Studies in the Chemistry of Dyes and their Adsorption by Fibres.

by

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S U M M A R Y.

The work described had the main purpose of gaining a better understanding of the mechanism by which dyes are sorbed by various substrates. A subsidiary aim was the development of new analytical procedures to simplify the determination of purity of the dyes used and for the detection of hydrogen bonding. Broadly, the work is classified into three main sections, dealing respectively with analysis of dyes, methods of detecting hydrogen bonds, and the study of the sorption of certain natural colouring matters by various fibres and of synthetic dyes by alumina (in the form of anodised aluminium) and cellulose.

An oxidative method for the analysis of azo dyes and some dyes of other classes is described. The results for the majority of dyes examined, agree closely with those obtained by titanous chloride analysis, and the new method has the advantage of being simple, rapid and clean in use. The procedure involves measurement of the volume of nitrogen produced on boiling the dye with a dilute solution of potassium dichromate and sulphuric acid. A still simpler, colorimetric method of determining water-soluble azo dyes uses ceric sulphate oxidation. It is useful for some dyes, but many do not react in simple proportion with the oxidant.

The use of the refractometer for detecting the complex ratios of hydrogen bond interaction in binary solutions of organic compounds is also described. This method appears equally useful

for detecting strongly or weakly-bonded complexes. The reality of the existence of many compounds so detected has been demonstrated by a variety of procedures, including molecular weight determination, preparation of solid complexes, and comparison with complexes previously reported, either by preparation in substance or detection by infra-red spectrophotometry.

The dielectric constant and refractive index methods of detecting complex-ratios in hydrogen-bond interactions have been applied to nearly two hundred and seventy pairs of compounds in a variety of solvents.

Intra- as well as inter-molecular bonds can be detected, and a qualitative estimate of their relative stability may be made. Alcoholic and phenolic hydroxy-, aldehyde, amido-, amino-, azo-, carboxylic and sulphonic acid, ester, keto-, nitro- and quinone groups are amongst those examined. Several compounds have been included to represent models of certain natural and synthetic polymers.

A number of inter- and intra-molecular bonds have been detected involving a hydrogen atom attached to carbon and activated by a neighbouring carbonyl oxygen atom. These include intermolecular bonds between certain esters, e.g., acetates, and azobenzene and quinone. Supporting evidence is quoted showing that this type of bond may be responsible for the sorption of dyes by cellulose acetate.

Numerous examples of shielding of groups by the solvent have been noted, e.g., water protects alcoholic groups against combination with a number of other solutes of low affinity, but not against phenol. The carbonyl oxygen atom

in ketones, amides, or aldehydes is for the same reason unable to form intermolecular complexes in benzene, ether or water, but it is reactive in carbon tetrachloride or dioxan. This was checked by examining the sorption of benzene-azo-α-naphthylamine and benzene-azo-β-naphthylamine on anodised aluminium. These compounds show little affinity for anodised aluminium, using benzene as a solvent, but on employing carbon tetrachloride or dioxan, sorption proceeds readily.

Bonding between water, used as a solute in anhydrous solvents, and several other compounds has been observed. With the amide or azo groups water acts as a cross-linking agent, each of its hydrogen atoms being attached to a separate molecule of the other solute.

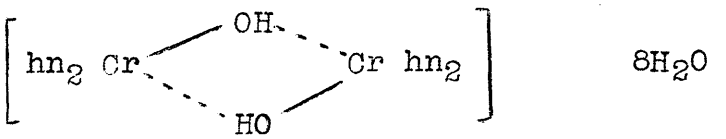
The reactions of the alkylamide group have been studied in view of their importance in the interpretation of the behaviour of proteins and nylon. This group appears to react, bifunctionally, in the enol form in organic solvents, but water stabilises the keto-form and it is then usually monofunctional, the carbonyl oxygen being protected by the solvent. A hydrogen atom on the carbon adjacent to the carbonyl group in the keto-form is shown also to be reactive and the bearing of this fact on the interpretation of the action of quinones in tanning proteins is discussed. The bonding properties of carbohydrates and their relation to sorption by cellulose, are also considered. The individual hydroxy- or ether groups in mono- and disaccharides in their normal ring structures, can form intermolecular bonds with other solutes in an anhydrous solvent (ethylene glycol), but not in water, even with phenol, on account of shielding by

the solvent. The nitrogen atom in some solutes can combine, in water, with the free aldehyde group in the open-chain form of glucose or cellobiose. It is shown that these facts are consistent with the sorption of dyes by cellulose from water being due to van der Waals attraction rather than by hydrogen bonds, as formerly supposed.

The sorption properties of haematein and its leuco compound, haematoxylin, the colouring principles of logwood have been examined. Haematoxylin is readily absorbed by acetate rayon, nylon, or wool, and comparison of the results with those of the hydrogen-bond detection procedure indicate that the sorption is due to such bonds. It is sorbed to only a negligible extent by viscose rayon, apparently because its molecule has insufficient physical attractive force to hold it to cellulose. Hydrogen bonding is also indicated as the mechanism of sorption of phenols and amines by the anodic film (alumina) on aluminium.

The lake-forming reactions of the Logwood and Brazilwood colouring matters with the more important mordanting methods have been investigated. The oxidised forms appear to be the lake-forming species; the leuco forms must first be oxidised by air or the mordanting salt before reaction can commence. Chromium and aluminium salts form water-soluble lakes when weak solutions of the colouring matters are boiled with chromates or dichromates, or aluminium chloride, respectively; these are respectively anionic and cationic and by a method of colorimetric titration their dye:metal ratios are shown

to be 2:1 in each case. Logwood with other metals, and brazilein with all the metals used, give insoluble lakes. By using chromic salts in alcohols, 1:1-complexes are formed. When dried down all the lakes are complex in structure, and even the previously water-soluble ones become irreversibly water-insoluble. The products in most cases appear to be mixtures of lakes in various stages of the reaction sequences, but by a consideration of the probable course of these sequences and a study of the elementary analyses, it has been possible to arrive at reasonable estimates of their composition. The insolubilisation which takes place on drying down the lakes in substance, and which is believed to take place also on the fibre, is attributed to condensation polymerisation of the 'olation' type, accompanied by loss of water. With the exception of lakes from chromic salts, which are largely 1:1-complexes, all the lakes have the 2:1-complex formation. When haematein is dyed on chrome-mordanted wool it at first forms the purple 1:1 complex, but within 5 min. (at b.p.) this unites with more haematein already on the fibre and forms 2:1-complex. Eventually after the full dyeing process, and drying, the deep blue or blue-black insoluble polymeric lake is produced. This appears to consist largely of a mixed complex of the probable structure



(hn = the haematein anion) with a considerable proportion of unolated complex, one molecule of water being hydrogen-bonded

to every free phenolic group. The (ferric) iron complex has a similar structure. It is suggested that the fastness of the dyed and mordanted fibres to wet treatments is attributable to the insolubility of these polymeric lakes.

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The Journal abbreviations used in this thesis are those current in the Journal of the Chemical Society, with the exception of that for the Journal of the Society of Dyers and Colourists (J.S.D.C).

INTRODUCTION

The general aim of the work described in this thesis was to examine various current theories of the mechanism of sorption in dyeing in much more detail than had been done before. Previous work, ably summarised by Vickerstaff ("The Physical Chemistry of Dyeing" Edinburgh, Oliver and Boyd Ltd., (1950)) in his monograph "The Physical Chemistry of Dyeing" has included very thorough investigations e.g. of the mechanism of electrovalent adsorption of anions by proteins, and of the influence of salts upon the sorption of dyes by protein and cellulose fibres. It is believed, however, that Van der Waals and hydrogen bond forces play a considerable part in the sorption of solutes by many fibrous and other solid substrates, but the detailed study of these processes has been somewhat neglected. Very little is known also about the state of metallic lakes in fibres dyed by the mordanting processes, and indeed the nature of these lakes has only been investigated in detail in the case of certain types of azodye and not with other varieties of lake-forming substance.

It was decided therefore to open investigations at first upon the general question of hydrogen bonding in relation to fibres. To do this the new technique for detecting such bonding between pairs of solutes in non-aqueous solution by dielectric constant measurement described by Giles, Rose and Vallance (J.C.S., 1952, 3799) was first examined. It had been found by Mclure (B.Sc., Thesis, Glasgow,1952) that by using the measurement of refractive index in place of the dielectric constant (a suggestion put forward by Rose at the conclusion of his work. (B.Sc., Thesis, Glasgow, 1950)), the

method could be extended to aqueous solutions, which could not be examined by the dielectric constant method. This was considered to be an important advance, because little was known about the influence of water on hydrogen bonding of solutes, nearly if not quite all previous work on intermolecular bonding having been done in absence of water. Yet water is the medium for virtually all sorption processes on fibres. This procedure was therefore taken up and a study of the hydrogen bonding properties of model compounds representing typical dyes and fibres both in non-aqueous and aqueous conditions, was commenced. The results proved to be so interesting and to reveal so much that was hitherto unsuspected, that it became a major part of the present research. Some of the new conclusions reached were checked by sorption experiments on fibres, particularly using certain natural colouring matters of the logwood and brazilwood class. These were chosen for two reasons: (a) they contain a high proportion of identifiable hydrogen-bonding groups and (b) some experience of their use in sorption experiments had already been gained by early workers in this laboratory, by Desai (Ph.D., Thesis, 1948; Gallacher, B.Sc. Thesis, Glasgow, 1948; Macneal B.Sc.,Thesis, Glasgow, 1949.) The formation and structure of metallic lakes in the fibre was also studied using these same colouring matters.

It was hoped to study the mechanism of sorption of azo dyes by a number of fibres, in order to confirm the usefulness of the conclusions reached as a result of the hydrogen bonding work, but unfortunately this section of the project had to be confined to a few experiments on cellulose, because so little time was available.

In anticipation, however, of this investigation being extended to cover a variety of azo dye structures, requiring much preparative work and analysis of products for purity, a preliminary research had been completed by which an improved method of analysis of azo and other dyes was worked out. In comparison with the hitherto used titanous salt procedure, this method while being equally reliable, is much simpler and more rapid, ~~by~~ Arshid (A.R.T.C. Thesis, 1951); Arshid, Desai, Giles, and McLintock (J.S.D.C., 1953, 69, 11).

THEORETICAL DISCUSSION

Theories of dyeing textile fibres :- A very large amount of work has been reported in investigations to determine the mechanism of dyeing natural and synthetic fibres and many theories have been put forward to explain the observed facts. It is therefore thought desirable to review briefly work on the dyeing mechanism of fibres in this section.

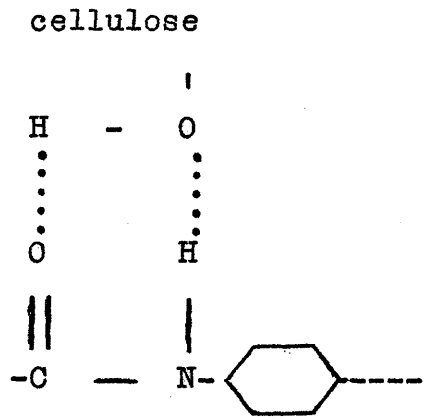
Cellulosic Fibres

By the investigations of Meyer and Mark (Ber; 1928, 61, 593), the structure of cellulose is established as consisting of β-glucose units joined together by oxygen bridges in 1:4 positions to form linear macromolecular chains of up to about 2000 units. These lie more or less parallel to each other, forming crystalline regions, here and there interspersed by amorphous regions. According to Crank (J.S.D.C., 1947, 63, 412) the dyeing of cellulose is considered to be a process of diffusion with absorption - i.e. accompanying a concentration C of ions free to diffuse is a concentration S of ions bound to the cellulose. The assumption that S bears a constant relationship to C forms the basis of existing theories of equilibrium dye absorption. From the surface electric potential of cellulose as calculated by Neale, and by adopting the same mathematical treatment as Neale, Crank derives expressions for the total surface charge, the total surface area (internal and external) of the cellulose, and the diffusion coefficient. Crank assumes that the charge due to the cellulose itself is independent of salt concentration and temperature. These modern theories are based mainly on the electrical theory of

dyeing as originated by Perrin (J.Chim. Phys., 1904,2,648; 1905, 3,100). Harrison (J.S.D.C., 1911,27,279) carried out experimental work on this subject, and came to the conclusion that in the case of the dyeing of cellulose with direct colours the diffusion of the dye ions relative to the cellulose is influenced by the electric charges in the same way as in the dyeing of fibres with other dyes, but the direct colour ions are not absorbed by, nor held to, the cellulose by electrical attraction, as appears to happen when wool is dyed with basic colours. The direct colour is considered to be mainly aggregated or coagulated within the pores of the cellulose in consequence of the adsorption of the sodium ions of the dye by the cellulose, assisted by the presence of salts and possibly by other factors to be considered later, while Lenher and Smith (J.Amer.Chem.Soc., 1935,57,504) have observed aggregation of dyes by the action of salts, the present popular idea is that this aggregation does not assist the dyeing, which is supposed to be due to a direct affinity between cellulose and colour ions of sufficient magnitude to overcome the electrical repulsion due to their charges. Mayer (Textilber; 1928,9,573) suggested that the dyes possessing a linear configuration, can lie close up to the cellulose molecule and the residual valency forces will thus be more effective in holding the two together than would be the case if the dye was not linear.

It is now generally supposed that the attachment of dyes to cellulosic fibres is due to hydrogen-bonding. Valkó (Kolloid-chemische Grundlagen der Textilveredlung, Berlin, 1937) suggested

that such linkages are formed between direct dyes and cellulose, the mode of union of substantive amide groupings, e.g., was visualised as :



Proteins

The early theory remains much the same to-day, though more is now known of the order of arrangement of the residues and the folded nature of the chains. The proteins consist essentially of polypeptide chain molecules produced by the linear condensation of α-amino acids, see, e.g., Astbury (J.S.D.C., 1933, 49, 168) and Speakman (ibid; 1933,49,180), also Speakman in "Fibre Science" (The Textile Institute, 1949, chap. XVI). Wool is built up of micelles lying parallel to the axis of the fibre and consisting of long folded parallel peptide chains held together by cystine and salt linkages. In silk these cross linkages are absent but the strength of the silk fibres is believed to be due to the formation of hydrogen-bonds and Van der Waals forces between the adjacent chains (Howitt, "Fibre Science" Chap. V). These can lie closely together as there are no bulky side chains present in the silk molecule.

Recent researches by Gralen (ibid; 1950,66,465) have shown that the outer surface of the wool fibre, known as the cuticle, is surrounded by a very thin smooth membrane, which is responsible for the low friction of dry wool fibres.

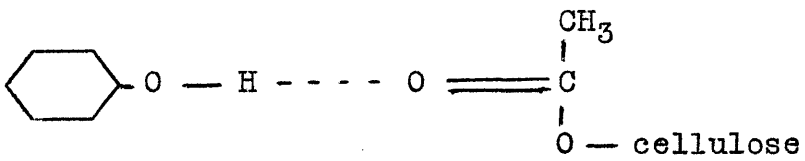
Knecht (ibid; 1904,20,238) proposed and Fort (ibid; 1916,32,33) developed the present chemical theory of wool dyeing, which has been proved basically correct as a result of detailed work by Speakman and his associates. Further work by Speakman and Stott (ibid; 1934,50,341) has shown that acid sorption by wool is a function of the pH of the bath and not of the molar concentration. He has also established that the maximum acid combining capacity of 1 g. of wool is about 0.82 ml. of N-acid at pH 1, which corresponds fairly closely with the number offree amino groups in wool. Speakman and Stott have shown that deaminated wool has a much reduced capacity for combination with acid, this combination being suggested as due to attachment with the imino groups in the protein chain. All these facts can be explained by Donnan's theory if it is assumed that the fibre forms the membrane and $R - NH_3^+$ ions formed by ionisation of the amino groups of theside-chains in the acid solution are the non-diffusible ions, Goodall (ibid; 1937,53,50).

From a series of recent investigations, it is now generally believed that from an acid solution, hydrogen and chloride ions (in the case of hydrochloric acid) are adsorbed by the basic and acidic groups respectively of the dye. The larger and more slowly diffusing dye ions then displace the chloride ions from the sites. The dye ions must have greater affinity for the absorption sites than the

chloride ions; this is believed to be due to the fact that in addition to the ionic link of the chloride ion, the dye anion is further able to form hydrogen bonds with the fibres (see Vickerstaff, "The Physical Chemistry of Dyeing,"Edinburgh and London; Oliver and Boyd, Ltd., 1950).

Cellulose Acetate.

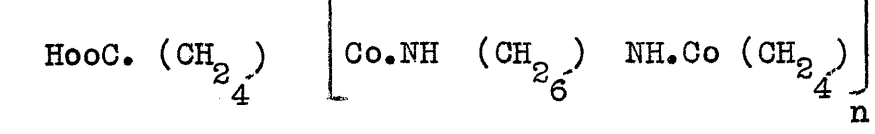
The dyeing behaviour of cellulose acetate rayon is completely different from that of the cellulose from which it is derived. Most of the direct cotton dyes and acid dyes leave the fibre completely uncoloured. This change appears to be due to the alteration in surface characteristics, whereas cellulose is highly hydrophilic, cellulose acetate is highly hydrophobic. From the work of Marsden and Urquhart (J.Text.Inst., 1945,33,T 105) on the sorption of phenols by acetate rayon, it appears that the mode of attachment may be by hydrogen bonding. The behaviour of acetate rayon towards phenol, o-nitrophenol and p-nitrophenol lends strong support to this assumption. The suitable polar group of a dye molecule could form a hydrogen bond with the carbonyl oxygen of the acetyl side chain, as shown below :



Nylon.

Nylon is an artificial fibre prepared by condensing hexamethylenediamine with adipic acid. Polymerisation proceeds until

a long chain compound of molecular weight 10-12,000 is obtained. This has a free carboxyl and amino group at respective ends of the chain, thus :-



Peters (J.S.D.C., 1947,63,388) has shown that at pH values of 3-6 the dyeing mechanism of nylon with acid dyes appears to be similar to that of wool, the only difference being that there are fewer basic sites available in the nylon molecule. Researches by Skinner and Vickerstaff (ibid; 1945,61,193) are in agreement with this and they state that nylon contains 0.05 milliequivalents of basic groups per gram.

In the pH range 3-6 it is evident that the dye is sorbed on the amino groups which terminate the polyamide chains. At lower pH values further combination can take place, probably on the weaker basic amide groups. This view has been supported by the work of Harris and Sookne (Bur.Stand.J.Res., 1941, 26 289) and further confirmed by Carlene, Fern and Vickerstaff (Symposium on recent advances in the theory and practice of Dyeing, S.D.C., 1947, P.24.), who also investigated the tendering effect of acid dyes on nylon.

Recently O'Brien *et al* and Peters (J.S.D.C., 1953,69,435), from investigations designed to reconcile Peter's earlier work with apparently conflicting evidence given by Remington and Gladding (J.Amer. Chem. Soc., 1950,72,2553) have concluded that the dye which is fixed to amide groups at low pH values catalyses hydrolysis of

the fibre at these positions, by the acid present, thus lowering its mol. wt. and increasing the number of free amino-groups.

The Hydrogen Bond

Though various hypotheses regarding the absorption of dyes and organic compounds on textile fibres other than proteins have been put forward, the modern theory which has gained much support is that of hydrogen bonding. In the present work, attempts have been made to verify this theory by absorption experiments and by examining model compounds corresponding to the structure of textile fibres and observing their combinations with various groups i.e. -N = N- , -OH-, acetyl etc., by the refractive index and dielectric constant methods. These are discussed in detail in the latter part of this thesis.

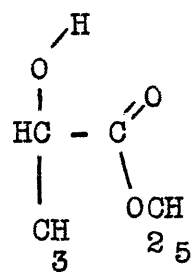
Below is given a brief review of the hydrogen-bonding mechanism. The unique property exhibited by the hydrogen atom in the formation of this bond is due to the fact that the positive hydrogen ion is a lone proton having no impeding shell of electrons around it. It can attract two anions between which it forms a bridge. In the early period it was thought that the bond was symmetrical, but this has been disproved largely by the work of Pauling (Proc.Nat.Acad.Sci., 1928,14,359), who has also shown that one hydrogen atom can form one hydrogen bond. He stated that because a hydrogen atom has only one stable orbital, it can form only one covalent link and therefore a hydrogen bond must be due to ionic forces. It is formed between the most electronegative atoms, the strength of the bond increasing with the electronegativity of the two bonded atons. e.g.,

fluorine > oxygen > nitrogen > chlorine.

It is found that hydroxy groups in phenols form a stronger bond than those of aliphatic alcohols. This has been explained on the basis that the higher electronegativity of the oxygen atom in the phenols is due to resonance.

For the formation of a hydrogen bond the hydrogen atom should be approximately directed towards the anion which is to be bonded, Robertson (Trans. Faraday Soc., 1940,36,913). The molecule should have a coplanar configuration, so that no steric hindrance may be offered to the approaching group in establishing contact closely enough to enable the bonding to occur. In general, formation of a six membered ring constitutes a favourable condition for hydrogen bonding.

Ethyl lactate -



does not form a strong hydrogen bond, because the O - O distance is large and the hydrogen atom of the hydroxyl group is not well directed towards the carbonyl oxygen atom.

The nature of the Attachment of Dye Lakes to Wool

This was discussed by Giles (J.S.D.C., 1944,60,303) who suggested that the normal mordanted chrome lakes on wool might be 1:1- complexes, the free co-ordinate valencies of the metal perhaps being attached to the fibre itself, so increasing the resistance to wet treatments. Later, however, Race, Rowe and Speakman (ibid; 1946,62,372) showed that the lakes of several typical mordant dyes, on the fibre have a 2:1 (dye : metal) ratio, which means that an

additional attachment to the fibre is doubtful, and they suggested that the increased wet-fastness of mordanted dyeings is simply due to the reduction of diffusion rate produced by the doubling of size of the dye molecule.

Section 1. Quantitative Analysis of Azo and other Dyes and Intermediates.

Since commercial dyes are not very pure and hence unlikely to give accurate measurements for absorption experiments and moreover it is advisable to know the degree of purity of a dye before putting it to its actual use, the author, in the first part of the thesis, deals with the analysis of dyes and intermediates.

If the absolute purity is required, a chemical analysis must be made on the sample. The direct colorimetric analysis of unknown samples against purified specimens, is not always easily applicable with water soluble dyes, the difficulty arising of purifying the samples, used for comparison to the required degree of purity. A simple and accurate analytical method for determining the purity of dyes, especially of water soluble types, is, therefore, of some general interest.

TITANOUS SALT ANALYSIS

The standard quantitative method for the analysis of water soluble dyes is the reduction process using titanous salt solutions, first proposed by Knecht, (~~ibid~~; J.S.D.C. 19, 169 (1903), ibid; 21, 292, (1905), ~~by Knecht~~.

Knecht and Hibbert, (ibid; 21, 344 (1905), Knecht and Hibbert, (ibid; 23, 285, (1907), Knecht (ibid; 25, 135, (1909), Knecht, (ibid; 27, 13 (1911), Knecht and Hibbert, (ibid; 31, 214 (1915), Knecht and Hibbert, (New Reduction Methods in Volumetric Analysis (London: Longmans Green & Co; 2nd edition, 1925.)

This method is suitable for almost all water-soluble azo dyes and

for some dyes of other water-soluble classes, as well as for certain intermediates, e.g. nitro and nitroso compounds. The results obtained by this method are fairly reliable, but there are a few objections to its use, including --

(a) The instability of the solutions of titanous chloride or sulphate which necessitates a complicated apparatus in order to prevent the reagent from oxidation. For this reason a continuous flow of hydrogen, prepared from granulated zinc and concentrated hydrochloric acid, is employed, even so, the strength of the reducing solution must be checked before every use, against a standard oxidising solution (ferric ammonium alum.)

(b) The need to use a dye solution containing 2N. hydrochloric acid, which causes the evolution of strongly acid vapours from the boiling solution during the titration.

(c) Many dyes do not show distinct colour change at the end point, and this necessitates a complication of the procedure by adding excess of reducing agent, at the boil, and then cooling and back-titrating with ferric ammonium alum.

(d) The necessity for carrying out the titration at the boil.

Oxidation with Potassium Dichromate and Sulphuric Acid

DYES

Desai and Giles (J.S.D.C., 65,639,(1949)) while conducting an investigation into the oxidation of azo compounds, found that a quantitative yield of nitrogen from water soluble azo dyes, not containing other nitrogen atoms, can be obtained by boiling in dilute

potassium dichromate - sulphuric acid solution, if groups containing nitrogen, other than the azo groups, were present in the dye, only a portion of the total nitrogen was recovered.

By using the new modified method, which is simple and of good accuracy, almost all types of azo dye, including those containing nitrogen in groups other than the azo group, can be analysed quantitatively. Certain other classes of dye can be determined as well. The reagents employed require no standardisation, and the apparatus (Fig. 3) is inexpensive, robust, and readily assembled. A number of representative dyes were analysed both by the new method and by means of titanous chloride. In a few cases the latter proved unsuitable or gave doubtful results, microanalysis by combustion was used as a check. The samples used were both old and new commercial products, laboratory preparations, crude and purified, and recrystallised commercial dyes. The results are given in Tables 1 and 2, from which the following general conclusions regarding the applicability of the new method may be drawn -

It appears to be suitable for all hydroxyazo dyes, whether water-soluble or water-insoluble, and for azo dyes without hydroxy groups if sulphonic acid groups are present. Unsulphonated azo dyes without hydroxy groups could not be estimated. It can be used successfully with methylene-blue and some triphenylmethane and anthraquinone dyes, although insufficient examples have been examined to determine whether it is applicable to the same extent as to azo dyes. It appears to be unsuitable for cyanine, vat, and water-insoluble anthraquinone dyes. Many of the dyes other than those of the azo class, can not be satisfactorily

TABLE I

Analytical Data on Water-soluble Azo Dyes

	C.I. No.	Dye Constitution: Base	Dye Constitution: Coupling Component	Sample used	Purity (%) found by $TiCl_3$	Purity (%) found by $K_2Cr_2O_7$	Purity (%) found by Microanalysis (N by combustion)
X	27	Aniline	2-Naphthol-6:8-disulphonic (G) acid	L.P.*	100	99·9	—
	28	Aniline	2-Naphthol-3:6-disulphonic (R) acid	L.P.	99	98·7	—
	31	Aniline	8-Acetamido-1-naphthol-3:6-disulphonic acid	Azo Geranine 2GS (ICI)	31	30·8	—
	39	*m*-Nitroaniline	R acid	L.P.	113†	99·4	—
	42	*p*-Nitroaniline	*N*-Ethyl-*N*-*p*-sulphobenzyl-aniline	Azo Cardinal G (A)	35†	36·2	35·5
	(64)	*p*-Toluidine	R acid	L.P. +	100	99·0	—
X	78	*m*-Xylidine	2-Naphthol-6-sulphonic (Schäffer's) acid	Scarlet 2R (B)	31	29·9	—
X	89	α-Naphthylamine	G acid	Recryst. sample of Crystal Ponceau heptahydrate (A)	100	100·1	—
	119	2-Methoxy-5-methyl-aniline	1-Naphthol-3:8-disulphonic acid	Eosamine B (A)	52	51·7	—
	148	Sulphanilic acid	Resorcinol	Resorcine Yellow (A)	60	59·8	—
	151	Sulphanilic acid	β-Naphthol	L.P. (crude)	61	61·3	—
	170	*o*-Aminophenol-*p*-sulphonic acid	1:5-Dihydroxynaphthalene	Diamond Black PV (By)	32	31·2	—
	176	1-Naphthylamine-4-sulphonic acid	β-Naphthol	Recryst. from Naphthalene Red J (ICI)	100	100·1	—
	182	1-Naphthylamine-4-sulphonic acid	Schäffer's acid	Naphthalene Red EAS (ICI)	48	48·0	—
	185	1-Naphthylamine-4-sulphonic acid	G acid	Recryst. from Naphthalene Scarlet 4R (ICI)	85	85·4	—
	266	*m*-Aminophenyltrimethyl-ammonium chloride	*m*-Toluidine, then β-naphthol	Janus Red B (MLB)	62	62·1	—
	518	Dianisidine	1-Amino-8-naphtholdisulphonic acid (2S acid)$_2$	Chlorazol Sky Blue FFS (ICI)	18	17·7	—
	—	*p*-Anisidine	R acid	L.P.	89·5	90·1	—
	—	*m*-Chloroaniline	R acid	L.P. +	68	67·8	—
	—	*p*-Chloroaniline	R acid	L.P. (99)	88	87·6 (100)	—
	—	*NN*-Dimethyl-*p*-phenylenediamine	R acid	L.P.	52·5	52·1	—
	—	*p*-Nitroaniline	R acid	L.P.	88†	88·5	—
	—	*p*-Phenetidine	R acid	L.P.	73	71·9	—
X	—	Benzidine	(R acid)$_2$	L.P.	41·5	40·8	—

* Laboratory preparation.
† Assuming the nitro group is not reduced.

\+ Purified by one passage through an ion-exchange (anionic and cationic) resin column.

x (Not done by the author).

TABLE 2.

Analytical Data on Miscellaneous Dyes

C.I. No.	Type and or Constitution of Dye		Sample used	Purity (%) found by— $TiCl_3$	$K_2Cr_2O_7$	Microanalysis (N by combustion)
	Base	Coupling Component(s)				
Water-insoluble Hydroxyazo Dyes						
24	Aniline	β-Naphthol	L.P. (recryst.)	99	99·4	—
38	*m*-Nitroaniline	β-Naphthol	L.P. (recryst.)	96	96·4	—
—	*m*-Chloroaniline	β-Naphthol	L.P. (recryst.)	*	99·1	—
—	*p*-Chloroaniline	β-Naphthol	L.P. (recryst.)	*	100	—
—	*NN*-dimethyl-*p*-phenylenediamine	β-Naphthol	L.P. (recryst.)	72	73·0	—
—	*p*-Phenetidine	β-Naphthol	L.P. (recryst.)	98	97·7	—
—	*p*-Toluidine	β-Naphthol	L.P. (recryst.)	96·5	94·7	—
Azo Compounds without Hydroxy Groups						
—	Azobenzene	—	Pure recryst.	—	16	—
15	Aminoazobenzine	—	Pure recryst.	—	25	—
—	4-Nitro-4′-*N*-phenylaminoazobenzene		Dispersol Fast Orange A (ICI)[10] (recryst.)	—	28	—
21	Aniline	*m*-Toluylenediamine	Chrysoidine RL (B)	90*	19	—
143	Sulphanilic acid	Diphenylamine	Recryst. commercial product	97	96·9	—
147	Na 4′-*N*-(2:4-dinitrophenyl)aminoazobenzene-4-sulphonate		Azo Flavine FF (B)	(65) *†	50·5	52·5
370	Benzidine	(1-Naphthylamine-4-sulphonic acid)$_2$	Congo Red WS (ICI)	56·5	56·7	—
495	Dianisidine	(1-Naphthylamine-4-sulphonic acid)$_2$	Benzopurpurine 10BS (ICI)	35	35·1	35·5
Sulphonated Triphenylmethane Class						
670	Na salt of 4-sulpho-4′:4″-bis(*N*-methyl-*N*-*p*-sulphobenzylamino)triphenylmethyl		Lissamine Green SFS (ICI)	73·5	74·8	—
735	Na salt of bis-*p*-dimethylaminophenyl-2:7-disulpho-1-naphthylmethyl		Lissamine Green VS (ICI)	65·5	66·9	—
Azine Class						
841	3:7-Diamino-2:8-dimethyl-5-phenyl(or *o*-tolyl)-phenazinium chloride		Safranine	—	‡	—
Thiazine Class						
922	3:7-Bisdimethylaminophenazathionium zinc chloride		Methylene Blue 2BS (ICI)	47‖	47·3‖	—
924	3:7-Bisdimethylamino-4-nitrophenazathionium zinc chloride		Methylene Green	—	‡	—
Anthraquinonoid Dyes						
1054	Sodium 1:5-diamino-4:8-dihydroxyanthraquinone-3:7-disulphonate		Alizarin Sapphire Blue B (CAC)	—	60·1	57·5
1076	Sodium salt of 1-amino-2-methyl-4-*o*-sulpho-*p*-methylanilinoanthraquinone		Solway Blue RNS	—	50·0	51·0
Na 1:4-Diaminoanthraquinone-2-sulphonate			L.P.	—	54·5	52·5

Several dyes of the Vat and Cyanine classes and an anthraquinonoid Disperse dye all gave very low yields of nitrogen.

* Titanous chloride in these cases gave abnormally high analytical figures.

† Partial reduction of the nitro groups takes place with $TiCl_3$, and the purity value obtained (based on no reduction of nitro groups) is unreliable.

‡ Very low yield of nitrogen.

‖ Calculated as fine dye.

estimated by titanous chloride analysis, and the microanalytical figures for nitrogen are not always sufficiently precise for giving purity data. So for these very reasons, the suitability of the new method for these dyes can not be assessed accurately, as no suitable standard of comparison is available by which to check the results.

The author has been unable to find any published record of the use of titanous salt analysis for either (1) nitroazo dyes or (11) water insoluble azo dyes. The present tests show that (1) give doubtful results in some cases with titanous chloride, owing to partial reduction of the nitro group; in several examples, no reduction of this group appeared to take place. The present dichromate oxidation method gives yields corresponding to the total nitrogen, including that of the nitro group. It is found that the water-insoluble azo dyes can be estimated quite satisfactorily in glacial acetic acid solution by means of titanous salts or the new method, and the results by the two methods are in agreement.

Intermediates

The present method was tested on the following intermediates - acetanilide, p-anisidine hydrochloride, diphenylamine, H-acid, p-nitroaniline, 2-nitronaphthalene - 4:8 - disulphonic acid. In all cases very low yields of nitrogen (3-15% of theoretical) were obtained. There is little structural resemblance between these compounds, and it is difficult to explain why as a class they do not decompose readily, while many dyes, of equally varied structures, give quantitative yields of nitrogen. A possible assumption is that coloured compounds, vix. dyes, decompose quantitatively, whereas

uncoloured intermediates do not. From the above facts, it appears that the ease of release of nitrogen is related to the structural characteristics conferring colour on the molecule.

Precision : Series of up to ten replications of analyses of dyes which decompose rapidly gave standard deviations of about 0.3.

Reaction Mechanism.

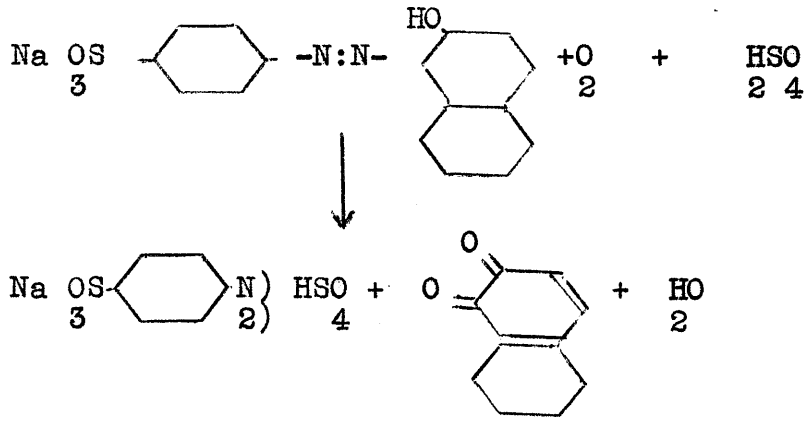
It is assumed that, in the case of the hydroxyazo dyes, the quinone hydrazone tautomer is preferentially attacked, and disruption first occurs of a C=N bond adjacent to the aromatic nucleus containing the hydroxy group, leading to the formation of a diazonium salt, which then loses nitrogen (J.S.D.C., 65,639,(1949) (Desai and Giles). The present method shows that the nitrogen in the azo group appears to be given off more rapidly than that in other groups in the molecule, thereby supporting the above supposition. After the decomposition of this group, a general break-up of the disruption products must occur. It has been noticed that o-hydroxyazo compounds decompose more rapidly than the para-isomers in the present procedure. This agrees with suggestions made by previous workers that the former exist largely as quinone hydrazones and the latter as the azo tautomers, e.g. Giles and Neustader, (J.C.S., 1864, (May, 1952)) Azo compounds containing neither hydroxy nor sulphonic acid groups must decompose in a different manner from hydroxy azo compounds, because they give low yields of nitrogen, not even corresponding to the azo group alone.

