	0·025569		
	0·025617		
iso-propyl "	0·020087	0.0206 η 25	(12)
n-propyl "	0·019666	0·02101 η 22·86	(13)
iso butyl "	0·033556	0·030658 η 27·77	(14)
iso γ methyl butyl "	0·037563	0·03798 η 25	(15)
Water		0·008948 η 25	(16)

TABLE 5.

Liquid	Magnetic susceptibility x $^{-}10^{6}$ I	 II	Ref.no.
n-butyl alcohol	·7908	·815	17a
		·81	b
		·79	c
		·811	d
		·810	e
iso-propyl "	·7939		
n-propyl "	·7870	·766	18
iso-butyl "	·8094	·798	18
		·834	17
iso γ methyl butyl "	·8060		

TABLE 6.

Liquid	Specific Heat I	 II	Ref.no.
n-butyl alcohol	·591 ($\simeq$25°C.)	·689 (20-114°C.)	19
iso-propyl "	·650	·7064 (24-100°C.)	19

Preparation of mixtures.

Sets of nine binary mixtures containing approximately 10%, 20%.... etc. gram molecules of one constituent, and 90%, 80%.... etc. gram molecules respectively of the other constituent were made up in the following way.

Flasks of about 100 cc. capacity were cleaned by washing with hot chromic acid. They were rinsed well with distilled water, and treated with a current of steam for one hour, and afterwards dried in an oven at 110°C. for at least one hour. They were stoppered up with well fitting corks and each was weighed empty. In order to make up 50 cc. of each mixture, the volume required, (as calculated from density values) of one constituent was added from a burette; the flasks with the liquid were weighed; the required volume of the second constituent was added, and the flasks containing the mixture reweighed. The mixtures were stored in the dark. Mixtures were prepared in this way, of n-butyl alcohol with each of the following: n and iso-propyl, iso-butyl, and iso γ methyl butyl alcohols.

Tables (7-10) give the weights, together with the gram molecular composition which has been calculated from the weighings for every mixture.

TABLE 7.

No of mixture.	Wt of n-butyl alcohol.	Wt of iso-propyl alcohol.	% gm.mol. n-butyl alcohol.	% gm.mol. iso propyl alcohol.
	gms.	gms.		
1	4·8254	34·2229	10·26	89·74
2	9·3102	29·9655	20·12	79·88
3	13·8802	26·0082	30·20	69·80
4	17·9397	21·4563	40·45	59·55
5	22·0360	17·6948	50·86	49·14
6	25·9952	14·0400	60·02	39·98
7	29·8114	8·8027	73·40	26·60
8	33·4180	6·9260	79·64	20·36
9	37·2287	3·2757	90·21	9·79

TABLE 8.

No. of mixture.	Wt of n-butyl alcohol	Wt of n-propyl alcohol.	% gm.mol. n-butyl alcohol.	% gm.mol. n-propyl alcohol.
	gms	gms.		
1	4·8712	35·2380	10·09	89·91
2	9·4391	30·6356	20·00	80·00
3	13·9260	26·2444	30·13	69·87
4	18·2658	21·9816	40·26	59·74
5	22·2300	17·9673	50·09	49·91
6	26·2298	14·0724	60·55	39·45
7	29·9072	14·1700	62·79	37·21
8	33·5756	6·8491	79·83	20·17
9	37·1364	3·3696	89·92	10·08

TABLE 9.

No. of mixture	Wt of n-butyl alcohol.	Wt of iso-butyl alcohol.	% gm.mol. n-butyl alcohol.	% gm.mol. iso butyl alcohol.
	gms	gms.		
1	3·9081	35·9102	9·82	90·18
2	7·9887	31·8179	20·07	79·93
3	11·9992	27·8280	30·10	69·90
4	16·1643	23·7930	40·46	59·54
5	20·0933	19·8819	50·26	49·74
6	24·1136	14·3983	62·61	37·39
7	28·1182	12·0672	70·24	29·76
8	32·1710	8·0331	80·01	19·99
9	36·2456	3·2458	91·78	8·22

TABLE 10.

No. of mixture.	Wt of n-butyl alcohol.	Wt of γ amyl alcohol.	% gm.mol. n-butyl alcohol.	% gm.mol. γ amyl alcohol.
	gms.	gms.		
1	3·3358	37·0325	10·33	89·67
2	7·0890	32·8941	20·40	79·60
3	10·5589	29·6980	29·77	70·23
4	14·5975	25·7581	40·26	59·74
5	18·4825	21·8369	50·05	49·95
6	22·6786	17·6386	60·46	39·54
7	26·7792	13·7090	69·96	30·04
8	31·2085	9·1909	80·15	19·85
9	36·6138	3·9300	91·72	8·28

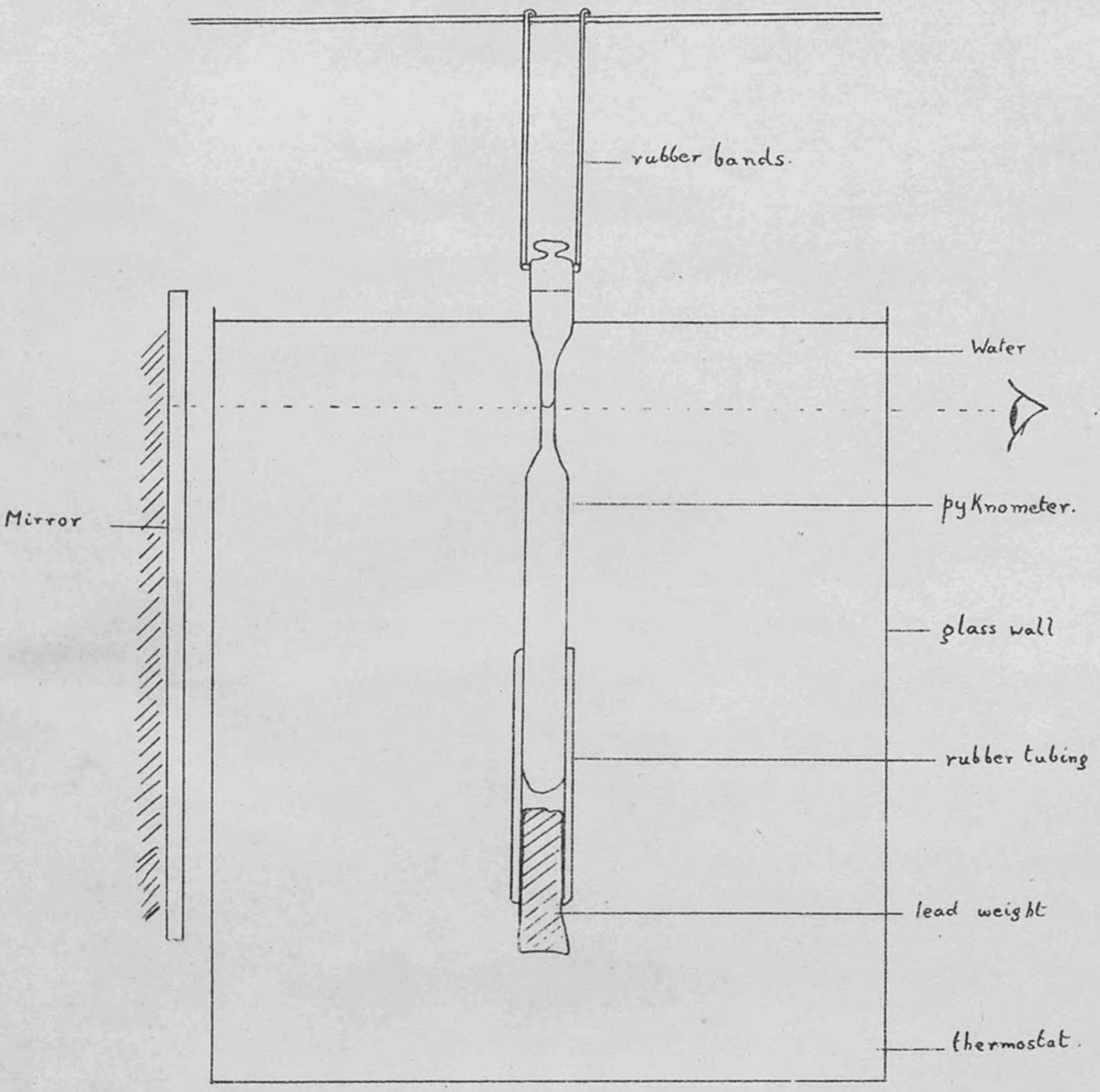

rubber bands.
Water
pyKnometer.
Mirror
glass wall
rubber tubing
lead weight
thermostat.

Fig. 1.

Determination of density.

Weights of equal volumes of water and each liquid were compared at the same temperature (25°C) by the following method.

Preliminary measurements shewed that to obtain results reliable to at least the fourth decimal place the pyknometer must be treated consistently on all occasions. The method described below, therefore, was adopted in all weighings of the pyknometer.

Each weighing was made to the fifth decimal place, by the oscillating method, on a Bunge balance fitted with a telescope and capable of weighing correctly to $^{1}/100$ mgm. The weights used were of quartz and platinum and these had been previously calibrated.

A pyknometer of about 2 cc. capacity was cleaned with chromic acid, washed with distilled water and dried. Before weighing it was hung in the thermostat at 25° for a few minutes, dried with a soft cloth, and left in a dessicator for 20-30 mins. After leaving in the balance case for another 10 mins. it was weighed as described above.

Freshly boiled, distilled water was poured into the pyknometer which was hung in a glass-walled thermostat at the required temperature for about $\frac{1}{4}$ hour. The vessel was held in a vertical position by means of a lead weight as shewn, (Fig.1.) and the level of the liquid adjusted so that the bottom of the meniscus was just touching the scratch on the neck when viewed in a mirror at the back of the thermostat. Any excess of water was carefully removed by means of a capillary tube and filter paper, the pyknometer was then dried, left in the dessicator and balance case for 20-30, and 10 minutes respectively, as before, and weighed. The level was re-adjusted and the vessel reweighed, the whole process repeated, and the average of nine results obtained.

The pure liquids and each mixture were dealt with in a similar way, at least two adjustments of level being made for each liquid.

The neck of the pyknometer used for the fourth set of results was of decidedly smaller bore than the other, and it was found unnecessary to make more than two adjustments.

Having found the weights of equal volumes of water, of the mixtures, and of their constituents, the density of each mixture compared to the density of water at 25°C. was calculated. The results of the determinations are given in Tables (11-14), and in the curves Fig. (5). In the case of the curves, the density is plotted as ordinate against the composition of the mixtures expressed in gram molecules.

A further set of curves (Fig.11) shewing the percentage deviation of the density of each mixture from the value calculated from the mixture law is also given.

Determination of refractive index.

A Pulfrich refractometer made by Zeiss was used to measure the refractive index of the pure liquids and liquid mixtures. The temperature was maintained at 25°C. by means of water circulating at that temperature in the cell containing the liquid and round the prism. All measurements were made using the D-line obtained from a sodium lamp.

The zero of the instrument was ascertained by use of the small prism let into the telescope, and the value obtained was used in correcting subsequent readings. To measure the angle made by the emergent ray with its original direction, the D-line was set in position near the cross wires, the telescope was then clamped, and the fine adjustment made with the micrometer screw. The reading to the nearest minute of arc was made directly from the vernier scale. This was repeated with a fresh quantity of the liquid, and the mean value taken.