Absorptiometric Analysis of Azo Dyes using Ceric Sulphate as Oxidant.

Ceric sulphate is a stable, clean, and convenient oxidising

agents (Vogel, A Text Book of Quantitative Inorganic Analysis (London: Longmans Green & Co., 2nd edition, 1951), Willard and Young, (J. Amer. Chem. Soc., 52,132 (1930), and later papers). It was found that solutions of many azo dyes are instantaneously decolorised by it in the cold. It has been reported by Desai and Giles, (J.S.D.C.,65,639,(1949)) that volumetric and potentiometric analysis of Orange II with ceric sulphate does not give conclusive results. In the present work an absorptiometer was used in assessing the decomposition of dyes by this reagent, and a simple analytical method suitable for routine analysis was worked out. The method is to add increasing quantities of 0.001N. ceric sulphate solution, acidified with sulphuric acid, to a series of aliquots of a dye solution, (a suitable strength being 0.05 - 0.1%). The solutions are then allowed to stand at room temperature for about 10 min. to ensure completion of the reaction, and are afterwards suitably diluted for optical density determination. A graph is then plotted of optical density against quantity of reagent added. With increase in the amount of oxidising agent, the depth of colour of the solution progressively decreases (ceric sulphate itself is pale yellow), and the graph, which is linear, may be readily extrapolated to zero optical density. The intercept on the x-axis should correspond to quantitative oxidation of the dye (Fig. 1.)

The decomposition of Orange II by ceric sulphate in presence of sulphuric acid was assumed by Desai and Giles, (J.S.D.C.,65,639 (1949)), to be represented by the equation



Only less than half the azo dyes examined have been found to give results approximately corresponding to this equation, as shown by Table 3, which summarises the experimental data obtained with a range of representative azo dyes.

In a few cases the dye is precipitated by addition of the acid ceric sulphate solution. (The presence of acid is necessary in ceric sulphate oxidation to avoid precipitation of basic salts). Various means of avoiding such precipitation were tried, e.g. use of emulsifying agents in the aqueous solutions, or of dioxan or pyridine as solvent, but no encouraging results were obtained, the oxidation being prevented in such circumstances.

* Shorter and Hinshelwood, (J.C.S., 3276 (1950)) find that oxidation of acetone by ceric sulphate involves transfer of electrons from the organic compound to the oxidising agent. They suggest that the enol form is attacked and successively hydroxylated.

Jones and Soper, (ibid; 802 (1935)) found that the active compound in acid ceric sulphate solutions is $H_3Ce(SO_4)_3OH$, which ionises as an acid.

Table 3.

Ceric Sulphate Oxidation of Azo Dyes.

C.I. No.	Dye	Oxygen required* (mol./mol.dye)
-	Aniline→ 1-Naphthol-5-sulphonic acid ...	0.8
-	o-Anisidine→ R acid	1.05
-	m-Chloroaniline→ R acid	1.1
-	p-Chloroaniline→ R acid	1.1
-	p-Nitroaniline→ R acid	0.8
31	Azo Geranine 2G..	1.0
57	Amidonaphthol Red 6B...	1.25
(64)	p-Toluidine→ R acid	1.0
119	Eosamine B.	1.6
126	Erika 2GN..	1.05
148	Resorcine Yellow	1.5
151	Orange II	1.0
170	Diamond Black PV	1.1 (?)+
176	Naphthalene Red J	0.8
182	Naphthalene Red EA	1.0
185	Naphthalene Scarlet 4R	1.2
518	Chlorazol Sky Blue FF	0.95
-	Cr complex of 2-Amino-4-chloro-phenol - 6 - sulphonic acid→ 3-Methyl-1-phenyl-5-pyrazolone	1.0

* Calculated from titanous chloride analysis data.

\+ Diamond Black PV gives a curve with an abrupt change of slope; extrapolation of the upper part of the curve gives this value.

Colorimetric Determination of Azo Dye Coupling Components

The improved procedure devised for the analysis of intermediates which can be used as diazo or coupling components for azo dyes, is based on the colorimetric method previously described by Cropper and Giles (J.S.D.C., 60,279 (1944)) for determining the strength of solutions of the Naphthol AS type. The new method is simple, rapid, and less tedious than the commonly employed diazo titration procedure, see Saunders (The Aromatic Diazo-Compounds and their Technical Applications (London: Edward Arnold & Co., 2nd edition 1949)) and it has given consistent results with a number of typical intermediate

The method involves the addition of successively increasing quantities of a diazotised solution to a series of equal aliquots of a solution of a second component, the end-point of the coupling reaction then being readily determined by measuring the optical density of the liquids, plotting the values against the volumes of diazo solution added, and noting at which point the maximum density is first reached. Table 4 shows the results, and in Fig. 2 are shown two typical curves.

Table 4.

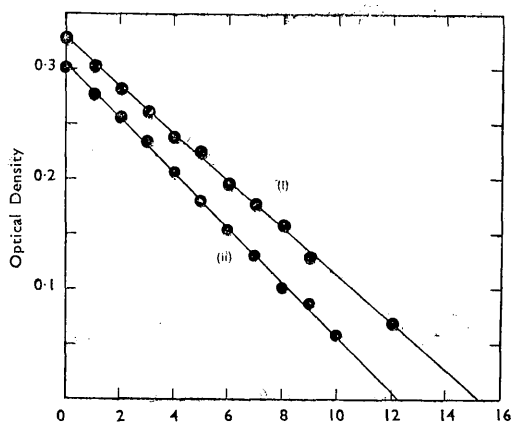
Colorimetric Determination of Azo Dye Coupling Components.

Compound	Quality	Purity (%) * (D)	(C)
a-Naphthol	...Recryst.	99	100.0
β-Naphthol	...Recryst.	100	100.5
1-Amino-8-naphthol-3:6-di-sulphonic acid (H acid)...	...Recryst.	85	86.0
1-Amino-8-naphthol-4:6-di-sulphonic acid (K acid)...	...Recryst.	63	63.5

Table 4. (continued.)

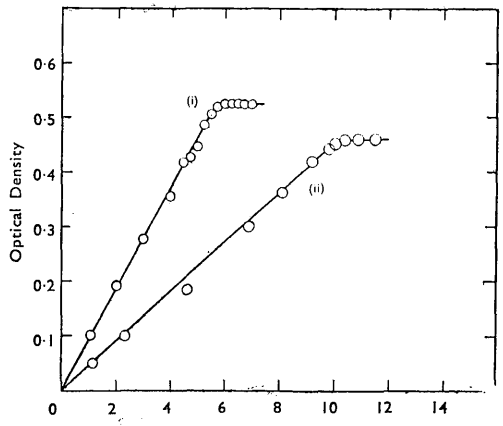
Compound	Quality	Purity (%) * (D)	(C)
2-Amino-8-naphthol-6-sulphonic acid (γ acid)...	Recryst.	73	72.0
2-Naphthol-3:6-disulphonic acid (R acid)...	Crude commercial	59	60.0
	Recryst.	72	72.5
2-Naphthol-6:8-disulphonic acid (G acid)	Recryst.	97	97.5
2-Naphthol-7-sulphonic acid (F acid)...	Recryst.	70	71.5
o-Anisidide of 3-hydroxy-2-naphthoic acid...	Commercial	-	97.5
o-Toluidide of 3-hydroxy-2-naphthoic acid...	Commercial	97	96.3

* (D) Direct diazo titration.
(C) Colorimetric titration.



Vol. of 0·0011 N. Ceric Sulphate added, c.c./5 c.c. dye soln.
(i) Naphthalene Red EAS (0·082% soln.)
(ii) Azo Geranine 2GS (0·103% soln.)

FIG. 1



0·001 N. Diazo Soln. (c.c.) added to 10 c.c. 0·001 N. Coupling Component
(i) R acid
(ii) β-naphthol

FIG. 2

DISCUSSION and CONCLUSIONS

The dichromate oxidation method described appears to be suitable for all azo dyes except the small number which contain neither a sulphonic acid group nor a hydroxy group and also for some nitrogen containing dyes of other classes, e.g. the triphenylmethane and anthraquinone classes. The method is simple and in most cases more rapid than the titanous salt reduction method.

The method is unsuitable for nitrogen - containing intermediates, but many of these may be determined readily by the colorimetric method also described in this thesis.

The ceric sulphate oxidation method is the simplest analytical procedure for azo dyes, and it could be used where a large number of routine purity determinations are required. Many dyes, however, do not react in simple stoichiometric proportion with the reagent, and unless improvements can be effected by future research, it will be necessary to have previously determined data available upon the required molar proportion of oxidant, e.g. as given in Table 3.

The colorimetric method described for azo dye coupling components is simple, rapid, and reliable, and is an improvement on the diazo titration procedure. It appears to be applicable to any second component, and while only compounds of this class have been studied in the present investigation, this method should be of equal value in determining bases in the form of their diazotised solutions.

Errors Due to Nitrogen - Containing Impurities.

The oxidative procedure is not expected to give reliable results with ~~these~~ dyes, having nitrogen - containing impurities, e.g. uncoupled diazo compound or its decomposition products. The

presence of such substances is believed to account for abnormally high nitrogen yields obtained from some laboratory preparations of azo dyes in the crude state, e.g. some dyes prepared from chloroanilines. After recrystallisation the analyses by dichromate and titanous chloride were in agreement. Thus, if there is any reason to suspect the presence of impurities of this type, it may still be necessary to analyse by titanous chloride as well as by dichromate. If the two methods are in agreement, it is probable that the true value has been found. If they are not, neither method can be entirely reliable, because some of the impurities in question, e.g. diazo compounds, also react with titanous salts. Possibly in certain of these cases the ceric sulphate method could be used as a check.

Experimental

Apparatus for Nitrogen Determination

The apparatus is shown in Fig. 3. F is a 50-c.c. round-bottomed flask heated by a Bunsen burner; C a small Liebig condenser approx. 7 in. long overall; N a 1.5-c.c. micronitrometer (Schiff's pattern); and D is a 250-c.c. Dewar flask containing solid carbon dioxide and fitted with a mercury safety valve M. The nitrometer is filled with 50% (by weight) aqueous potassium hydroxide containing barium hydroxide (1 g. per 100 g. of potassium hydroxide) to prevent frothing, Cumming, Hopper, and Wheeler (Systematic Organic Chemistry (London: Constable & Co. 4th edition 1950): P.465) by removing traces of carbonate particles*.

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* The liquid is allowed to stand several days before use, and the traces of solid carbonate which have settled to the bottom are removed by decantation.

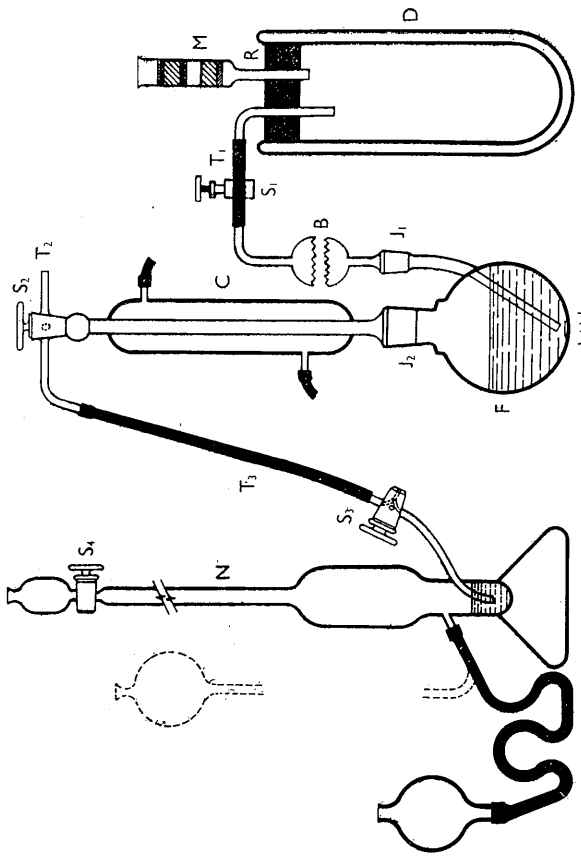
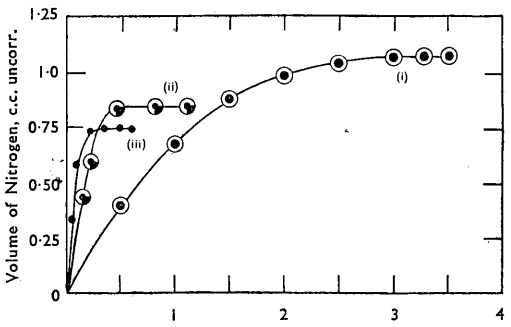


FIG. 3—Apparatus for Nitrogen Determination



(i) Lissamine Green SF (slow)
(ii) Chlorazol Sky Blue FFS (medium)
(iii) Resorcine Yellow (fast)

FIG. 4—Rate of Nitrogen Evolution

The glass lead-in tube and the condenser are connected to the reaction flask F by means of standard ground-glass joints, J_1, J_2 (in the present apparatus these are of B 7 and B 10 designation respectively); S_3, S_4 are the glass stopcocks+ of the nitrometer, S_3 being a three-way cock with one exit to the atmosphere. S_2 is a three-way glass stopcock+; when this is in one position the flask is connected with the nitrometer; when it is in the other position the flask is connected either to the atmosphere or to a vacuum pump through the short glass side-arm T_2; B is a bulb of sufficient capacity to prevent sucking-back of the liquid into D; T_1 and T_3 are rubber connecting tubes. The carbon dioxide supply is regulated by a screw-clip+ S_1; R is a rubber bung.

The mercury valve M is of the usual construction, as shown, with a fused-in sintered glass disc at the bottom, having layers placed upon it in the following order - 1 cm. of mercury, then an air space (2-3 cm.), a plug of tightly packed cotton wool, a layer of intimately mixed charcoal and iodine, and finally another plug of cotton wool, Cumming, Hopper, and Wheeler, (Systematic Organic Chemistry (London: Constable & Co., 4th edition 1950): P. 468.). This valve both regulates the maximum pressure of carbon dioxide (which may be increased if desired by increasing the thickness of the mercury layer) and prevents the escape of mercury vapour into the atmosphere.

To perform an analysis, the order of procedure is as follows -

(i) Charge D with solid carbon dioxide, by gently ramming down the

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+Good results have been obtained with a clip and stopcocks of normal pattern, but long-handled precision stopcocks of the type recommended by the American Specification Committee (Royer, Alber, Hallet,

(cont.)

+ Spikes, and Kuck (Ind. Eng Chem; Anal Ed; 13,574 (1941) Royer, Alber, Hallet, and Kuck (ibid; 15,476 (1943)) would give a more critical control of gas flow.

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finely powdered material until the vessel is filled to capacity. Insert the bung, and allow excess gas to escape to the atmosphere through the mercury valve for 2 hr. before use. This ensures an air-free supply.

(ii) In F place 5 c.c. of 5 N. sulphuric acid, 5 c.c. of 10% (wt./vol.) potassium dichromate solution, and a suitable amount of dye solution * (usually 2-10 c.c. of 0.01% solution) to produce Ca. 1 c.c. of nitrogen.

(iii) Sweep out the apparatus with carbon dioxide until free from air, as follows - With the nitrometer reservoir in the lowered position and S_4 closed, open S_3 to the air and turn S_2 to connect C with S_3. Open S_1 fully and pass a steady stream of gas for 5 min., then open S_4 and raise the reservoir to fill N with the potassium hydroxide solution. Close S_4, lower the reservoir, open S_3 to N, and pass a slow stream of carbon dioxide again, observing whether all the air has been removed by noting the size and velocity of the bubbles rising in N.

(iv) Begin oxidation by boiling the contents of F, a very slow stream of gas being passed to prevent sucking-back of the liquid +.

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* Normally in water, but glacial acetic acid is used for water-insoluble azo dyes.

+ It is advisable to open S_3 to the atmosphere for a short time while the flask is warming up, but to close it before b.p. is actually reached, in order to allow the escape of any dissolved air in the reaction liquid.

(v) When oxidation is complete, which is shown by the diminution in size of the gas bubbles in N almost to vanishing point, increase the carbon dioxide flow for 1 min. to complete the collection of nitrogen; then remove the burner, close S_3, open S_2 to the atmosphere, and read the volume of gas in N after allowing it to stand 15 min. to cool to room temperature.

It is advisable to plot a rough curve showing the rate of evolution of nitrogen, by observations of the nitrometer reading at intervals during the experiment. The curve will readily indicate the time for which the analysis should be continued. In Fig. 4 are reproduced typical curves showing the rate of evolution of nitrogen from various dyes.

Period of Oxidation

For specifying the length of time required to complete the oxidation, the soluble azo dyes may be divided roughly into three classes -

(a) Dyes without additional nitrogen-containing groups; these are oxidised in 10 min. (in a few cases even in 3 min.).

(b) Dyes with nitrogen-containing groups in addition to the azo group; these require a slightly longer treatment, but are completely oxidised in about 30 min. The higher the ratio of azo to amino groups, the more rapid appears to be the decomposition.

(c) Dyes which are precipitated by the oxidising solution and do not redissolve on boiling. These should be boiled for 2 hr. to complete the oxidation. Only a few examples of this class have been encountered, e.g. Congo red and benzopurpurin. (Some dyes are precipitated in the cold, but redissolve on boiling. These are included in Class (b).) The triphenylmethane and anthraquinone

dyes appear to decompose slowly and may require 2-3 hr. for analysis*.

The whole procedure occupies about 30 min. with dyes in Class (a) and 50 min. with those in Class (b). The extended period required for Class (c) dyes is no great inconvenience, because the apparatus can be left without attention during the boiling process, provided the rate of flow of carbon dioxide has been correctly adjusted and is low. It is important, however, when testing these dyes, to ensure that the carbon dioxide is completely free from air, and a check should be made by passing the gas into the filled nitrometer for 15 min. before starting the experiment. No measurable volume of gas should collect.

Even if the gas supply does contain traces of impurity, a fairly reliable result can sometimes be obtained by plotting the rate of gas collection and noting the point at which the slope of the curve finally becomes constant. This represents the point at which nitrogen evolution from the dye has ceased; thereafter the gas which collects at a constant rate is impurity.

PREPARATION AND STANDARDISATION OF CERIC SULPHATE SOLUTION

Ceric sulphate is very stable, and no special precautions are necessary for storing it in solution. The technical-quality material may be used; this is readily standardised by means of potassium dichromate, using ammonium ferrous sulphate as intermediate standard with N-phenylanthranilic (diphenylamine-2-carboxylic) acid as indicator.+

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* Many attempts were made to accelerate nitrogen evolution from dyes whose decomposition is slow, e.g. by the use of increased concentrations of acid and/or potassium dichromate, or the use of high concentrations of ferric chloride as an additional oxidising agent in order to raise the b.p. of the reaction mixture, but no success was achieved.

(cont.)

+ With dichromate as the titrant, because the indicator is effective only in presence of ferrous ions.

The 0.001N. ceric sulphate solution is made strongly (N.) acid with sulphuric acid; 4 mol. of the salt ($Ce(SO_4)_2$) yield 1 mol. of oxygen.

COLORIMETRIC DETERMINATION OF AZO DYE COUPLING COMPONENTS

PURIFICATION OF INTERMEDIATES- The naphthalenesulphonic acids were purified by precipitation with acid from alkaline solution, followed by recrystallisation from water; β-naphthol (m.p. 122°C.) by sublimation; and α-naphthol (m.p. 94°C.) by recrystallisation from aqueous ethanol. Some coupling components were used in the original commercial state.

Solutions are prepared as follows -

SULPHANILIC ACID (01. N.)- Dissolve 17.32 g. of pure sulphanilic acid in boiling water (400 c.c.), adding sufficient sodium carbonate to make the solution slightly alkaline (Brilliant Yellow paper), filter hot, cool, dilute to 1000 c.c., and store in the dark.

DIAZO SOLUTION (0.001 N.)- Add 2 c.c. of concentrated hydrochloric acid to 5.0 c.c. of 0.1 N. sulphanilic acid, followed by 5.2 c.c. of 0.1 N. sodium nitrite solution. Neutralise to Congo red paper with sodium acetate, and dilute to 500 c.c. with ice-cold water.

~~XXXXXXX~~ COUPLING COMPONENT SOLUTION (0.001 N.) - The solution should contain 5 g. of sodium hydroxide per 1000 c.c. Unsulphonated naphthols are dissolved in boiling aqueous ethanol containing sodium hydroxide, and the solutions diluted with aqueous ethanol.

Method of Test

Pipette 10-c.c. portions of coupling component solution into a series

of graduated flasks, of a capacity (usually 100-500 c.c.) required to give solutions having optical densities suitable for direct reading on an absorptiometer. Add successively increasing quantities of diazo solution, and allow the mixtures to stand for 30 min., to ensure complete coupling, before diluting. Use aqueous ethanol for diluting the solutions from unsulphonated coupling components. After examining the solutions on the absorptiometer, read off the purity of the test sample directly from the curve of optical density against volume of diazo solution added. In the present work good results have been obtained with both a one-cell (EEL) and a two-cell (Spekker) absorptiometer.

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Distilled water and analytical-quality reagents were used in the present work, except where otherwise stated. Microanalyses for nitrogen were by Dr. A.C. Syme (Glasgow) and Drs. Weiler and Strauss (Oxford).

Section 2.

THE STRUCTURE OF THE METALLIC LAKES OF THE BRAZILWOOD AND LOGWOOD DYES.

The logwood and brazilwood colouring matters are of no value unless combined with a metallic mordant. Only then do they develop full colour and fastness properties. The reactions they undergo in the mordanting processes have not, so far as the author is aware, been fully elucidated and as they are of both theoretical and technical interest and importance, an investigation designed to throw some light on their mechanism was undertaken.

Lake Structures: General considerations.

The various mordanting metals all give shades of dull blue or reddish blue with logwood colouring matters on the fibre, deepening to black with a characteristic bluish or purplish cast in the heaviest shades. The brazilwood colouring matters when mordanted are dull purple or purple-brown in tone.

The determination of the constitution of the majority of the lakes of these colouring matters has proved a somewhat complex problem. These substances are black, amorphous, infusible, virtually insoluble in all solvents and often appear to be mixtures. In order to arrive at a conclusion regarding their probable constitution one has to rely entirely on elementary analyses and an estimate of the probable sequence of intersections between the reactive groups and metal atoms concerned, based on a consideration of their known chemical properties. Proceeding on

these lines, a series of probable constitutional formulae has been drawn up (IV - XIII) which satisfy the criteria mentioned and, moreover, show a general consistency of pattern throughout.

In order to avoid unnecessary complexity, the proposed formulae (IV - XIII) are given in a simplified form, in which aq = H_2O ; bn = the monavalent brazilein ion or radical; bn = the divalent brazilein radical ; hn = the monavalent haematein ion or radical ; and hn = the trivalent haematein radical.

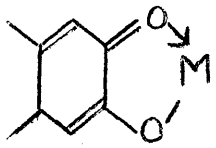
Nature of the Reactive Groups concerned in Lake Formation.

The oxidised forms, brazilein and haematein, rather than the leuco-compounds appear to be the lake-forming agents. Lakes can be formed from the latter, but the reactions almost certainly involve prior oxidation of the leuco-compound by air and/or the metal salt used. The relative lake-forming tendencies of haematoxylin and haematein can be demonstrated in a rather striking way by boiling, in an open beaker an aqueous solution of the former containing some aluminium chloride and a little sodium hydrosulphite to ensure absence of oxygen. After a time the clear colourless solution becomes turbid, owing to the formation of a white precipitate of sulphur, and instantly afterwards it becomes deep purple. Purple is the colour of the aluminium lake, which clearly cannot be formed until all the reducing agent has been destroyed by air and the haematoxylin has thus been left free to be air oxidised to haematein.

Further, the anions of the colouring matters, rather than the neutral molecules, must be the reactive species, because lake formation is promoted by alkaline conditions and retarded in acid

solutions. The retardation in acid must be due to competition for the colour anion between the metal cation and the hydrogen ion of the acid. Moreover, in aqueous solution, all the 6-covalent metals examined form 2:1-(dye:metal) complexes (x)but in organic solvents, e.g. ethanol, in which, of course, the degree of ionisation will be less than in water, the reaction appears to be retarded, so that mainly 1:1 complexes are formed.

Each colouring matter molecule must therefore form a chelate ring with a metal atom thus:-



It is, further, necessary to consider the possible reactivity of the additional phenolic groups in the molecule(+) especially since Haematein has a pair of o-phenolic groups which might act as an additional chelating centre. Morgan and Smith (J. Chem. Soc. Trans., 119, 704, (1921); 121, 160 (1922); 125, 1731 (1924)) found that when two potential chelating centres are present in an anthraquinone dye molecule, only one forms a true chelate ring when treated with a cobaltammine salt, the other being partially

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(x)Copper, the only 4-covalent metal examined, appears to form 1:1-complexes in water.

(+)The alcoholic group will probably not react with metals. The shade of the chromium lakes is not significantly affected when this group is alkylated (Duff).

reactive, forming a salt linkage. Weinland and Dottinger (Z. anorg. Chem., 102, 223 (1918); Weinland and Walter, ibid., 126, 141 (1923); Shuttleworth, J. Soc. Leather Trades Chemists, 32, 116 (1948)), by treating alkaline catechol solutions with metal salts, obtained chelate compounds of the type $M(C_6H_4O_2)_2K^+$ where M = Co" or Cu" and of the type $M(C_6H_4O_2)_3K^+$ where M = Cr" , and Shuttleworth examined the reactivity of phenol itself and several di-and trihydric phenols with a basic chromic sulphate. Only those having two phenolic groups in the o-position formed complexes with the salt. The present results, discussed below, are consistent with some combination of phenolic groups in haematein and brazilein with copper and perhaps with chromium in one instance, but not with iron.

A more detailed discussion of the proposed constitutions of the present series of lakes now follows.

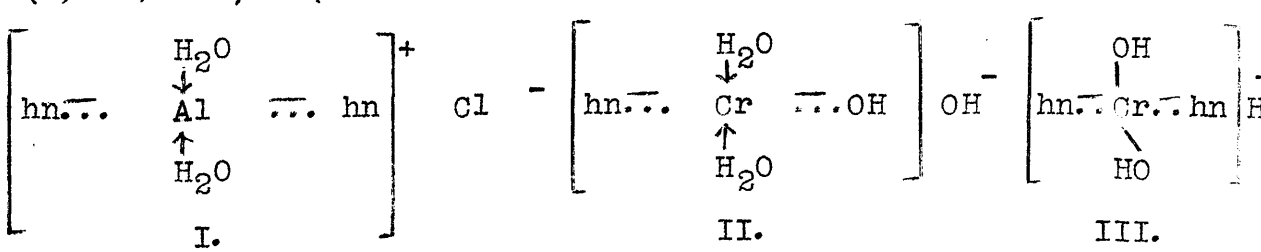
Water-soluble Haematein Lakes.

These are formed when dilute (0.1%) aqueous solutions of the colouring matter are boiled with aluminium chloride, or with potassium chromate or dichromate. A purple cationic and a blue anionic complex are obtained respectively. By plotting the optical density of the peak absorption wavelength of a series of solutions each containing the same amount of colouring matter, but increasing quantities of the metal salt, curves are obtained (Fig. 5) from which the ratio, dye:metal, in each type of complex can be read off.

If the ratios so obtained are examined (see Table 5) it is seen that they tend towards 2:1 (dye:metal) in every case. Disturbing factors must, however, be affecting the formation of these

complexes because none of the ratios is a simple integer. This can be accounted for as follows. The chromate or dichromate ion must first be reduced to the chromic salt state, and this means that some colouring matter must be oxidised and destroyed (x) before the remainder can enter into complex formation. The effect will be to <u>increase</u> the apparent dye:metal ratio. This is, in fact, seen in three of the lakes listed in Table 5. The small increase is indicative of a very complete destruction of a proportion of the haematoxylin or haematein concerned. The other three lakes, however, give ratios appreciably less than the theoretical. These three, all chromium lakes, are observed to be formed less readily in the boiling solutions than that from haematoxylin and chromate, and the low ratio can be accounted for by the presence of a proportion of a purple chromium lake, which can be detected both by chromatographic and spectrographic analysis (See Fig. 6, curve b), and which is believed to be a cationic 1:1-complex formed as a first stage in the production of the 2:1-complex. These complexes are formulated as they exist in the dilute solutions, as follows

(I, II, III):- (hn = the haematein radical)



I. II. III.

(x) This applies both to haematein and haematoxylin. Even the oxidation of two mols. of the latter is insufficient to reduce one mol. K_2CrO_4 or $\frac{1}{2}$ mol. $K_2Cr_2O_7$ to the Cr''' state.

~~XXXXXXXX~~

TABLE 5

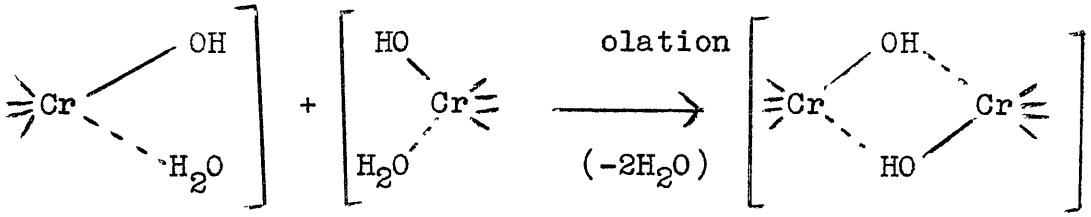
Analytical Ratios of Water-soluble Logwood Lakes.

Colouring Matter (a)	Metal Salt.	Complex Ratio.	
		Metal atoms: 2 mols.(a) (See Fig. 5).	Mols.(a): 1 metal atom.
Haematoxylin	$AlCl_3$	0.975	2.05
	K_2CrO_4	0.975	2.05
	$K_2Cr_2O_7$	1.250	1.60
Haematein	$AlCl_3$	0.975	2.05
	K_2CrO_4	1.250	1.60
	$K_2Cr_2O_7$	1.025	1.95

The lakes from other metals or from brazilin and brazilein were found to be too unstable in water to be examined by the colorimetric method. In most cases they tend to precipitate wholly or partially as soon as formed and the use of organic solvents or dispersing agents did not prevent this.

Water-insolubilisation Processes.

The lakes once prepared in substance and dried, have become virtually insoluble in all solvents, except by destruction in concentrated mineral acids and alkalies. Their insolubilisation is attributed to the operation of one or more of three processes:
(a) the formation of neutral, unionised complexes. Simple neutral complexes are an intermediate stage between the cationic and anionic forms and are likely to be less soluble than either of these. The analytical data support the assumption that they occur in some of the materials prepared,
(b) the formation of complex salts between cationic lakes and anions of colouring matter, and (c) "olation", when the dilute solutions of the water-soluble blue chromic lake are evaporated to dryness the lake cannot be redissolved in water. It is also noticed that the same water-soluble blue lake flocculates out of solution in the cold on standing several days. These facts point to the operation of the form of condensation polymerisation known as "olation", which takes place in aqueous chromic salt solutions on standing, or by heating:-



If this occurs when the lake solutions are concentrated and evaporated to dryness it could account for the insolubility of the final products of reaction of the colouring matters with chromate, dichromate, and iron salts, as discussed below.

Water content.

The lakes were not intensively dried and it has been assumed that therefore one water molecule will remain bound, by a hydrogen bond, to each free phenolic group in the molecules.(x) The analytical data are quite consistent with this assumption.

The actual products obtained will now be discussed.

Lakes from Chromic Salts.

Deep purple solutions are obtained when chromic salts and brazilein or haematein are boiled in alcoholic or "Cellosolve" solutions. These are considered to be 1:1-complexes, for the following reasons:-

(i) The colorimetric analysis of ~~ethanol~~ solutions (Fig.5) gives evidence of a 1:1-complex, (with CrO_3).

(ii) The 2:1-complex is blue. It would be expected that the smaller molecule of the 1:1-complex would have a less deep (i.e. a redder) shade.

(iii) The use of organic solvents will reduce ionisation and decrease the velocity of reaction between metal salt and colouring matter, thus favouring the production of only the smaller complexes, which must of course represent an early stage in the formation of the 2:1-complex.

(x)The ratio of combination between a water molecule and a phenolic group in non-aqueous solution is 1:1 (Arshid, Giles, McLure, Ogilvie and Rose, to be published).

(iv) The aqueous solutions of the blue chromium lakes in the early stages of boiling contain some purple component, and the colorimetric data demonstrate that some component with a lower ratio than 2:1 must be present.

(v) A purple lake appears to be formed at an early stage in the reaction between haematein and potassium dichromate on wool, because patterns mordanted with this salt and dyed for short periods (ca. 60 sec.), or at a low temperature, with haematein, assume a purplish colour, quite unlike the normal blue of mordanted haematein at low shade depths. (See Fig. 7 which is discussed more fully below).

All these facts support the assumption that a purple 1:1-complex is an intermediate stage in the reaction between haematein and metal salt which ultimately leads to the formation of the blue 2:1-lake. The analytical data are also consistent with the purple compounds being mixtures of 1:1-complexes, the cationic lakes being associated with unchanged haematein anions.

Lakes in Substance from Chromic Salts.

If excess of colouring matter is present from the start, as it has been in the present preparations using chromic chloride, etc., any cationic lake formed will be accompanied in the solution by gegenions of inorganic and organic (i.e. colouring matter) anions. The salt formed with the latter will be less soluble than that formed with the inorganic anion, so that in the prolonged extraction process following the evaporation of the original solution it will remain and the other be washed away. Even if excess of colouring matter is not used, a consideration of the typical equilibria:-

$$hn^{-}H^{+} + \left[Cr\ aq_6\right]^{+++}\ Cl_3^{-}$$

$$\left[hn\ Cr\ aq_4\right]^{++}\ Cl_2^{-} + aq_2 + HCl$$

$$\left[hn\ Cr\ (OH)\ aq_3\right]^{+}\ Cl^{-} + aq_2 + 2HCl$$

will show that as the reaction mixture is concentrated the equilibria will tend to move back towards the initial state, i.e., more haematein anion will be formed, leading to the precipitation of more of its salt with the cationic lake. In any case, such complex salts could be expected to be present in the final product, as indeed, they do appear to be. Thus, the substances obtained from haematein and brazilein by reaction with normal (hexaquo-) chromic chloride ($Cr\ aq_6, Cl_3$), or chromic fluoride, have analyses and properties consistent with compositions of cationic lakes corresponding to 30 parts of IVa and 70 parts of IVb, and 67 parts of Va and 33 parts of Vb respectively. When a salt in which some chlorine is in the inner complex is employed ($Cr\ Cl_2\ aq_4, Cl$), the chlorine is retained by the metal and is found in the lake. The analyses suggest the presence of some cationic and some neutral non-ionic lake, and the properties and analyses of the products are consistent with mixtures of 70 parts (VIa) with 30 parts (VIb) for the haematein derivative and 25 parts VIIa with 75 parts VIIb for the brazilein derivative, though it may well be that more complex mixtures than these are actually present, and the actual compositions obtained must be dependent, amongst other conditions, upon the physical state of the reactants, which at least in the case of

brazilein, are not wholly in solution at the start of the reaction.

Insoluble Lakes from Chromate and Dichromate.

It has already been noted that in the first stages of their formation, in dilute aqueous solution, the lakes formed from potassium chromate or dichromate consist of 2:1-complexes with some 1:1-complexes in admixture. The insolubilisation which accompanies drying is assumed to be due to olation and the analyses correspond to a product consisting of about equal parts of the olated anionic lake (VIIIb) and the unolated complex (VIIIa). The presence of chromic cations (as in VIIIb) can in fact be demonstrated by the detection of chromium in dilute hydrochloric acid which has been shaken up with the solid lake, in the cold. The substance is, in fact, a form of ion-exchange resin.

It is known that olation of inorganic chromium salts can proceed further than the condensation of two basic chrome complexes, and higher polymers can be formed.

The lake prepared from hexamminochromic nitrate and haematein in water appears to have the same composition as that made from dichromate. All the ammonia molecules associated with the chromium atom are thus replaced either by haematein or hydroxyl ions (x).