The refractive index was read from tables supplied with the instrument. Tables (15-18) shew the results from which refractive index - gm. molecular composition, and refractive index - deviation curves have been drawn. See Figs. (6 and 11.)

Determination of viscosity.

The viscosity of the pure liquids and of each mixture was determined at 25°C, using an Ostwald viscosimeter constructed according to the specification 118/1923 of the British Engineering Standards Association. The instrument chosen was of such a size that the minimum time of flow of the liquid was not less than 60 secs, this being within the limit of the value required by Reynold's criterion for non-turbulent flow as deduced from the dimensions of the viscosimeter. Namely

$$v < \frac{1000\eta}{rd}$$

where v = velocity in cm/sec.
η = viscosity of liquid.
d = density of liquid.
r = radius of tube.

The viscosities of n and iso-butyl, and amyl alcohols were high, and in order to economise time a larger viscosimeter was used to measure the viscosities of these alcohols. This viscosimeter was of such a size that the minimum time of flow of the liquids was still 60 secs., n-butyl alcohol being taken as the standard liquid in place of water. The viscosity of the n-butyl alcohol was determined as previously, using the small viscosimeter with water as the standard liquid.

Before using a viscosimeter, it was cleaned with chromic acid to remove every trace of grease, and then rinsed thoroughly with distilled water. In order to dry it, a current of dust-free air was drawn through it for about 30 mins.

A quantity of freshly boiled distilled water was measured out at 25°C. by means of a pipette. This was fashioned with a drawn-out end, to facillitate insertion into the viscosimeter, and with a narrow neck to enable an exact volume of liquid to be introduced.

The viscosimeter was hung in a thermostat of water at 25°C, for about 10 mins. after which period the time taken for the liquid to flow through the viscosimeter was noted by means of a stop-watch reading correctly to $^1/_5$ sec. Since all subsequent viscosity values must depend upon the time of flow of water, a larger number of readings were made with this liquid than with others. The average of 4-6 readings differing by not more than $^3/_5$ sec. was taken; a fresh quantity of water was put into the viscosimeter after drying as before, and the process was repeated. The mean of five averages obtained by using fresh quantities of liquid was finally taken.

Each liquid was dealt with in a similar way, but fewer readings were taken. In the case of the pure liquids, the mean of values obtained from two or three fresh quantities of the liquid was considered to give sufficiently accurate results.

When using the larger viscosimeter, to avoid the use of large quantities of expensive liquids, in most cases only one quantity of liquid was used, but an average of ten readings was made.

Having obtained in this way the time of flow of equal volumes of water and liquids, and knowing the densities of these liquids and assuming the viscosity of water at 25°C to be $8{\cdot}95 \times 10^{-3}$ (21 and 22), the viscosity of the liquids were calculated from the following formula:-

$$n_l = \frac{d_l t_l}{d_w t_w} \times 8{\cdot}95 \times 10^{-3}$$

where d_l = density of liquid (d^{25}_{25})

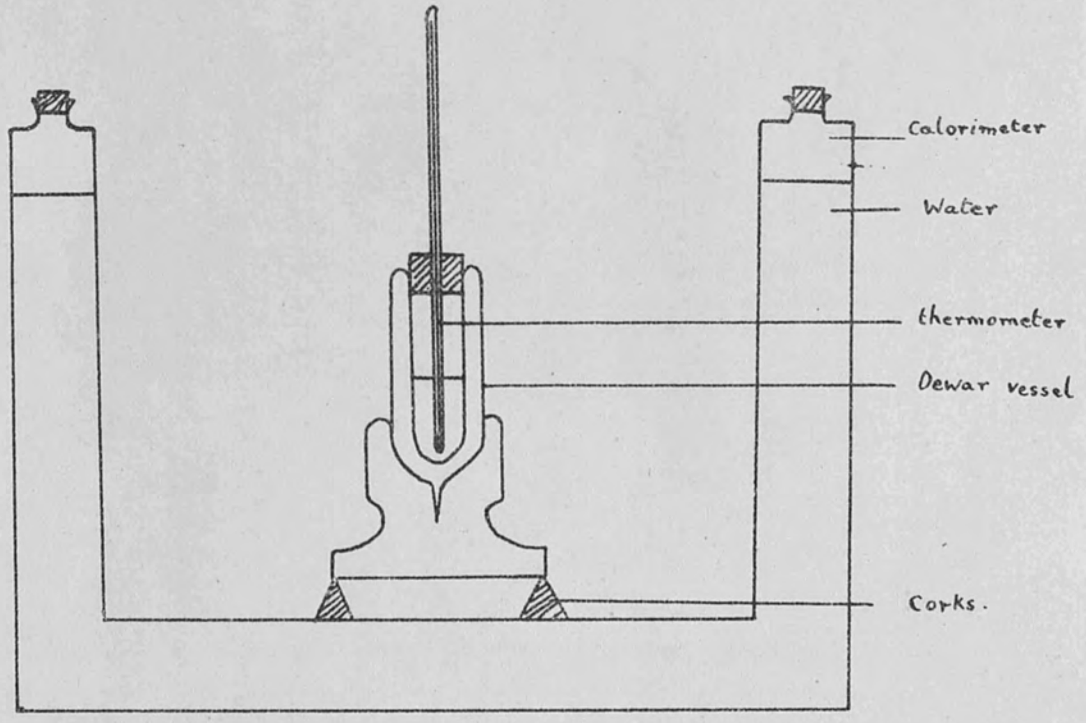
d_w = density of water at 25°C.

t_l = time of flow of liquid in secs.

t_w = time of flow of water in secs.

The results, shewing viscosity and also percentage gram molecular deviation values, are tabulated in Tables (19-22). Viscosity-composition, and deviation-composition curves are shewn in Figs. (7,8 and 11).

Fig. 2



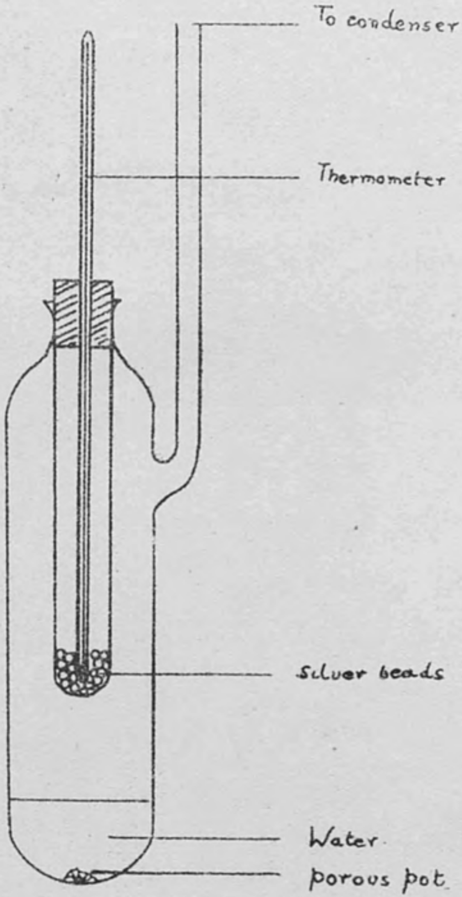


Fig. 3.

Determination of heat of mixing.

In calculating the heat of mixing from experimental results, the specific heat of the mixture is required. Hence the method employed was one which involved the determination of the specific heat of each liquid mixture.

Standardised thermometers reading to $\frac{1}{10}$°C were used, and were read to the nearest $\frac{1}{100}$°C. To guard against loss of heat the calorimeter, which was a small Dewar vessel, was placed on a stand resting on corks inside a large copper calorimeter, see Fig. (2).

The water equivalent of the Dewar vessel and thermometer, which was used as stirrer, was first determined. The volume of water used for this, and subsequently the volume of liquid mixtures measured out, was kept constant in order that the loss of heat inevitably occurring by contact with the glass, should be the same for each determination. The Dewar vessel was weighed empty; 30 cc. of water were added and the vessel was reweighed. A thermometer passing easily through a cork which fitted the neck, was placed in the liquid and the vessel was left in the calorimeter until the temperature was steady. Meanwhile silver beads of known weight were heated in a double-walled boiling tube as shewn in Fig. (3). To avoid superheating, it was found necessary to insert an asbestos pad between the tube and retort holder when boiling the water contained in the outer jacket. When the temperature was constant it was noted, the thermometer was removed, and the beads quickly tipped into the Dewar vessel. The liquid was stirred well with the thermometer already in the vessel, and the temperature was taken every ½ min. from ½ min. after the time of mixing until the fall became regular. By plotting a time-temperature graph, and extrapolating, the temperature at the time of mixing and hence the water equivalent, was obtained. An average was taken, of five results agreeing closely.

To determine the heat of mixing of two liquids, the Dewar vessel and a small flask each fitted with a cork were weighed empty. The amounts of liquids calculated to give 30 cc. of mixture of the required composition were run in to each respectively from a burette. The vessels were reweighed and left in the calorimeter until the temperatures were steady. These were then noted, the liquids were mixed, and the temperature at the time of mixing obtained by extrapolation, as before.

The specific heat of the liquid mixture was then determined by the method of mixing used for obtaining the water equivalent of the calorimeter as described above. The specific heats of the two pure liquids were determined in a similar way. The usual formula, see (1), as given below, was used in the calculation. The mean of a number of results was taken, and a specific heat-composition curve was drawn. The curve was found to be approximately a straight line.

Using this graph, and the following formula (2), the heats of mixing of n-butyl alcohol and iso-propyl alcohols in a number of different proportions were determined.

$$S_m = \frac{1}{W_m} \left(\frac{W_s S_s \ (t_2 - t_3)}{t_3 - t_1} \ - W \right) \qquad (1)$$

where S_m = specific heat of the liquid.

W_m = wt. of liquid.

W_s = " " silver.

W = water equivalent of calorimeter and stirrer.

t_1 = initial temperature of liquid.

t_2 = " " " silver.

t_3 = temperature at time of mixing.

$$H = \frac{S_m(W_m)(t_3 - \frac{t_1 + t_2}{2}) \ + \ W(t_3 - t_1)}{W_m} \qquad (2)$$

where H = heat of mixing of the liquids.

W_m = weight of mixture.

$t_1 t_2$ = initial temperatures of the liquids in calorimeter and other vessel respectively.

t_3 = temperature of mixture.

S_m = specific heat of the mixture at t_3.

It was found that the temperature changes on mixing n-butyl and iso-propyl alcohols were very small and always less than 1°C. With the apparatus available the obtaining of values giving smooth curves would have required taking the mean of a very large number of experiments. This was not possible with the limited time and materials at disposal. Assuming the heat of mixing of the other alcohols under consideration to be of the same order as that of n-butyl and iso-propyl alcohols, the method was rejected as being unreliable.

The results obtained for n-butyl and iso-propyl alcohols are given in Tables (23 and 24), and specific heat-composition and heat of mixing composition curves are shewn in Fig.(9).

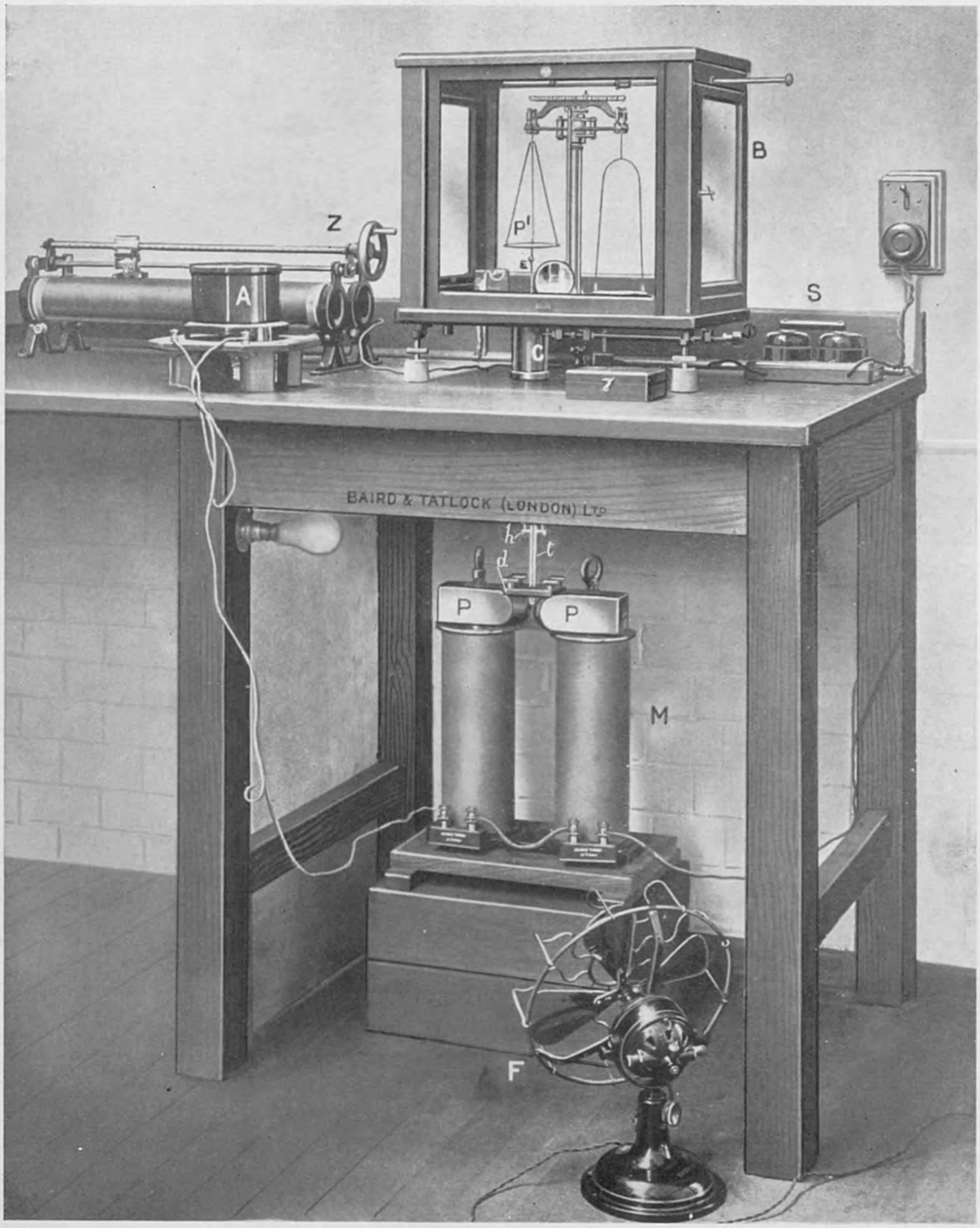
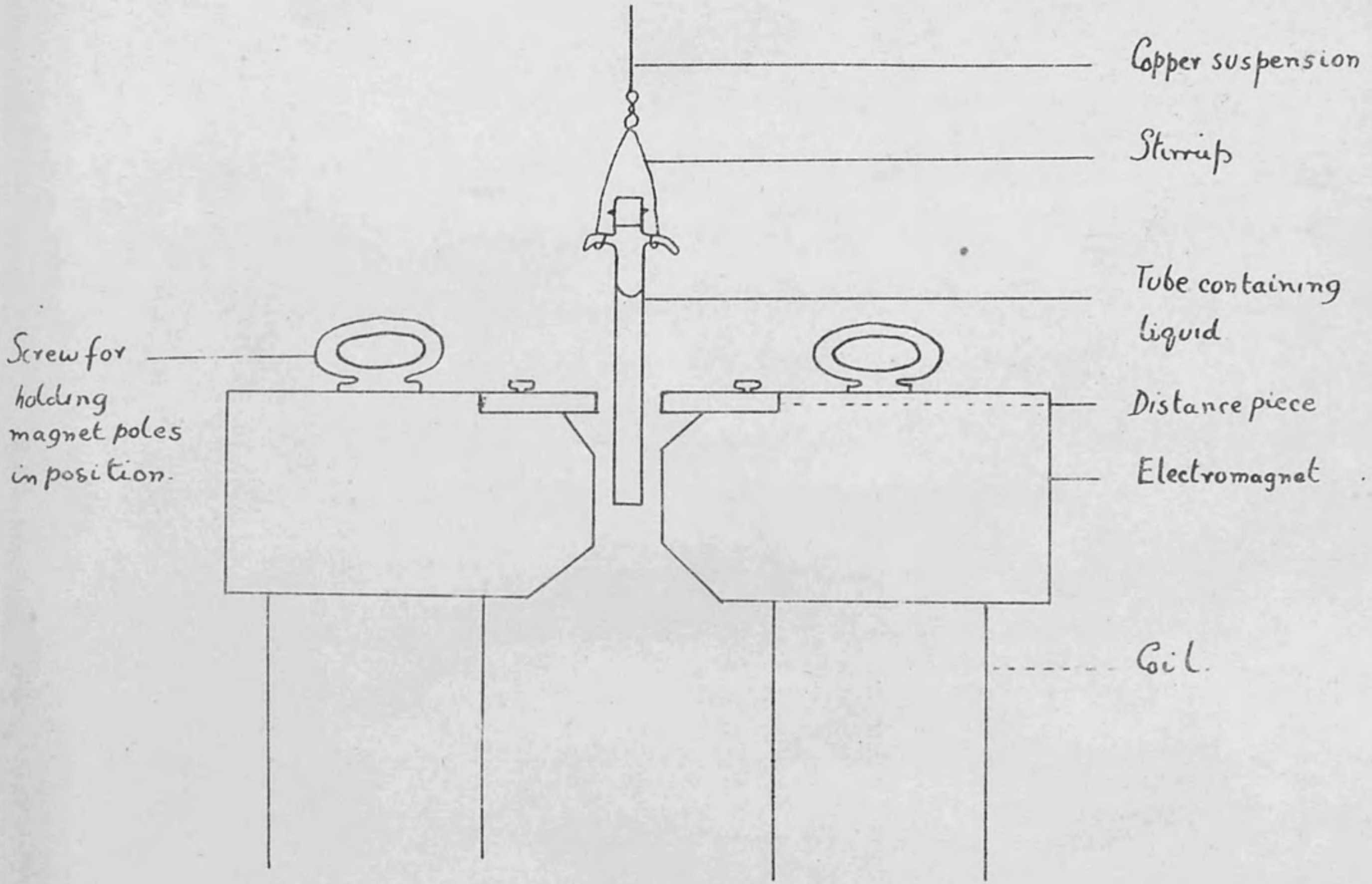
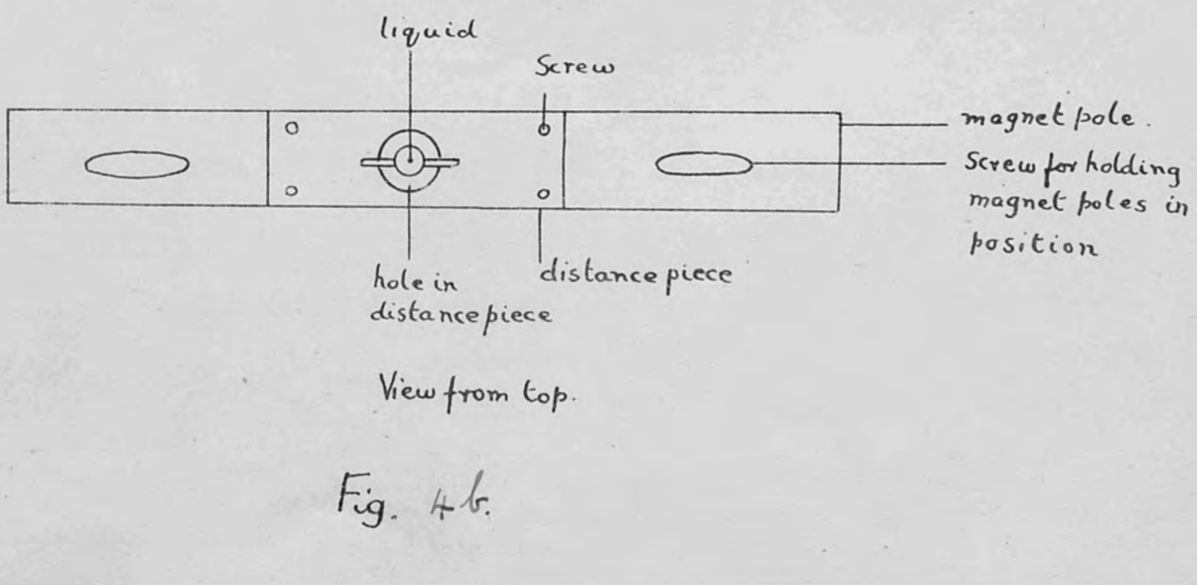


FIG. 4a.



Side view



View from top.

Fig. 4b.

Determination of Magnetic Susceptibility.

For the measurement of the magnetic susceptibility of the liquids under consideration, the Guoy method was used, and the apparatus shewn in Fig. (4a). A column of liquid of constant length was suspended in a homogeneous field between the poles P of an electromagnet M, so that one end of the column was in the maximum field and the other end in a region of no magnetic field, and the pull exerted on the liquid was determined by weighing.

The balance B used for the purpose was of the Bunge type, modified so that the lever D was worked from the right-hand side, while the fine copper wire E carrying the vessel and liquid to be weighed passed up through a hole in the bench to the beam of the balance. The vessel (t) was of glass, shaped with arms as shewn in Fig. (4b.), and was hung between the poles of the magnet by means of a copper stirrup (h). This was attached to the suspension in such a way that the position of the glass tube could be readjusted so that the inside meniscus of the bottom of the tube was level with a mark on the centre of the pole piece of the magnet. The distance between the pole pieces was maintained by a brass distance-piece (d) with a circular hole through which the tube containing the liquid hung. The metal plate was kept in its position on the pole pieces by means of screws.

A current of 3 amps. passing through magnet coils of 20,000 turns produced a field of about 5,400 gauss. The current was controlled by a resistance Z connected with a two-pole switch (S), and was registered on an ammeter A. The field was explored in preliminary experiments and was found to be uniform for at least 2 mm. on either side of the centre, very nearly uniform for about 1 cm. on either side of the mark, and was negligible at a region 6·5 cms. above.

The pull on a known volume of liquid was determined in the following way. The tube was weighed in and out of the magnetic field. The liquid was measured out and added by means of a pipette, and the apparatus was again weighed in and out of the field. The values of the pull on the empty tube were redetermined throughout the course of the experiments and were found not to differ from each other more than those determined on the same day. An average was therefore taken, and this was used throughout the determinations and was subtracted in each case from the total pull of the liquid and tube.