(x) This conforms with the fact (Martell and Calvin, Chemistry of the Metal Chelate Compounds (New York: Prentice-Hall, Inc., 1952)) that neutral nitrogen and negative oxygen have about equal co-ordinating affinity for metals, so that, e.g., a co-ordinated ammonia molecule would not be replaced by water molecule, but might be replaced by hydroxyl ion or haematein anion.

Lakes from Copper Sulphate.

These are readily formed as dark blue or violet precipitates by addition of the metal salt to solutions of haematein or brazilein, respectively. They are probably 1:1-complexes of 4-covalent copper (a possible formula for the haematein lake is shown at X) and may contain some cuprous ion stabilised by chelation, but no formulation could be found corresponding to the elementary analyses.

Lakes from Ferric Ammonium Alum.

The composition of the haematein lake appears to be very similar to the products from potassium dichromate, i.e., it is an olated anionic 2:1-complex (XIa) associated with the corresponding unolated compound (XIb). By shaking with cold dilute hydrochloric acid, some of the latter is removed and can be detected in the extract. The analysis of the brazilein product suggests that it may be a mixture of the olated complex (XIIb) with some of the ~~cationic (XIIa) and~~ anionic (XIIa) complex~~es~~, as in the case of the chromium compound.

Nature of the Lake-forming Reactions in the Fibre.

The processes which produce the inert, insoluble lakes when the liquid reaction mixtures are evaporated to dryness must also operate when mordanted and dyed fibres are dried. It is thus expected that the lakes in fibres will be very similar complex mixtures to

those whose composition has already been discussed (x), and the full formulation of the most important product, logwood black on a dichromate mordant, is probably close to that shown (XIII). During the dyeing process the simpler anionic 2:1-lake (III) may be formed in the fibre and, indeed, aqueous solutions of this lake will dye wool the characteristic having blue shade which logwood displays at low shade depths. Even before the blue complex is formed, however, it is preceded by the formation of the purple 1:1-complex, and if logwood dyed patterns on a chrome mordant are examined during the first few minutes of immersion in the bath the shade is seen to be a dull purple, which later changes to blue and black. In order to study these colour changes more precisely, a number of woollen patterns mordanted and dyed with haematein under different conditions were examined spectrophoto-metrically. The reflectance curves are low and rather indeterminate (Fig. 7) but the following conclusions can be drawn from them:

(x) Race, Rowe and Speakman, J.S.D.C., 62, 372 (1946) found that the ratio, dye molecules: chromium atoms in chrome mordanted wool dyed with several typical dyes was almost exactly 2:1. Their measurements were made by comparing the amount of dye absorbed with the amount of non-extractable chromium. This method would give exact 2:1-ratios even if the actual lakes were polymerised structures of the type here proposed. They attributed the improved wash-fastness of mordanted dyeings to the doubling of size of the dye molecule by complex formation.

(i) the purple shade in the early stages of dyeing represents a mixture of cationic 1:1-lake and free haematein anion (7a-d), but these soon combine together to form the blue 2:1-complex (7d-e). This can be confirmed by removing a purple pattern from the bath and boiling it in water. Its colour changes to blue (7f). When the fibre remains in the dyebath the change is complete in 5-10 min. A similar sequence of events takes place when chrome alum is used as mordant, but the blue lake then forms more slowly and the dyed shades, even after normal dyeing periods, have a pronounced reddish tone.

Clearly the metal salt and colouring matter are at first absorbed by the fibre more rapidly than they can combine to form the lake, but as their concentration in the water inside the fibre increases, so does their rate of mutual reaction, so that after 5-10 min. the lake forms in the fibre as rapidly as the components are absorbed. It can readily be demonstrated that when wool is boiled in weak mixed aqueous solutions of colouring matter and mordant, lake formation is much more rapid in the fibre itself than it is in the solution in absence of fibre.

It seems likely that the large insoluble complex of logwood black in the fibre must be held therein by purely mechanical forces aided perhaps by van der Waals' attraction, and not by chemical bonds with the substrate. This is the conclusion which Race, Rowe and Speakman also reached regarding the retention of the chromium lakes of synthetic mordant dyes in wool.

E X P E R I M E N T A L.

Preparation and Examination of Lakes.

In Solution.

Colorimetric determinations were made as follows :
(i) 2:1-lakes, by adding 0.1% aqueous potassium chromate or dichromate, or aluminium chloride solution to 10 c.c. of 0.1 per cent aqueous haematoxylin or haematein solution, in a series of increasing quantities. The mixtures were then boiled for 60 sec., cooled and diluted for measurement on the photoelectric absorptiometer with the appropriate filter. A curve is obtained consisting of two straight lines (Fig. 5) intersecting at a point corresponding to the ratio of components in the complex. The results are summarised in Table (5) above.
(ii) 1:1-lake. By a similar process using solutions of 0.1% chromium chloride hexahydrate and 0.1% haematein respectively in ethanol. Dilution was made with ethanol.

Tests of sign of ionic charge.

Two simple qualitative methods have been used to determine the sign of charge on the water soluble lakes: (i) examination of the effect of the solutions on anodised aluminium and powdered silica (quartz). These are positively and negatively charged, in water, and are coloured only by anions and cations, respectively; (ii) examination of the rate of spread of a drop of solution upon filter papers previously impregnated with cationic and anionic surface-active agents, and dried. Anionic lakes are retained by the first and cationic lakes by the second.

An attempt was made to confirm the magnitude of the ionic charge by passage of the solutions through columns of the appropriate ion-exchange resins, followed by electrometric titration, but consistent results were not obtained in successive experiments. This may have been due to some incipient precipitation occurring in the resin columns.

Brazilein lakes are all insufficiently water soluble for colorimetric analysis to be applicable.

In Substance.

Chromium (1:1-) complexes.

(a) From Hexaquochromic chloride or chromic fluoride.

A mixture of 2.5g haematein dissolved in 60 c.c. ethanol and either (i) 1.4 g. hexaquochromic chloride ($CrCl_3,6H_2O$) in 30 c.c. ethanol, or (ii) 0.8 g. chromium fluoride in 50 c.c. water, was refluxed for 12-15 hr. and then evaporated to dryness. The residue was (Soxhlet) extracted with isopropyl alcohol for three days to remove free haematein and chromium chloride, then warmed with a little ether to complete the removal of impurities, separated by filtration, and dried at 100-110°C. for 24 hrs. Partially soluble in hot water, more so in dilute mineral acid. Wool is dyed a dull purple shade.

Found: H,4.5, Cr, 5.95 (mean of 14 preparations by different operators; (Desai, Connelly, Duff etc., Private communication), range 5.4 - 6.8); $(C_{16}H_{11}O_6)_3$ Cr, $10H_2O$ (IVa) requires H, 4.7; Cr, 4.6; $(C_{16}H11O_6)_2$ Cr (OH), $7H_2O$(IVb) requires H,4.7; Cr, 6.55; 30 parts (IVa) + 70 parts (IVb) requires H,4.7; Cr, 6.0%.

A brazilein lake was similarly prepared, from hexaquochromic chloride, the colouring matter being partly in solution and partly in suspension in the solvent (ethanol). Soxhlet extraction was by "Cellosolve". Found: Cr, 5.8; $(C_{16}H_{11}O_5)_3$ Cr, $7H_2O$ (Va) requires Cr, 5.1; $(C_{16}H_{11}O_5)_2$ Cr(OH), $5H_2O$ (Vb) requires Cr, 7.2; 67 parts (Va) + 33 parts (Vb) requires Cr, 5.75%.

(b) From "Chromic chloride tetrahydrate", $[CrCl_2(H_2O)_4]$ Cl.

A mixture of solutions of 1.25 g. haematein in 80 c.c. ethanol and 0.85 g. of the chromic salt in 50 c.c. ethanol was refluxed 24 hr. The purple solution was evaporated to dryness at 40°C., and the residue (Soxhlet) extracted for several hours with isopropanol, until no more coloured materials passed into the extract. Finally, the material was washed with ether and dried in a vacuum desiccator. The dark purple amorphous product was partially soluble in hot water, and more so in dilute acid solutions and quite soluble in concentrated mineral acids; it was insoluble in organic solvents. The aqueous solutions coloured wool and silica purple, but did not affect anodised aluminium. Found: Cr, 12.0, 11.8; Cl present, but no Cl-ion;

$(C_{16}H_{11}O_6)CrCl_2,4H_2O$(VIa) requires Cr, 10.6;
$(C_{16}H_{11}O_6)$ $Cr_2(OH)_2(Cl)_3$, $7H_2O$ (VIb) requires Cr, 15.3; 70 parts (VIa) + 30 parts (VIb) require Cr, 12.0%.

The brazilein lake was similarly prepared, the colouring matter being only partly dissolved in the reaction mixture. Found: Cr, 15.4, 15.1; $(C_{16}H_{11}O_5)$ $CrCl_2$ $3H_2O$(VIIa) requires Cr, 11.3; $(C_{16}H_{11}O_5)$ $Cr_2Cl_3(OH)_2$ $6H_2O$(VIIb) requires Cr, 16.4; 25 parts (VIIa) + 75 parts (VIIb) requires Cr, 15.1%.

Chromium (2:1-) complexes.

(a) From Potassium dichromate. Haematoxylin (10 g.), dissolved in 500 c.c. water, was mixed with 3 g. potassium dichromate dissolved in 100 c.c. water, and the mixture boiled a few min. to precipitate the flocculent blue-black lake, which was then separated by filtration and well washed with hot water, followed by drying at 110°C.

Found: C, 46.5; H, 4.2; Cr, 9.2; $(C_{16}H_{11}O_6)_2(OH)_2\ Cr_2 10H_2O$ (VIIIa) requires C, 42.0; H, 4.6; Cr, 11.4 $(C_{16}H_{11}O_6)_4\ (OH)_2\ Cr_2,\ 8H_2O$ (VIIIb) requires C, 52.5; H, 4.25; Cr, 7.10; 50 parts (VIIIa) + 50 parts (VIIIb) requires C, 47.3; H, 4.4; Cr, 9.3%

(b) From hexamminochromic nitrate. Aqueous solutions of mixtures of haematein and hexamminochromic nitrate, heated on the boiling water bath several hr. deposited a dark bluish-black precipitate, which was filtered off, washed well with water and dried. Found, Cr. 9.3, 8.9, 9.1%, in successive preparations. N absent. The composition probably resembles that of the product prepared by dichromate.

(c) From potassium chromate in aqueous alcoholic solution.

A solution of 1.6 g. haematein in 100 c.c. methanol was mixed with a solution of 0.73 g. potassium chromate in 60 c.c. water and boiled under reflux 14 hr. The mixture was then evaporated to dryness at 40°C., finely ground, boiled under reflux with water (18 hr.), Soxhlet extracted with "Cellosolve" until

the extracts were no longer coloured, washed with ether, and dried at 100-120°C. for 10 hrs. Found: Cr, 8.8, 8.4; this product may therefore be very similar to that made in aqueous solution.

A lake was similarly prepared from brazilein (0.95g) in 75 c.c. ethanol and 0.62 g. potassium chromate in 45 c.c. water, refluxed for 10 hr. Found: Cr, 10.1, 9.9; $(C_{16}H_{11}O_5)\ O_7Cr_3 5H_2O$ (IXa) requires Cr, 24.5; $(C_{16}H_{11}O_5)\ 2\ (OH)_2\ Cr_2,\ 28H_2O$ (IXb) requires Cr, 12.3; $(C_{16}H_{11}O_5)_4\ Cr\ (OH)_2\ 4H_2O$ (IXc) requires Cr, 7.8%. The product is probably a mixture of these three complexes.

Copper lakes.

(a) Solutions of 1 g. haematein in 75 c.c. ethanol and 0.5 g. cupric sulphate crystals in 25 c.c. water were mixed and boiled under reflux 15 hr. The liquor was then evaporated to dryness at 40°C. and the residue first repeatedly washed with aqueous ethanol and then refluxed with aqueous ethanol 9 hr., then dried in a vacuum desiccator. The product was insoluble in water and organic solvents. In concentrated sulphuric acid it gave a deep red solution, and in 10% aqueous potassium hydroxide, a reddish blue solution. Hot suspensions of the lake coloured both anodised aluminium and silica on standing.

Found: Cu, 11.1, 10.9: 11.2 (by combustion) 15.25 (second prep.); C, 42.65; H, 4.05; SO_4 absent; the material is possibly a mixture of cuprous and cupric lakes with some metal oxide or hydroxide. $(C_{16}H_{11}O_6)_2\ Cu_2 6H_2O$ (X) requires Cu = 15.4%.

A brazilein lake was similarly prepared, using 0.6 g. copper sulphate in 40 c.c. water, and refluxing 13 hr. Subsequent washing was with hot water, followed by refluxing 5 hr. with methanol. Found: Cu, 11.35, 11.5 (x) (17.6% second prep.): (x) Cu, 12.5 by combustion.

C, 46.1; H, 3.95; this material may also be a mixture containing oxide or hydroxide. (Second prep. using 0.25 g. $CuSO_4$).

Iron Lakes.

(a) Haematoxylin (1.1g). dissolved in 40 c.c. water, was mixed with ferric ammonium sulphate (0.65g), dissolved in 30 c.c. water and boiled under reflux 6 hr. The mixture was then evaporated to dryness at 40°C, well washed with hot water and then refluxed with aqueous ethanol several hr., then separated by filtration, washed with aqueous ethanol, and dried in a vacuum desiccator. An aqueous suspension coloured anodised aluminium, but not silica. Found: Fe, 9.0, 9.25.

(b) A solution of haematein (0.5g) in 40 c.c. methanol was mixed with a solution of 0.32 g. ferric ammonium sulphate in 20 c.c. water and boiled under reflux 15 hr. The mixture was then evaporated to dryness at 40°C., repeatedly washed with hot water, then refluxed with aqueous "Cellosolve" (6 hr.), washed with water, then ether, and then dried at 100°C. An aqueous suspension did not colour either anodised aluminium or silica.

Found: Fe, 9.2. the constitution must therefore be identical with that of the lake from haematoxylin.

(c) Brazilein (1 g.) dissolved in a mixture of 25 c.c. "Cellosolve" and 50 c.c. water was mixed with a solution of 0.75 g. ferric ammonium alum in 40 c.c. water and boiled under reflux 16 hr. The mixture was then evaporated to dryness at 50°C., the residue repeatedly washed with boiling water and then boiled under reflux

13 hr. with aqueous ethanol. It was then filtered off, washed with hot water, then with methanol and finally with ether, and dried in a vacuum desiccator. A second preparation was purified by refluxing first with water, then with "Cellosolve". Found: Fe, 9.1, 9.15 (in different preparations).

The constitutions of all these lakes are probably similar to those of the complexes from dichromate, i.e., mixtures of XIa and XIb and of XIIa and XIIb.

Tin.

Haematein (1.52g) dissolved in methanol (80 c.c.) was mixed with stanuous chloride (0.72 g) dissolved in 40 c.c. water containing a little hydrochloric acid, and boiled under reflux 25 hr. The late which had precipitated was separated by filtration well washed with hot dilute hydrochloric acid to remove unreacted tin salt, then (Soxhlet) extracted several days with ethanol to remove unreacted haematein, and finally washed with ether and dried in a vacuum desiccator. The brazilein lake was similarly prepared. Both these compounds gave very considerably greater analyses for tin than could normally be accounted for. It is assumed they were contaminated with basic inorganic tin salts.

Determination of metals in lakes.

Chromium.

Besides the weighing of the ash after micro-combustion in oxygen, the following methods were used to determine chromium:- (a) A known weight of lake was fused with sodium peroxide in a nickel crucible. The mass, after cooling, was leached out with

boiling water, the solution filtered, boiled to remove oxygen, and acidified with hydrochloric acid to convert chromate to dichromate. The solution was then diluted to a given volume; to an aliquot portion a little concentrated hydrochloric acid was added, followed by potassium iodide crystals, and the liberated iodine was titrated with 0.1 N. sodium thiosulphate solution, using starch indicator. The accuracy of the method was checked by determination of a known chromium salt.

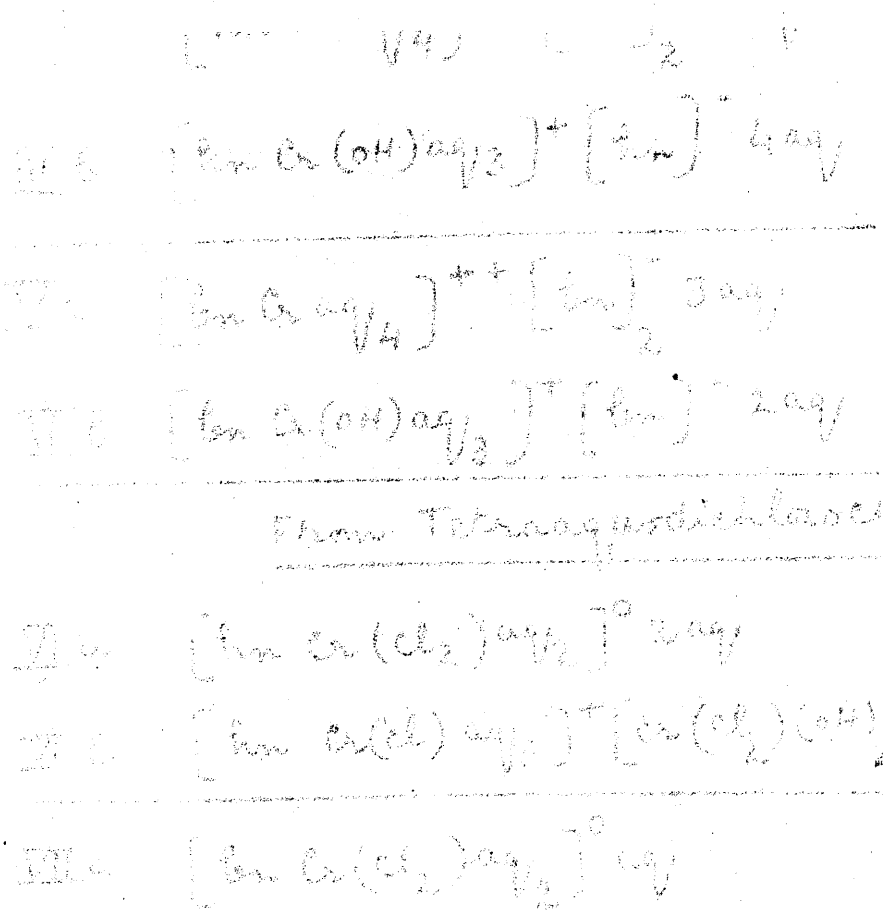
(b) Ashing in a platinum crucible. This gave high values, presumably due to incomplete combustion or to carbide formation. Better values were obtained if the crucible was allowed to cool from time to time and the ash moistened with a few c.c. of ethanol.

Copper and Iron.

0.05 G. of the lake was ignited to constant weight in a porcelain crucible, the residue cooled, 10 c.c. sulphuric acid (S.G.1.84) added and the mixture carefully stirred into 100 c.c. cold water. 25 c.c. aliquot portions of the solution were then taken for titration with 0.1N sodium thiosulphate solution, after addition of ca. 3g. potassium iodide crystals, using starch indicator. For the iron analysis, a small quantity of a suspension of cuprous iodide was also added to the mixture before titration. Copper was also determined by direct weighing of the ash after micro-combustion in oxygen.

Spectrophotometric measurements of solutions were made on a Unicam SP500 photoelectric spectrophotometer and absorptiometric determinations on either a Hilger Spekker or an E.E.L. photoelectric absorptiometer. The reflectance spectra of dyed fabrics were made

on the Hardy automatic recording spectrophotometer in the Dyehouse laboratories of Imperial Chemical Industries Ltd., Dyestuffs Division. They were measured against magnesium oxide using a double fabric layer with a matt black backing.



Proposed Structures of Brazilein and Haematein Lakes

Chromium (1:1) Complexes

From Hexaquochromic chloride

IV a $[hn\ Cr\ aq_4]^{++}\ [hn]_2^{-}\ 6\ aq$

IV b $[hn\ Cr(OH)\ aq_3]^{+}\ [hn]^{-}\ 4\ aq$

V a $[bn\ Cr\ aq_4]^{++}\ [bn]_2^{-}\ 3\ aq$

V b $[bn\ Cr(OH)\ aq_3]^{+}\ [bn]^{-}\ 2\ aq$

From Tetraaquodichlorochromic chloride

VI a $[hn\ cr(cl_2)\ aq_2]^{0}\ 2\ aq$

VI b $[hn\ cr(cl)\ aq_3]^{+}\ [cr(cl_2)(OH)_2\ aq_2]^{-}\ 2\ aq$

VII a $[bn\ Cr(cl_2)\ aq_2]^{0}\ aq$

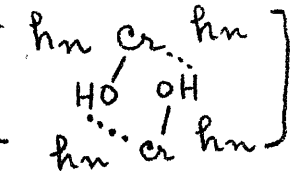
VII b $[bn\ Cr(cl)\ aq_3]^{+}\ [cr(cl_2)(OH)_2\ aq_2]^{-}\ aq$

Lakes - continued

Chromium complexes from chromates and dichromates

VIII a $\left[hn\ Cr(OH)_2\ hn \right]^{-} \left[Cr(OH)_2\ aq_4 \right]^{+} 4\,aq$

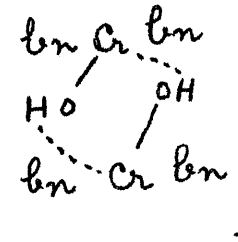
VIII b



8 aq

IX a $\left[bn\ Cr\ aq_4 \right]^{++} \left[Cr_2O_7 \right]^{--} aq$

IX b



12 aq

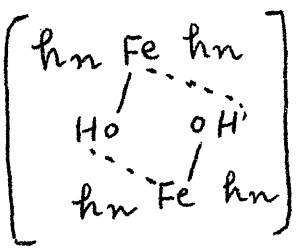
IX c $\left[bn\ Cr(OH)_2\ bn \right]^{-} \left[Cr(OH)_2\ aq_4 \right]^{+} 2\,aq$

From Copper Sulphate

X $\left[Cu(aq_2) = \underline{hn} \cdots Cu(aq_2) \right]^{+} \left[hn \right]^{-} 2\,aq$

From Ferric Ammonium Sulphate

XI a



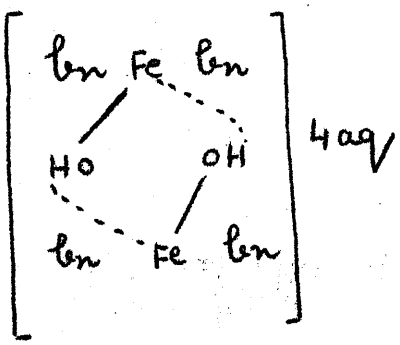
8 aq

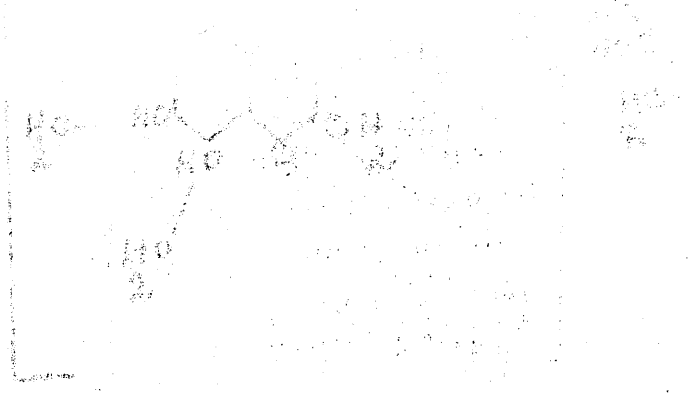
Lakes - continued

XI b $\left[bn\,Fe(OH)_2\,bn \right]^- \left[Fe(OH)_2 \right]^+ 4aq$

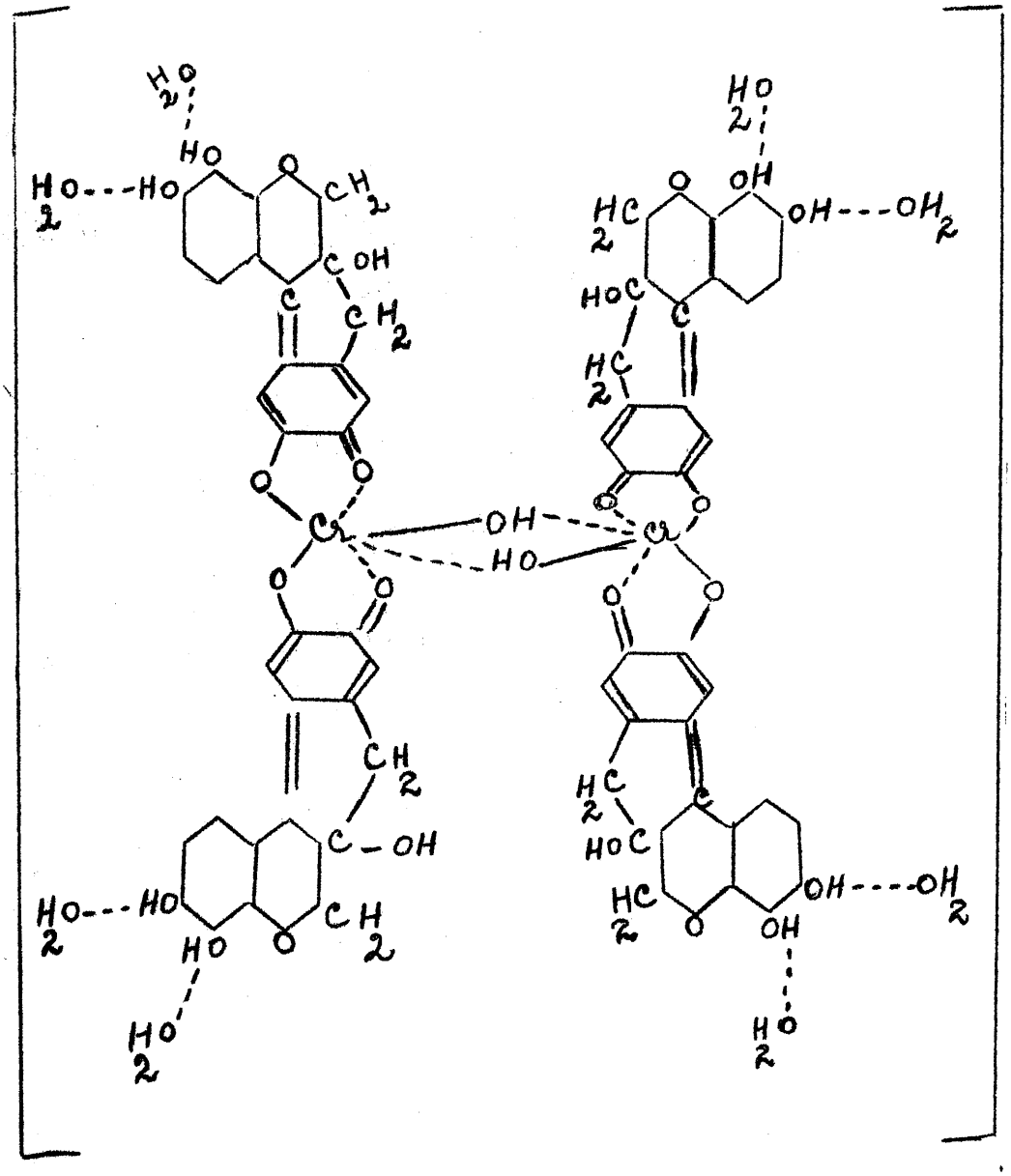
XII a $\left[bn\,Fe(OH)_2\,bn \right]^- \left[Fe(OH)_2\,aq_4 \right]^+ 2aq$

XII b





XIII Probable Structure



XIII Probable Structure of Logwood Black.

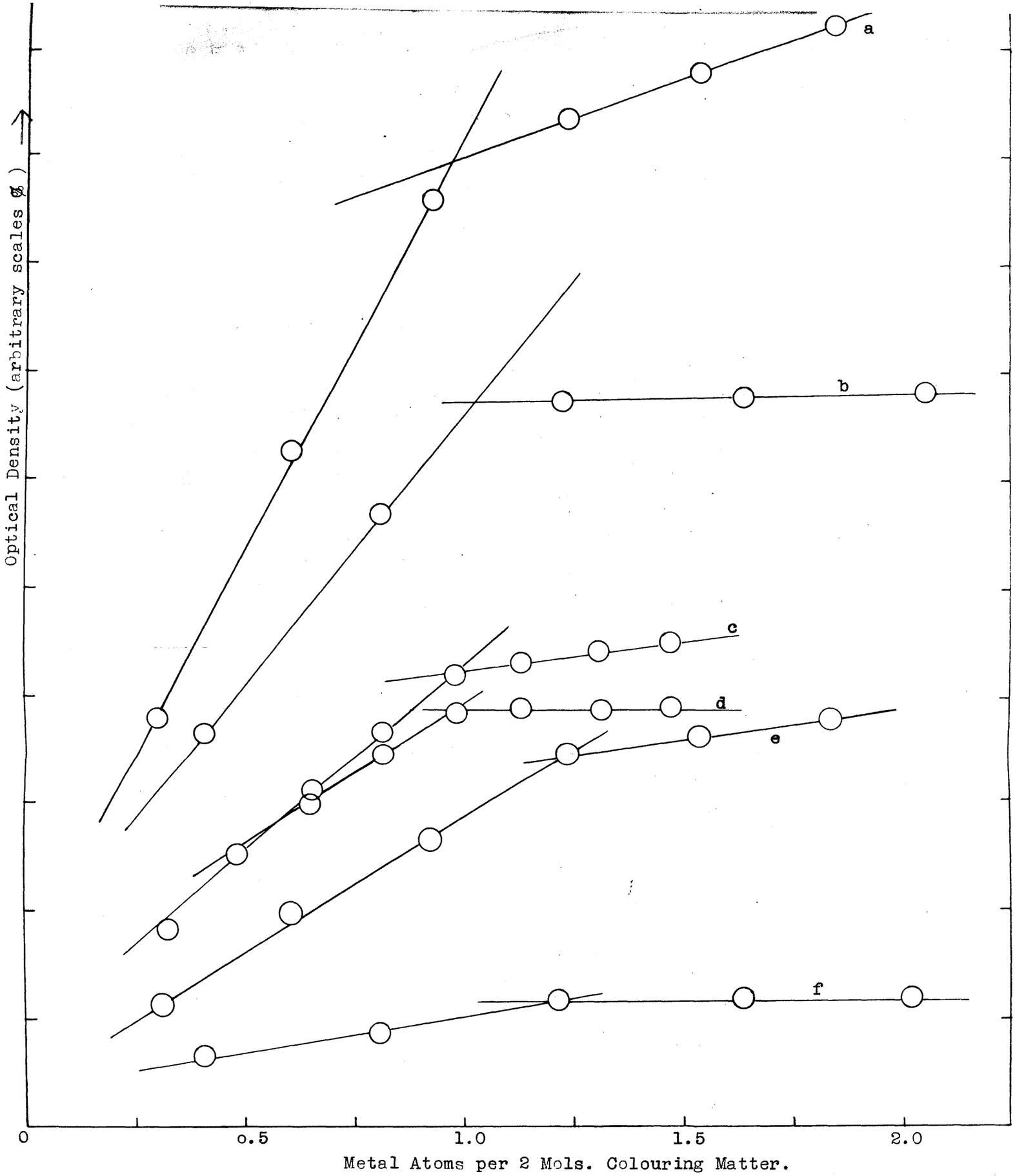
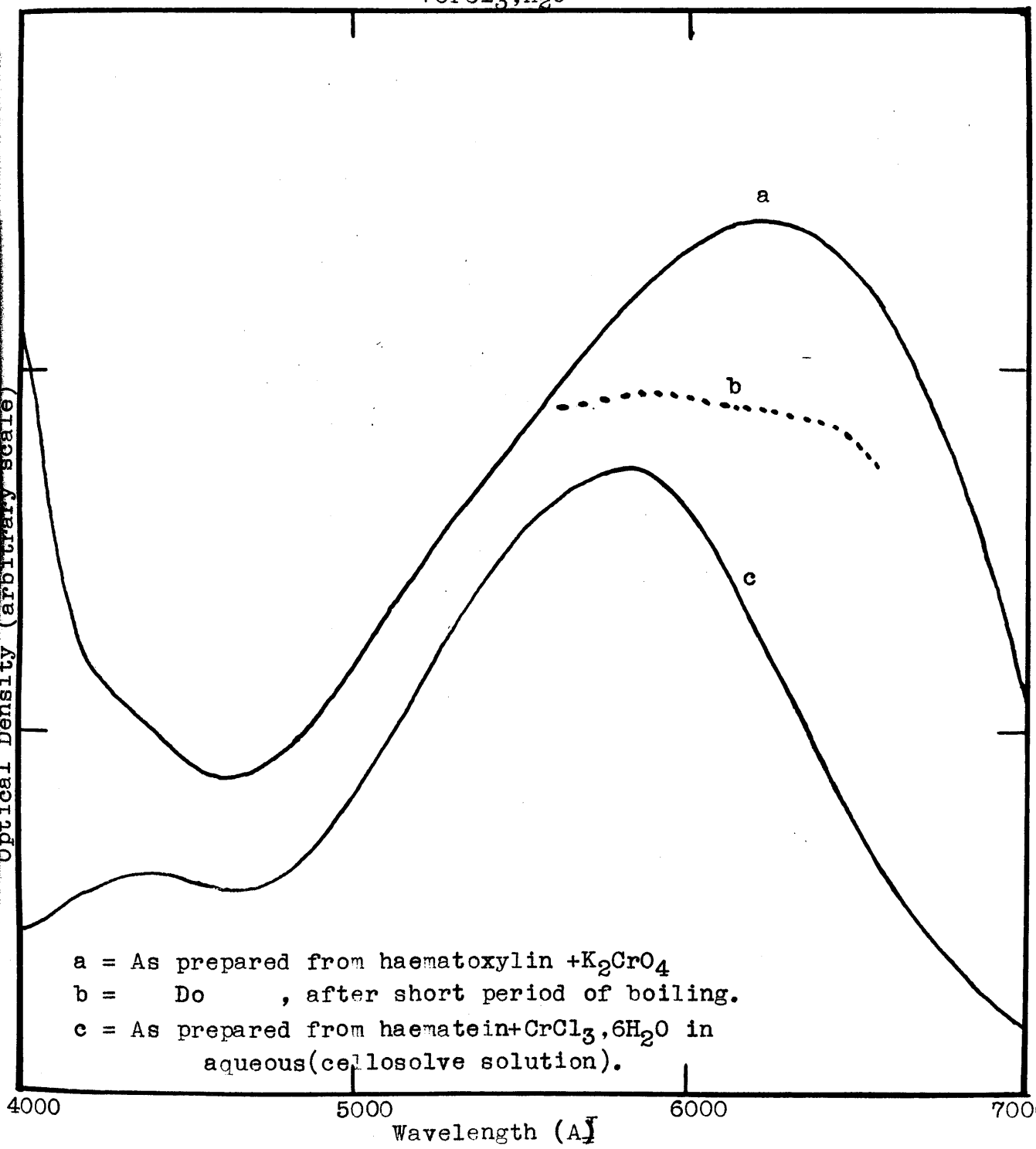


Fig. 5 . Colorimetric Determination of Metal:Dye Ratio in Water-Soluble Logwood Lakes

a) Haematoxylin+K_2CrO_4
b) Haematein+$K_2Cr_2O_7$
c) " +$AlCl_3$
d) Haematoxylin+$AlCl_3$
e) Haematein+K_2CrO_4
f) Haematoxylin+$K_2Cr_2O_7$

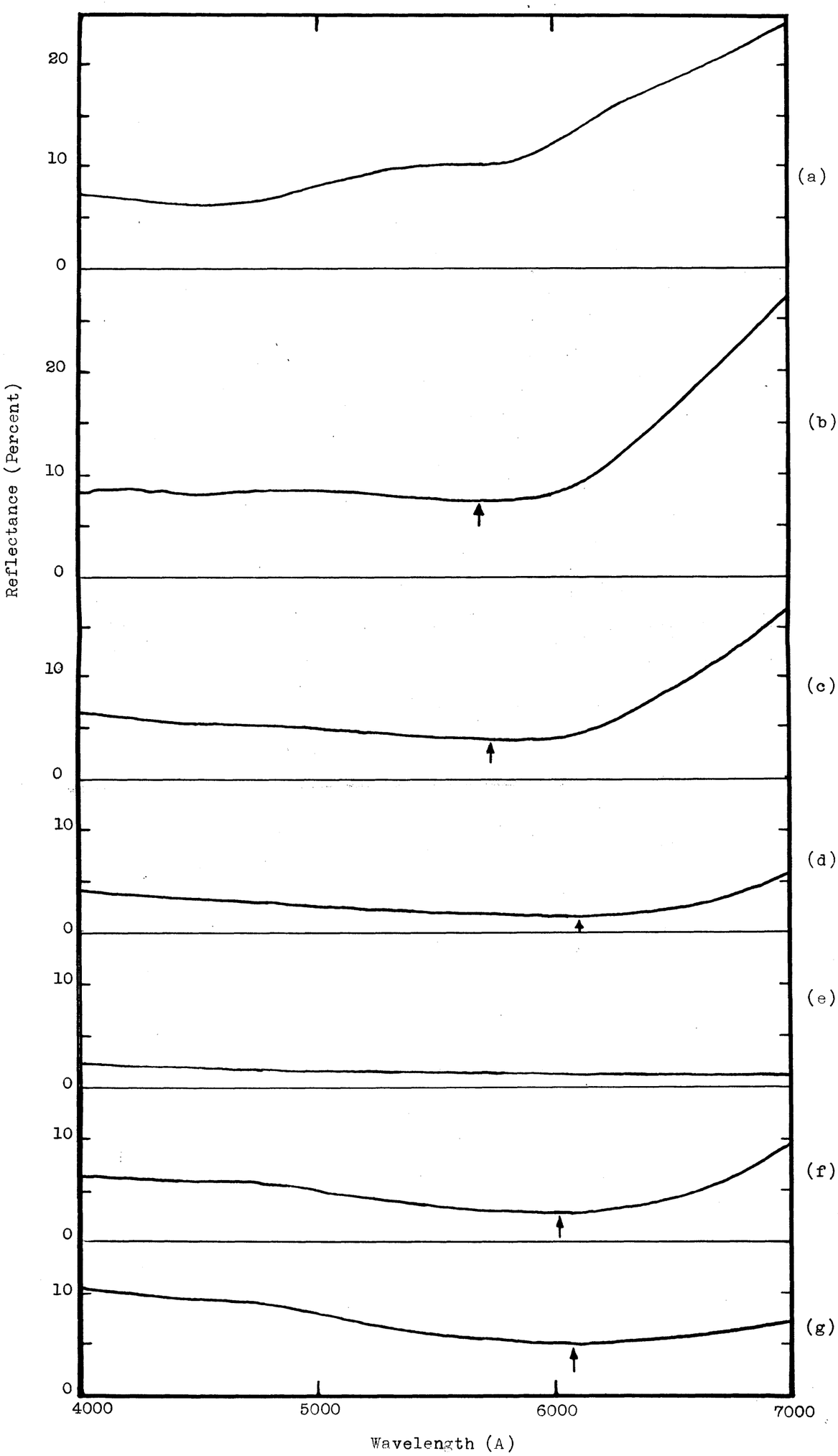
✱ Several of the curves have been displaced vertically, for clarity.

Fig. 6 . Spectral absorption curves of soluble Chromium Lakes of Logwood+K_2CrO_4 +$CrCl_3,H_2O$



a = As prepared from haematoxylin +K_2CrO_4
b = Do , after short period of boiling.
c = As prepared from haematein+$CrCl_3,6H_2O$ in aqueous(cellosolve solution).

Fig. 7 . Reflectance Spectra of Potassium Dichromate-mordanted woolen (flannel) Fabric Dyed with Haematein under various conditions. (The arrows indicate the appromixate position of the minima in the original traces).



a) Dyeing of 3% Haematein, unmordanted.
b) Fabric mordanted in Acid Potassium Dichromate, then Dyed 30 seconds with Haematein (3% on weight of fabric).
c) As (b), but dyed 2 minutes (Dull purple shade)
d) As (b), but " 5 " (Bluish purple shade)
e) As (b), " " 60 minutes (Full black shade)
f) Treated as (c), then rinsed and boiled 5 minutes in water.
g) Fabric Dyed in solution of Preformed water-soluble Blue (cr) lake of Haematein with K_2CrO_4

PART II

Studies in Hydrogen-bond Formation.

Section 1. The use of Refractive Index Measurement to Detect Intermolecular Complex - Formation in Solution.

Section 2. The Examination of the Inter - and Intramolecular Bonding Properties of Water and a variety of Organic Compounds.

PART II.

Section 1. STUDIES IN HYDROGEN-BOND FORMATION.

The Use of Refractive Index Measurement to detect Intermolecular Complex-Formation in Solution.

Giles, Rose and Vallance's paper (J.C.S., 1952, 3799) described preliminary experiments upon the use of dielectric constant measurements to detect intermolecular hydrogen-bonding between pairs of organic solutes in non-aqueous solutions. Plots of dielectric constant against molar ratio of the solutes (at constant total molarity) were shown to be linear, changes of slope occurring at ratios corresponding to the composition of intermolecular complexes.

The present work describes an alternative method of detecting complex formation which may be used with both non-aqueous and aqueous solutions. The results obtained by the two methods are compared and a detailed examination is described of the validity of their interpretation as evidence of the presence of hydrogen-bond complexes.

Use of Refractive Index Measurements.

It was desired to extend the work already described, to include aqueous solutions. The dielectric constant method is unsuitable for these, and consideration was therefore given to the measurement of some other physical constant. The refractive index appeared to fulfil the criterion of ready determination to a high degree of precision with small amounts of materials. By the Maxwell law, the square of the refractive index of a substance is

equal to its dielectric constant, and therefore this parameter should, like the dielectric constant, vary linearly with the concentration of a solution (See Appendix I). It is known, however, that some pure liquids, water particularly, deviate considerably from the Maxwell law, more especially if measurements of the two constants are not made with radiation of the same frequency (x). Moreover, it was proposed to use dilute solutions, not pure liquids, in the present research, and it was therefore necessary to examine empirically the relationship between the square of the refractive index and the concentration of non-aqueous and aqueous solutions over the range of concentrations likely to be employed in the present research. The results of this examination are summarised in Figs. 1A and 2A, which show that the relationship is quite linear, for a variety of typical compounds in both non-aqueous and aqueous solutions up to at least double the maximum concentration (0.25 M.) used in the present work.

This test was then followed by one for additivity. Fig. 3A shows that the square of refractive index is truly additive for binary solutions, of constant molarity, of azobenzene and benzoquinone, two substances not capable of hydrogen-bond interaction.

(x) For a discussion, see Remick, "Electronic Interpretations of Organic Chemistry", London, Chapman and Hall, Ltd., 1943. Appendix II.

When, however, substances which are capable of interaction are examined, viz. azobenzene and phenol (Fig.6A), the curve is linear, but shows two distinct slope changes, corresponding to intermolecular complexes of 1:1- and 1:2-ratio, exactly as found by the dielectric constant method, Giles, Rose and Vallance (J.C.S., 1952, 3799). An examination of some 33 different non-aqueous binary solutions, of which details are given in Section 2, then revealed that identical evidence of interaction is given in every case by the dielectric constant and the refractive index methods. Further, it was found that aqueous solutions give the same type of curves, with evidence of complex formation in appropriate cases, when examined by the latter method.

Previous Work.- The author has been unable to trace any previous use in this manner of refractive index determinations, but Pushin and Matavulj (Z.physikal Chem., 1932, A158, 290; A161, 341; A162, 415); Pushin and Rikovski (ibid., 1932, A161, 336); Pushin, Matavulj, Rikovski and Nenadovic (Bull.Soc.chim.Belgrade, 1940-46, 11, 72; through Chem.Abs., 1948, 42, 2167); and Pushin, Matavulj and Rikovski (ibid., 1948, 13, 38, 165, 173; through Chem.Abs., 1951, 45, 6475; 1952, 46, 2894), using binary mixtures of certain organic liquids, plotted values of refractive index directly against molar composition. They observed many examples of systematic variation from arithmetic mean values, and obtained curves showing in many cases maxima corresponding to intermolecular complex formation. They detected, e.g., complexes of piperidine with phenols; of acetic acid with certain primary, secondary and

tertiary amines (in several cases corresponding to known solid complexes); of acetic acid (1 mol.) with 1 mol. of phenylhydrazine, piperidine, pyridine, or quinoline respectively; of acetic acid (2 mols.) with aniline (1 mol.); of aniline (1 mol.) with (1 mol.) phenol or o-chlorophenol; of formic acid (2 mols.) with (1 mol.) aniline, mono- or dimethylaniline, pyridine or quinoline respectively; and benzylamine (1 mol.) with (probably 1 mol.) thymol; and undefined complexes of quinol with o- and p-chlorophenol, cresols, guaicol or thymol; no complexes were detected between aniline and p-chlorophenol, cresols or guaicol. Evidence of molecular association of a second component mixed with benzene or toluene was obtained in some cases.

Confirmation of Complex-formation by other Methods.

There were thus good grounds for believing that either of the present methods gives valid evidence of the presence of hydrogen-bond complexes, but it was considered that confirmation of this belief by as many other independent methods as possible would be desirable. Accordingly, a variety of procedures has been adopted in order to check the validity of the evidence the author presents. These include; (a) comparison with the composition of known solid complexes; (b) molecular weight determinations; (c) comparison with infra-red spectrophotometric data; (d) examination of compounds known to contain strong chelate bonds; (e) a study of certain interactions in monolayers; (f) comparison with certain sorption experiments on solid substrates; (g) an examination of the results as a whole, to detect whether simple integral ratios of combination are always returned, and to

evaluate their overall consistency and relation to previously known behaviour of the groups and molecules concerned; (h) a further study of the theoretical basis of the curves obtained. The results of this work are now discussed in detail.

(a) Solid complexes.- In Table IA a number of solid complexes between alcohols or phenols and other organic compounds, described by Pfeiffer ("Organische Molekülverbindungen", Stuttgart, F. Enke, 2nd edn., 1932) are shown, in comparison with identical or closely similar complexes detected in solution by the present methods.

Table IA.

Intermolecular Complexes of Hydroxylic Compounds.

Components	Molar Ratio	
	As solid (Pfeiffer)	In solution (present work) +
Aldehydes and Ketones		
Acetaldehyde + ethanol	1:1	1:1 (W)
Benzaldehyde + ethanol		1:1 (W)
Acetone + methanol		1:2 (C)
Acetone + phenol	1:2	x (E,W)
Diisobutyl ketone + phenol		1:2 (D)
Amide		
Urea + phenol	1:2	(1:1); 2:1; 1:3(El)
Amine		
Aniline + phenol	1:1	(1:2) (B) x (W)
Carboxylic acids		
Acetic acid + phenol		1:1 (T)
Benzoic acid + phenol		1:1 (T)
Trichloroacetic acid + phenol	1:1	
Esters		
Dimethyl oxalate + phenol	1:2; 1:4	
Dimethyl terephthalate + phenol		1:4 (T)
Ethylene glycol dibenzoate + phenol		1:4 (T)
Quinone		
Benzoquinone + phenol	1:2	(1:2) (T)
Benzoquinone + quinol	1:1	1:1 (D)

+ Solvents: B = benzene; C = carbon tetrachloride; D = dioxan; E = diethyl ether; El = ethanol; W = water.

x No complex detected.

It does not of course follow that the same type of complex will always exist both in the crystalline state and in solution, and in fact a number of examples in Table IA show that the solvent itself may quite prevent interaction. (This point will be considered more fully in Section 2). Nevertheless, there is good agreement between the data from the different sources.

It was hoped that this information could be supplemented by examination of solid complexes prepared from the solutions used in the present work. Only two such solutions have actually been found satisfactorily to deposit solid complexes, viz., ether or toluene solutions of diethylamine with p-nitrophenol and resorcinol respectively. These complexes when previously prepared (Giles, Rose and Vallance, J.C.S., 1952, 3799) returned analyses not exactly corresponding to an integral ratio of the components. The discrepancies were attributed to possible selective solution of one component by the washing solvent. The preparations were carried out with suitable precautions and the elementary analyses correspond with integral ratios of components (1:2 in both cases). On account of precipitation, refractive index measurements cannot be carried out with solutions in the same solvent used for their preparation, but by using dioxan as a solvent in which the complexes are quite soluble, no precipitation occurs and curves can be obtained (Fig.4A) which show changes of slope corresponding to the analyses of the solids, though in one case (resorcinol) the change is not very definite. Solutions in water give evidence of complexes of different integral ratios.

(b) Molecular weight determination.- Four pairs of compounds were selected for examination by the f.p. method in benzene. One of these, azobenzene + phenol, was chosen because, when examined by both the present methods (see above) it appears to form two distinct complexes of different ratio; the other three, because they appear to form complexes by the less common mechanism of bonding through hydrogen attached to carbon. From data plotted on the basis shown (Figs. 6A-9A) viz., apparent mol.wt. of combined solute vs. molar ratio, the presence of an intermolecular complex should normally be demonstrated by a maximum in the curve at the appropriate ratio(s). In fact, all the expected discontinuities are evident, though in three of the five instances they are only just so. In two systems (Figs. 7A and 8A) minima are obtained, i.e., complex formation lowers the apparent molecular weight. Low mol. wt. values can be attributed to solvation of solute by solvent (cf. Skau and Wakeham in "Physical Methods of Organic Chemistry" Vol. I, ed: Weissberger, New York, Interscience Publishers, Inc., 1945. Chap. 1). The azobenzene-phenol system is clearly made complex by association of the phenol itself and the curve is difficult to interpret. Even so, the discontinuities are above the theoretical line for no combination, and monomeric phenol molecules. The high intermediate sections of the curve must represent complex-separation on freezing, which can in fact be observed owing to the colour of azobenzene.

It may also be mentioned that Pushin and Matavulj (loc.cit.) confirmed the molar ratios of complexes detected in binary liquid mixtures, by f.p. determinations, and Laurent (Compt.rend.,1935,

201, 554) obtained a solid complex of phenol and aniline with a molar ratio (2:1) the same as found by dielectric constant determination, and also confirmed by cryoscopic measurement.

(c) Infra-red spectrophotometry. Flett (J.S.D.C.) 1952,68,59) and Tsuboi (Bull. Chem. Soc Japan. 1952, 25, 60) have given thermodynamic data for hydrogen-bond formation between pairs of armmatic compounds in carbon tetrachloride solutions, obtained by infra-red spectrophotometry. They determined heats, etc., of reaction by the method of measuring the change in height of an absorption band with change in temperature. This does not actually give an unequivocal measure of the ratio of components in the complex, but this ratio can usually be estimated, at least if the number of participating molecules is not more than about three or four, from the magnitude of the heat changes. In Table 2A some of Flett's and Tsuboi's data for compounds most resembling those the author has examined, are compared with the present results. The systems studied are closely similar and in one example (azobenzene + benzyl alcohol, c.f. Fig. 5A) are in fact identical. In all cases the two methods give parallel results.

Table 2A.

Comparison of present results with Flett's and Tsuboi's determinations.

Complex between	Molar ratio and Solvent		
	Flett (χ_c)	Tsuboi (χ_c)	Present Method
nizole, benzyl alcohol	1:1 (?)		
nisole, phenol			1:1 (B)
enzaldehyde, phenol		1:1 (?)	1:1 (W)
enzyl acetate, phenol	1:1 (?)		
isoPropyl acetate, phenol			1:1 (T)
N-n-Butylpropionamide, diethylamine			1:1 (T)
N-n-Butylpropionamide, ethanol			1:1 (T)
imethylformamide, diethylamine			1:1 (B)
imethylformamide, diphenylamine	1:1 (?)		
imethylformamide, phenol	1:1 (?)		1:1 (B;D;W)
zobenzene, benzylalcohol	1:1 (?)		1:1 (C)
Nitrobenzene, phenol		1:1 (?)	1:2 (B)

: Ratios assumed

olvents: B = benzene; C = carbon tetrachloride; D = dioxan;
T = toluene; W = water

In the present work a series of binary solutions (0.2M.) of azobenzene and phenol in carbon tetrachloride was examined in two infra-red spectrophotometers. In a double-beam apparatus (Brownlie, J.Sci.Instrum., 1950, 27, 215) with a sodium chloride prism, the height of the main band of the fundamental OH-stretching frequency was recorded, and in a single-beam apparatus, with a quartz prism, the height of the first overtone of the OH-stretching frequency was recorded. An attempt was made to plot the values obtained against the molar ratios of solutes, but unfortunately in both cases the experimental errors in the intensity measurements proved to be greater than any systematic variations due to solute interaction, and no firm conclusions could be drawn from the results.

(d) Chelated compounds. - If true complex formation is shown by these methods, then the masking of the reactivities of pairs of individual groups in a molecule by chelation should be capable of demonstration thereby, since it will lead to a corresponding reduction in the number of possible intermolecular bonds. This has been tested and found to apply in a number of cases, which will be discussed in Section 2, but a particular example may be quoted here. This is the evidence that phenol forms, with nitrobenzene, p-nitrophenol and o-nitrophenol, 2:1, 3:1 and 1:1-complexes, respectively (Fig.10A). These are

formulated in Fig. 11A :-

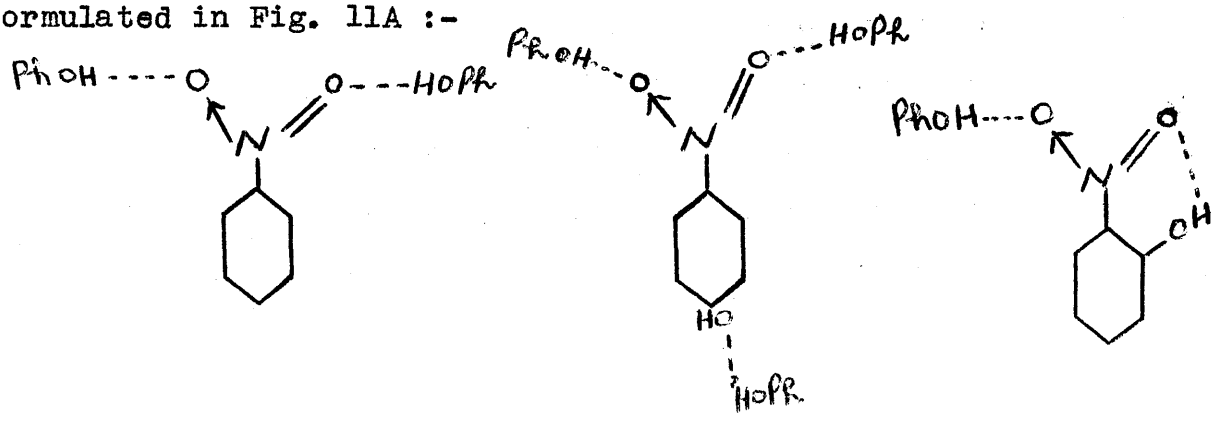


Fig. 11A. Complexes between Phenol and Nitrocompounds.

(e) Monolayer experiments.- Hydrogen-bond formation between some of the types of molecule used in the present work has been detected by interactions in monolayers on various aqueous solutions (Giles and Neustadter, J.C.S; 1952, 3806; Allingham, Giles and Neustadter, Faraday Society Discussion, 1953, in the press; Cameron, unpublished). The results of experiments by the different procedures are in some cases directly comparable. Particular examples are as follows:

(i) Quinol as solute in the water phase greatly increases apparent molecular area of monolayers of alkyl benzeneazo-β-naphthol and N-alkylacetamide derivatives; this is attributed to cross-linking through the phenolic groups of quinol. In agreement with this, a sulphonated benzeneazo-naphthol compound and acetamide both show evidence of 2:1-complexes with quinol in water.

(ii) Some dihydric phenols of large molecular size as solutes in the water phase greatly increase the apparent molecular

area of a monolayer of a surface-active benzoquinone derivative, but quinol itself produces only a slight increase. This is attributed to 1:1-quinhydrone complex formation in which solute and monolayer molecules lie close-packed side-by-side. In confirmation, a 1:1-complex is demonstrated by refractive index measurements on benzenoquinone-quinol solutions in dioxan (Fig.17A). Water cannot be used because the quinhydrone complex immediately separates out from aqueous solutions.

(iii) The evidence of the present methods regarding the bonding of hydrogen attached to carbon in the acetyl and other ester groups and the bonding properties of carbohydrates in water is supported by monolayer experiments. This is discussed in Section 2 and elsewhere (Allingham et al, loc.cit.).

(f) Sorption Experiments.- The heat changes associated with sorption of phenol from water solution on nylon or cellulose acetate lend support to the deductions made directly from the results of the present work. This is discussed in Section 2.

((g) Consistency of results.- More than 270 pairs of substances have now been examined by the two present methods. Many of these show more than one change of slope in the curve. In every case these changes occur at simple integral molar ratios, within the limits of experimental error. Moreover, in almost all cases, the formation of the complexes can be explained by a simple interpretation

of the known behaviour of the groups concerned. This matter will be discussed fully in section 2. Particular comparison may be made, on the one hand, of the donor properties of O and N atoms, as revealed by this work, e.g., (a)both N and H atoms in diethylamine and both O atoms in the nitro group may combine simultaneously with phenol, and (b) the quinone or keto-O atom may form two intermolecular bonds simultaneously; and, on the other hand, of certain parallel conclusions from X-ray and infra-red measurements (See Pauling, op. cit.). The latter show that both O and H atoms in the hydroxy-groups in the resorcinal crystal can be intermolecularly bonded at the same time, that both oxygen atoms in the nitro-group can intramolcularly bond with hydroxy-groups, simultaneously, and that an oxygen atom of anthraquinone can chelate with two hydroxy-groups at once.

(h) Theoretical Treatment.-The theoretical treatment given by Giles, Rose and Vallance (J.C.S., 1952, 3799) (Appendix) showed that linear curves with a change of slope at the point of complex formation are to be expected if the value of K for the reaction is high, i.e. if the complex is very stable, and in the particular case of a 1:1-complex. Many of the complexes now detected, however, cannot be very stable, and indeed Flett (loc.cit.) has already shown that in 12 binary systems (in carbon tetrachloride), similar to these the author has examined the values of K are often quite low, the lowest, at room temperature, being 3.82, yet the present curves are always

apparently linear, within the limits of accuracy of the method. It was therefore necessary to re-examine the theoretical basis of the method in an entirely general way with a view to determining whether unstable complexes also should be theoretically detectable. At the same time the opportunity was taken to examine cases where a complex other than 1:1 ratio, or more than one complex present simultaneously occur.

A fuller treatment is given in an Appendix which has been submitted to J.C.S., together with the paper, but ~~that~~ it is too long to quote in full. The mathematical analysis was kindly made by Mr. J.C. Eaton. It is there shown that the graph of the physical constant used against solute molar ratio, can be expressed simply in terms of a deviation $z(S_{xy}-S_x-S_y)$ where z is the number of molecules of complex Xm Yn formed, and S_{xy} etc., are the slopes of the curves for the constants of the respective individual components of the solution. The graph of z against the number of molecules of X present, consists of two straight lines, intersecting at the point corresponding to the composition of the complex, only of $K=\infty$, but for all values of K the graph has a single maximum at this same point. This will give a maximum or a minimum in the curves as plotted in this work, according as the value of $(S_{xy}-S_x-S_y)$ is positive or negative. Thus in the special circumstance where $S_{xy} = S_x + S_y$, i.e., where the physical constant of the complex is the additive value of these of its components, no deviation at all should occur. This has been experienced in practice as recorded below, but it appears

to take place only at one temperature, and at temperatures above and below this, deviations are observed. The graphs for all the systems studied are thus strictly not linear, but it will be seen from the figures that the deviations from linearity are barely discernible.

The argument may be extended to cases in which two compounds, X and Y, combine to form more than one complex, e.g., XY and X_2Y. Here there are two equilibria co-existing in the solution :-

$$X + Y = XY, \text{ and}$$

$$XY + X = X_2Y,$$

and the concentrations of the reactants will adjust themselves so that the equilibrium constants in the mixture are the same as in the separate systems. The curve can therefore be divided into halves, one of which, between X = Y and X = 0 has no change of slope, and the other between X = Y and Y = 0 has one corresponding to X_2Y. A similar treatment may, in fact, be applied to conditions where more than two complexes can be formed, and in the present work (section 2) as many as three have sometimes been detected in the same solution.

All of the tests applied have therefore supported the interpretations of the results given by the present methods. The new procedures therefore appear to offer a reliable and simple means of studying the hydrogen-bonding properties of organic compounds of many types, and in the succeeding section the results of tests with a wide variety of compounds will be given and discussed.

Survey of Methods of Detection of Hydrogen Bonds.- A fuller

description of many of these methods is given in a review by Hunter (Ann. Reports,1946, 43, 141). At this point it is appropiate to evaluate the utility of the present methods in comparison with those hitherto used for detecting hydrogen-bonds. These and their applicability may be summarised as follows:-

(a) Radiation Methods.- Electron diffraction (low pressure vapours); X-ray diffraction (crystals); infra-red spectrophotometry (vapours pure liquids, solutions, solids).

(b) Methods involving Studies of Various Physical and Chemical Properties.-e.g., f.p., b.p., or solubility determinations on pure substances and observations of chemical reactivity (detection of association and intermolecular bonding); Measurement of mutual solubilities of acceptor and donor compounds, and of dielectric constant or refractive index of binary liquid mixtures.

Present Methods.- The present procedures appear somewhat more versatile than most of the other methods listed above. They can be used with any substance which can be brought into solution in either an organic solvent or water to a concentration which may be at least as low as 0.01 M., and the total volume of solution required for complete examination may, with suitable apparatus, be reduced to less than 2 c.c. Moreover, in many cases they appear capable of giving information not determinable, or determinable only with difficulty, by other methods. Even infra-red spectroscopy, perhaps now the most widely used method, cannot satisfactorily be employed with such a variety of solvents as can the present method and requires costly and elaborate equipment.

In section 2 it is shown that the nature of the solvent may be very important in determining the type of intermolecular complex formed, and by studying the influence of different solvents upon a given system, useful information can be obtained upon the relative strength of a number of inter- and intra-molecular bonds.

The results are most consistently explained in terms of hydrogen bonding and there appears little or no reason to suppose that other forms of intermolecular association are responsible for the effects observed.

EXPERIMENTAL.

Materials.- The organic solvents used were dried by the usual methods, in the laboratory, except dioxan, which was of the "specially dried" quality (B.D.H.) used for Karl Fisher titrations.

Instruments.- The dielectric constant meter (Fig.12A) used in the present work incorporates a Y 63 electron-ray ("magic-eye") tuning indicator and is based on the circuits used by Alexander (Electronics 1945, 18, No.4, 116), Bender (J.Chem.Educ., 1946, 23, 179), and Fischer (Anal.Chem., 1947, 19, 835). The triode portion of the indicator is used as the oscillator, and the target electrode as the resonance detector. The target, coated with fluorescent material, is positive with respect to the cathode. The resulting electron stream from cathode to target is influenced by a control electrode grid (internally connected with the triode anode), which, when it is made negative with respect to the target, deflects the electron stream, producing a shadow on the target, the normal "open eye". The angle of the shadow is reduced by making the

control electrode more positive. In the non-oscillating position the anode current produces a large potential difference across the anode resistor R_2, which holds the anode and control electrode potentials at a low value with respect to the target; the "eye" is then open. When the anode and grid circuits are brought to resonance, the anode current decreases and therefore the potential difference across R_2 drops. Consequently, the potential of the control electrode with respect to the cathode, rises - it becomes less negative with respect to the target and the "eye" closes. The most convenient reference point for making measurements is the critical off-resonance capacity setting when the "eye" just flicks open or shut with increase or decrease of capacity respectively.

The following are the values of the components used: C_1,350uuf; C_2,12.5uuf; C_3,25uuf; (C_4 is the dielectric cell); C_5, C_7, 0.01 uf; C_6, 0.001uf; C_8, C_9, 2uf; R_1, 1 megohm, R_2, 42,000 ohms; X, 4.55 Mc./s. quartz crystal; L_1 11 turns of 20 S.W.G. enamelled copper wire close-wound on a 1-in former; L_2, small R.F. choke; L_3, 7-Henry 50-ma choke. The condensers C_1 and C_2 are fitted with low-geared vernier dials. The dielectric cell (C_4) is constructed from a 12-uuf variable condenser, with silvered plates, by stripping all but one plate from the stator and all but two plates from the rotor. A brass stop is fitted so that the plates cannot be opened more than about half the maximum extent. The cell unit is connected to the main circuit by a short, screened cable. For use, the condenser plate assembly is submerged in about 20 c.c. of the liquid under test, contained in a small glass beaker.

Calibration of Instrument.- The instrument is switched on 15 minutes before use. It is first necessary to determine the value of the scale readings of the fine tuning condenser,(C_2) against the main condenser (C_1). This procedure is repeated several times with a series of settings of C_1, the corresponding values of C_1 and C_2 being noted. In use, when the resonance position is reached, the reading of C_2, corrected to its value on C_1, is added to that of C_1.

The instrument is then calibrated, first with air and then with a series of pure liquids of known dielectric constant, as follows. With the plates of the measuring cell condenser open, in air, the anode and grid circuits are brought to resonance (the "eye" just flicks shut at this point), by tuning first with C_1 and then with C_2. The measuring cell plates are now closed, and C_1 and C_2 again adjusted to resonance. The difference between the two readings of C_1, each corrected by addition of the respective readings of C_2, gives the maximum capacitance increment in the measuring cell with air dielectric. The procedure is then repeated with the measuring cell filled with each liquid in turn. The dielectric constant of any liquid is given by the ratio of the maximum capacitance increments of the cell filled with that liquid and with air.(This method of measurement by using capacitance increments eliminates errors due to stray capacities between the cell,leads,and chassis.) The typical series of calibration readings in Table 3A shows that the plot of dial readings (i.e.,values of C_1 corrected as described above)against dielectric constant is virtually linear over a wide range. In the present work,where only the relative

values of dielectric constant of a series of liquids are required, a simpler procedure may be followed: readings are taken only with the condenser plates closed, and they may then be plotted directly against the molar ratios of the solutes in the solutions used.

TABLE 3A Calibration of instrument.

Dielectric	Air	Benzene	Ethyl ether	Chloroform	Pyridine	Acetone
Dielectric constant	1.00	2.88	4.33	4.95	12.50	21.30
Max. capacitance increment of cell (dial reading)	128.2	125.0	122.0	120.1	99.1	77.8

The solutions of the two solutes to be examined were prepared and stored until required in ground-glass-stoppered tubes, then measured quickly in succession in the instrument at room temperature. After each solution had been measured, the plates were carefully washed with successive changes of pure dry ether and finally well dried in an air stream. A few typical results are shown in Fig. 13A.

The following refractometers were employed, both with sodium light: Bellingham and Stanley (Abbe type, reading 10^{-4} unit) and Zeiss (Pulfrich type, reading 10^{-5} unit). These require respectively ca 0.1 and 1.0c.c. liquid for each determination. The Pulfrich type of instrument is preferred on account of its greater precision, especially for aqueous solutions in which the variation in n often occurs only in the fourth decimal place. In all cases a mean of at least two or three independent readings (in special cases up to six) was taken for each solution.

Procedure. The general procedure was adopted in the following manner:- Some 8-12 or more separate binary solutions of differing molar ratios

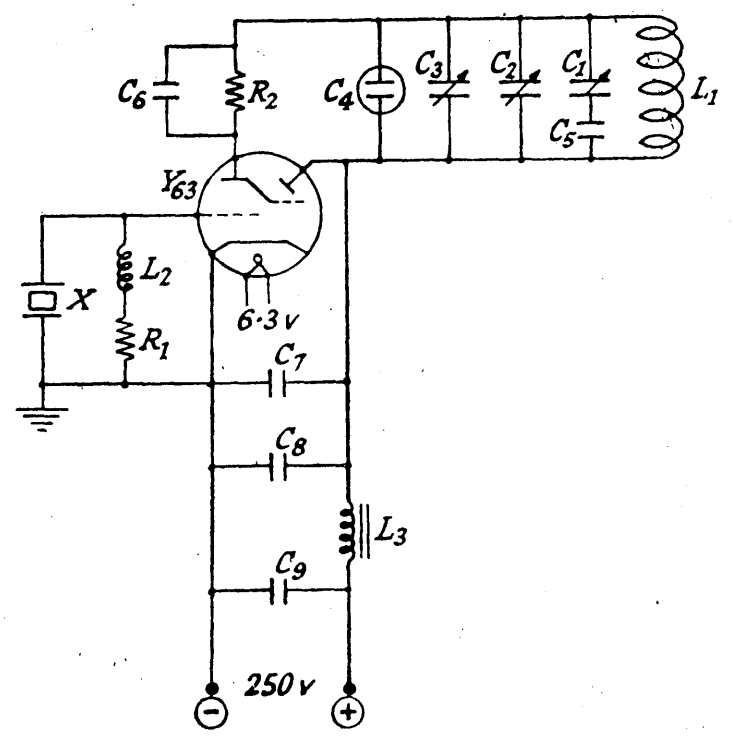


Fig. 12A

were
~~being~~ used for each pair of solutes. Experiments were repeated in many cases where the position of the change of slope on the curve was uncertain, but normally one set of determinations is sufficient.

Preparations of Solid Complexes.- Concentrated solutions in toluene of diethylamine and either p-nitrophenol or resorcinol respectively, were mixed and the crystalline precipitates collected, carefully washed with a minimum quantity of ether and dried in vacuo. The p-nitrophenol complex separates out at once, that from the resorcinol only slowly and the mixed solutions were left to stand several days in the cold before the precipitate was collected. (p-Nitrophenol complex, yellow needles, m.p. 90 C., Found: C, 54.8; H,5.9; N,11.85; $C_{16}H_{21}O_6N_3$ requires C, 54,9; H, 6.0; N, 12. 0%; resorcinol complex, buff platelets m.p. 119 C Found: C, 65.6
H, 8.27; N, 4.81; $C_{16}H_{23}O_4N$ requires C, 65.5; H, 7.85; N,4.8%). * (75a)

Difficulties.- Two particular sources of error are liable to occur in the use of the present methods. These are: (a) the slow rate of mutual solution of some liquids. On account of the small quantities of solute used, complete dissolution in the solvent is sometimes difficult to observe, and some apparently homogeneous solutions, e.g. of glycerol in dioxan, gave irregular results until complete solution was ensured by prior warming and then cooling before use; (b) the evaporation of organic solvents. On account of the rapidity with which results can be obtained, most of the experiments can be carried out at room temperature. With water as solvent no difficulties arise, but when using many of the organic solvents, e.g., toluene or dioxan, difficulties may be experienced when the temperature rises above ca. 18°C., due to their rapid evaporation, and it may then be necessary to circulate cooled water from a thermostat through the apparatus.

*

Determination of "Apparent Molecular Weight".- The Beckmann f.p. method was used, with "molecular weight quality" benzene. From each pair of compounds a series of binary solutions of constant total molarity (0.1) was prepared. The apparent molecular weight, i.e. the value obtained on the assumption that only a single compound is present, is equal to the sum of the product of the true mol.wt. of each solute into its respective molar fraction, the molar fraction for the complex being calculated on the basis of the maximum possible value of unity, for complete reaction. The points shown in the Figs. (6A-9A) are each the mean of two or three separate determinations.

For the dielectric constant apparatus a modified cell design would require to be used if temperature regulation is desired, and the simple microthermostat incorporating a thermistor control, recently described by Marshall (J.S.D.C., 1953, 69, 202) may prove of value for this purpose.

When the temperature is changed, the "kink" in the curves often changes from a maximum to a minimum; this can be shown to be due to the different effects of temperature upon the physical constant values of the various components of the system, (see above). Thus at some intermediate temperature it must in these cases disappear, and if this should occur at the particular temperature used for experiment it might be assumed, in absence of other evidence, that no complex could be formed between the solutes concerned. Therefore, in certain instances where it was important to establish beyond doubt the reality of negative results with a particular group, determinations were made at more than one temperature with one pair of solutes, and/or with a solute containing the group under study and a variety of second solutes all in the same solvent, since it is very unlikely that if a negative result occured fortuitiously it would do so at the same temperature with a range of compounds.