To obtain reliable results certain other precautions were necessary. Weighings were made by the oscillation method, using standardised weights, and allowing only small amplitudes. In this way swinging of the tube out of a uniform field was prevented. The magnet and apparatus below the bench was boarded in, and the suspension up to the base of the balance was surrounded by a copper tube C, to shield from draughts and sudden changes of temperature. The substance was weighed in and out of the magnetic field very rapidly, so that readings should be made at the same temperature as nearly as possible. The temperature of the air between the poles was noted before and after each reading by means of a thermometer placed between the poles, and results were considered untrustworthy if the temperature differed by more than 1°C during the determination. In order to avoid heating of the coils and hence production of convection currents which would affect the weighings, the electric current was kept on for as short a time as possible, and the magnet was cooled by means of an electric fan F. after each time of using. Results to the 5th place of decimals were obtained, but as the last figure was not entirely reliable a large number of readings agreeing within ·04 or ·05 mgm. were obtained, and the average taken.

The magnetic susceptibility was calculated from the following formula:- (20)

$$10^6 \chi = \frac{0{\cdot}03 \ell A + \alpha F}{W}$$

where χ = magnetic susceptibility.

$\cdot 03 \times 10^{-6}$ = volume susceptibility of air.

W = weight of substance in gms.

F = pull of substance in mgms.

A = area of cross section of tube.

ℓ = length of liquid column.

α = constant for apparatus.

$$= \frac{2\ell \times 981 \times 10^6}{H_1^2 \times 100} \text{ C.G.S. units.}$$

H_1 = field at bottom of cylinder, depending on the distance between the pole pieces.

Preliminary experiments gave $\underline{\alpha = \cdot 520}$ for distance piece used.

[Mean of 16 determinations.]

when $\ell = 7{\cdot}75$ cms.

Hence

$$H_1 = \frac{\sqrt{2 \times 7{\cdot}75 \times 981 \times 10^3}}{\cdot 520}$$

$$= \underline{5408 \text{ gauss}}.$$

For other lengths of material used:

$$\alpha' = \frac{\cdot 520 \times l}{7 \cdot 75}$$

where α' = new constant.
l' = new length of column.

For 1st mixture $l_1 = 8{\cdot}5$ cms.
$\therefore \alpha = \cdot 570$
$\cdot 03 l_A = \cdot 12379$

For remaining mixtures
$\alpha = \cdot 566$
$\cdot 03 l_A = \cdot 12256$

In Tables (25-28) the results are recorded, and Figs. (10 and 11) shew magnetic-susceptibility-composition, and deviation-composition curves.

TABLES OF RESULTS.

Density.

TABLE 11.

Mixture. N-butyl and iso-propyl alcohols.

No. of mixture	Wt of mixture	$^{25}d_{25}$ (expt.)	$^{25}d_{25}$ (cal^d)	% gm.mol. deviation from cal^d
iso-propyl alcohol	1·56845	0·78343	-	
1	1·57498	0·78662	0·78604	0·073
2	1·58052	0·78946	0·78855	0·115
3	1·58646	0·79242	0·79111	0·165
4	1·59227	0·79533	0·79372	0·203
5	1·59715	0·79776	0·79637	0·174
6	1·60145	0·79991	0·79870	0·150
7	1·60799	0·80318	0·80211	0·133
8	1·61087	0·80462	0·80370	0·114
9	1·61513	0·80675	0·80639	0·046
n-butyl alcohol	1·61940	0·80888	-	

TABLE 12.

Mixture. N-butyl and n-propyl alcohols.

No. of mixture	Wt of mixture	$^{25}d_{25}$ (expt.)	$^{25}d_{25}$ (cal^d)	% gm.mol. deviation from cal^d
n-propyl alcohol	1·60635	0·80236	-	
1	1·60826	0·80331	0·80297	·042
2	1·60963	0·80402	0·80357	·056
3	1·61083	0·80460	0·80418	·052
4	1·61252	0·80544	0·80480	·079
5	1·61374	0·80605	0·80544	·076
6	1·61470	0·80653	0·80602	·063
7	1·61489	0·80663	0·80616	·058
8	1·61634	0·80735	0·80719	·020
9	1·61746	0·80792	0·80780	·015
n-butyl alcohol	1·61847	0·80841	-	

TABLE 13.

Mixture. N-butyl and iso-butyl alcohols.

No. of mixture	Wt of mixture	$^{25}d_{25}$ (expt.)	$^{25}d_{25}$ (cal^d)	% gm.mol. deviation from cal^d
iso-butyl alcohol	1·60245	0·80041	-	
1	1·60396	0·80117	0·80121	-
2	1·60601	0·80219	0·80201	·002
3	1·60748	0·80292	0·80280	·001
4	1·60904	0·80378	0·80364	·001
5	1·61045	0·80441	0·80442	-
6	1·61235	0·80536	0·80541	·001
7	1·61389	0·80613	0·80601	·001
8	1·61505	0·80671	0·80677	·001
9	1·61724	0·80780	0·80773	·001
n-butyl alcohol	1·61842	0·80839	-	

TABLE 14.

Mixture. N-butyl and iso γ methyl butyl alcohols.

No. of mixture	Wt of mixture	$^{25}d_{25}$ (exp^{t})	$^{25}d_{25}$ (cal^{d})	% gm.mol. deviation from cal^{d}
γ amyl alcohol	1·65931	0·81286	-	
1	1·65839	0·81241	0·81239	·002
2	1·65738	0·81191	0·81192	·001
3	1·65662	0·81153	0·81149	·005
4	1·65577	0·81112	0·81101	·013
5	1·65484	0·81067	0·81056	·013
6	1·65416	0·81033	0·81008	·031
7	1·65322	0·80988	0·80965	·028
8	1·65190	0·80923	0·80918	·006
9	1·65085	0·80871	0·80865	·007
n-butyl alcohol	1·64994	0·80827	-	

Average wt. of water at 25° contained in pyknometer used for the three first mixtures = 2·00202 gms.

[This was the result of nine determinations, the extreme values being 2.00173 - 2·00223.]

Average wt. of water at 25° contained in pyknometer (which was not the same instrument as used above) used for fourth mixture = 2·04132 gms.

Refractive Index.

TABLE 15.

Mixture. N-butyl and iso-propyl alcohols.

No. of mixture	i	$n_{D_{25}}$ (expt.)	$n_{D_{25}}$ (cal^{d})	% gm.mol. deviation from cal^{d}
iso-propyl alcohol	58°37'	1·37538	-	-
1	58°8·1'	1·37810	1·37765	·033
2	57°39'	1·38086	1·37983	·075
3	57°14'	1·38325	1·38205	·087
4	56°51'	1·38560	1·38431	·093
5	56°28'	1·38767	1·38661	·077
6	56°74'	1·38967	1·38865	·073
7	55°40'	1·39233	1·39159	·053
8	55°24·2'	1·39386	1·39297	·060
9	55°4·3'	1·39580	1·39531	·036
n-butyl alcohol	54°47.2'	1·39747	-	

TABLE 16.

Mixture. N-butyl and n-propyl alcohols.

No. of mixture	i	$^{n}D_{25}$ (expt.)	$^{n}D_{25}$ (cal^{d})	% gm.mol. deviation from cal^{d}
n-propyl alcohol	57°12·4'	1·38343	-	-
1	56°54·3'	1·38513	1·38485	·020
2	56°37·4'	1·38674	1·38624	·036
3	56°22·4'	1·38820	1·38762	·041
4	56°5·15'	1·38987	1·38910	·055
5	55°50·6'	1·39128	1·39049	·057
6	55°37·15'	1·39259	1·39195	·046
7	55°33·65'	1·39293	1·39226	·048
8	55°12·0'	1·39504	1·39465	·029
9	54°58·6'	1·39634	1·39607	·019
n-butyl alcohol	54°47·0'	1·39749	-	-

TABLE 17.

Mixture. N-butyl and iso-butyl alcohols.

No.of mixture	i	$^{n}D_{25}$ (expt.)	$^{n}D_{25}$ (cal^{d})	% gm.mol. deviation from cal^{d}
iso-butyl alcohol	55°24·0'	1·39387	-	-
1	55°20·0'	1·39426	1·39422	·003
2	55°15·0'	1·39474	1·39460	·010
3	55°10·5'	1·39518	1·39496	·016
4	55° 7·5'	1·39548	1·39533	·011
5	55°3·75'	1·39584	1·39569	·011
6	54°58·25'	1·39638	1·39615	·017
7	54°56·25'	1·39658	1·39641	·012
8	54°53·5'	1·39690	1·39667	·016
9	54°49·75'	1·39719	1·39719	0
n-butyl alcohol	54°47·25'	1·39749	-	-

TABLE 18.

Mixture. N-butyl and iso γ methyl butyl alcohols.

No. of mixture	i	$^{n}D_{25}$ (expt.)	$^{n}D_{25}$ (cal^{d})	% gm.mol. deviation from cal^{d}
γ amyl alcohol	53°2·5'	1·40781	-	-
1	53°10·0'	1·40706	1·40674	·029
2	53°18·0'	1·40625	1·40570	·039
3	53°30·0'	1·40538	1·40474	·046
4	53°39·8'	1·40449	1·40365	·053
5	53°46·0'	1·40350	1·40264	·061
6	53°59·5'	1·40216	1·40157	·044
7	54° 8·5'	1·40128	1·40059	·048
8	54°20·5'	1·40010	1·39954	·040
9	54°34·5'	1·39871	1·39834	·026
n-butyl alcohol	54°47·0'	1·39749	-	-

Viscosity.

TABLE 19.

Mixture. N-butyl and iso propyl alcohols.

No. of mixture	Time of flow. (secs)	Viscosity $(\eta 25)$ expt. $(x10^3)$	Viscosity $(\eta 25)$ cal^d $(x10^3)$	% gm.mol. deviation from cal^d
Water	108·8			
iso-propyl alcohol	312·4	2·0087		
1	317·9	2·0571	2·0656	0·41
2	324·1	2·1048	2·1202	0·74
3	329·1	2·1452	2·1760	1·41
4	337·4	2·2074	2·2328	1·14
5	345·7	2·2686	2·2904	0·95
6	353·7	2·3274	2·3413	0·59
7	363·5	2·4017	2·4154	0·56
8	368·2	2·4371	2·4500	0·53
9	377·6	2·5059	2·5085	0·10
n-butyl alcohol	385·2			

TABLE 20.

Mixture. N-butyl and n-propyl alcohols.

No. of mixture	Time of flow. (secs)	Viscosity (η_{25}) expt. $(x10^3)$	Viscosity (η_{25}) Cal^d $(x10^3)$	% gm.mol. deviation from cal^d
Water	83·9			
n-propyl alcohol	229·7	1·9666		
1	235·5	2·0241	2·0280	0·19
2	242·9	2·0816	2·0883	0·32
3	248·8	2·1355	2·1499	0·65
4	255·6	2·1945	2·2115	0·72
5	262·2	2·2540	2·2713	0·76
6	269·7	2·3189	2·3350	0·70
7	270·3	2·3261	2·3486	0·90
8	283·0	2·4316	2·4523	0·82
9	289·4	2·4941	2·5137	0·78
n-butyl alcohol	299·3	2·5750		

TABLE 21.

Mixture. N-butyl and iso-butyl alcohols.

No.of mixture	Time of flow (secs)	Viscosity (η_{25}) expt. (x10^3)	Viscosity (η_{25}) cal^d (x10^3)	% gm.mol. deviation from cal^d
*Water	83·9			
*n-butyl alcohol	296·5			
iso-butyl "	90·0	3·3556		
1	86·8	3·2385	3·2771	1·18
2	83·05	3·1106	3·1962	2·67
3	80·6	3·0157	3·1142	3·16
4	78·4	2·9354	3·0324	3·20
5	76·3	2·8590	2·9542	3·22
6	73·9	2·7724	2·8555	2·91
7	72·6	2·7262	2·7946	2·44
8	71·1	2·6719	2·7166	1·64
9	69·4	2·6076	2·6225	0·56
n-butyl alcohol	67·9	2·5569		

*Small viscosimeter used.

TABLE 22.

Mixture. N-butyl and γ methyl butyl alcohols.

No. of mixture	Time of flow (secs)	Viscosity ($_{25}$) expt. (x10^3)	Viscosity ($_{25}$) cal^d (x10^3)	% gm.mol. deviation from cal^d
*Water	83·9			
*n-butyl alcohol	297·1			
γ-amyl alcohol	100·4	3·7563		
1	96·6	3·6200	3·6329	0·36
2	92·7	3·4722	3·5117	1·12
3	89·3	3·3432	3·4006	1·68
4	85·8	3·2105	3·2754	1·98
5	82·7	3·0928	3·1580	2·06
6	79·5	2·9719	3·0340	2·04
7	76·3	2·8507	2·9207	2·39
8	73·55	2·7457	2·7988	1·93
9	70·1	2·6152	2·6606	1·69
n-butyl alcohol	68·7	2·5617		

*Small viscosimeter used.

Specific Heat and Heat of Mixing.

TABLE 23.

Mixture. n-butyl and iso-propyl alcohols.

% composition of mixture (gm. mols.) Iso-propyl alcohol.	n-butyl alcohol	Specific heat
100	0	·650
9·7	90·3	·649
21·3	78·7	·636
29·9	70·1	·627
39·6	60·4	·625
49·85	50·15	·625
58·25	41·75	·614
69·9	30·1	·603
80·0	20·0	·606
86·4	13·6	·588
0	100	·591

TABLE 24.

Mixture. N-butyl and Iso-propyl alcohols.

No. of mixture	Weight of		% gm.mol.comp^n of mixture		S_m	t_1	t_2	t_3	Heat of mixing
	Iso-propyl alcohol	n-butyl alcohol	Iso-propyl alcohol	n-butyl alcohol					
	gms.	gms.							
1	20·4610	2·8904	89·7	10·3	·644	18·6	18·1	18·61	·168
2	18·1020	5·4639	77·9$_5$	22·0$_5$	·637	18·1	17·5	18·2	·269
3	15·4523	9·2897	67·2	32·8	·631	16·7	17·0	17·01	·143
Average 2 and 3			72·6	27·4					·206
4	13·0513	10·6527	60·4	39·6	·627	15·3	15·9	15·9	·262
6	9·0123	15·5056	41·7$_5$	58·25	·615$_5$	17·78	17·1	17·8	·224
7	6·2133	17·9070	30·0	70·0	·608$_5$	17·31	16·5	17·3	·231
8	4·0389	20·1095	19·9	80·1	·602$_5$	16·4	16·0	16·5	·121
9	1·9685	19·5220	11·1	88·9	·599	15·2	15·32	15·32	·055

Magnetic Susceptibility.

Pull on empty tube = 1·08 mgms.

[Average of 13 determinations differing by not more than ·17 mgm.]

TABLE 25.

Mixture. N-butyl and iso-propyl alcohols.

No. of mixture	Mean pull. mgms (Corrected)	Wt of substance gms	Temp. °C	Magnetic susceptibility $-10^6\chi$		% deviation from cal^d
				(exp^t)	(cal^d)	
Iso-propyl alcohol	4·28	3·22877	20	·7939		
1	4·31	3·25181	19	·7936	·7936	0
2	4·32	3·25198	21	·7952	·7934	·23
3	4·33	3·26142	20	·7947	·7932	·19
4	4·37	3·27078	21	·7963	·7929	·43
5	4·35	3·27691	22	·7974	·7927	·59
6	4·37	3·28417	23	·7962	·7925	·47
7	4·40	3·29191	23	·7975	·7921	·68
8	4·42	3·31700	19	·7969	·7920	·62
9	4·42	3·32704	19	·7944	·7917	·34
n-butyl alcohol	4·41	3·32631	20	·7916		

TABLE 26.

Mixture. N-butyl and n-propyl alcohols.

No. of mixture	Mean pull mgms. (Corrected)	Wt of substance gms	Temp. °C	Magnetic susceptibility $-10^6\chi$ (exp^t)	(cal^d)	% deviation from cal^d
n-propyl alcohol	4·35	3·28382	23	·7870		
1	4·36	3·28950	22	·7874	·7874	0
2	4·37	3·29518	25	·7878	·7879	0
3	4·37	3·28634	25	·7899	·7881	·23
4	4·38	3·29150	23	·7905	·7884	·27
5	4·40	3·29666	24	·7926	·7888	·48
6	4·42	3·30456	22	·7941	·7892	·61
7	4·42	3·30448	23	·7941	·7893	·60
8	4·41	3·31351	26	·7940	·7899	·51
9	4·41	3·31502	27	·7933	·7902	·39
n-butyl alcohol	4·41	3·30771	24	·7916		

TABLE 27.

Mixture. N-butyl and iso butyl alcohols.

No. of mixture	Mean pull (mgms) (Corrected)	Wt of substance gms	Temp. °C	Magnetic susceptibility $-10^6\chi$		% deviation from cal^d
				(exp^t)	(cal^d)	
iso-butyl alcohol	4·48	3·28434	22	·8094	-	
1	4·49	3·28725	22	·8102	·8075	·33
2	4·50	3·29101	23	·8111	·8055	·69
3	4·51	3·29885	23	·8112	·8036	·94
4	4·50	3·29518	20	·8101	·8016	1·06
5	4·49	3·29813	21	·8080	·7997	1·04
6	4·49	3·30109	22	·8069	·7992	1·1
7	4·46	3·29936	29	·8025	·7958	·91
8	4·46	3·31068	22	·7995	·7939	·7
9	4·43	3·31658	19	·7925	·7916	·01
n-butyl alcohol	4·41	3·31406	26	·7900		

TABLE 28.

Mixture. N-butyl and iso γ methyl butyl alcohols.

No. of mixture	Mean pull mgms (Corrected)	Wt of substance gms	Temp. °C	Magnetic susceptibility $-10^6\chi$		% deviation from cald
				(exp^t)	(cal^d)	
γ amyl alcohol	4·52	3·32610	21	·8060	-	-
1	4·51	3·31796	23	·8056	·8032	·30
2	4·50	3·31044	23	·8057	·8003	·67
3	4·47	3·30274	26	·8031	·7975	·70
4	4·47	3·31521	22	·8001	·7926	·97
5	4·46	3·31644	23	·7974	·7918	·71
6	4·45	3·31380	24	·7965	·7890	·97
7	4·44	3·31748	25	·7945	·7861	1·06
8	4·40	3·31757	23	·7868	·7833	·44
9	4·37	3·31078	23	·7833	·7799	·43
n-butyl alcohol	4·33	3·30539	24	·7776	-	-

Density · composition curves.

n butyl alcohol with
iso propyl alcohol – in black
n propyl – red
iso butyl – violet
iso methyl butyl – green.

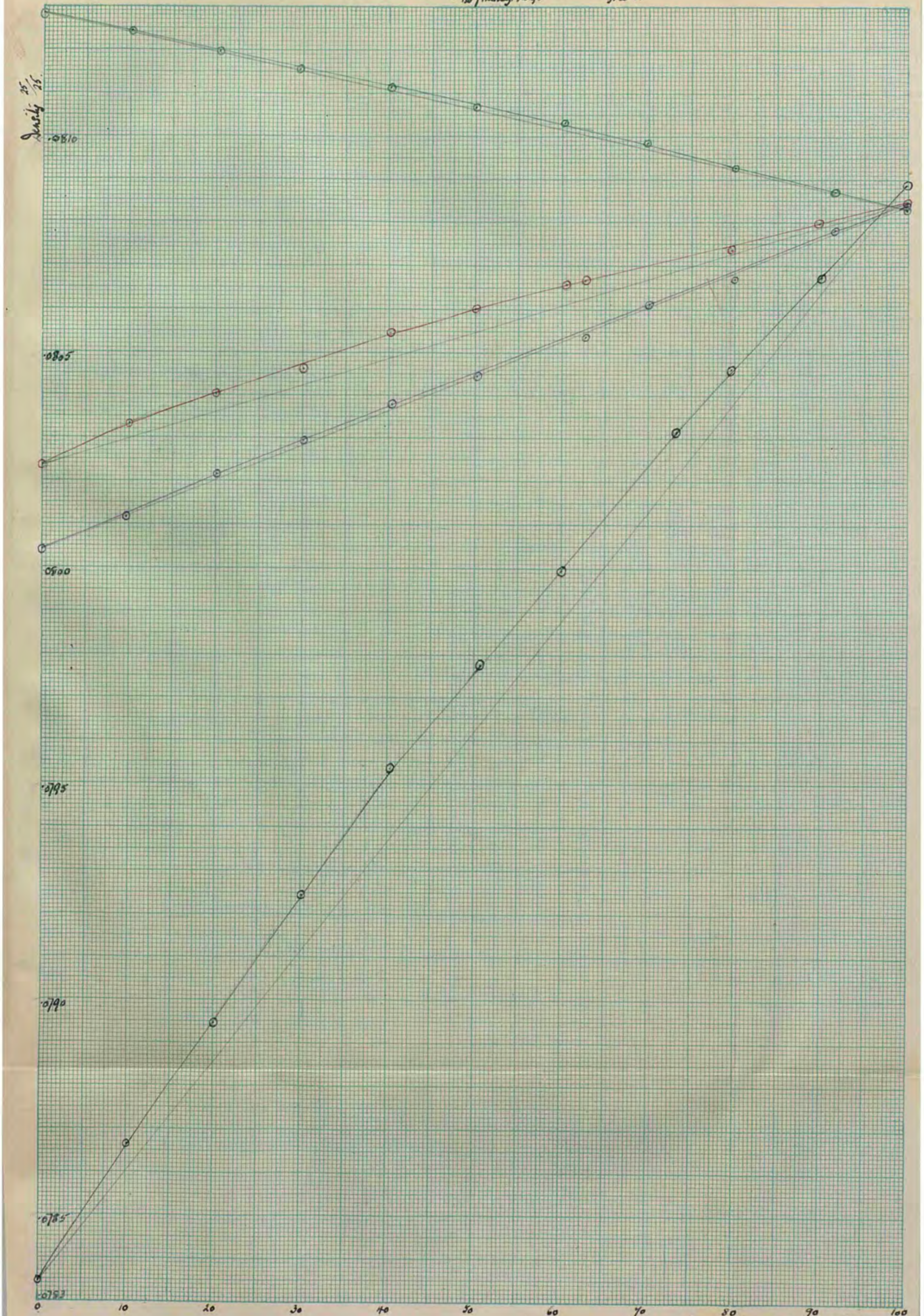


FIG. 5.

Refractivity-composition curves.

Mixtures of n butyl alcohol with
iso propyl alcohol in black
n-propyl. " - red
iso-butyl " - violet
iso methyl butyl - green.