Several of the complexes whose existence is difficult to detect because of the very slight slope change they impart to the curves (see Section 2) might thus be detected more readily at some other temperature.

Scale of Experiments.- The author has usually used solutions of 0.25 or 0.1M concentration. In certain instances where solubility is low or the amount of material available was small, solutions as weak as 0.01 M. have been used quite satisfactorily, the curves still showing no loss

of distinctions of slope changes. The quantity of any one solution required for a complete experiment can be as little as 5-2 c.c. when a refractometer is used.

Analytical use.- The Square of refractive index, rather than the refractive index itself, having as it does, a linear relation with concentration, at least over the lower ranges, is obviously more suitable for use in the quantitive analysis of solutions. It might prove to be of particular value in the analysis of solutions of a number of aliphatic compounds unsuitable for absorptiometric determination. Preliminary experiments have, in fact, demonstrated the value of this method of analysis in determining sorption isotherms.

Polarimetry.- Some attempts were made to detect bonding between amino-acids and glucose in aqueous solutions by measurement of specific rotation in a polarimeter, but the acids were insufficiently soluble to give any useful result.

Appendix 1.

Relation between Concentration of a Solution and its Dielectric Constant and Refractive Index.

It is thought desirable to state more precisely the theoretical basis for these relationships. In the first place, it is necessary to consider a polar solute in solutions as dilute as those used here as being equivalent to a gas, and thus having a dielectric constant very nearly equal to unity. The equation of the molecular polarisation derived from the Clausius Mosotti law, viz.,

$$P = \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{M}{d}$$

where M= the molecular weight and d= the density of the gas (or here the concentration of a dilute solution), then becomes

$$P \simeq \frac{(\epsilon - 1)}{3} \frac{M}{d}$$

and M and P being constant, it follows that there is a linear relation between ϵ and d at any given temperature.

At optical frequencies, $\epsilon = n^2$ (both in theory and practice), so that n^2 should be approximately proportinnal to molar concentration in dilute solution, as it is so found here. Further, over very small ranges, n is approximately proportional to n^2 (because $(1+x)^2 \simeq 1+2x$ if x is very small) and the value of n itself can, in fact, be used in plotting the curves for a number of the systems examined here, though the use of n^2 is preferable both for theoretical reasons and because it gives a linear relation with concentration over wider ranges.

Section 2. (Part II)

The Examination of the Inter- and Intramolecular Bonding Properties of Water and of a Variety of Organic Compounds.

It has been shown in Section 1 (Part II) that determinations of dielectric constant or refractive index can be used to demonstrate the ratio in which solutes form hydrogen-bond complexes in binary solution. In this section the results of the application of these procedures to the study of the hydrogen-bonding properties of a large number of organic substances, and of water, in a variety of solvents, are described.-

The aim of this work has been to disclose new information upon the reactivity of many typical substituent groups, particularly as it affects their behaviour in sorption on solid substrates from various solvents, including water. Little information is available upon hydrogen bonding in presence of water, yet the sorption of organic compounds from aqueous solution is a process of high importance, both in the laboratory and in the useful arts.

Compounds Used, etc.- Simple compounds, for the most part, have again been employed in this work, chosen particularly to enable an examination to be made of the reactions of typical groups found in certain natural and synthetic polymers, especially fibres.
E.G. N-n-butylpropionamide and other alkylamides have been used to represent the peptide link in proteins and nylons; glucose, cellobiose, various aliphatic alcohols, tetramethylglucopyranose, etc., to enable the reactions of the groups in cellulose to be studied; N-acetyl-glucosamine to represent chitin; ethyl acetate, glucose penta-acetate

and isopropyl acetate to represent cellulose acetate; and dimethyl terephthalate and ethylene glycol dibenzoate to represent polyethylene terephthalate (Terylene). A number of aromatic azo-compounds, both of water-soluble and water-insoluble types, and examples of certain groups not previously examined, e.g., aldehyde and quinone groups, including one compound (2:3-benzanthranol) which is a quinone with a single oxygen atom, were also included. Amongst the hydroxy-compounds used is haematoxylin (Colour Index No. 1246), a complex bis-o-dihydric-phenol). The ability to use aqueous solutions has now enabled a wider range of compounds to be examined than in the earlier investigation, and in addition to its use as a solvent, water has been used as a solute in conjunction with a number of typical organic compounds, with successful and interesting results.

Some of the results of the earlier work suggested that the present procedure should provide useful evidence not only of inter-molecular, but also of intramolecular or chelate, bonds, and by including in this work a number of selected compounds the author has been able to show that it does indeed do so.

DISCUSSION

Table 4A shows the full results in summary form, and a discussion of some of their implications follows. A few typical curves are shown in Figs. 14A, 15A, and 16A. Tables 8A-18A give the detailed and comprehensive data of refractive index and dielectric constant measurements.

Protective Influence of Solvents.- It was reported by Giles, Rose and Vallance (J.C.S., 1952, 3799) that no evidence could be obtained of intermolecular bonding involving the ketone group. Nevertheless the formation of this type of bond is possible; e.g., Badger and Bauer (J. Chem. Phys., 1936, 4, 469, 711; 1937, 5, 839), detected bonding between acetone and methanol, by infra-red spectrophotometry of binary mixtures, or solutions in carbon tetrachloride. The earlier experiments were made with solutions in benzene and it was thought that the solvent might be inhibiting complex-formation. As a result of the further work now described it appears that benzene as a solvent does prevent the ketone group from forming bonds, and so do both ether and water, but not either carbon tetrachloride or dioxan. (A bond between the ketone group and water itself is in fact evidenced in dioxan solutions).

A study of Table 4A reveals a number of other examples of the protective effect of a solvent preventing hydrogen bonding between various individual groups, and some of these examples are summarised in Table 5A.

TABLE 4A

Solutes a	Solutes b	Solution Solvent	Solution Total mol concn.	Method(s) Temp. (°C.) for n	Mol.ratio of complex (a:b)
		ACETATES			
α-D-Glucose--penta-acetate	Aniline	T	0.1	ε, n 20	(1:1)
	Anisole	T	0.1	ε, n 20	(1:1)
	Azobenzene	T	0.1	ε, n 20	2:1; 1:1
	Benzoquinone	T	0.1	ε, n 20	(2:1)
	Diethylamine	T	0.1	ε, n 22	(1:1)
	o-Nitrophenol	D	0.1	n 20	1:1
	Phenol	D	0.1	n 20	1:1; (1:5); 1:6
	Triethylamine	T	0.1	n 20	1:1
		D	0.1	n 20	1:1; 1:6
Ethyl Acetate	Azobenzene	T	0.1	n 17	4:1
	o-Nitrophenol	P	0.1	n 20	(1:1)
		T	0.1	n 14	1:1
Glyceryl triacetate	Diethylamine	D	0.1	n 15	(1:3)
		T	0.1	n 12	1:1
isoPropyl acetate	Anisole	D	0.1	n 20	1:1
	Azobenzene	D	0.1	n 19	4:1
	Benzoquinone	T	0.2	ε, n 20	2:1[xxx]
	3-Methoxybenz-anthrone (Duranol Brilliant Yellow 6G)	D	0.01	n 20	(2:1)

TABLE 4A (continued)

	o-Nitrophenol	D	0.1		n 19	1:1
		T	0.1		n 20	1:1; (1:2)
	Phenol	T	0.2	€	n 20	1:1
ACIDS						
Acetic acid	Phenol	T	0.25	€	n 20	1:1 xxx
Benzoic acid		T	0.25	€	n 20	(1:1)
Naphthalene 1-sulphonic acid		W	0.1		n 20	xx
2-Naphthol-3:6-disulphonic acid		W	0.1		n 20	1:1
1-Naphthylamine -3:8-disulphonic acid		W	0.1		n 20	xx
ALCOHOLS						
Methanol	Phenol	D	0.1		n 20	1:1 xxx
		W	0.25		n 20	1:1
Ethanol	Water	D	0.1	€	n 20	1:1
	Phenol	T	0.25	€	n 19	1:1
		W	0.25		n 20	1:1
isoButanol	Phenol	D	0.1		n 21	1:1
n-Amyl alcohol		D	0.1		n 21	1:1
Ethylene Glycol	Methanol	D	0.1		n 20	1:1 xxx
	Phenol	W	0.25		n 20	1:1; (1:2)
	Sulphanilic acid-β-naphthol	W	0.1		n 24	(xx)
Glycerol	Methanol	D	0.1		n 20	(1:1)
		W	0.25		n 20,35	xx

TABLE 4A (continued)

	Phenol	W	0.25	n 20	1:1; 1:3
	Triethylamine	W	0.25	n 22	(xx)
	Water	D	0.1	n 20	1:1
Erythritol	Methanol	W	0.25	n 21	xx
		Cs	0.05	n 18°	1:1
	Phenol	W	0.25	n 19°	1:1; 1:4
Mannitol		W	0.25	n 19°	1:6
	Water	EG	0.1	n 18	1:1
	Phenol	EG	0.1	n 22	(1:1); 1:6
1-5-Pentane diol	Methanol	D	0.1	n 18	1:2
n-Pentanol	Phenol	D	0.1	n 21	1:1

ALDEHYDES AND KETONES

Acetaldehyde	Azobenzene	T	0.1	n 20	2:1
	Diethylamine	W	0.25	n 20	1:1
	Ethanol	W	0.25	n 20	(xx)
	Phenol	W	0.25	n 20	(xx)
Benzaldehyde	Diethylamine	W	0.25	n 19	(1:1)
	Ethanol	W	0.25	n 20	(1:1)
	Phenol	W	0.25	n 20	(1:1)
Acetone	Aniline	B	0.3	€	xx
	Diethylamine	B	0.2	€	xx
	Phenol	E	0.25	€	xx
		W	0.1	n 20	xx
	Methanol	C	0.25	n 20	(1:2)
	Triethylamine	W	0.25	n 21	xx
	Quinol	E	0.25	€	xx

TABLE 4A (continued)

Benzophenone	Phenol	B	0.25	n 18	xx	xxxx
	Acetic acid	D	0.25	n 19	1:1	
Diisobutyl ketone	Benzaldehyde	D	0.25	n 19	1:2	
	Benzoic acid	D	0.25	n 20	1:1; 2:1	
	Phenol	D	0.25	c, n 20	1:2	
	Propionic acid	D	0.1	n 20	1:1	
	Trimethylacetic acid	D	0.25	n 20	1:1	
	Formic acid	D	0.25	n 20	1:2	

AMIDES

Acetamide	Benzoquinone	T + El	0.044	n 20	1:1	
		W	0.1	n 20	2:1	
	Haematoxylin	Acetone	0.3	c	(2:1)	
	Phenol	W	0.25	n 22	1:1	
	Quinol	W	0.25	n 20	2:1	
N-n-Butylpropionamide	Diethylamine	T	0.2	c, n 20	(1:2)	
	Ethanol	T	0.2	c, n 20	1:1	xxx
	Urea	El	0.1	n 20	1:1	
	1-Hydroxyanthraquinone	B	0.1	c	xx	
Diethylacetamide	Azobenzene	T	0.1	n 20	4:1	
Dimethylacetamide	Azobenzene	T	0.1	n 14	4:1	
	Benzoquinone	T	0.1	n 14	4:1	
Dimethylformamide	Aniline	B	0.25	c, n 20	2:1	
	Diethylamine	B	0.25	c	1:1	
	Haematoxylin	W	0.05	n 20	4:1	

TABLE 4A (continued)

	Phenol	B	0.25	∈	1:1
		W	0.25	n 19,35	1:1
Urea	Phenol	El	0.2	n 20	2:1; (1:1); 1:3
		AMINES			
Aniline	Anisole	B	0.25	∈	xx
	Diethylamine	W	0.25	n 18	1:1
	Phenol	B	0.25	∈, n 21	(1:2)[xxxxx]
	Phenol	W	0.25	n 17	xx
	Triethylamine	W	0.25	n 19	(1:1)
Diethylamine	p-Nitrophenol	D	0.1	n 20	1:2
		W	0.1	n 20	1:2; 2:1
	Phenol	B	0.25	∈	1:1
	Phenol	W	0.25	n 18,20	1:1[xxx]
		D	0.1	n 20	1:1; (1:2)
	Resorcinol	W	0.25	n 20	2:1
Triethylamine	Ethanol	W	0.25	n 21	xx
	Resorcinol	T	0.25	n 20	2:1
		AZO COMPOUNDS			
Aniline→α-Naphthylamine	Phenol	T	0.1	∈, n 20	(1:3; 1:4)
Aniline → β-Naphthol	Aniline	B	0.25	∈	2:1
	Pyridine	B	0.25	∈	xx

TABLE 4A (continued)

	Resorcinol	E	0.25	∈	2:1; 1:1
	Phenol	B	0.25	∈	1:1;(1:2)
	Trichloroethylene	T	0.1	∈, n 20	1:2
	Quinol	D	0.1	∈, n 20	1:1;(2:1)
Aniline → B-Naphthylamine	Phenol	T	0.1	∈, n 20	1:2[xxx]
Azobenzene	Acetone	D	0.1	n 18	xx
	Aniline	B	0.25	n 19	2:1[xxxx]
	Benzoquinone	T	0.1	n 19	xx
	Benzyl alcohol	C	0.1	n 20	1:1
	Diethylamine	B	0.25	n 19	1:1[xxxx]
	Phenol	B	0.25	n 19	1:1; 1:2[xxxx]
	Triethylamine	D	0.1	n 18	xx
Sulphanilic acid→ α-Naphthol	Phenol	W	0.25	n 20	1:1; 1:2; 1:3
Sulphanilic acid→ B-Naphthol	Ethylene glycol	W	0.1	n 20	xx
	Glycine	W	0.1	n 19	1:1
	Phenol	W	0.25	n 18	1:1
	Quinol	W	0.1	n 20	2:1

CARBOHYDRATES AND RELATED COMPOUNDS

N-Acetyl-D-glucosamine	Aniline	W	0.25	n 18	(2:1)
	Aniline→2-naphthol-3:6-disulphonic acid	W	0.01	n 20	(1:1)
	Azobenzene 4-sulphonic acid	W	0.1	n 22	1:1
	Diethylamine	W	0.25	n 20	(1:1)

TABLE 4A (continued)

	Dimethylformamide	W	0.25	n 19	1:1
	Methanol	W	0.25	n 19	1:1
		EG	0.1	n 18	1:1; (1:4)
	B-Naphthol	EG	0.05	n 18	(1:1); 1:4
	Phenol	W	0.25	n 18	1:1
		EG	0.05	n 16,18	1:1;1:4
	Triethylamine	W	0.25	n 20	1:1
	Quinol	W	0.25	n 20	2:1
D-Cellobiose	Aniline	W	0.25	n 16	1:1
	Azobenzene 4-sulphonic acid	W	0.1	n 22	(2:1)
D-Cellobiose	Diethylamine	W	0.25	n 19	(1:1)
	Dimethylformamide	W	0.25	n 15	1:1
	Pyridine	W	0.25	n 15	(1:1)
	Quinol	W	0.25	n 16	(xx)
	Triethylamine	W	0.25	n 15	(1:1)
D-Fructose	Ethanol	W	0.25	n 20	(xx)
	Phemol	W	0.25	n 21	xx
	Triethylamine	W	0.25	n 20	xx
D-Glucose	Acetamide	W	0.25	n 22	1:1
	Aniline	W	0.25	n 18	2:1
	Azobenzene 4-sulphonic acid	W	0.1	n 19	(2:1)
	Diethylamine	W	0.25	n 19	1:1
	Dimethylformamide	W	0.25	n 18	1:1
	Ethanol	W	0.25	n 20	xx
	Methanol	W	0.25	n 20	xx
	p-Nitrophenol	W	0.1	n 20	2:1
	Phenol	W	0.25	n 20,35	xx

TABLE 4A (continued)

	Phenol	EG	0.1	n 20	1:6
	Pyridine	W	0.25	n 19	(1:1)
	Triethylamine	W	0.25	n 20	1:1
	Quinol	W	0.25	n 17	xx
	Water	EG	0.1	n 14	1:6; (2:1)
Sucrose	Triethylamine	W	0.25	n 20	xx
2:3:4:6 Tetra-methylgluco-pyranose	Water	D	0.05	n 20	2:1; 1:2
Ternary Solution					
D-Glucose (1mol) ≡ Triethylamine (1 mol)	Phenol	W	0.25	n 13	1:1; 1:6

ESTERS: (AROMATIC)

Dimethyl terephthalate	Phenol	T	0.1	n 18	1:4
	Triethylamine	T	0.1	n 18	1:4[xxx]
Ethylene glycol dibenzoate	Phenol	T	0.1	n 22	1:4[xxx]
	Triethylamine	T	0.1	n 20	1:4

ETHERS, PHENOLS

Anisole	Phenol	B	0.25	∈	(1:1)
Catechol	Methanol	D	0.1	n 20	1:2[xxx]
	Phenol	W	0.25	n 17	(1:1); 1:2
Diethyl ether	Triethylamine	D	0.1	n 22	1:2
Haematoxylin	Phenol	D	0.25	∈	1:5[xxx]
Pyrogallol	Phenol	W	0.25	n 20	(1:1); 1:3

TABLE 4A (continued)

Quinol	Methanol	D	0.1	n 20	(1:2)
	Phenol	W	0.25	n 19,35	1:2
NITRO-COMPOUNDS					
Nitrobenzene	Phenol	B	0.25	∈	1:2
o-Nitrophenol	Diethylamine	B	0.25	∈, n 18	1:1
	Phenol	B	0.25	∈	1:1
p-Nitrophenol	Phenol	B	0.25	∈	1:3
QUINONES					
2:3-Benz-9-anthrone	N-n-Butylpropionamide	D	0.01	n 20	1:2
	Phenol	D	0.01	n 20	1:1[xxx]
Benzoquinone	Anisole	D	0.1	n 20	1:2
	N-n-Butylpropionamide	T	0.2	∈, n 20	1:4[xxx]
	Phenol	T	0.25	∈, n 19	(1:2)
	Quinol	D	0.1	n 20	1:1
1:4:5:8-Tetraaminoanthraquinone (Duranol Brilliant Blue CB)	Phenol	D	0.01	∈	2:1[xxx]
	isoPropylacetate	D	0.01	∈	(2:1)
WATER					
Water	Aniline	D	0.25	∈, n 20	(2:1)
	Aniline→ β-Naphthol	D	0.1	∈, n 20	1:2

TABLE 4A (continued)

Azobenzene	D	0.1 ϵ,	n 20	1:1; 2:1
Benzophenone	D	0.2 ϵ,	n 20	1:2
N-n-Butylpropionamide	D	0.2 ϵ,	n 20	1:2[xxx]
Diisobutyl ketone	D	0.1 ϵ,	n 20	(1:1 or 1:2)
Phenol	D	0.2	n 20	1:1; 1:2
isoPropyl acetate	D	0.1	n 20	2:1; 1:2
Styrene	D	0.2	n 20	1:2[xxx]
Urea	El	0.2	n 20	1:2

MISCELLANEOUS

Phenol	4-chlorophenoxy acetic acid	D	0.05	n 23	1:1
	α-(4-chlorophenoxy)-propionic-acid	D	0.05	n 21	1:1
	α-(4-chlorophenoxy)-butyric acid	D	0.05	n 23	1:1
Di-isobutyl-ketone	α-(4-chlorophenoxy)--isobutyric acid	D	0.05	n 19	(1:1),0
	α-(2:4-dichlorophenoxyl)--propionic acid	D	0.05	n 19	1:1
	α-(2:6-dichlorophenoxy)--propionic acid	D	0.05	n 19	1:1
Triethylamine	2:6-dichlorophenoxy acetic acid	D	0.05	n 19	2:1, 1:2

TABLE 4A (continued)

Solvents: A = acetone; B = benzene; C = carbon tetrachloride; Cs = 'Cellosolve' (ethylene glycol monoethyl ether); D = dioxan; E = diethyl ether; El = ethanol; EG = ethylene glycol; M = methanol; P = petroleum ether, b.p. 80-100°C; T = toluene; W = water.

Methods: ϵ = dielectric constant; n = refractive index.

x	Data in parentheses denote less certain indications, due to small change in slope.
xx	No evidence of complex formation
xxx	These curves show particularly pronounced changes of slope.
xxxx	Results by dielectric constant method reported by Giles, Rose and Vallance (J.C.S., 1952, 3799).
xxxxx	This complex reported also by Laurent (Giles, Rose and Vallance, J.C.S., 1952, 3799.)
xxx	Also: Azobenzene (B) with aniline, N-n-butylpropionamide phenol; catechol (E) with phenol; diethylamine with aniline (B), o-nitrophenol (B) or resorcinol (E); quinol (E) with N-n-butylpropionamide or phenol.(see Giles, Rose and Vallance, J.C.S., 1952, 3799).

TABLE 5A

Protective Effect of Solvents.

Group Protected.	Solvent.	Second Solute.
$-SO_3H$	W	Phenol
C=O (in aldehydyes, amides, ketones)	B,E,W	Phenol, etc.
C=O in dimethylformamide	B,D,W	Phenol, etc.
(Alk-)OH, -O	W	Alk-CH, $-NH_2$, -CHO, etc.

Effect of Sulphonic Acid Groups upon Bonding.- Unsulphonated azo-compounds can form intermolecular bonds between the azo-group and either (a) amide groups (see Table 4A) in non-aqueous solvents, or (b) alcoholic groups in the water sub-phase when the azo-compound is spread as a monolayer thereon (Giles and Neustadter, J.C.S., 1952,3806; Allingham, Giles and Neustadter, Faraday Soc., Discussion, 1953, in the press). Sulphonated azo-compounds do not appear to interact in water either with alcoholic groups (see Table 4A) or with the amide groups of amino-acids (Derbyshire and Marshall, Faraday Soc., ibid.)* These facts show that the sulphonic acid group interaction of an azo-group in the same molecule, with other solutes of low affinity. This could be attributed either to the protective effect of the solvated water surrounding the anion or to a reduction in electronegativity at the azo-nitrogen atoms. Phenols have high enough affinity to interact with the sulphonated compounds.

* The heats of reaction of several amino acids with either hydrochloric acid or the free acid of a sulphonated o-hydroxyazo-dye (Naphthalene Orange G) in water, were found to be the same. Derbyshire and Marshall interpreted this as evidence that no interaction occurs between the groupings in the amino acids and the dye.

The 1:1-complex which glycine forms with a sulphonated azo compound (Table 4A) must represent interaction between the amino group and the sulphonic acid anion, and not with the azo-group.

Water as a solvent.- By the use of the refractive index method, hydrogen bonding is as readily detected in aqueous as in non-aqueous solutions, numerous examples of its use for this purpose being shown in Table 4A. Apart from the evidence of the protective effect of the solvent discussed above, the results demonstrate that the molar ratios of hydrogen-bond complexes between given solutes is often, but not always the same in water as in non-aqueous solvents. Cf., e.g., the ratios in which phenol combines with quinol or the azo-group, respectively; in benzene the azo-group forms either 1:1- or 1:2- complexes with phenol (Section 1, Part II), in the water-soluble azo-compound (sulphanilic acid -α- naphthol) it does the same (a 1:3-complex is also formed by reaction with the 4-hydroxy group).

A comparison of the interaction-ratios of di-or tri-ethylamine with p-nitrophenol or resorcinol (Section 1, and Table 4A) (refractive index method) with those of the solid complexes also reveals interesting facts regarding the effect of water as solvent. In non-aqueous solution diethylamine combines with two molecules of the phenol, no doubt these being attached to both atoms of the NH residue. In presence of water, only one phenol molecule is bound by each amine group (i.e. giving 2:1 amine-phenol complex). Evidently the hydrogen atom of the amino group is protected by attachment to water (cf. the reactivity of alkylamides discussed below).

Water as Solute.- Water enters so intimately into almost all reactions involving fibres that its bonding properties towards a number of the model compounds used to represent fibres are of especial

interest. It appears to act either monofunctionally as monomer or dimer, or bifunctionally as a cross-linking agent. The evidence of cross-linking action between pairs of azo-groups is supported by experiments in monolayers (Giles and Neustädter, J.C.S., 1952, 918, Allingham, Giles and Nustädter, 1953, in the press).

Bonds with Hydrogen attached to Carbon.-Hydrogen attached to carbon forms bonds less readily than when attached to nitrogen or oxygen, and a neighbouring group of powerful electron-attracting nature is usually required to facilitate the reaction. Thus Earp and Glasstone (J.C.S., 1935, 1709, 1720) detected bonding between oxygen in ether, and hydrogen attached to aliphatic carbon activated by chlorine atoms or a negative group, e.g., a phenol or nitrophenyl group.

The enormously greater solubility of CH_2X_2 or CHX_3 compounds (e.g., X = Br, Cl, or F) in O- or N-donor solvents, compared with that predicted from Raoult's law, is also attributable to bonding through CH(Zellhoeffer, Copley, and Marvel, J.Amer. Chem. Soc., 1938, 60, 1337, Copley, Zellhoeffer and Marvel, ibid., 2666, 2(14); and this has been confirmed by infra-red spectrphotometry (Buswell, Rodebusch and Roy, ibid 2528; Gordy, J.Chem. Phys., 1939,7(163) and by determination of data on heats of mixing (Copley and Holley, J.Amer. Chem. Soc., 1939, 61, 1599), which also demonstrated similar bonding between acetylene or phenylacetylene and donor solvents. Hydrogen bonds on carbon exists also in liquid hydrogen cyanide (Pauling, The Nature of the Chemical Bond, Ithaca, N:Y., Cornell Univ. Press, 2nd ed., 1944).

A Chelate bond involving hydrogen attached to carbon has also been suggested between methyl and nitro-groups in o-nitrotoluene

(Sidgwick and Callow, J.C.S., 1924, 125, 527); between CO and the hydrogen attached to the carbon atoms of ~~the~~ propiophenone and higher ketones (Evans, J.C.S., 1936, 785); and in the anions of n-butyric and higher saturated aliphatic acids (Dippy, J.C.S., 1938, 1222).

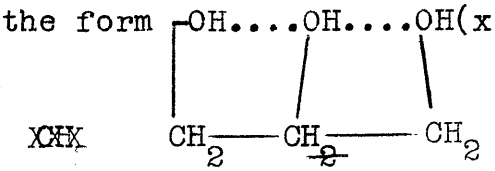
Recently, Jones and Badger (J. Amer. Chem. Soc., 1951, 73, 3132, cf., Badger, J.Chem. Phys., 1940, 8, 228) have given evidence from infra-red spectrophotometry, of supposed intermolecular bonding between methanol and hydrogen of aromatic rings in benzene and other hydrocarbons, in binary solutions in organic solvents.

The possible importance of this type of bond in the reactions of fibres appears hitherto to have received little or no attention. The present results, however, supported by other related investigations seem to indicate that the carbonyl group in carboxylic acids and in acetyl compounds, aldehydes and alklamides can activate neighbouring CH groups sufficiently to cause bonding, and, perhaps, thereby to initiate certain types of sorption by fibres. This matter is discussed below.

Water appears to form a bond with hydrogen of an ethylene linkage in styrene (cf the well known enhancement of hydrophilic properties of alkyl chains by introduction of such linkages). A bond between a hydrogen atom of trichloroethylene and the azo-group in 1-benzene-azo-2-naphthol is also detected, which could account for the high solubility of unsulphonated azo-compounds in this solvent.

Chelation in Aromatic compounds.- The ability of these methods to detect chelation in aromatic compounds is seen by an inspection of many results of the present investigations, e.g. it is shown by the behaviour of nitrophenols (Section 1), 1-hydroxyanthraquinone (Table 4A) and o-hydroxy- and o- aminoazo- compounds. An attempt was made

to detect chelation between hydroxy- and sulphonic acid groups, but the compounds used proved unsuitable. No chelation was detected (in water) in 2-naphthol-3:6-disulphonic acid. 2-Naphthol-1-sodium sulphonate is too soluble in water for examination, though this fact itself is indicative of chelation. Chelation between these groups has received little attention, but Shetty (Textilø.- Rundschau, 1950, 5, 399) has detected its presence by an examination of the water-solubility and lake-forming properties of some sulphonated hydroxyazo-compounds.

Chelation in Polyhydric Alcohols.- Weak, 5-membered chelate rings exist in o-dyhydric phenols. Their instability is shown by infra-red spectroscopy (Pauling, op.cit.) and it is also made evident by the reactivity which such pairs of groups show towards phenol. There is no evidence available that chelation between vicinal hydroxy-groups in aliphatic compounds is equally familiar. The rather surprising behaviour at first observed between glycerol and methanol in water, and later investigated in some detail by an examination of several other alcohols (Table 6A) now seem to be most rationally interpreted by supposing that such a form of chelation is present in some of these compounds in certain solvents. Glycerol, e.g., may be supposed to react in the form  one hydrogen atom only (x) being free for intermolecular bonding. On this hypothesis, ethylene glycol, erythritol and mannitol should also be monofunctional towards, e.g., methanol or water. On the other hand 1:5-pentane diol, which cannot contain such an internal bond, should be bifunctional. Further, a powerful hydrogen-bonding second solute, e.g., phenol, might be expected to

disrupt the weak chelate rings and unite with each hydroxy-group in all these alcohols. An inspection of the detailed results (Table 4A and 6A) will show that the facts are in accordance with each ~~other~~ of these predictions.

In the solutions ~~it is~~ examined ~~that~~ the chelate molecules are of course subject to constant bombardment by a large excess of solvent molecules. It was therefore hoped that by examining their reactivity in the presence of solvents of different polarity a qualitative estimate of the stability of the chelate rings could be obtained. This has in fact proved to be so. It is found that 6-membered chelate rings in aromatic compounds are stable towards all the solvents and second solutes examined, whereas 5- and 7- membered rings in aliphatic or aromatic compounds being, as they are, under greater strain, can be disrupted by a suitable choice of a solvent and/or second solute.

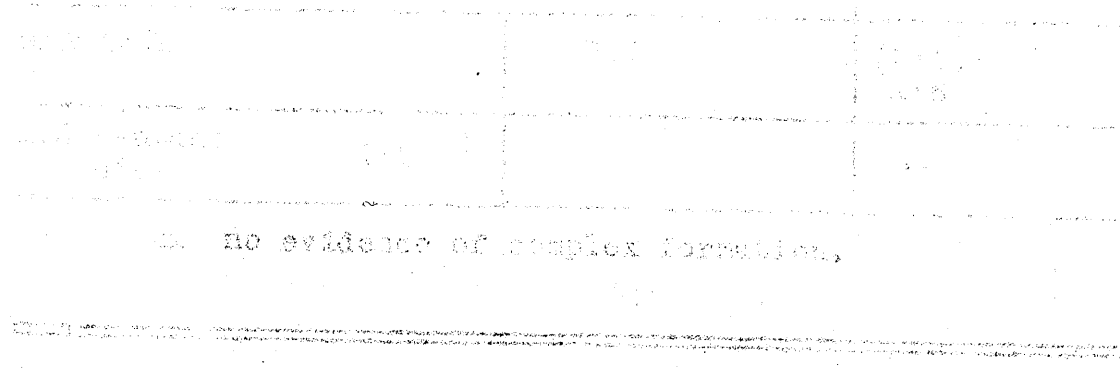


TABLE 6A

MOLAR RATIO OF COMPLEXES FORMED BY STRAIGHT-CHAIN ALCOHOLS.

First Solute.	Second Solute and Solvent.									
	Methanol in			Water in			Phenol in			
	Cs	D	W	EG	D	D	EG	T	D	W
Methanol						1:1				1:1
Ethanol					1:1			1:1		1:1
iso-Butanol									1:1	
n Pentanol									1:1	
Ethylene glycol		1:1								1:1; (1:2)
Glycerol		(1:1)	xx		1:1					1:1; 1:3
Erythritol	1:1		xx							1:1; 1:4
Mannitol				1:1			(1:1); 1:6			1:6
1:5-Pentane diol		1:2								

xx no evidence of complex formation.

The Reactivity of the Amide group.- The intermolecular bonding reactions of the alkylamide group are of high importance in the study of e.g., protein structure, the tanning of proteins, and the water sorption and dyeing properties of nylon and proteins. The information which the present work discloses upon this subject is set out in Table 7A. A pattern of behaviour is then evident, which may be expressed in the following generalisation: the alkylamide group reacts normally in the enol (.C(OH):N.) form, which is bifunctional. It seems to react in the keto form when the amide hydrogen atoms are both replaced by alkyl groups, as of course would be expected, or when one or both are bounded to water (as a solvent) and the keto oxygen atom is then unreactive, being protected by the solvent, in benzene or water. Both forms can interact with a variety of other groups. Note that when the second solute is symmetrically bifunctional, a 1:1 interaction ratio is interpreted as evidence of a 2:2-complex (Giles, Rose and Vallance, J.C.S. 1952, 3799).

The powerful swelling action of the phenols on nylon is clearly due to pairs of interamide hydrogen bonds being disrupted and replaced by bulky phenol molecules. Dihydric phenols are cross-linking agents and therefore less effective in swelling.

Footnote.

Buswell, Rodesbusch and Roy (J.Amer. Chem. Soc.) 1938,60, 2444) in infra-red spectroscopic studies observed, that monosubstituted amides, e.g., N-ethylacetamide, associate and enolise in CCl_4 solution.

Table 7A.

Intermolecular Reactivity of the Alkylamide Group.

Amide (a)	Group (b)	Mol.ratio of complex (a:b):solvent	Probable tautomeric form
$H:CO.NMe_2$	-OH	1:1 n	keto
	$-NH_2$	2:1 n	keto
	-NH	1:1 n	keto
	-CHO xx	1:1 w	keto
P.CO.NH.Bu.	-OH	1:2 n	enol
	=O xxx	2:1 n	enol
	$-NO_2$	1:1 n	enol
	$-N_2-$	1:1 n	enol
	Urea	1:1 n	enol
$CH_3.CO.N(CH_3)_2$	=O xxx	2:1 n	keto
$CH_3.CO.NH_2$	-OH	1:2 n	enol
		1:1 w	keto
	=O xxx	1:1 w	keto
		1:2 n xxxx	enol

n = non-aqueous: w - water.

xx In glucose and cellobiose.

xxx Quinone group.

xxxx Interpreting a 1:1 ratio as evidence of a 2:2 complex.

The several examples discovered of bonding by hydrogen attached to carbon activated by a neighbouring carbonyl group provided the opportunity to investigate the possibility of this

type of bond occurring with alkylamides. Both diethyl and dimethylacetamide were examined and are shown to be capable of bonding with azobenzene[≠] or benzoquinone; this must clearly be evidence of bonding by a hydrogen (x) attached to carbon, e.g., $H_2\overset{(x)}{C}H{:}CO.N(CH_2)_2$, neither carbonyl oxygen nor the nitrogen can be responsible, since, e.g., acetone and diethylamine, in the same solvent, are unreactive towards azobenzene. If hydrogen in this position is reactive, hydrogen attached to carbon in the protein chain may be so also; this would open up additional possibilities of hydrogen-bond cross-linking in protein structures. Kandar (Bull. Chem. Soc., Japan, 1950, 23, 4, 137; through J. Text. Inst., 1951, 42, A 575; Chem. Researches (Japan, 1951, 9 133; through Chem. Abs., 1951, 45, 7610) has in fact proposed an α-keratin model embodying CH...N bonds.

So far, no experiments have been made to establish the existence of this type of bond when the normal amide group is present in water, though it may exist in the acetamide-benzoquinone system.