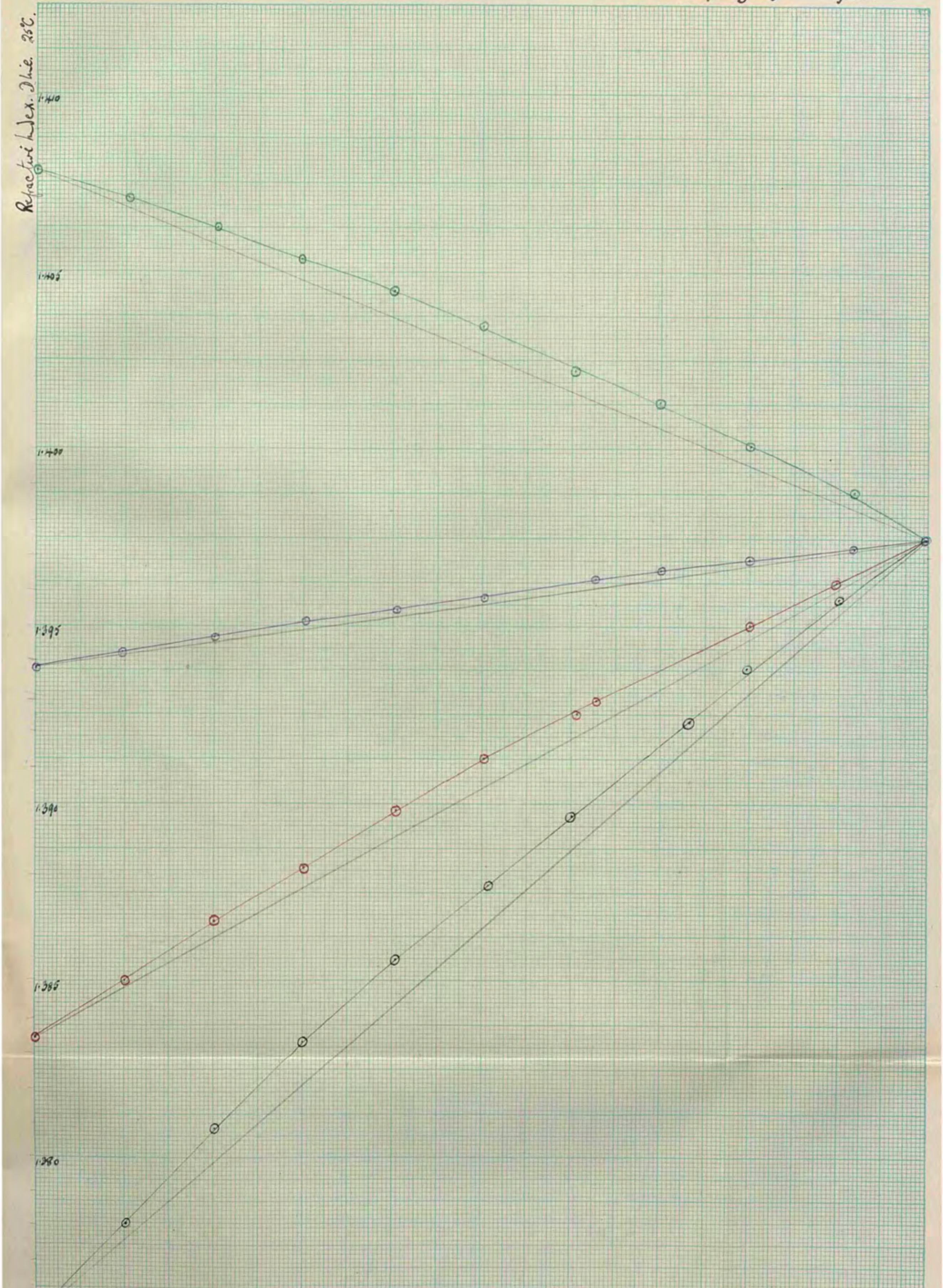


FIG. 6

Viscosity - composition curves.

Mixtures of n butyl alcohol with { iso propyl alcohol - in black
n .. .. - red

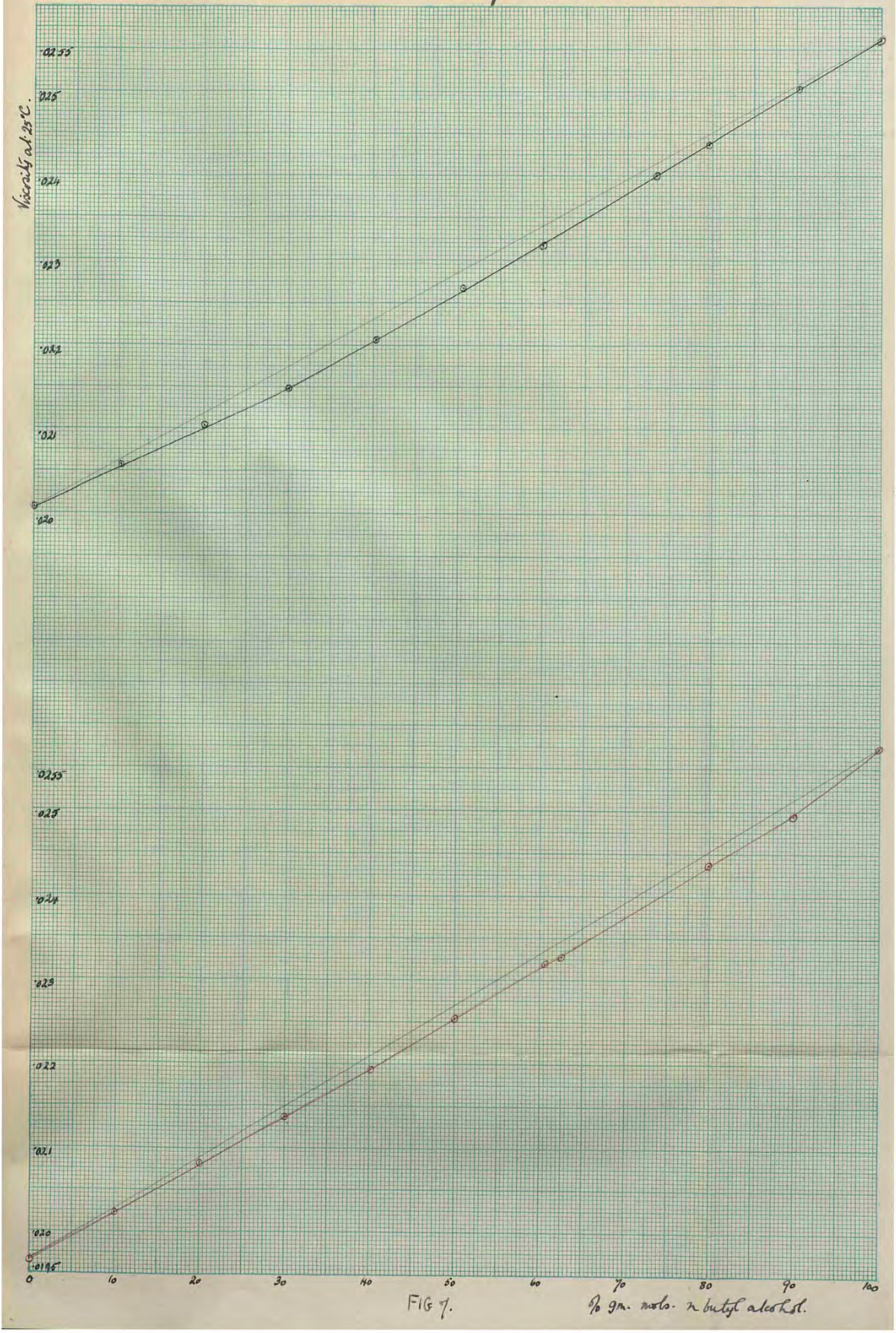


FIG 7.

Viscosity-composition curves. Mixtures of n-butyl alcohol with { isobutyl alcohol - in violet. / isomethylbutyl - green.

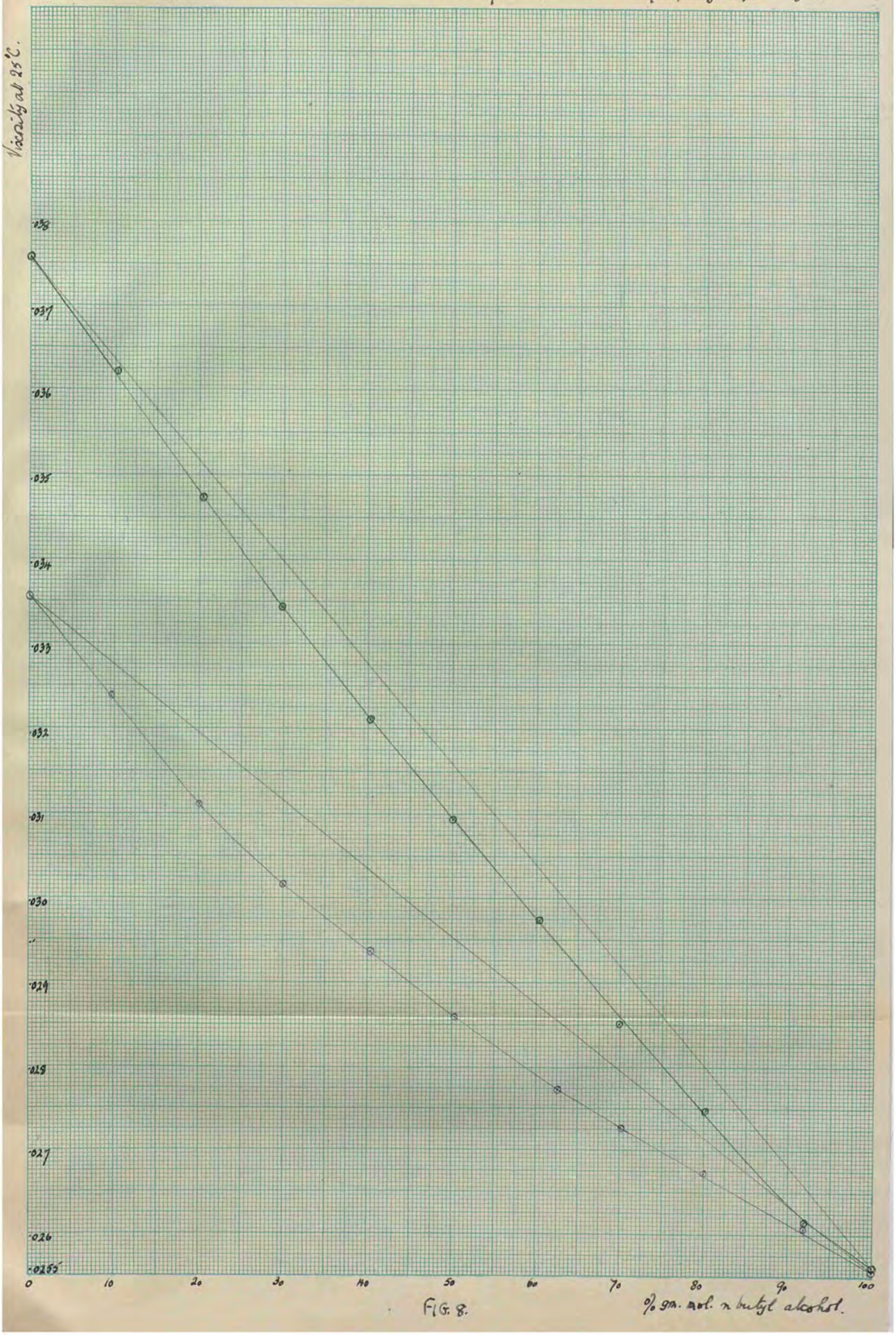


FIG. 8.