The Hydrogen-bonding Properties of Carbohydrates.- Glucose and cellobiose in water react alike, monofunctionally. If the pyranose ring-structures of these compounds were operative, it would be expected that the cellobiose molecule would combine with

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≠ If this is so, then the 4:1-complex observed must represent two atoms bonded to each nitrogen, while this behaviour is well known (the author is not aware that it has) in the case of oxygen (cf. Pauling, loc. cit.) previously been reported for nitrogen.

twice as many molecules of a second solute as glucose does. In the open-chain form, however, both compounds have a single aldehyde group and it must therefore be this group which forms intermolecular bonds in water, a conclusion supported by the similarity of the reactions of acetaldehyde. The equilibrium in water between the open-chain form of glucose and the α- and β-ring structures is normally strongly in favour of the latter, only a small percentage of open-chain compound being present. If the aldehyde group enters into complex-formation the equilibrium will be disturbed and more open-chain molecules will be formed, until their proportion is sufficient to have a perceptible effect upon the curves examined. If the aldehyde group does not react with a solute, e.g., phenol (in water), then the equilibrium is undisturbed, the glucose molecule remaining largely in the ring configuration. The keto-group unlike the aldehyde-group, is protected against intermolecular bonding in water by the solvent. It is therefore to be expected that the ketose sugars would not form complexes at all in water, and indeed neither fructrose nor sucrose does so.

The hydroxy-group in aliphatic alcohols in water is protected against reaction with other alcoholic groups, amino-groups, etc., this is illustrated by a number of examples in Table 4A. Thus the absence of any apparent reaction of carbohydrate hydroxy-groups towards, e.g. alcohols and amines in water is understandable. The phenolic hydroxy-group does, however, react with alcoholic groups in water, and can in fact disrupt

5-membered chelate rings to do so. Yet in spite of repeated examination of its behaviour with glucose in aqueous solution, the author has been unable to detect any evidence that phenol unites with the glucosidic hydroxy-groups.(x) It does combine with each of the six hydroxy-groups in the straight-chain alcohol, mannitol, even though these must be capable of chelation, and there seems consequently no reason to doubt that it would do so in the straight-chain form of glucose. For the reason discussed above the ring-structures of glucose should predominate in presence of phenol, and this leads to the conclusion that the hydroxy-groups in these structures differ in reactivity in aqueous solution from those in the open-chain molecule. The difference cannot be due to the presence of chelate bonds in the ring structures; the evidence both of the experimental work (c.f. the reaction of water in ethylene glycol solution) with glucose (6:1-complex) and mannitol (1:1 complex) respectively and of an examination of models shows these are not present. The reduced affinity for phenol must represent an enhanced affinity for water of the ring-forms of glucose.

It is thus postulated that the shape of the ring molecule favours the retention of a more strongly-bound atmosphere of water

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(x) The 2:1-complex with p-nitrophenol is attributed to bonding of the -CHO group to each oxygen atom in the $-NO_2$ group. The phenolic group has enhanced acidity and the consequent increased solution by water may account for it not reacting with open-chain glucosidic hydroxy-groups.

than the straight-chain molecule can retain. A comparison of the ring form of glucose with the open-chain form, in the crumpled state in which it most probably exists in water, shows that the solvated water molecules on either side of the ring can approach more closely to each other, and thus exert a stronger mutual attraction, than those across the diameter of the crumpled chain. (The shortest distances of separation across the two molecules are about 4A and 6.5A respectively). The resulting increased protection of the ring form against attack by other solutes may be a factor in the preference shown by Nature for this structure in the carbohydrates. The deduction that the ring form more strongly attracts water receives some support also from the fact that the equilibrium in water so favours the ring-structures when it might be expected that the open-chain form would be more stable, both by reason of its higher statistical probability and the presence of a series of chelate rings.

These observations upon the bonding properties of carbohydrates may be used to re-interpret some of the known facts of the substantivity of water-soluble dyes for cellulose, which hitherto has been attributed to a hydrogen-bonding mechanism(x) (See the Summary given by Vickerstaff in "The Physical Chemistry of Dyeing" Edinburgh, Oliver and Boyd, Ltd., 1950). It has now

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(x) Marsden and Urquhart (J.Text.Inst., 1942, 33, T105) found that phenol is completely unabsorbed by cellulose from aqueous solution, in agreement with the present observation of its unreactivity towards glucose.

been suggested, and the suggestion has been supported by a re-examination of known facts and by certain experiments in monolayers, that dye molecules are held to cellulose molecules principally by van der Waals attraction, the water surrounding the fibre molecules effectively preventing direct hydrogen-bond interaction (Allingham, Giles and Neustädter, Faraday Society Discussion, 1953, in the press). Some direct bonding may perhaps take place on subsequent drying of the dyed material, but this has no connection with the sorption mechanism in presence of water.

Further Experiments with Glucose.-

It was desired, if possible, to detect the reactivity of the hydroxy-and ether groups in glucose more selectively, and thus to obtain additional evidence in support of the conclusions already reached. This aim was achieved by the use of tetramethyl-glucopyranose, which is soluble in non-aqueous solvents, but retains one hydroxy-group, and by the discovery that ethylene glycol can be used with good results as a non-aqueous solvent for glucose. Both water and phenol were found to form 6:1-complexes with glucose in this solvent, from which it is inferred (i) that protection by the solvent is indeed the cause of the non-reactivity of the hydroxy- and ether groups in water; and (ii) that no chelate rings are present, since in the same solvent the chelate rings persist in mannitol (See Table 5A water as second solute). This must mean that the ring-form of glucose is the form reacting in ethylene glycol. Tetramethylglucopyranose forms both 1:2- and 2:1-complexes with water (in dioxan). The 2:1-complex must represent cross-linkin of two pyranose molecules (probably at the hydroxy-groups) by a water

bridge, and its detection is thus evidence that such water bridges might exist in cellulose; in the 1:2-complex, one water molecule may be attached to both the hydroxy and aldehyde groups of the straight chain molecule (x), or a water dimer to one active centre, probably the hydroxy-group.

Use of Ternary Solution containing Glucose.- An additional confirmation of the conclusions upon the behaviour of glucose was sought by the use of a ternary solution, in the following manner:- Phenol as one solute in water was used in the normal way, with glucose as a second solute, but to every solution triethylamine was also added, in equimolar proportion to the glucose present. By the process already outlined, the amine should stabilise the open-chain glucose molecule rather than the pyranose ring, and thus, by analogy with the open-chain alcohols, the hydroxy-groups should be available for the combination with phenol even in water. This proves to be so, 6:1- and 1:1-complexes being formed between phenol and the amine-glucose mixture (Fig.18A). (The 1:1-complex must represent interaction of phenol and amine alone; the 6:1 complex must be evidence that five phenol molecules are occupied with hydroxy-groups and the sixth either with the amine nitrogen or the aldehyde oxygen). This experiment thus

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(x) The hydroxy-group in the ring-structure is accompanied by five ether groups, each of which would seem to have similar reactivity. One should, therefore, expect a 1:6-ratio complex for this structure as for glucose itself with water in glycol solution.

gives evidence in favour of the open-chains structure for the 1:1-glucose complexes and also, indirectly, of the suggested greater affinity for water of the hydroxy-groups when in the pyranose ring.

Reactivity of the Azo Group.- Chelation of this group with o-amino- or hydroxy-groups is evident and the 6-membered chelate ring is stable both in organic solvents and water. The ready formation of intermolecular bonds by this group may be responsible for the sorption of azo-dyes by cellulose acetate or polyethylene terephthalate (Terylene).

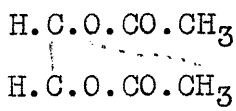
Sorption by Cellulose Acetate.- It was previously supposed that a hydrogen bond between cellulose acetate and phenol (Marsden and Urquhart, loc.cit.) or dyes (Vickerstaff, op. cit.) was located on the carbonyl oxygen atom of the acetate residue. The present and related results (Allingham et. al. loc. cit.; Cameron et. al. private communication) point to the bond being located on hydrogen attached to carbon of the acetyl residue, in the case of donor solutes if not with phenol, etc., also. Supporting evidence (to be published) is provided, e.g., by bonding by the low apparent heat of sorption of phenol (from aqueous solution) on cellulose acetate (2.5 kcal. per mol. compared with 3.5 kcal. for sorption on nylon, where the bond is believed to be -NH...O. Cameron et al. private communication).

Esters.- The fact that aliphatic acetates, and the aromatic esters examined, can interact with compounds containing no free hydrogen, e.g., azobenzene or benzoquinone may be interpreted as evidence of a bond through hydrogen attached to the carbon atom

of the ester group, this being activated by the adjacent carbonyl oxygen atom.

Not only, however, do the present results indicate the presence of intermolecular C...H bonds, but they appear to demonstrate that such bonds can establish chelate rings in certain compounds.

Chelation through Hydrogen on Carbon:- Penta-acetyl glucose, like glucose itself, appears to react in the open-chain aldehyde form. In toluene solution the acetyl groups are unreactive, yet they are reactive when dioxan is the solvent, and the acetyl group in ethyl or isopropyl acetate can form complexes in both dioxan and toluene. It seems clear that there is another example in penta-acetyl glucose of a series of weak chelate rings, which are stable in toluene but are broken even by the weakly polar solvent, dioxan. They are thus even less stable than those in the polyhydric alcohols. It is demonstratable by scale models that a series of 7-membered rings can be formed in this compound, leaving no free hydrogen as end-group (except that of the aldehyde group), thus:



This hypothesis is supported by the test with triacetyl glycerol (triacetin), which was found to combine with only one molecule of a second solute (diethylamine) in toluene, but with three in dioxan. 7-membered chelate rings, stable in toluene and unstable in dioxan apparently therefore exist in this compound also.

Intermolecular Chelation of the Keto-group.- In order to check the validity of the hypothesis put forward by Evans and Dippy (loc. cit.) and referred to above, regarding internal chelation involving hydrogen on carbon in ketones and aliphatic acids, respectively, the behaviour of certain carboxylic acids in forming intermolecular bonds with a keto-group was examined. When not protected by the solvent, this group normally forms 1:2-complexes, e.g., with benzoic or formic acid, methanol or phenol. These may be formulated, e.g., as in Fig. 19A(a).

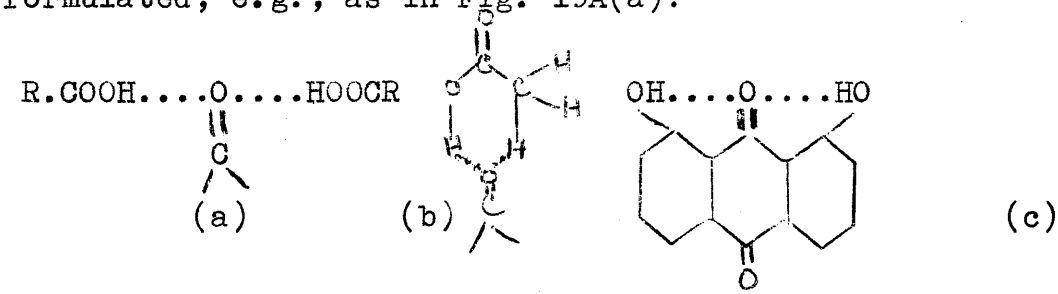


Fig.19A. Bifunctionality of keto and quinone oxygen atoms.

The oxygen atom thus behaves bifunctionally as it does in forming the chelate rings in 1:8-dihydroxyanthraquinone (Pauling, loc.cit.). Fig.19A(c). The compounds which have an α or a β -CH group, however, i.e. acetic, propionic and trimethylacetic acids, form only 1:1-complexes, and for these, intermolecular chelate rings (6-,6-and 7- membered respectively) may be formulated (cf.Fig.19A(b)), which are in fact, very similar to the intermolecular chelate compounds Evan and Dippy have suggested. Though by no means conclusive, this evidence is regarded as supporting the possibility of bonds being formed through hydrogen on carbon in this class of compound. The 1:1-benzoic acid-ketone complex cannot be formulated as a chelate complex without including a hydrogen atom

of the benzene ring and there is little evidence that this is justified.(x)

The Reactivity of N-Acetylglucosamine.- A knowledge of the bonding reactions of this substance should assist in the interpretation of the sorption phenomena of the natural polymer, chitin, of which it is the principal building unit. The monofunctionality of its complex-formation with various second solutes in water (Table 4A) is consistent with a reaction at either the ether oxygen atom amines or with the nitrogen atom (with hydroxyl compounds), all other positions (including the amino-hydrogen atom), being solvent protected. In ethylene glycol three of the four hydroxy-groups appear to be reactive also. The fourth is probably involved in an intramolecular bond (a in Fig. 20A). Darmon and Rudall (Faraday Soc. Discussions, No. 9, 1950, 251) obtained evidence of the possible existence of this bond (and of unbonded $>$NH groups) in chitin, in studies with polarised infra-red and X-radiation. Being 7-membered it is probably unstable in water. The complexes in water are probably formed either with the aldehyde group of the open-chain tautomer, or with the amino-nitrogen atom.

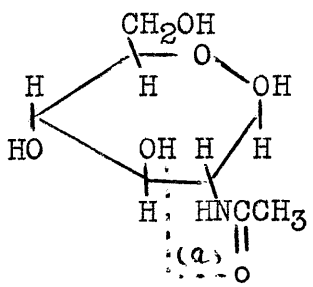


Fig. 20A. Suggested intramolecular bond in N-acetylglucosamine.

(x) Jones and Badger's results (vide supra) were obtained in organic solvents.

EXPERIMENTAL.

Materials.- All the compounds used were either of analytical reagent quality or were purified in the laboratory, from commercial or laboratory-prepared products. The naphthalene sulphonic acids were purified by recrystallisation from water and the two Duranol dyes by Soxhlet extraction with benzene, followed by recrystallisation. All solvents were completely dried. The dioxan and methanol were of the "specially dried" quality (B.D.H.) used for Karl Fischer titrations. Ethylene glycol was first fractionated and then passed through a column of activated alumina.

2:3-Benz-9-anthranol was prepared by Fieser's method (J.Amer.Chem.Soc., 1931, 53, 2329). It formed buff crystals, m.p.176°C., and would not couple with diazo solutions; thus it exists as a quinone and not an enol.

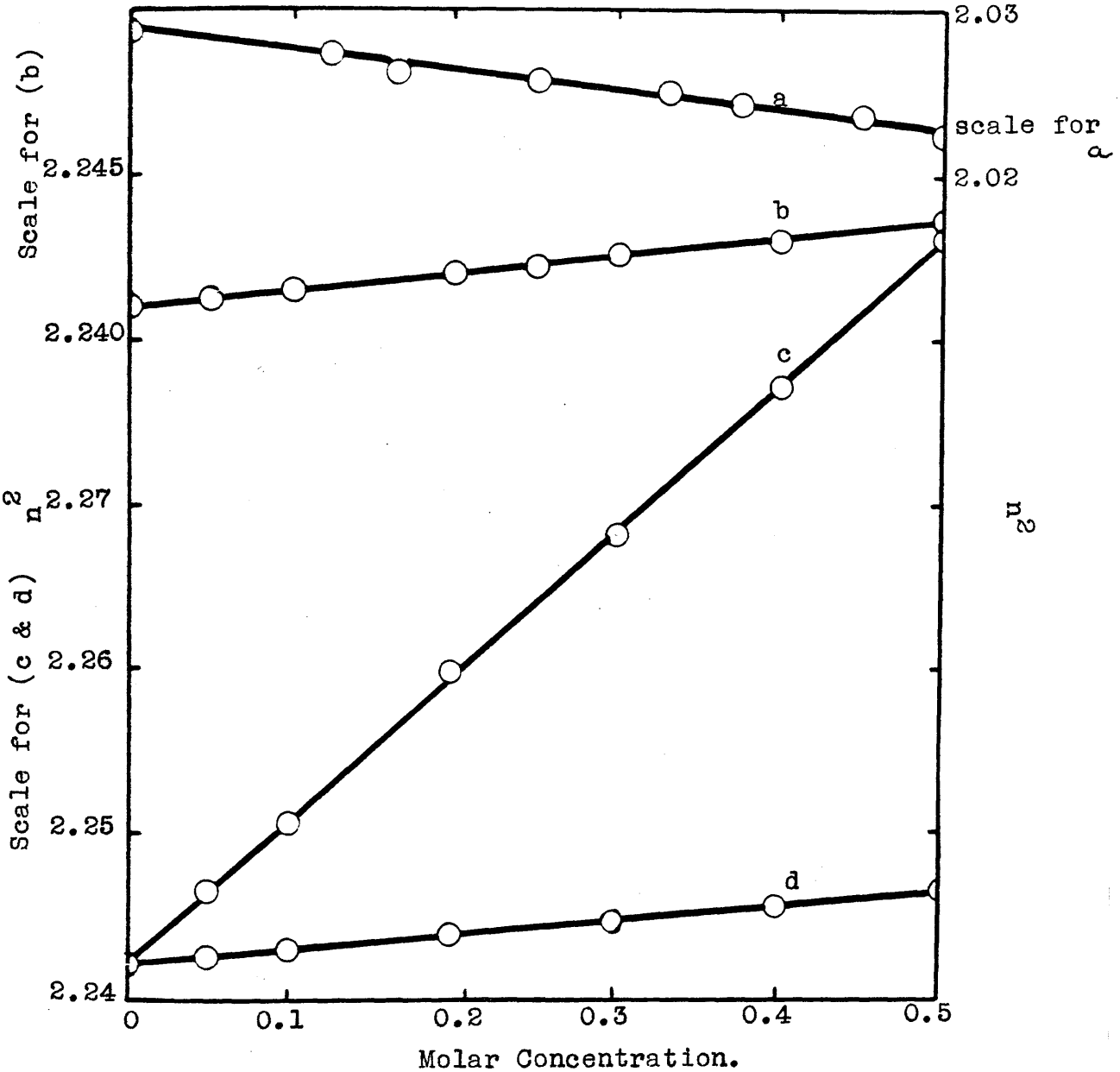
Azobenzene 4-Sulphonic Acid.- This was prepared by treating azobenzene (1 part) with 20% oleum (5 parts) at 130°C. for 15 min., followed by cooling, drowning in cold water, and recrystallisation from water. Orange plates, m.p. 127°C.

N-Diethylacetamide.- This was prepared in small yield from acetyl chloride and diethylamine, by the method used for N-n-butyl-propionamide, given by Giles, Rose and Vallance (J.C.S., 1952, 3799) B.p.180°C. (the sample of N-dimethyl-acetamide was kindly supplied by Dr. M.A.T. Rogers).

Instruments and Procedure.- These have already been described in Section 1.

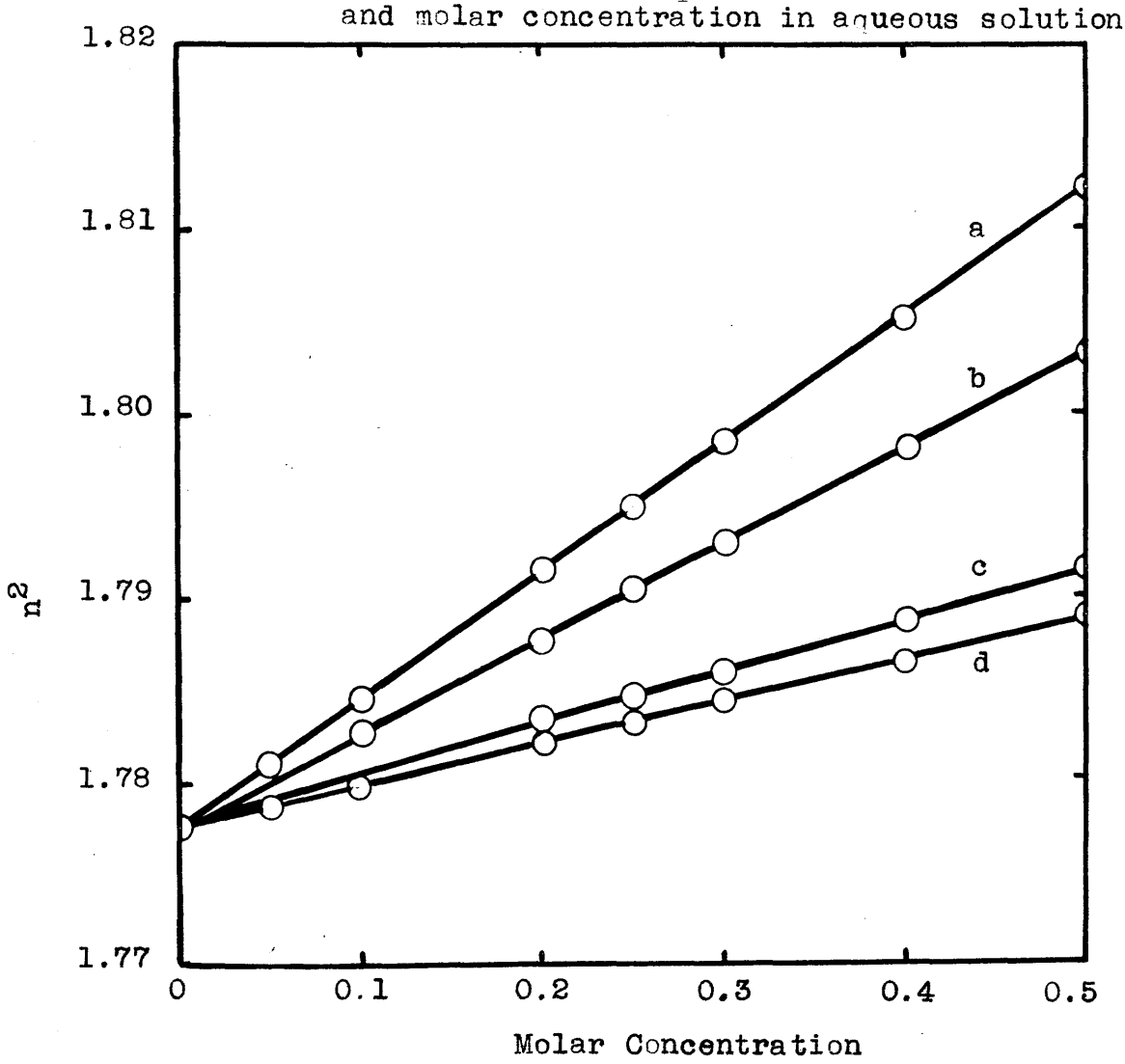
Where necessary, the conclusions reached have been checked by using Catalin (Stuart) type atomic models.

Fig. 1A . Relation between square of refractive index and molar concentration in non-aqueous solutions.



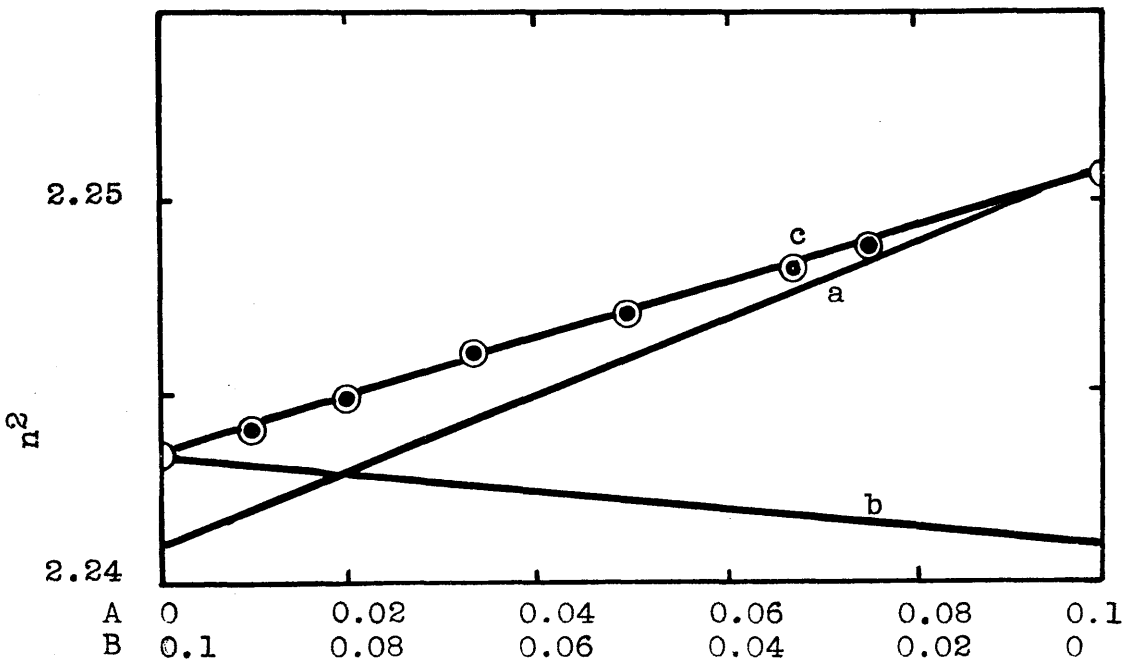
a) = Water in dioxan (20°C.)
b) = Phenol in toluene (19°C.)
c) = Azobenzene in toluene (19°C.)
d) = Benzoquinone in toluene. (19°C.)

Fig. 2A .Relation between square of refractive index and molar concentration in aqueous solutions.



a = Glucose or Manitol (19°C) c=Glycerol(20° C).
b = Phenol (19° C). d=Dimethylformamide(19° C).

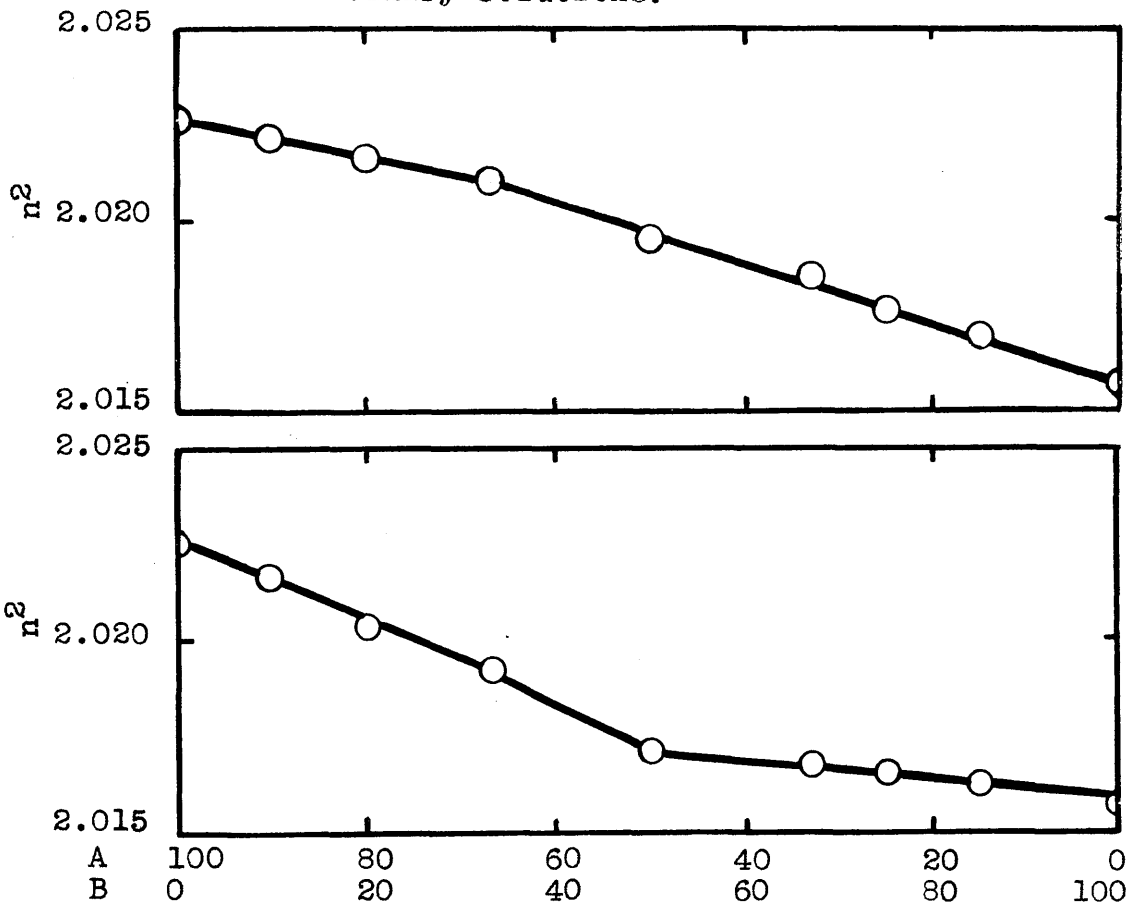
Fig. 3A. Additivity of square of refractive index for non-interacting solutes.



a) Curve for benzoquinone alone.
b) Curve for Azobenzene alone.
c) Curve for binary solutions of A+B.

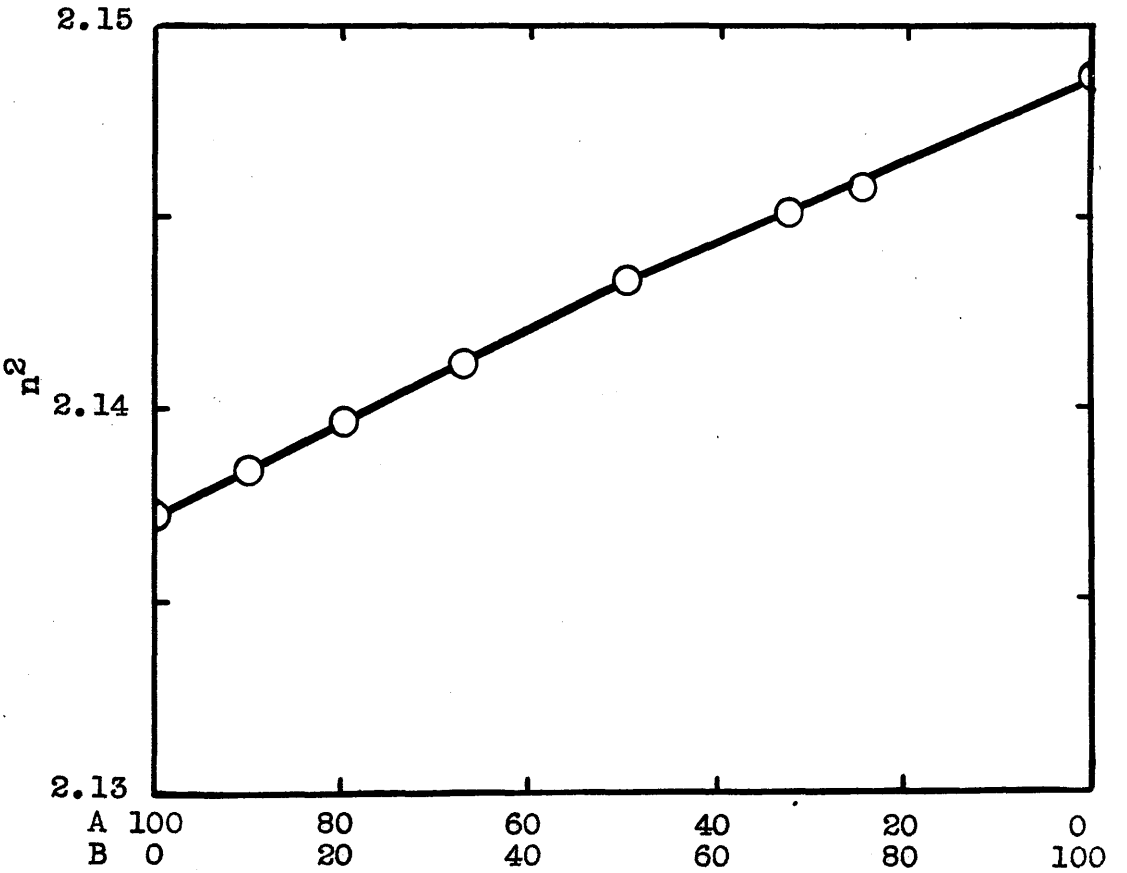
A= Benzoquinone;
B= Azobenzene.

Fig.4A . Relation between square of refractive index and Component ratio in binary solutions.



Top:- A=p-Nitrophenol; B= Diethylamine.(D,20° C).
Bottom:- A=Resorcinol; B= Diethylamine.(D,20° C).

Fig. 5A . Relation between square of refractive index and component ratio in binary solutions.



A = Benzyl alcohol; B = Azobenzene. (CCl_4)

Fig. 6A . Relation between molar ratio, square of refractive index, and apparent molecular weight in binary solutions of azobenzene and phenol.

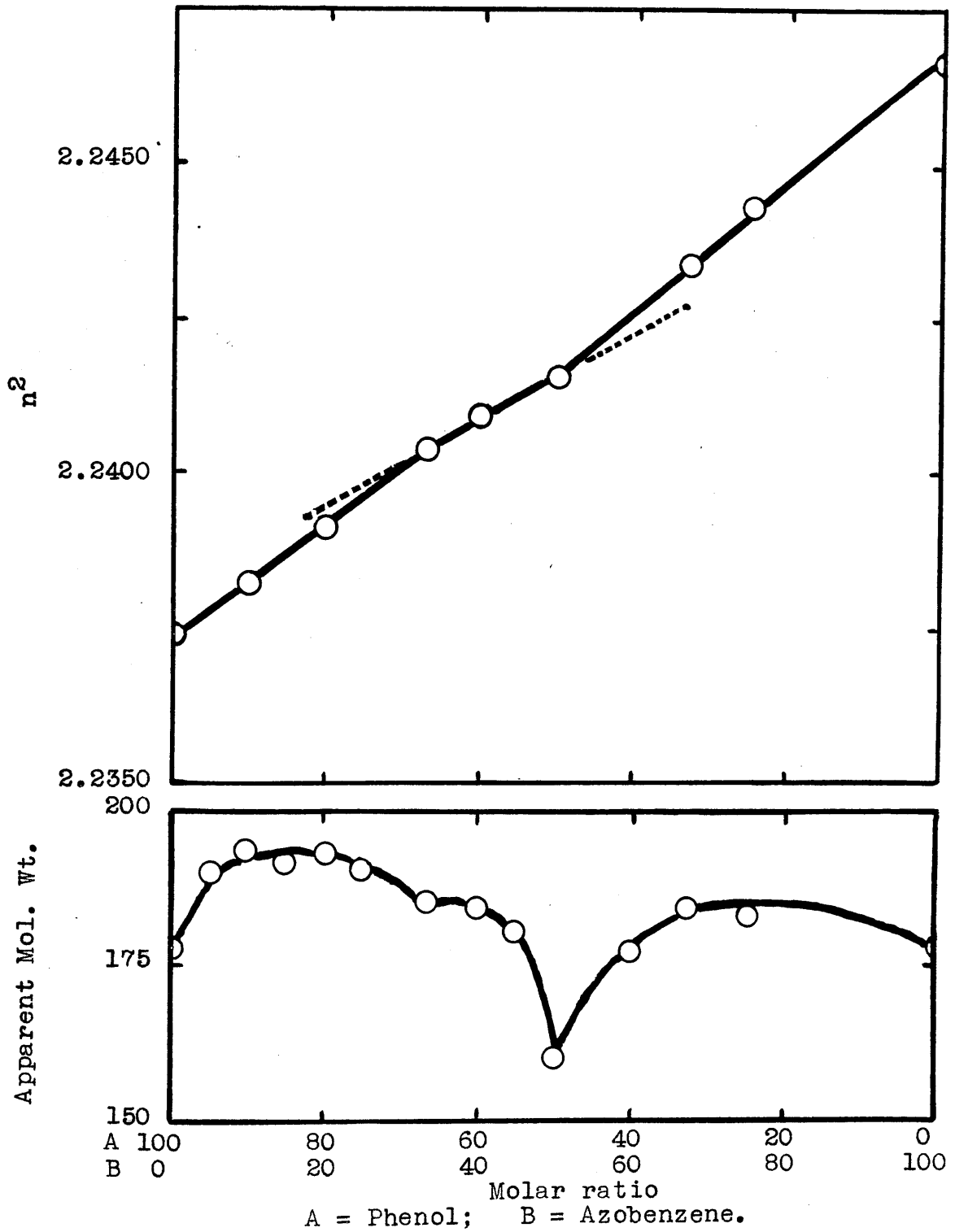
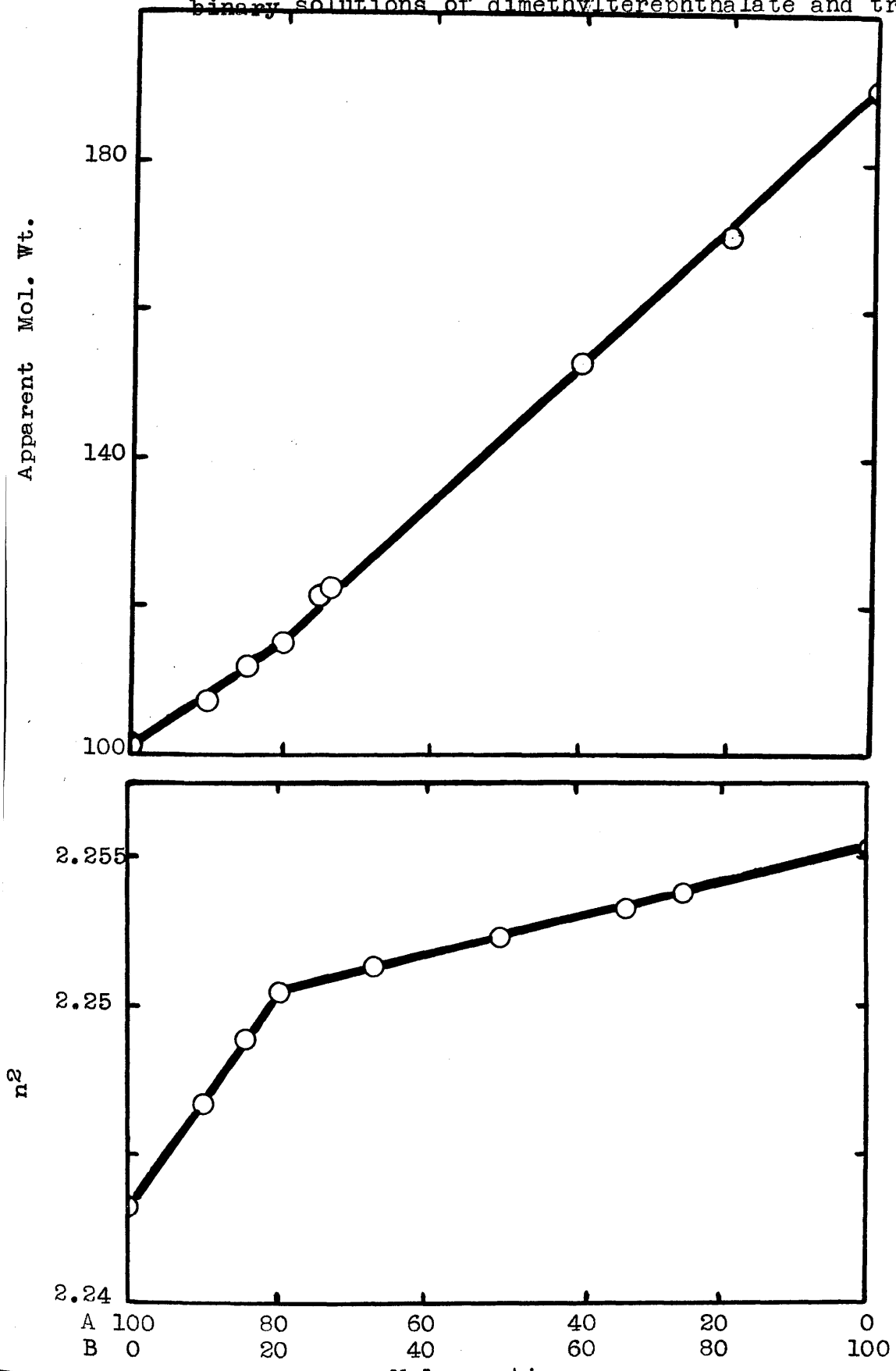
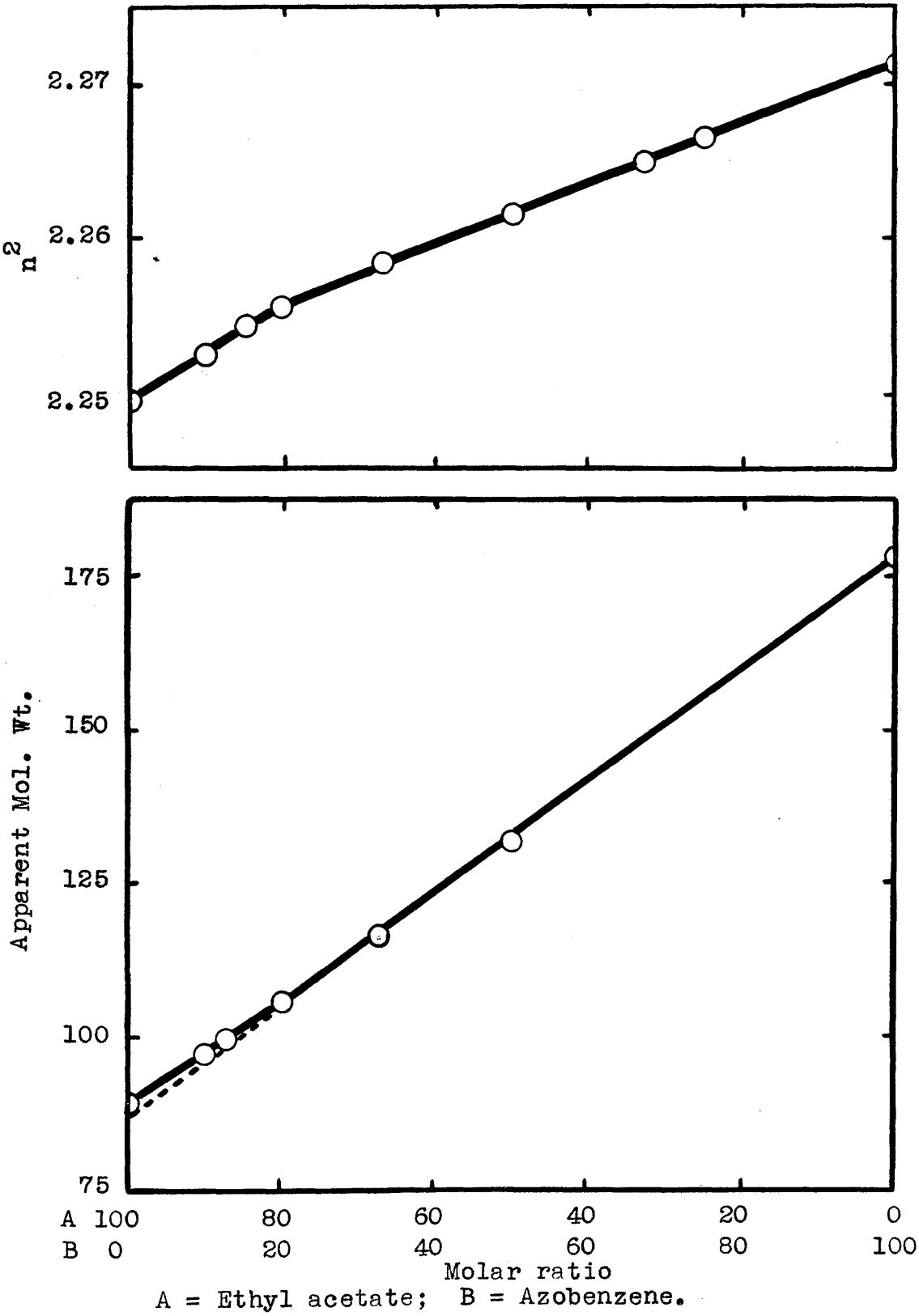


Fig. 7A . Relation between molar ratios, square of refractive index and apparent molecular weight in binary solutions of dimethylterephthalate and triethylamine.



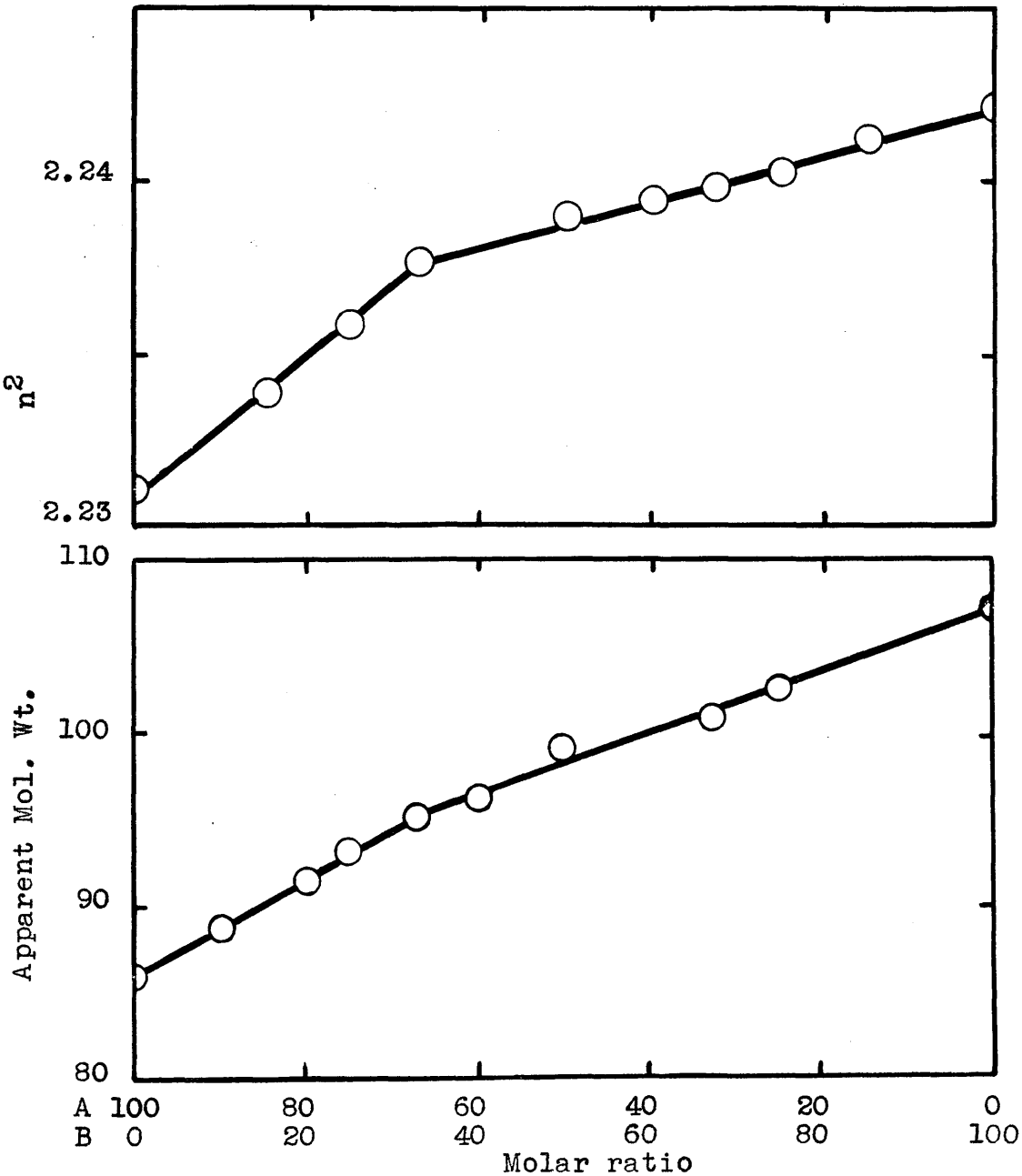
= Triethylamine; B = Dimethylterephthalate.

Fig. 8A . Relation between molar ratio, square of refractive index, and apparent molecular weight in binary solutions of azobenzene and ethyl acetate.



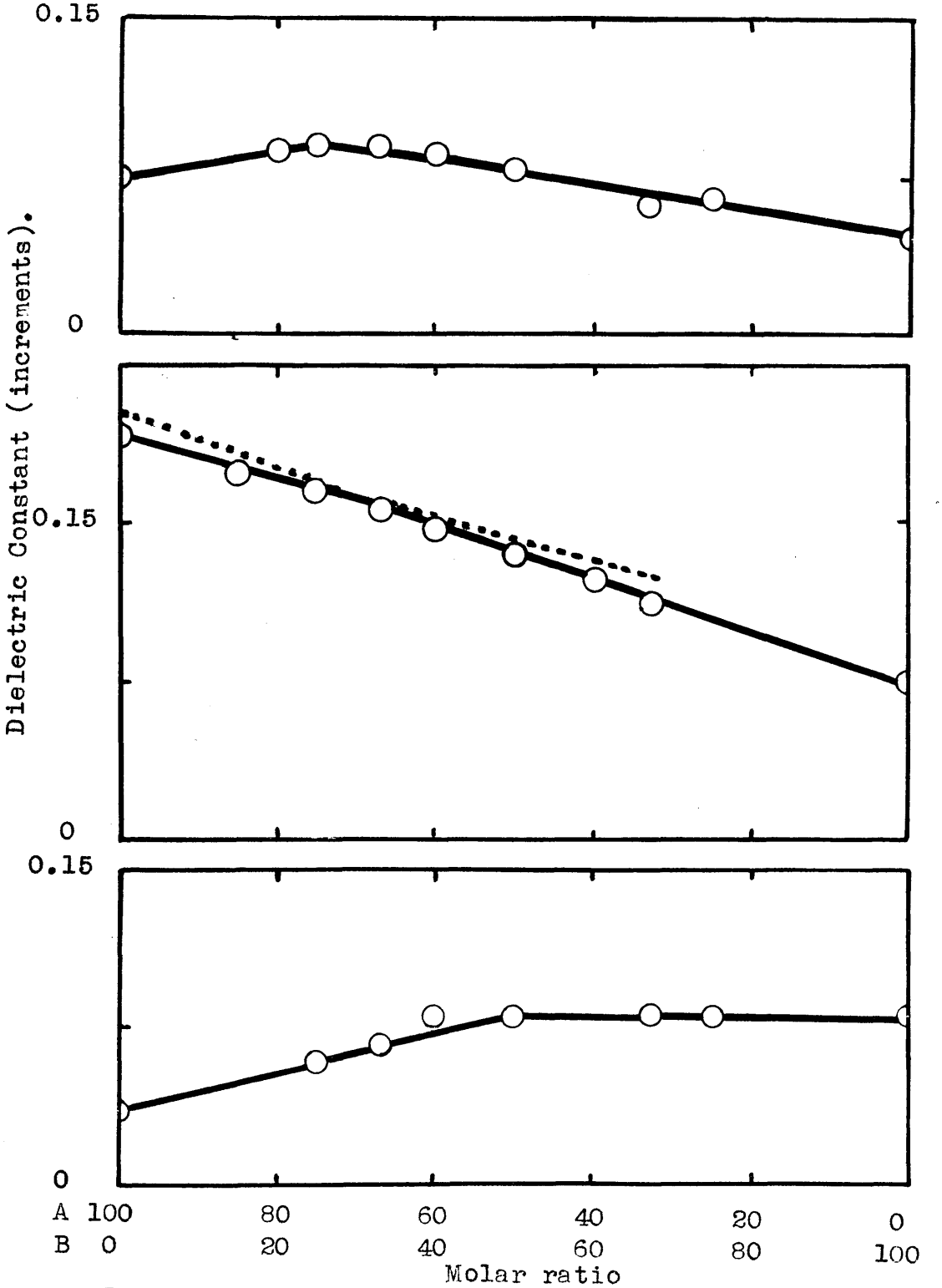
A = Ethyl acetate; B = Azobenzene.

Fig. 9A . Relation between molar ratio, square of refractive index, and apparent molecular weight in binary solutions of benzoquinone and alkyl acetates.



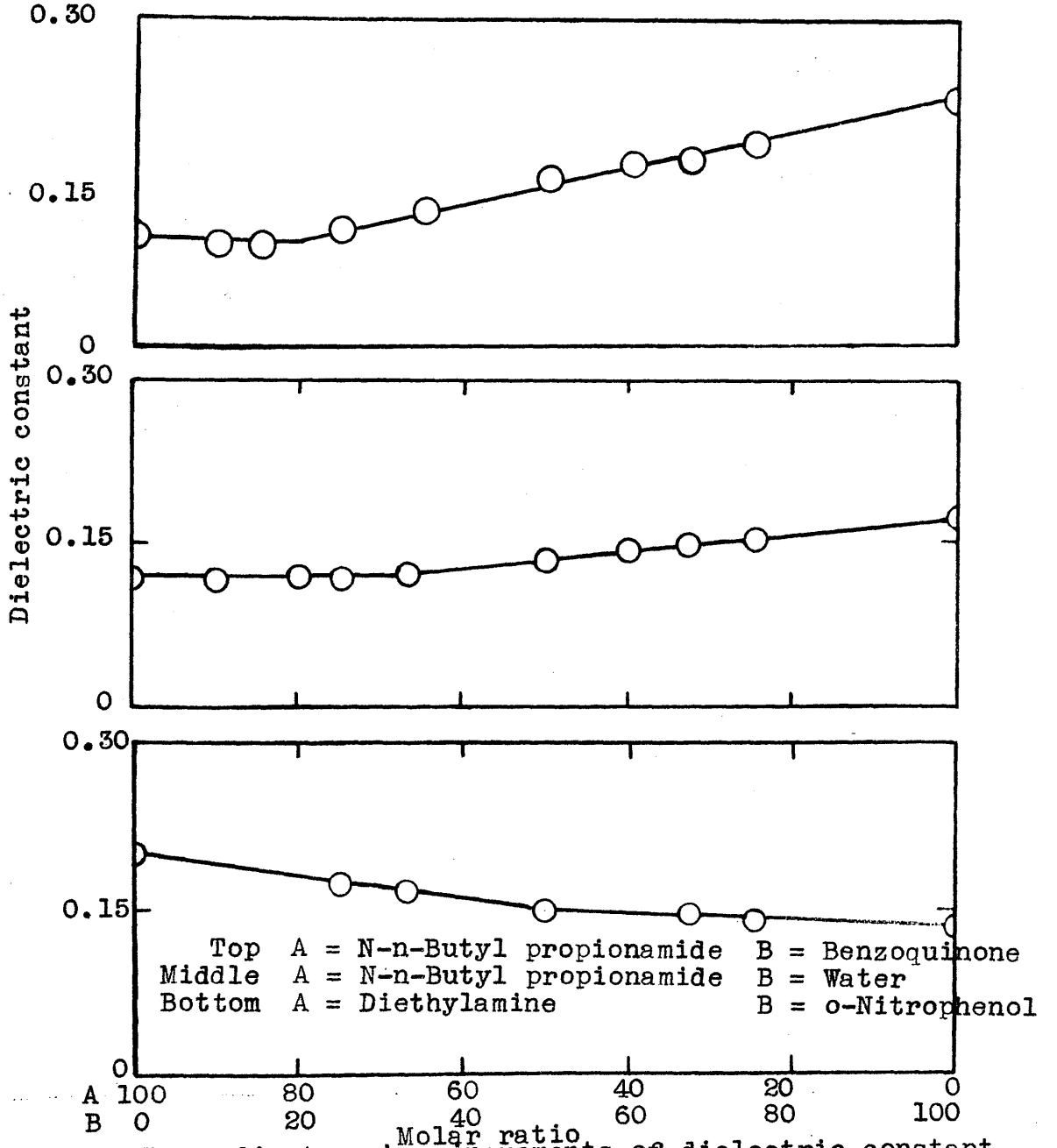
Top : A = iso-Propyl Acetate; B = Benzoquinone.
Bottom : A = Ethyl Acetate; B = Benzoquinone.

Fig. 10A. Detection of intramolecular bonds by dielectric constant method.



Top = A = Phenol; B = p - Nitrophenol.
Middle = A = Phenol; B = Nitrobenzene.
Bottom = A = Phenol; B = o - Nitrophenol.

Fig. 13A. Relations between dielectric constant * and component ratio in binary solutions.



* The ordinates show increments of dielectric constant on arbitrary base lines, not absolute values.

Fig. 14A . Relation between square of refractive index and component ratio, in binary solutions.

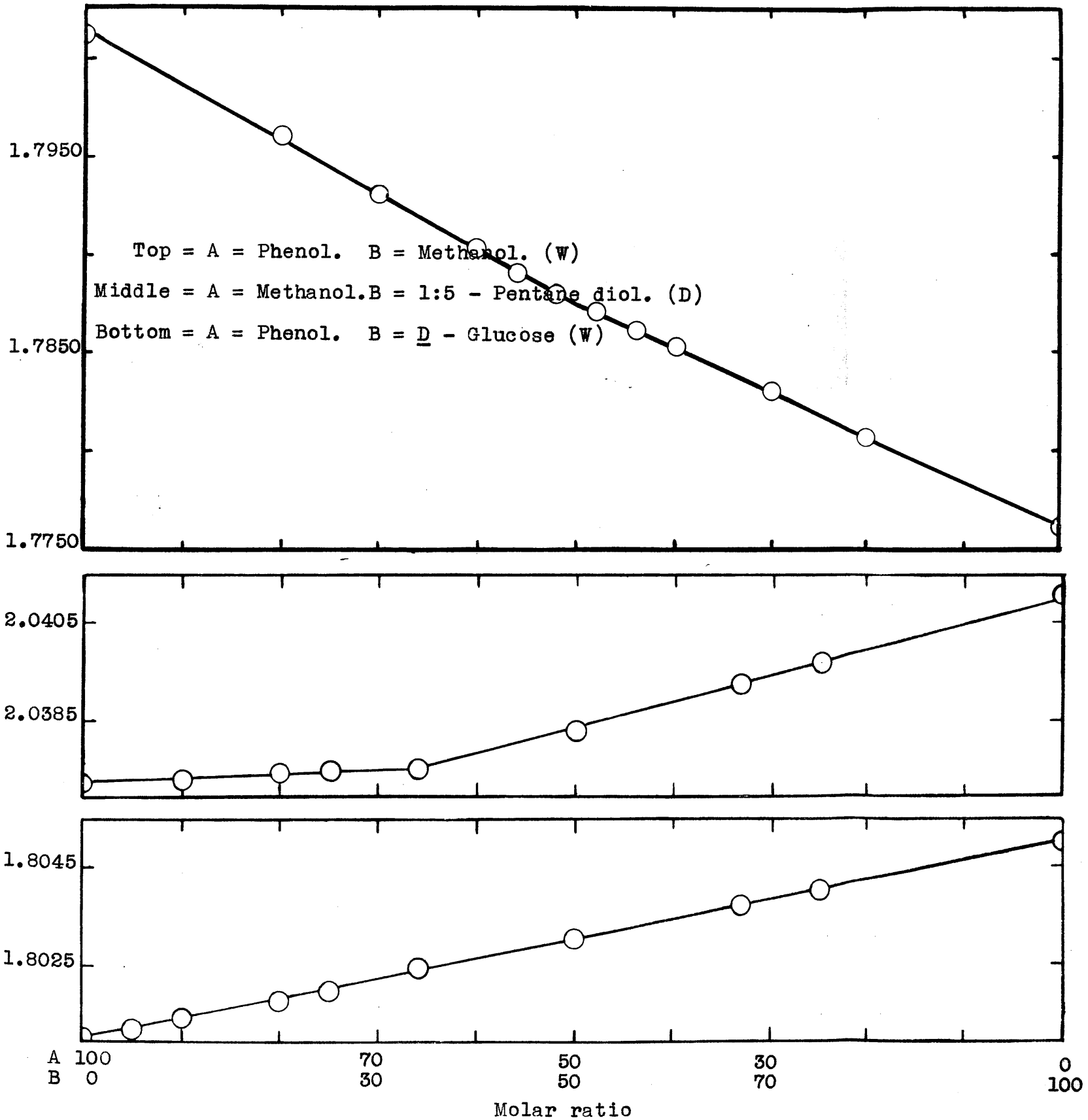


Fig. 15A . Relation between square of refractive index and component ratio in binary solutions.

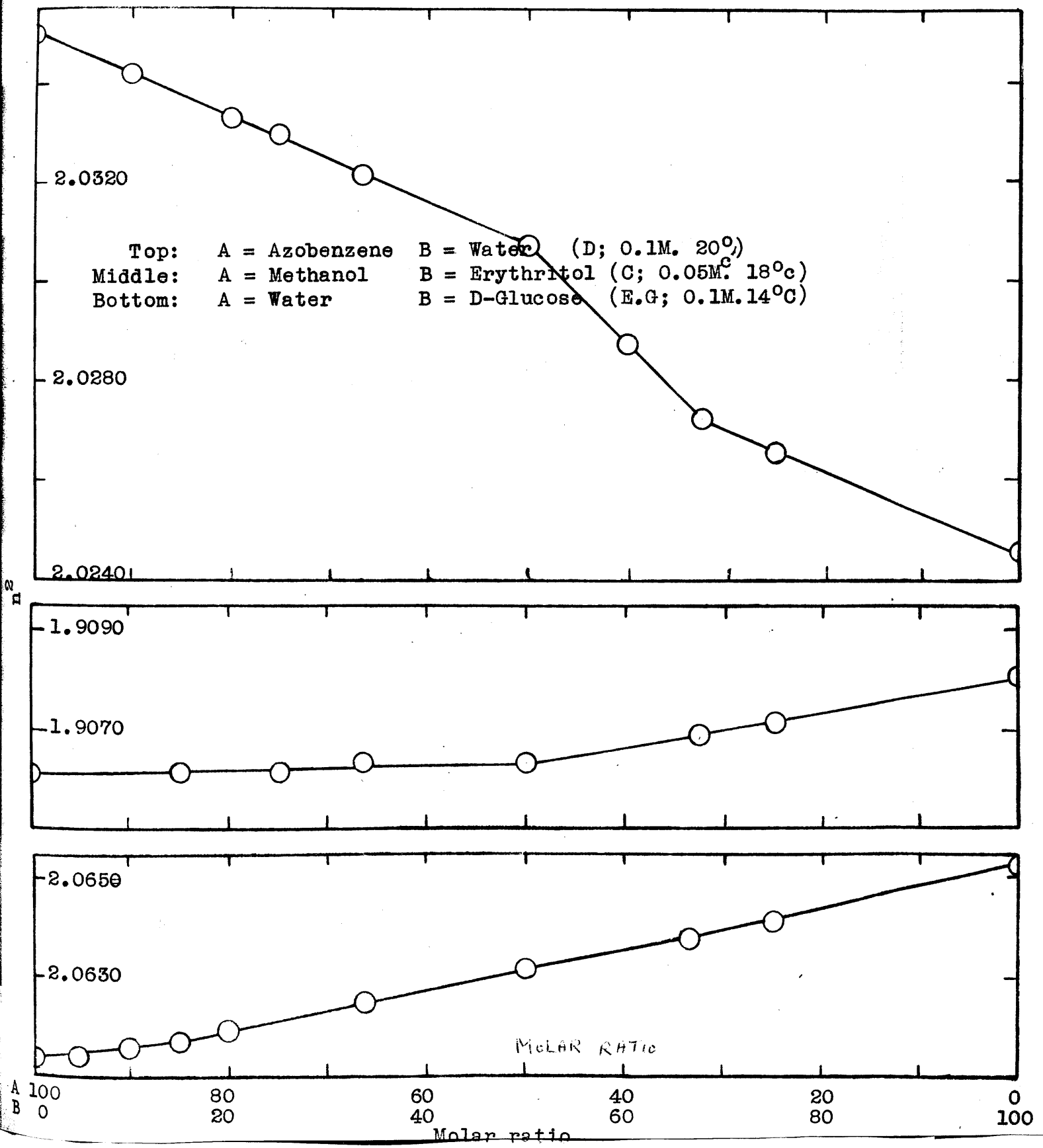
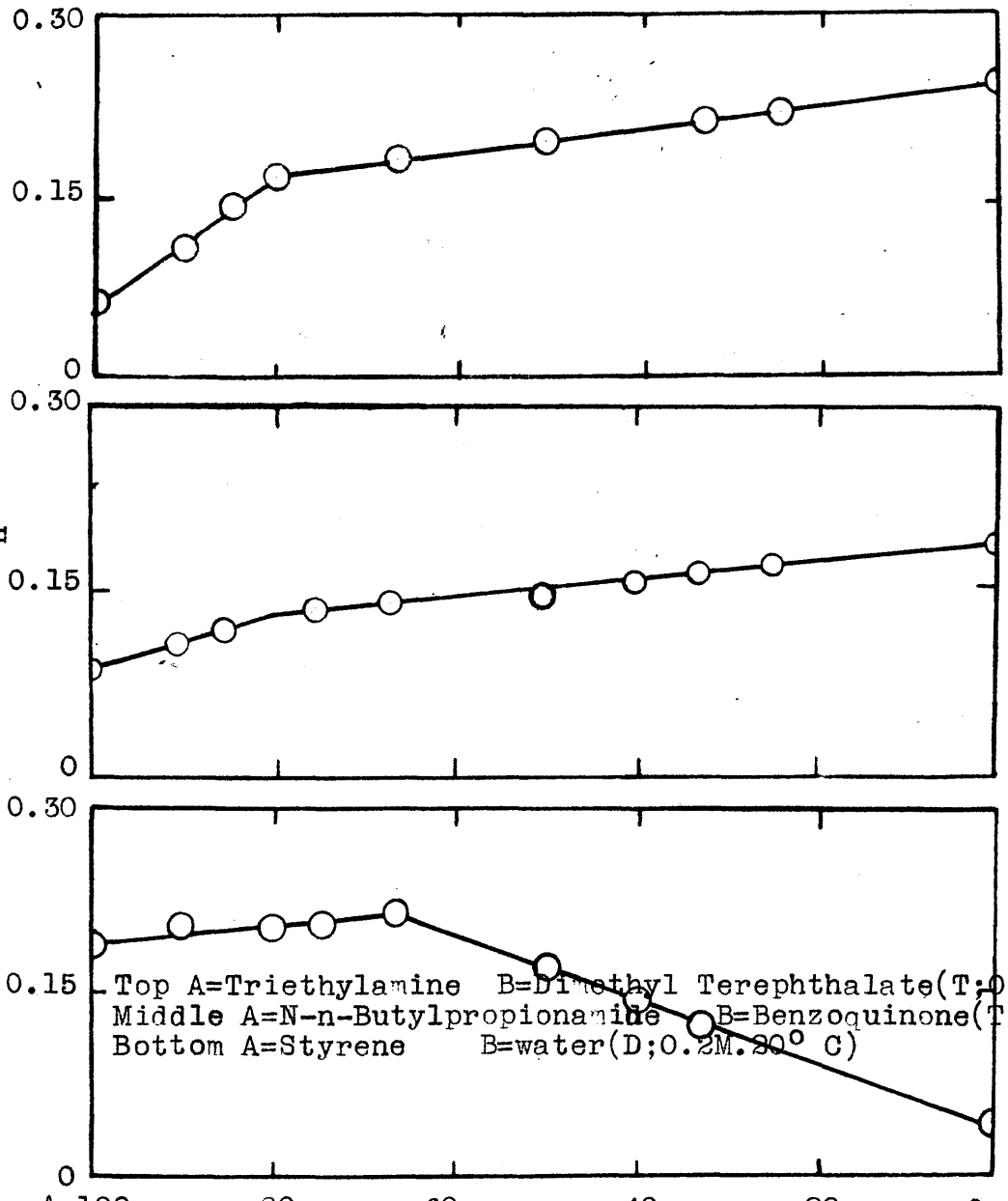
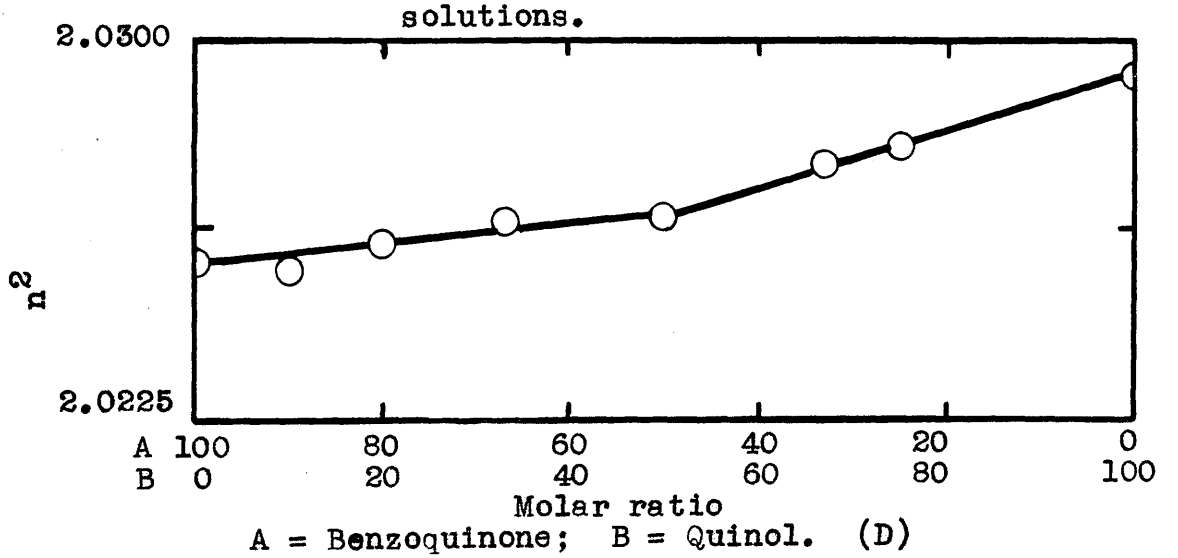


Fig.16A . Relation between square of refractive index* and component ratio in binary solutions.



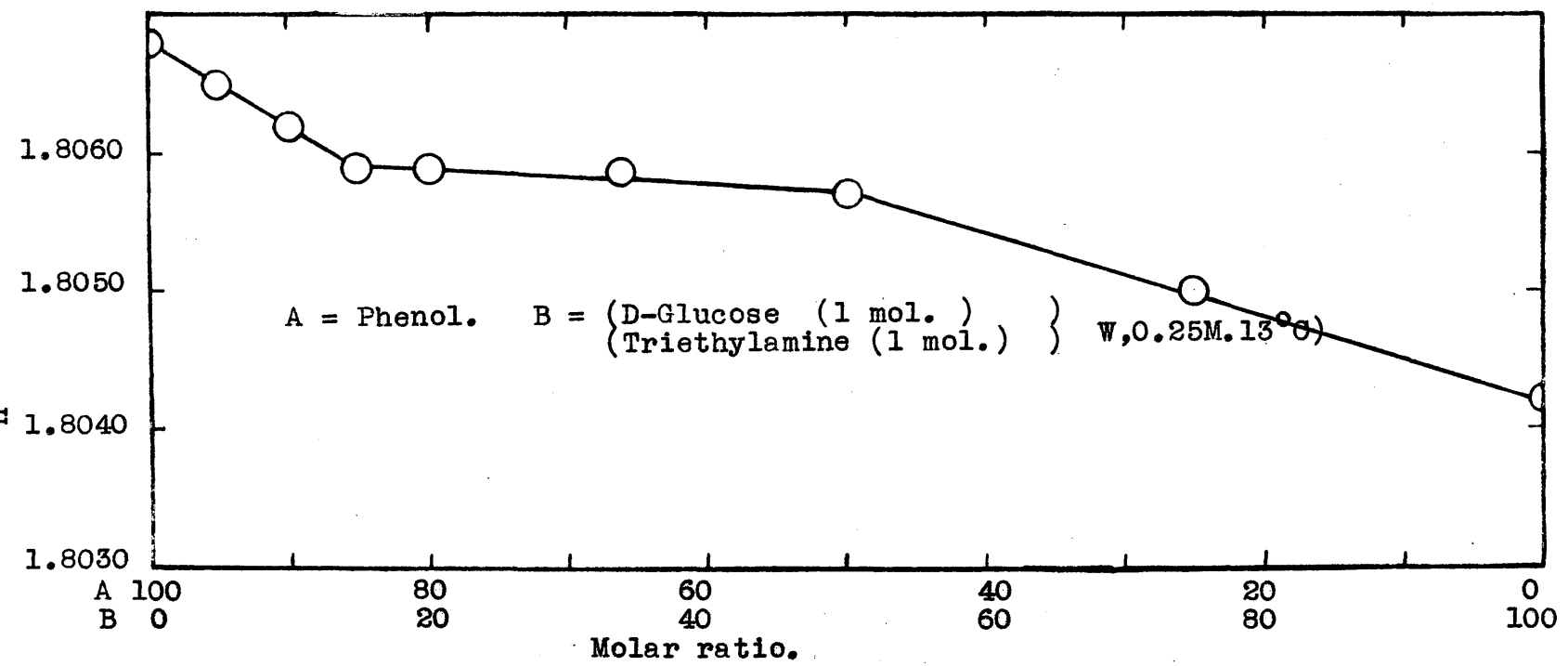
*The ordinates show increments of square of refractive index, on arbitrary base lines. not absolute values.