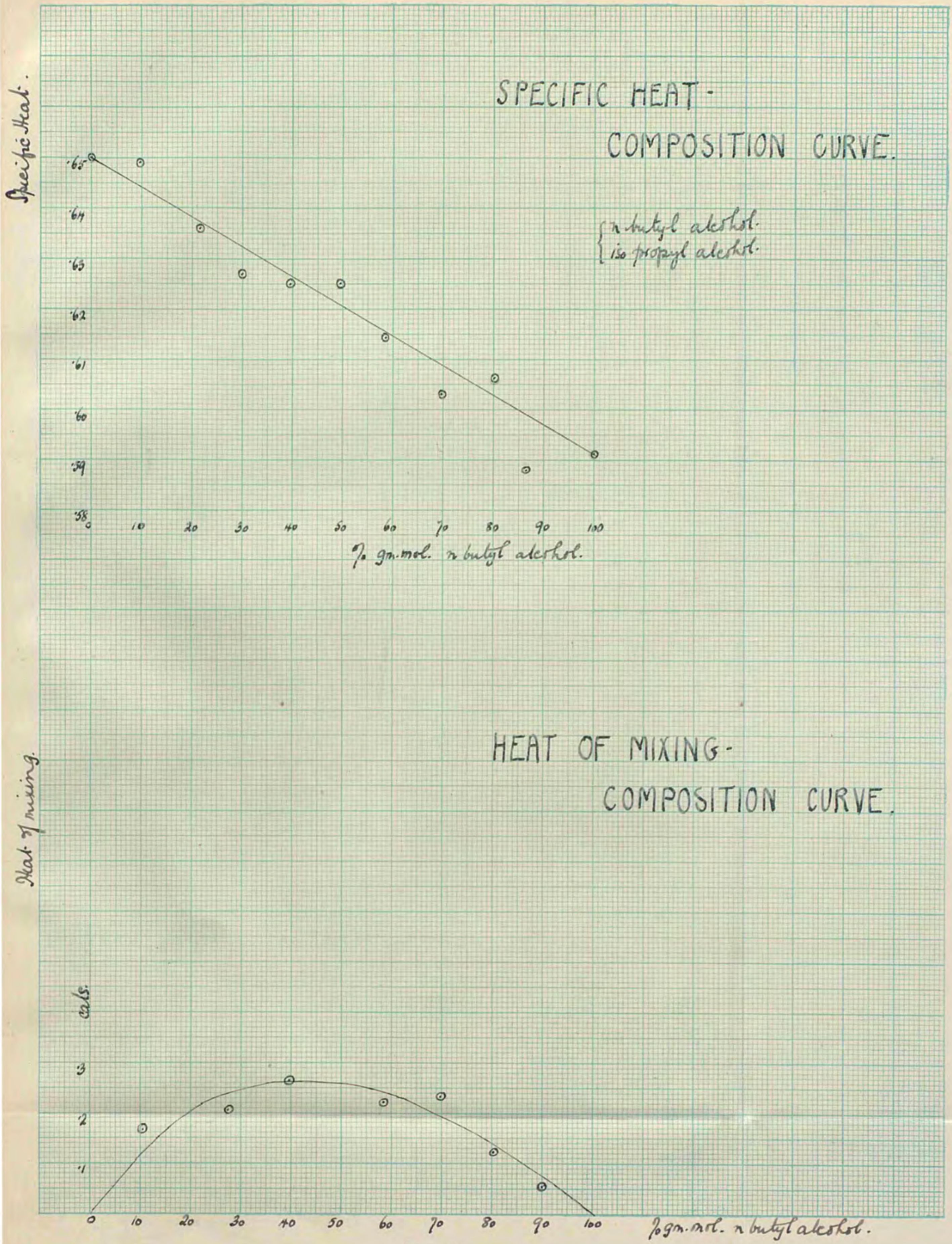

SPECIFIC HEAT - COMPOSITION CURVE.
Specific Heat.
n butyl alcohol.
iso propyl alcohol.
·65
·64
·63
·62
·61
·60
·59
·58
0
10
20
30
40
50
60
70
80
90
100
% gm.mol. n butyl alcohol.
HEAT OF MIXING - COMPOSITION CURVE.
Heat of mixing.
Cals.
·3
·2
·1
0
10
20
30
40
50
60
70
80
90
100
% gm.mol. n butyl alcohol.

Fig. 9.

Magnetic susceptibility-composition curves. n butyl alcohol with { isopropyl alcohol in black
n " " red
iso butyl " " violet
γ methyl butyl " " green.

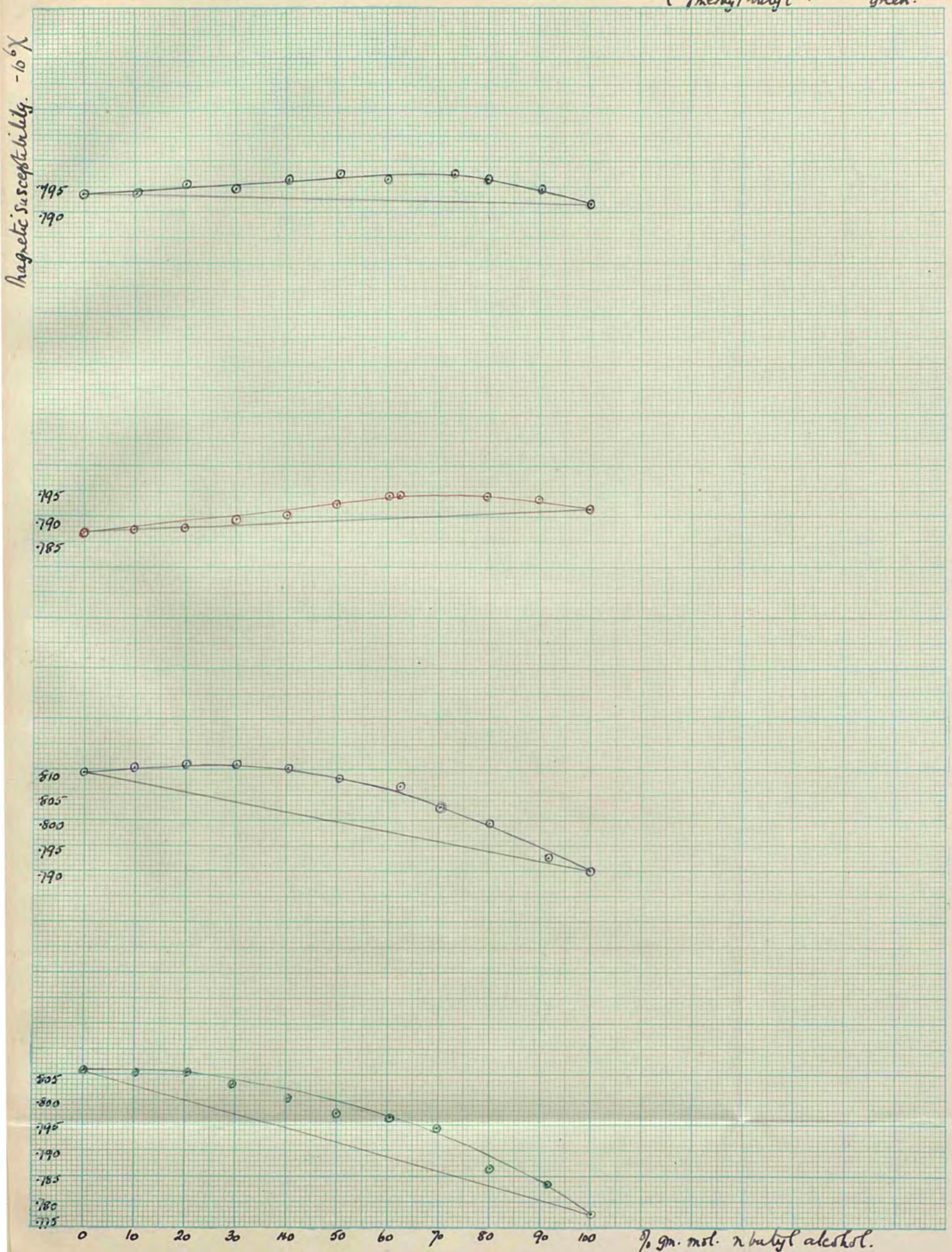


Fig. 10

Deviation-composition curves. n. butyl alcohol with {iso propyl alcohol – in black
n iso butyl " red
iso butyl " violet
iso methylbutyl – green.

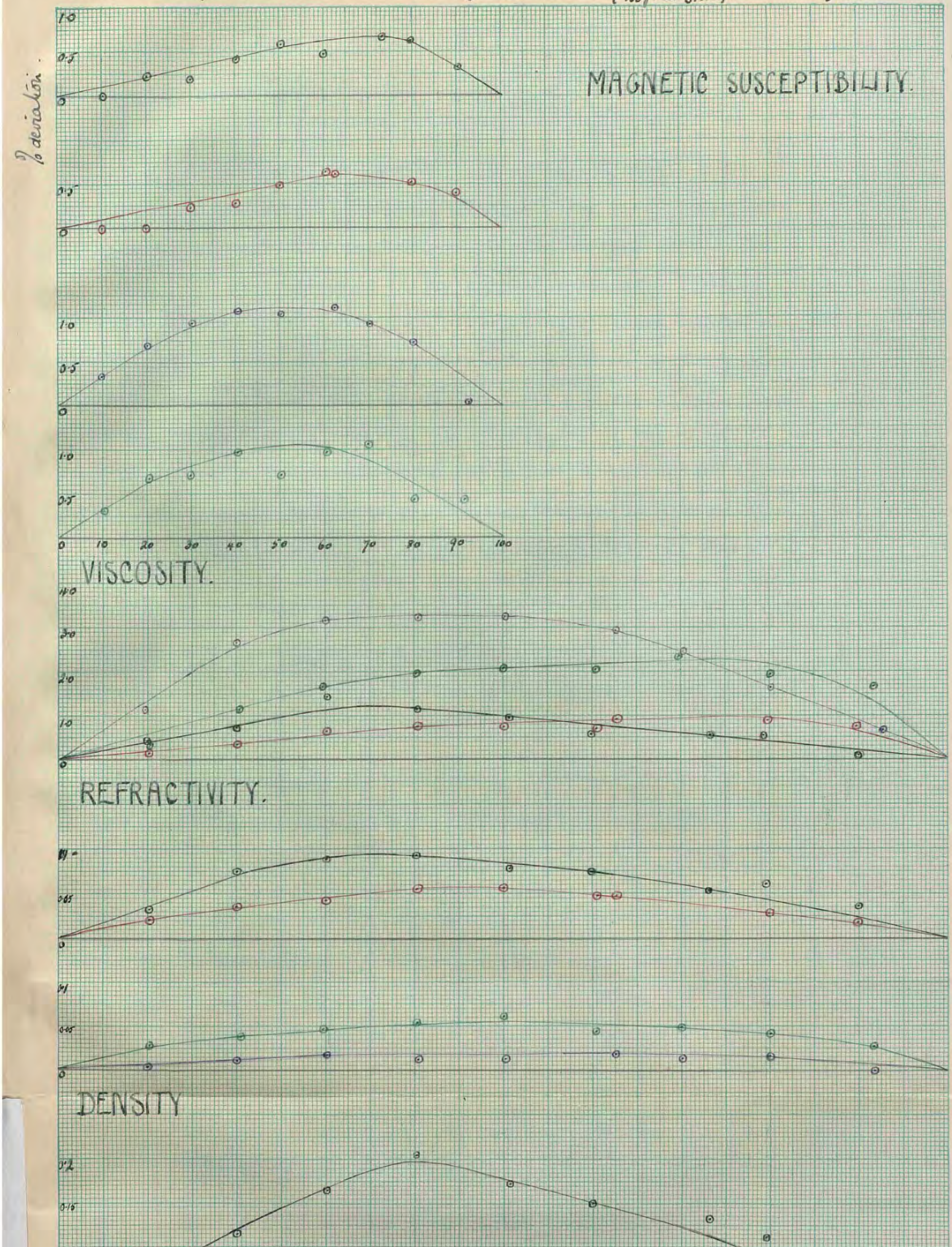


FIG. II.

Discussion of results.

It is a recognised fact that as a class alcohols are associated compounds, the lower members being more associated than the higher. The alcohols dealt with in this thesis were some of the lower members of the aliphatic series. It was expected that investigation of property-composition curves of mixtures of these alcohols would yield results indicating deviations from the additive mixture law. It was thought that by comparing results obtained using mixtures of one alcohol with others in the series above and below it, some light might be shed upon the nature of the changes taking place on mixing, and upon the electronic and magnetic relationships of the molecules.

In Table (29) a list of the results obtained is given, shewing the approximate composition of the mixtures with maximum deviation of the experimental values from the values as calculated by the additive law. Table (30) shews the percentage deviation in each case for mixtures of this composition.

TABLE 29.

Mixture.	% gm.mol.composition of mixture with max^m deviat^n.				
n-butyl alcohol and	Density	Refractivity	Viscosity	Magnetic Suscept^y	Heat of mixing
iso-propyl "	40	40	30	70	40
n-propyl "	40	40	70	70	
iso-butyl "	Indefinite	60	40	50	
γ methyl butyl "	60	50	70	60	

TABLE 30.

Mixture.	Maximum % deviation of mixtures of composition given in Table 29.			
n-butyl alcohol and				
iso-propyl "	0·2	0·09	1·2	0·8
n-propyl "	0·79	0·06	0·8	0·7
iso-butyl "	0·002	0·02	3·2	1·2
γ methyl butyl "	0·03	0·06	2·4	1·1

Consideration of property-composition curves for each mixture.

1. n-butyl and iso-propyl alcohols.

All curves indicate that association occurs to a small extent between these two alcohols on mixing. Density, refractivity, and viscosity measurements give curves with mixtures of maximum deviation having the larger proportion of iso-propyl alcohol and therefore indicate some de-association of the latter. The loss of symmetry of the curves is counteracted to some extent by the higher degree of association of the pure propyl alcohol over that of the n-butyl alcohol.

The magnetic susceptibility curve shews a maximum at about 70% n-butyl alcohol, suggesting de-association of this liquid. This might be only apparent, due to the influence of the greater degree of association of the iso-propyl alcohol over that of the n-butyl alcohol, but it is unlikely that this would have so marked an effect.

2. n-butyl and n-propyl alcohols.

Density and refractivity curves indicate the amount of association of n-butyl alcohol with n-propyl alcohol to be less than with the iso compound. The occurrence of de-association of the n-propyl alcohol, less than in the last case is inferred by the shift in position of the maximum deviation.

Viscosity and magnetic curves also indicate association between the two alcohols as taking place. The composition of the mixtures at maximum deviation intimates de-association of the n-butyl alcohol by the addition of the n-propyl alcohol.

n and iso-butyl alcohols.

Although from density and refractivity results it is made evident that practically no association between the two compounds n- and iso-butyl alcohols occurs on mixing them, from both viscosity and magnetic susceptibility measurements an amount of association between them, greater than in either of the two former cases would be inferred.

The shape of the viscosity composition curve suggests very slight de-association of the iso-compound, while the symmetry of the magnetic susceptibility curve apparently negatives this.

n-butyl and iso-γ-methyl butyl alcohols.

Density and refractivity curves give indication of very slight association between n-butyl alcohol and the amyl alcohol on mixing. Since n-butyl alcohol is likely to be slightly more associated than the other constituent, the symmetry of the curves suggest very slight de-association of the n-butyl alcohol occurring.

Viscosity and magnetic susceptibility curves indicate association between the two alcohols, and slight de-association of n-butyl alcohol.

Consideration of Tables (29 and 30) indicate that:

1. Every mixture shews at least some departure from the additive mixture law, that is, none of the pairs of liquids examined can be regarded as ideal.

2. Deviation values for viscosity and magnetic susceptibility are much greater than those for density and refractivity.

3. In the case of density and refractivity, the order of deviations in ascending magnitude is given by mixtures of n-butyl alcohol with iso-butyl, iso γ methyl butyl, n and iso-propyl alcohols respectively. In the case of viscosity and magnetic susceptibility this order is completely changed (practically reversed), n and iso-propyl alcohols having similar low values, while those of iso γ methyl butyl and iso-butyl alcohols are in ascending order.

4. The position of maximum deviation in density and refractivity-composition curves is similar.

5. There is a general tendency throughout density, refractivity and viscosity curves, for the position of maximum deviation to shift gradually towards the larger percentage of n-butyl alcohol in the mixtures of n-butyl alcohol with iso, normal propyl, iso-butyl, iso γ methyl butyl alcohols respectively.

This shift occurs in the reverse direction in the magnetic susceptibility curves.

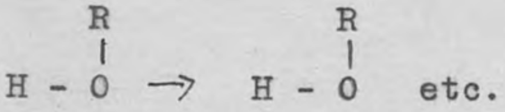
6. On the whole, the density and refractivity curves resemble one another, while viscosity and magnetic susceptibility curves appear distinct from these and are like each other in certain respects.

A consideration of the above lead to the conclusions:-

a. All the curves indicate very slight mutual effects occurring on mixing n-butyl alcohol with another alcohol. It is probable that since the substances are associated liquids and the molecules are in a high state of complexity that some such result as slight association and de-association might occur, but owing to the various forces at work the exact nature of such changes is difficult to deduce.

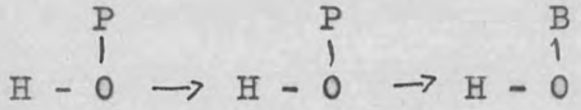
The results appear however, on the whole, to indicate that de-association of one alcohol is occasioned by the addition of an alcohol of higher molecular weight.

In the light of modern electronic views on valency, the oxygen atom in hydroxy compounds is capable of donating two electrons to a hydrogen atom belonging to another molecule thus:



$$H - \overset{\overset{R}{|}}{O} \rightarrow H - \overset{\overset{R}{|}}{O} \quad \text{etc.}$$

Various associated molecules consisting of the alcohols might result on mixing such compounds. Taking propyl and butyl alcohols as an example, the coordinated compound might be of the type:



$$H-\overset{\overset{P}{|}}{O} \rightarrow H-\overset{\overset{P}{|}}{O} \rightarrow H-\overset{\overset{B}{|}}{O}$$

[P and B representing a propyl and butyl group respectively], where in the associated molecule there is a larger proportion of the alcohol with lower molecular weight. Since the pure liquids, before mixing, are associated in varying degrees, it is not an easy matter to postulate the state of the resulting mixture, the number of possibilities being far too great. Information on this point could doubtless be obtained from measurements of the dipole moment of the individual alcohols and the mixture shewing maximum divergence from the simple law, that is for the mixture which probably contains the greatest quantity of co-ordinated compound.

b. It is known that viscosity is a property extremely sensitive to constitutive changes, and it is significant that the viscosity and magnetic susceptibility curves obtained present so much similarity. It is noticed moreover that the viscosities and molecular susceptibilities of the liquids are in the same order. These values are given below. (Table 31.)

TABLE 31.

Liquid	Viscosity (25°)	Molecular susceptibility
n-propyl alcohol	·01967	47·22
iso " "	·02009	47·63
n-butyl "	·02563	58·58
iso " "	·03356	$59{\cdot}89_5$
iso γ methyl butyl "	·03756	70·93

It is calculated, using the results obtained from the determination of the magnetic susceptibility of iso-propyl alcohol that:

(i) an error of ·05 mgm. pull caused an alteration of about $\cdot 004 \times 10^{-6}_{m}$ in magnetic susceptibility.

$\simeq \cdot 5\%$.

(ii) " " ·06 gms. in weighing or measuring out the liquid caused an alteration of approximately ·5%.

Thus the results can be considered as accurate to within 1%. Yet the maximum deviation was only 1%, so that considering also the small degree in variation in the magnetic susceptibility it is not surprising that the curves do not altogether agree with those obtained by different methods. That it has been possible to obtain results giving curves is indicative that the method should prove highly applicable to the investigation of changes occurring on mixing liquids which have more divergent susceptibility values.

c. The diamagnetism of the alcohols considered is a resultant of two effects. One is due to the Larmor precession, and increases regularly with increasing molecular weight, while the other depends on the presence of the dipole and this for the monohydric alcohols is practically constant. The molecular susceptibilities of a particular group of elements (provided that the type of linkage remains the same) should therefore give a constant value.

Table (32) shews molecular susceptibilities of the alcohols calculated from Pascal's atomic susceptibility values (21), compared with those obtained experimentally by him and by certain other workers. χ_{CH_2} values as deduced from experimental work described in this thesis are also given and are seen to be in fair agreement with Pascal's figures.

TABLE 32.

Alcohol	Molecular suscept^{y} (cal^{d} from Pascal's atomic suscept^{y} values.) $-10^6\chi$	$-10^6\chi_{CH_2}$ Pascal	Molecular susceptibility (Experimental - various workers) $-10^6\chi$		$-10^6\chi_{CH_2}$ Watkins
n-propyl	46·4		45·96 (Pascal)	47·22 (Watkins)	
n-butyl	58·3	11·9	59·94 (Faraday (Quincke (Henrichsen	58·58 "	11·36
			58·46 (Becquerel)		
iso-propyl	46·4			47·63 "	12·26
iso-butyl	58·3		59·05 (Pascal)	59·89 "	
γ methyl butyl	70·2			70·93	11·05

It will be noticed that in the two cases considered, the molecular susceptibility of the iso compound exceeds that of the normal compound. The difference in the values is $-0{\cdot}41 \times 10^{-6}$ for propyl alcohol, and $-0{\cdot}31 \times 10^{-6}$ for butyl alcohol, and at least some such constitutive effect is to be expected since the packing of the elements in the iso compound is closer than in the normal compound. That the effect is in the same direction as that caused by increase in molecular weight appears rational.

Conclusions.

I. Association, to a small extent, takes place between n-butyl alcohol and either iso, normal propyl, iso butyl, and iso γ methyl butyl alcohols on mixing.

De-association of one alcohol is occasioned by the addition of an alcohol of higher molecular weight.

II. It is highly probable that magnetic susceptibility measurements will yield valuable results indicating the changes which occur on mixing two liquids.

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