Fig.17A . Relation between square of refractive index and component ratio in binary solutions.



A = Benzoquinone; B = Quinol. (D)

Fig. 18A. Relation between square of refractive index and component ratio in ternary solution.



PART III.

Sorption Studies.

Section 1. The Sorption of Logwood Colouring Matters by Fibres.

Section 2. Miscellaneous Sorption Data.

PART III. SORPTION STUDIES.

Section 1. The Sorption of Logwood Colouring Matters by Fibres.

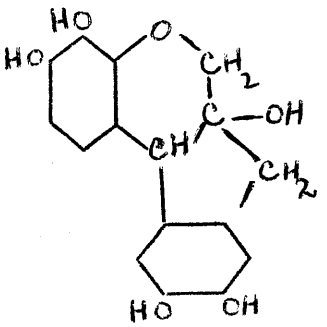
The investigations made in recent years upon the theoretical basis of dyeing mechanisms have been concerned with synthetic dyes, usually sulphonated azo dyes. Little or no attention has been paid to the use of natural colouring matters. Scientific research has thus reflected the prevailing technical practice, for the natural products are now of much less importance. Nevertheless a study of the dyeing processes of the natural materials should have some intrinsic interest, not only because of the former importance of these products, but also because the structural features responsible for their colour and dyeing properties differ markedly, in most cases, from those of their synthetic counterparts.

A systematic investigation has therefore been undertaken to elucidate the details of the processes by which logwood black in particular is formed in the fibre. This natural colouring matter is still widely used and moreover, its molecular structure has some resemblance to that of natural tannins, so that its reactions with protein fibres and metals may have interest in other directions. The history and properties of the material are admirably summarised by Bird and Newsome, J.S.D.C., 66, 423 (1950), who made very thorough investigations to establish the dyeing and mordanting methods necessary to promote the best fastness properties. Logwood is the heartwood of the tree Haematoxylon campeachianum, grown mainly in the West Indies. Introduced to Europe by the

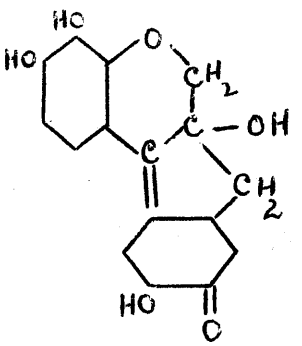
Spanish after their American conquests, its use became so well established that by the middle of the nineteenth century it had become the most important of all dyes, but with the increasing use of synthetic products, often of superior fastness properties, its importance has declined, though it is still in quite widespread use, and indeed is the only natural colouring matter which is now consumed in large quantities.

When mordanted with chromium logwood produces a shade of black with an attractive bluish cast, and it can be used on wool, silk, leather, nylon and acetate rayon. Aluminium, copper, iron and tin have been used as mordants in earlier times, but chromium is almost exclusively used to-day. The colouring principle of logwood is haematoxylin (IB(a))(C.I. No. 1246), which is itself colourless, but is readily oxidised to the dark brown coloured haematein (IB(b)).

IB(a)



Haematoxylin



IB(b)

Haematein

The structures of all these compounds were first fully determined by Perkin and Robinson, J.C.S.Trans., 93, 489, 1115 (1908) (see Perkin and Everest, The Natural Organic Colouring Matters (London: Longmans Green and Co. Ltd., 1918), though they

have never been synthesised. The Brazil wood colouring matters produce reddish-purple to brown shades on chromium mordant, of indifferent fastness properties and of little current importance.

The Apparent heat of sorption.

The heat change observed when a solute is sorbed by a fibre, which is actually the algebraic sum of the changes involved in removing the solute from solution and then attaching it to the surface, and which is here referred to as the apparent heat of sorption, is useful for certain comparative purposes when studying the nature of bonds formed during sorption. While it gives no true indication of the actual heat of formation of the bond which unites solute and fibre, it can be used in comparing the nature of attachment of different solutes on the same fibre, or of the same solutes on different fibres and it appears to be additive (Cameron, Giles, Lockhart, and Moodie, to be published). It has been used in this way in the present work, and has been determined ~~from a derivation of the Van't Hoff equation:-~~ as described below

$\Delta H_{as} = \left[RT_1T_2 / (T_1-T_2)\right] \ln C_{B2}/C_{B1}$, where ΔH_{as} is the apparent heat of solution and C_{B1}, C_{B2} are bath concentrations (strictly, activites, but only dilute solutions are used) in equilibrium, at temperatures T_1 and T_2 respectively, with a given concentration in the fibre.

Determination of Apparent Heat of Sorption.

This has been measured by a derivation of the Van't Hoff equation, relating the change of heat of reaction with temperature to the equilibrium constant k, of a reversible reaction:-

$$\Delta H^{\circ}/_{RT} = C - \ln k$$

If measurements are taken at two temperatures, T_1 and T_2, sufficiently close for ΔH° to be regarded as constant, we have

$$\Delta H^{\circ}/_{RT_2} - \Delta H^{\circ}/_{RT_1} = -\ln {}^{C_{F_2}}/_{C_{B_2}F} + \ln {}^{C_{F_1}}/_{C_{B_1}F}$$

where C_{B_1}, C_{F_1} etc. are the concentrations (strictly the activities) of the solute in the bath and the fibre, respectively, and F is the activity of the fibre itself. If dilute solutions are used and two values of bath concentration, C_{B_1} and C_{B_2}, at the two temperatures are selected from the isotherms such that the concentration of solute in the fibre in both cases is identical, then we have :-

$$\Delta H^{\circ} = \left[RT_2T_1/(T_1 - T_2)\right] \ln C_{B_2} / C_{B_1}$$

Sorption Mechanism : Haematoxylin.

In order to obtain an insight into the chemistry of their attachment to the fibre, isotherms for the sorption of the various colouring matters were obtained at various temperatures, the period required for equilibrium to be reached having first been ascertained by rate measurements.

Haematoxylin and brazilin. Typical isotherms for haematoxylin are shown in Figs. 1B and 2B. An interpretation of these follows.

Cellulose.

The substantivity of haematoxylin for cellulose is so low as to be hardly measureable. This is clearly owing to the molecule

not being sufficiently long for the cellulose molecule to exert an appreciable attractive force upon it when the two are adlineated. Its molecule is, in fact, of comparable length to those of simple monoazo dyes, which also have virtually no substantivity, for the same reason.

Cellulose Acetate.

Sorption of dyes by this fibre is believed to take place through hydrogen bonds between its acetyl groups and suitable groups, e.g., OH, NH_2, in the dye.(x) Haematoxylin obviously has a number of possible hydrogen-bonding sites in its molecule. All four hydroxy-groups should be effective, since the chelate bond uniting pairs of o-hydroxy groups is 5-membered and weak (Pauling) so it is likely to be broken in water. Dielectric constant measurements in a solvent (Fig. 3B) made by the method of Giles, Rose and Vallance(J.C.S. 1952, 3799) show that haematoxylin has five groups capable of combining with phenol (the fifth must be either the ether oxygen or the alcoholic group). There is also an abundance of acetyl groups in the fibre available as sorption sites. One should thus expect at least all four hydroxy-groups in the compound to be attached to the fibre, for which it will therefore act as a cross-linking agent. It is, in fact, sorbed to a much less extent (of the order of 5

(x) It has recently been suggested (Allingham et al) that the bond may in some cases, if not in all, lie between the $-CH_3$ of the acetyl group and O or N in the dye.

per cent by weight) than in phenol (>100 per cent by weight, Marsden and Urquhart).(J. Text. Inst., 1942, 33 T105)

The apparent heat of sorption of phenol for cellulose acetate is given by Marsden and Urquhart as about -3k cal. per mol. but that of haematoxylin for this fibre varies over a range of -4.5 to -8.5 k cal. per mol, from determinations made from the $\int$-shaped isotherms of Fig. 1B. If this represents the formation of four hydrogen bonds their individual apparent heat of formation is clearly less than that reported by Marsden and Urquhart, J. Text. Inst., 1942, 33, T105 for phenol, but the sorption isotherms of phenol for cellulose acetate (Fig.4B) gave a value of Ca - 1.5 k cal. per mol., and on calculating on the basis of four hydrogen bonds, the value falls within the range of the value determined for haematoxylin on cellulose acetate. (Apparent heat of sorption of phenol for cellulose acetate as determined by (Cameron, Private Communication) =-2.5 k cal. per mol).

Nylon, Wool.

The internal hydrogen bonds in these fibres appear to be too strong to be broken by many groups in solutes (Allingham, Giles and Neustädter, in the press), but phenolic groups are in many cases able to break them, and thus to form new bonds with the fibre molecule; e.g., phenol itself, which readily swells and dissolves nylon. Haematoxylin should therefore be able to act as a cross-linking agent for nylon or wool. It is found, e.g., that, by a similar method to that reported above for haematoxylin and phenol, four molecules of dimethylformamide

can become associated with one of haematoxylin. The apparent heat of sorption of phenol, from aqueous solution, by nylon is about -3 ± 0.5 k cal. per mol. (Brand and Laidlaw, theses, Glasgow 1949), so that if a nylon molecule behaves like the amide group in dimethylformamide, one should expect a value for haematoxylin lying between -10 and -14 k cal. per mol. Actually the isotherms (Fig. 1B) give a value of ca -13 ± 1 k cal., which is in good agreement with prediction. The bonds are probably of NH---O type rather than OH---O, because (a) the $>C=O$ group may be preferentially protected by water (Arshid, Giles, McLure, Ogilvie and Rose, to be published) and (b) the data agree with the apparent heat of formation (ca -3.3 k cal. per mol.) of NH---O bonds by sorption from water derived indirectly, from experiments on α-Al_2O_3(x) (Arshid, Mehta, private communication).

The corresponding value for wool, however, derived from the isotherms of Fig. 2B, is about -13 k cal. per mol., which is also in good agreement with prediction.

Owing to the small quantity of brazilin available and the difficulty of analysing it (unlike haematoxylin it does not form water-soluble lakes) no sorption experiments were made with it, but there seems no reason to doubt that it would show very similar behaviour to haematoxylin, especially as brazilein and haematein behave almost identically in sorption (Desai, Ph.D. thesis 1948).

(x) -4.5 k cal. for OH---O from toluene or water; -3.3 k cal. for NH---O from toluene.

Absorption data of haematoxylin for cellulose acetate, nylon and wool are given in Tables 1B, 2B and 3B respectively. Table 4B gives the data of phenol for cellulose acetate.

TABLE 1B.

Temp. 60°C.		Temp. 50°C.	
Equilibrium Concentration g/l	Absorption m. mol. /g.		
3.80	0.033	3.60	0.066
5.50	0.088	5.20	0.133
6.90	0.183	6.50	0.256
8.72	0.213	8.0	0.333

TABLE 2B.

Temp. 60°C.		Temp. 50°C.	
Equilibrium Concentration g/l	Absorption m. mol. /g.		
1.32	0.113	1.2	0.133
3.12	0.146	2.85	0.191
6.92	0.180	6.60	0.233
10.6	0.199	8.50	0.249
		10.40	0.266

TABLE 3B.

Temp. 58°C.		Temp. 51°C.	
Equilibrium Concentration g/l.	Absorption m. mol./g.		
3.80	0.033	3.40	0.099
9.20	0.132	8.40	0.264
10.70	0.214	12.0	0.495
13.0	0.33		

TABLE 4B.

Temp. 50°C.		Temp. 30°C.	
Equilibrium Concentration g/l.	Absorption m. mol./g.		
1.356	0.343	1.288	0.378
4.666	0.709	4.467	0.816
6.294	0.907	6.113	1.004
7.906	1.114	7.635	1.258

Absorption of haematoxylin on silk was tried without success, because of the difficulty of a precipitate occurring on keeping haematoxylin with silk for a prolonged period of 5-6 hours at a temperature of 50°-60°C.

Haematoxylin is a true phenol and not an acid. Its titration curve shows no change in sorption values over a wide range of pH value (Fig. 5B), for being uncharged, its molecule is uninfluenced by the charge on the fibre. The haematein anions, on the other hand, are unable to penetrate the fibre against its normal negative charge, until this has been reversed by acid. The molecule is almost entirely dissociated on the alkaline side of pH 5 and so neither undissociated molecules nor anions enter the fibre in any numbers.

EXPERIMENTAL.

Preparation and Purification of Materials.

Haematoxylin.

The commercial pure product (100g.), a buff-coloured powder, was dissolved in 500 c.c. boiling water containing a little sulphur dioxide; the solution was clarified with charcoal, filtered and cooled. The long thin colourless needles which separated were washed with water containing a little sulphur dioxide and dried in a desiccator. The product separating from concentrated solutions is a monohydrate, the stable form in air; on rapid heating this loses water and melts at 140°C. Slow heating produces an anhydrous form, m.p. 240°C. (decomp.). From dilute aqueous solutions a trihydrate separates, m.p. ca.100°C. (depending on rate of heating). This slowly changes to the monohydrate on keeping.

Haematein.

Pure commercial haematoxylin (100g.) was dissolved in 1250 c.c. hot water, 125 c.c. ethanol added and the solution cooled; 140 c.c. of sodium hydroxide solution (40%) W/V) were then added, with stirring and cooling to below 25°C., followed gradually by addition of 37 c.c. aqueous hydrogen peroxide (100 vol.) in 50 c.c. of water. After five minutes the solution was neutralised with dilute hydrochloric acid (10%) and acidified with dilute acetic acid (25%). An amorphous brown precipitate of haematein settled out, which was filtered, washed with water and then gently warmed on a water bath in 700 c.c. of water, whereby it was changed into the crystalline form. The crystals

were filtered off, washed with methanol and dried. Yield, about 70%.

Several other methods were also used, but all gave low yields. They included oxidation of alkaline solutions of extracts of logwood chips or of pure haematoxylin by air bubbling for $>$ 6 hr., and recrystallisation of dried commercial "red haematein paste" from ethanol, after addition of ether to remove tarry matter.

Haematein forms minute red-brown platelets, with a greenish lustre (m.p. 210-216°C.). It is sparingly soluble in hot water (2.1 g/l. at 60°C). Care must be taken to avoid over-heating when dissolving this compound in water, owing to the danger of oxidative decomposition.

Brazilin. (By D.J. Duff)

A mixture of 100 g. "Brazil Wood Extract O" powder, 200 c.c. water and 25 c.c. sodium bisulphite solution (25% SO_2) was heated on the water bath until solution was complete, then diluted with water to 400 c.c. The liquid was then transferred to a continuous ether-extraction apparatus and extracted for several consecutive days with fresh ether, the extract being withdrawn each day and the whole finally evaporated to dryness and the residue recrystallised first from acetone and then from water. The yield is small because much of the product is retained by resinous matter and cannot be crystallised.

Brazilin forms colourless leaflets (changing to a pale cream colour in air) of monohydrate, m.p.175°C. (The Colour Index mentions also a hydrate with $1\frac{1}{2}H_2O$, giving needle-shaped crystals).

Cellulose acetate.

Powdered secondary cellulose acetate (acetyl value 53.6%) was used.

Nylon.

(15 fil. 45 den. bright drawn yarn) was scoured in a 0.5/100 solution of a non-ionic detergent (Lissapol N) with addition of a little ammonia, at 60°C. for 15 min., then well rinsed in distilled water.

Silk.

Raw domestic silk fibre was treated in 3/100 soap solution at b.p. for 1 hr., then again in 1/100 soap solution at b.p. for 30 min., well rinsed in distilled water, and dried. Before use, traces of yellowish solvent-soluble colouring matter were removed by Soxhlet extraction with toluene.

Viscose Rayon.

Courtaulds "Fibro" staple fibre was scoured in weak Lissapol N solution, then well rinsed in distilled water.

Wool.

Root ends of a Lincoln fleece (or in some experiments, woollen fabric cut in small pieces) were scoured in a dilute solution of Lissapol N at 60°C. for 5 min., rinsed first in hot and then in cold distilled water, dried at 95°C., and extracted with ether in a Soxhlet apparatus for 24 hr.

Before use all fibres were first oven-dried at 100-110°C., then allowed to condition in air at room temperature for 24 hr. and stored in stoppered bottles.

Sorption Experiments.

For most of the sorption experiments, except those made at b.p., the fibre samples (1 g.) were each treated with 20 c.c. of liquid in tightly stoppered test-tubes, which were fixed by phosphor-bronze spring clips to a shaft mechanically rotated at 25 r.p.m. under water in a thermostat tank. By this means they were given a constant and regular end-over-end agitation. Even so, when loose fibres are used, some difficulty is experienced in obtaining adequate movement and penetration of the fibres, which tend to stick as a lump at the end of the tube. This difficulty was surmounted by use of a perforated glass tube fibre-holder, of caterpillar shape (Fig. 6B). This is designed to fit loosely inside the test tube. The fibre is packed into the holder and the ends plugged with glass wool or polythene. During agitation the holder falls to and fro in the test tube, with a regular motion, out of phase with the movement of the liquor which is thus caused to pulsate into and out of the fibre *via* the perforations.

Haematoxylin.

The fibre (1 g.) was placed in a ground-glass stoppered test tube containing 20 c.c. of haematoxylin solution, to which was added a trace of sodium hydrosulphite to prevent oxidation. The liquor after the test was filtered through glass wool and the filtrate and water washings combined and brought to pH 5.9 by cautious addition of ammonia. This is the best value for satisfactory lake formation. A slight excess over the theoretical

quantity of 5% potassium chromate solution was then added, the mixture boiled 30 sec. and the solution of the blue lake so formed determined colorimetrically after suitable dilution with water.

Some experiments were carried out without the addition of sodium-hydrosulphite and the lakes from line dye bath (for estimation), prepared directly instead of bringing them just to pH 5-9, but in all such cases blank solutions of haematoxylin were kept along with the tubes (set for absorption) in order to ensure that there was no oxidation.

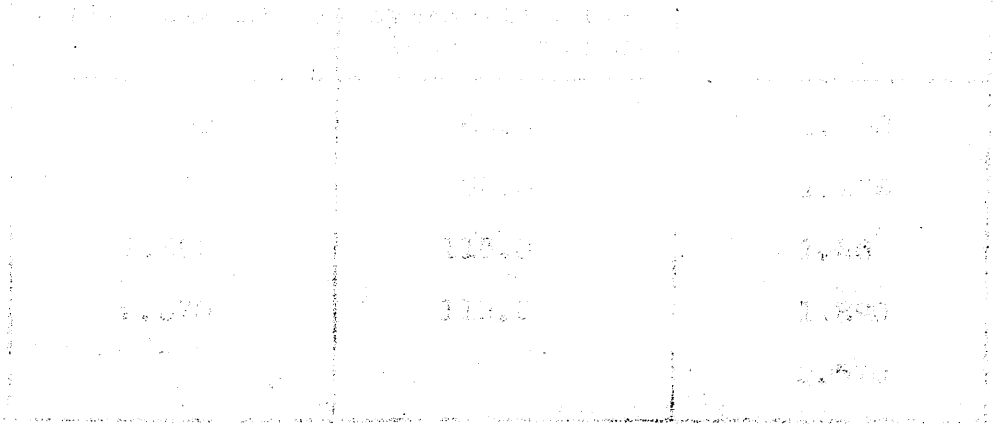
Haematein.

The pure colouring matter (2.0 g) was pasted with "Cellosolve" and added to boiling distilled water (1L), after addition of a trace of sodium hydrosulphite to remove oxygen. After boiling 15 mins. to effect complete solution, the solution was allowed to stand a few hr., filtered and stored under carbon dioxide in a well-stoppered bottle. For preparing the baths, at lower pH values both the stock solution of colouring matter and the water used for dilution were first brought to the same pH value with dilute sulphuric acid. It is essential to remove all air to avoid oxidation during the tests. For the experiments at lower temperatures this was ensured by passing a brisk stream of carbon dioxide through the liquor for 2 min. just before closure of the tubes by rubber stoppers. For the experiments, at b.p., flasks and reflux condensers were used, and a gentle stream of carbon dioxide was passed into the liquor throughout the experiment and allowed to escape up the condenser. The residual bath

liquors were analysed by the direct colormetric method, after making the liquors slightly alkaline with ammonia.

Padding process.

The good solubility of haematoxylin and the results of the sorption and lake-forming experiments suggested that the compound could be applied satisfactorily to wool from a fairly strong aqueous solution by padding, the lake thereafter being formed by passing the treated fabric immediately into a boiling solution of potassium chromate. This proved to be practicable on the laboratory scale, but no further trials of the method were attempted.



Section 2 (Part III). Miscellaneous Sorption Data.

Sorption on Anodised Aluminium.

Experimental and Discussion.

Dodecyl-aniline → R-acid.

Dodecyl-aniline → R-acid was prepared and purified (purity 85%) and sorption isotherms on anodised aluminium were determined (Table 5B).

TABLE 5B.

Temp. 60°C.		Temp. 50°C.	
Equilibrium Concentration. Milli Mols/Litre.	Sorption. Milli Mols of dye/KG. of anodised aluminium.	Equilibrium Concentration.	Sorption.
0.590	65.0	0.590	80.0
1.235	85.0	1.235	114.0
1.890	113.0	1.56	126.0
2.570	119.0	1.890	138.0
		2.570	149.0

Calculated heat of reaction ΔH = - 9.3 K Cal/Mol.

Aniline → R-acid.

A laboratory prepared sample of the dye was prepared and used to determine the sorption isotherms on anodised aluminium.

TABLE 6B.

Temp. 52° C.		Temp. 30° C. ?	
Equilibrium Concentration Milli Mols/Litre.	Sorption on the foil Milli Mols/KG	Equilibrium Concentration	Sorption on the foil.
0.II75	76.2	0.0875	79.6
0.230	II8.I	0.205	I36.7
0.400	I28.4	0.325	I88.9
0.575	I27.9	0.505	I89.7

Calculated heat of reaction $\Delta H = -4.8$ K Cal/Mol. ?

It was decided to trace the effect of the long chain, substituted in the dodecyl-aniline → Racid molecule, on sorption by comparing it with aniline → R-acid, having a similar configuration. The values of heats of reaction of both the compounds indicate a higher value for dodecyl-aniline → R-acid, which may be accounted for by increased van der Waals attraction. It was originally believed that the heavy long chain on dodecyl-aniline → R-acid molecule would be causing steric hindrance, hence exposure of less sites for hydrogen-bonding, but from the results, this is not the case.

The Sorption curves of dodecyl-aniline → R-acid and aniline → R-acid are shown in Figures 7B and 8B respectively.

2:4 - Dinitrophenol.

Sorption of 2:4 - Dinitrophenol on anodised aluminium

was studied with a view to finding whether the nitro groups present in the molecule have any effect on sorption. The heat of reaction obtained for 2:4 - dinitrophenol is -4.0 K Cal/mol., whereas that of phenol is -4.5 K Cal/mol; thus showing there is unlikely to be the attachment of nitro groups to anodised aluminium.

As the values of heats of reaction for both the compounds are nearly the same, it appears that the hydroxy group, common to both the compounds, is effective in the mode of attachment.

The sorption data of 2:4 - dinitrophenol and phenol are shown below in Tables 7B and 8B and curves in Figures 8B and 9B respectively.

2:4 - Dinitrophenol.

TABLE 7B.

Temp. 60°C.		Temp. 50°C.	
Equilibrium Concentration Milli Mols/Litre.	Sorption. Milli Mols/KG. of anodised aluminium.	Equilibrium Concentration.	Sorption.
0.442	136.7	0.4077	156.2
0.7473	351.4	0.6624	390.6
1.155	507.6	1.086	546.7
1.783	537.3	1.655	609.1

Phenol.

TABLE 8B.

Temp. 57°C.		Temp. 46°C.	
Equilibrium Concentration G/Litre	Sorption Milli Mols/G.	Equilibrium Concentration	Sorption
4.86	0.8418	4.83	1.159
8.875	6.836	8.85	8.183
13.9	7.50	18.7	8.772
18.91	7.432		

Analysis of phenol.

Phenol was determined by the bromine method. Approximately decinormal bromine solution was prepared by dissolving 2.76 g. of potassium bromate and 15.0 g. of potassium bromide in distilled water and diluting to one litre. This solution was standardised against decinormal sodium thiosulphate solution by adding potassium iodide and hydrochloric acid and titrating the liberated iodine in the usual manner. The volume of phenol solution to be titrated was measured in a 500 c.c. glass stoppered bottle and 50 c.c. of distilled water and 5 c.c. of hydrochloric acid were added to it. The standard bromine solution was added from a burette with constant shaking until a permanent yellow colour was obtained. 10 c.c. of 10% potassium iodide solution was then added. The free iodine was titrated against decinormal

sodium thiorsulphate solution, using starch as an indicator. From the amount of bromine solution consumed by phenol, the amount of phenol can be calculated according to the following relationship:-

1c.c. of $N/_{10}$ bromine solution $\equiv$ 0.0015675 g. phenol.

Effect of Solvents on Sorption.

It is shown in the hydrogen-bonding part above that organic solvents have an appreciable effect on the bonding affinities of solutes. They may similarly affect sorption. This point was examined in a few sorption experiments.

Benzene - azo - $\underline{\alpha}$ naphthylamine and benzene - azo - $\underline{B}$ naphthylamine were found to show no sorption on anodised aluminium, using dry benzene as a solvent. But by employing carbon tetrachloride as a solvent, a fair amount of sorption of both compounds was observed. The solvent (benzene) may be protecting the effective (amino-) group in the compounds, thus preventing it from combining with the substrate. The sorption curves for benzene - azo - $\underline{\alpha}$ naphthylamine and benzene - azo - $\underline{B}$ naphthylamine are illustrated in Figure 10B, and quantitative data are given in Tables 9B and 10B.

Benzene ⌒ azo - α naphthylamine.

TABLE 9B.

Temp. 60°C.		Temp. 50°C. ?	
Equilibrium Concentration Milli Mols/Litre.	Sorption. Mille Mols/ KG.	Equilibrium Concentration. Milli Mols/Litre.	Sorption. Milli/Mols/ KG.
0.1518	12.34	0.2683	24.77
0.2784	20.6	0.3643	28.3
0.5667	32.9	0.4554	35.4
0.7691	34.5	0.7491	42.4

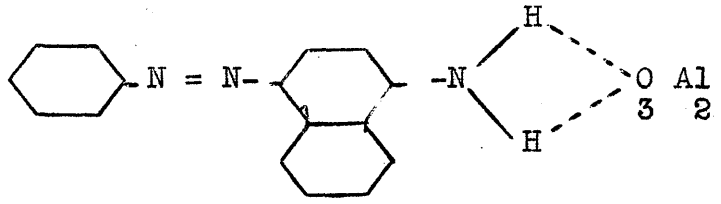
Benzene ⌒ azo - β - naphthylamine.

TABLE 10B.

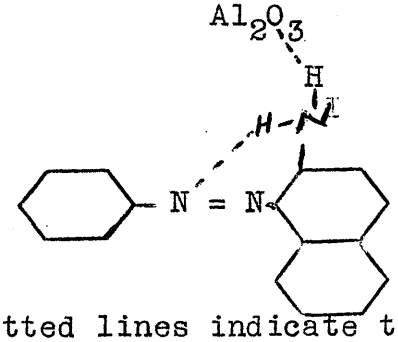
Temp. 50°C.		Temp. 40°C. ?	
Equilibrium Concentration	Sorption	Equilibrium Concentration	Sorption
0.1498	6.64	0.1498	6.86
0.2885	8.30	0.3846	11.44
0.3848	11.06	0.4839	12.58
0.5851	12.17	0.5851	12.58
0.7894	11.06	0.7854	13.73

Absorptiometric measurements were made on the Unicam SP500 absorptiometer at a wavelength of 4200A (α-compound) and 4350A (β -compound)&heats of reaction obtained. These values ⁎ suggest that there are two hydrogen bonds operative in benzene - azo-α-naphthylamine (a) but only one in the case of benzene - azo - β - naphthylamine. This could be explained as due to chelation between one of the nitrogen atoms of the azo group and a hydrogen from amino group, thus leaving only one hydrogen atom free to bond with anodised aluminium (b).

(a)



(b)



The dotted lines indicate the position of hydrogen-bonds. The results obtained appear to be quite in agreement with the theoretical interpretation.

The sorption of phenol on anodised aluminium, using ethanol as a solvent, was also examined. Solutions of varying concentrations, ranging from 5 g/l. to 20 g./l. were tried at two different temperatures, 35°C. and 40°C. for 72 and 48 hours, respectively, but no absorption was found at all.

⁎ (ΔH -6.5 K cal/mol for α compound and - 3.0 K cal/mol for β compound)?

Use of Bridging Compounds.

Benzene - azo - α - naphthylamine in benzene (dry) showed no attachment to anodised aluminium, but on the addition of quinol to the dye solution, sorption appeared to occur, and was measured quantitatively. A 0.5 g./l. dye solution was prepared and different volumes of this solution, each containing 0.02 g. of quinol were employed for absorption. The results are given in Table 11B and absorption isotherms are shown in Fig. 11B.

The value of ΔH obtained is ca -8.5 to -9 Kcal/mol. Bonding may be due to cross-linking through quinol, which could be illustrated as below.

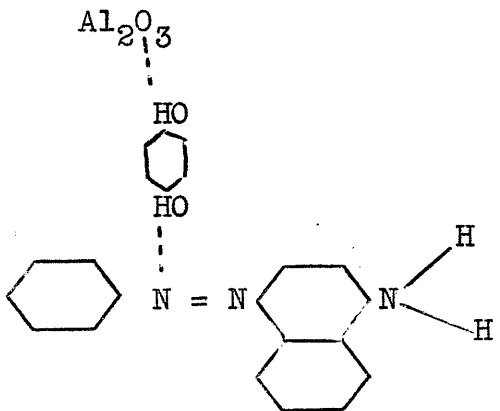


TABLE 11B.

Temp. 50° C.		Temp. 40° C.	
Equilibrium Concentration. Milli Mols/Litre.	Sorption. Milli Mols/ KG.	Equilibrium Concentration.	Sorption.
0.1518	6.50	0.3674	23.85
0.3825	14.20	0.5567	32.23
0.5716	22.70	0.7570	33.52
0.7674	27.08		

Without further knowledge of the apparent heats of formation of the OH...O and NH...O bonds from benzene solution, it appears that the present values are of the right magnitude.

Benzoquinone. This was used with the addition of resorcinol to act as a bridging compound, using dry dioxan as solvent. (Benzoquinone itself showed no affinity for anodised aluminium), but the dyebaths, after absorption gave very erratic absorptiometric results. This may be due to catalytic decomposition of the solution, which could have been confirmed by observing the absorption curves on the spectrophotometer before and after sorption, but this was not found possible because of the difficulty of measuring the absorption spectra below wavelength of 3000 Å.

B-Naphthyl acetate. As stated already in the hydrogen-bonding section, the hydrogen atom of the acetyl group shows an activity towards donor compounds, and it was thought that sorption of B-naphthyl acetate might thus be observed on anodised aluminium. The solvent employed was tert-butyl alcohol. The results obtained were very erratic; this may be attributed to the decomposition of the compound. (An ester of a phenol may be converted into an ortho- or para-hydroxy ketone or a mixture of both, by treatment with aluminium chloride. Some reaction of the same nature may be taking place with the aluminium oxide film). Ten different solutions of varying concentrations at different temperatures were observed, but the results obtained were very unsatisfactory. Methyl B-naphthol in ethanol and dimethyl terephthalate in toluene were tried also, but the same difficulty was encountered, which

suggests that catalytic decomposition may be taking place in all cases.

Absorption Studies on Cellulose.

Cotton.- Loose cotton was scoured in an anionic detergent Lissapol C (I.C.I.) (3 g./l.) and sodium carbonate (2g./l.) for about an hour at 80°C. and then thoroughly rinsed in cold water, to which a few drops of dilute acetic acid were added in order to neutralise any traces of alkali. The washed cotton was dried and conditioned for 48 hours at room temperature before it was used.

Solutes.- The dyes, benzeneazo→R-acid, p-nitro-benzeneazo → R-acid and o-nitro benzeneazo →R-acid were prepared and purified and the purity values checked by the oxidation method. p-Nitrophenol, naphthalene - β - sulphonic acid and anthracene - α - sulphonic acid were recrystallised from water. (Anthracene - α - sulphonic acid was prepared in the laboratory by R.V.R. Subramanian).

p-Nitro benzeneazo→R-acid.- The dye was tried in order to investigate its mode of attachment to the fibre. Stock solution (2g./l.) of the dye was prepared and different volumes of this solution, giving varying original concentrations, were kept in the thermostat at 30°C. and 50°C. for 96 and 72 hours respectively in presence of cotton, under agitation, in order to ensure complete absorption.

The data are given in the table below and absorption isotherms are shown in Fig. 12B.

TABLE 12B.

Temp. 30°C.		Temp. 50°C.	
Equilibrium Concentration G/L.	Absorption Milli Mols/KG.	Equilibrium Concentration	Absorption
0.60	164.5	0.48	45.6
1.32	307	0.72	68.4
1.7	329	1.94	136.8

The maximum absorption obtained is 329 m.mol./kg. The corrected value of ΔH is probably about -15 to -20 Kcal./mol).

O-Nitro benzeneazo→R-acid and benzeneazo→R-acid showed very little affinity, ~~which~~ could not be measured quantitatively. No explanation can be given for the behaviour of these dyes without further evidence. Either hydrogen bonding with free carboxyl group in the cellulose or van der Wall's attraction may be operating.

Anthracene-α - sulphonic acid.- It was hoped to measure the substantivity of anthracene-α- sulphonic acid. Maximum absorption values of ca 24 m.mol./kg. were found at both 50°C. and 60°C. This certainly suggests that hydrogen bonds are not involved, as of course, would not be expected. The absorption appears to be due to ion exchange. By neutralising the acid with dilute sodium hydroxide and then measuring its absorption, it was thought that different values might be obtained, but the results were the same as before. The results are shown in Table 13B and absorption

curves in Fig. 13B.

TABLE 13B.

Temp. 50°C.		Temp. 60°C.	
Equilibrium Concentration Milli Mols/L.	Absorption Milli Mols/KG.	Equilibrium Concentration	Absorption
1.852	9.3	1.502	4.9
2.674	23.3	1.841	9.7
3.634	24.1	2.674	23.3
		3.643	23.3

p-Nitrophenol.- The absorption of p-nitrophenol was examined both in water as well as dry toluene. Cotton was dried at 110°C. in an electric oven for 24 hours and then kept in various p-nitrophenol solutions (in toluene), of varying concentrations, at 50°C. and 60°C. for 48 and 24 hours, respectively. The solutions were measured on the "Spekker" absorptiometer, using ultra violet light. The optical density of solutions after keeping in contact with the fibre were somewhat higher than they were in the original solutions. This might be due to solvent evaporation, but on using water as a solvent, the optical density of the solutions was much higher than the original ones. This was repeated several times at different temperatures, but the same difficulty was encountered. This may be due to catalytic decomposition of p-nitrophenol. No further work was attempted with this substance.

Naphthalene - β-sulphonic acid.

The solutions were determined by titrating against 0.033N. sodium hydroxide solution using phenolphthalein as indicator. The maximum absorption at 50° and 60°C. (0.168 milli mols/G) was found to be the same, so, as with anthracene -α-sulphonic acid, absorption may be due to ionic exchange.

Wool.

α -Naphthol, β-naphthol, naphthalene and anthracene were tried as solutes in tests on wool, using various organic solvents, e.g., dry benzene, carbon tetrachloride, but none showed any affinity for wool.

It is supposed that the two hydrocarbons have insufficient van der Waal's attraction for the fibre and the naphthols may have too low hydrogen-bonding affinity to swell the fibre in the dry state.

These tests on wool were merely preliminary runs made in an attempt to correlate hydrogen-bonding data with sorption work, but no time was available to continue this part of the work.

Note. At a later stage in the work it was discovered that a thermostat apparatus had been behaving irregularly for the period covered by a few experiments. The sorption data concerned are believed to be reliable, but the recorded temperatures are probably incorrect. As there was insufficient time to repeat these experiments, the results obtained are recorded here and the appropriate temperature readings and some calculated heats of reaction are marked (?) doubtful.

Fig. 1B . Absorption Isotherms of haematoxylin on Nylon and Cellulose Acetate.

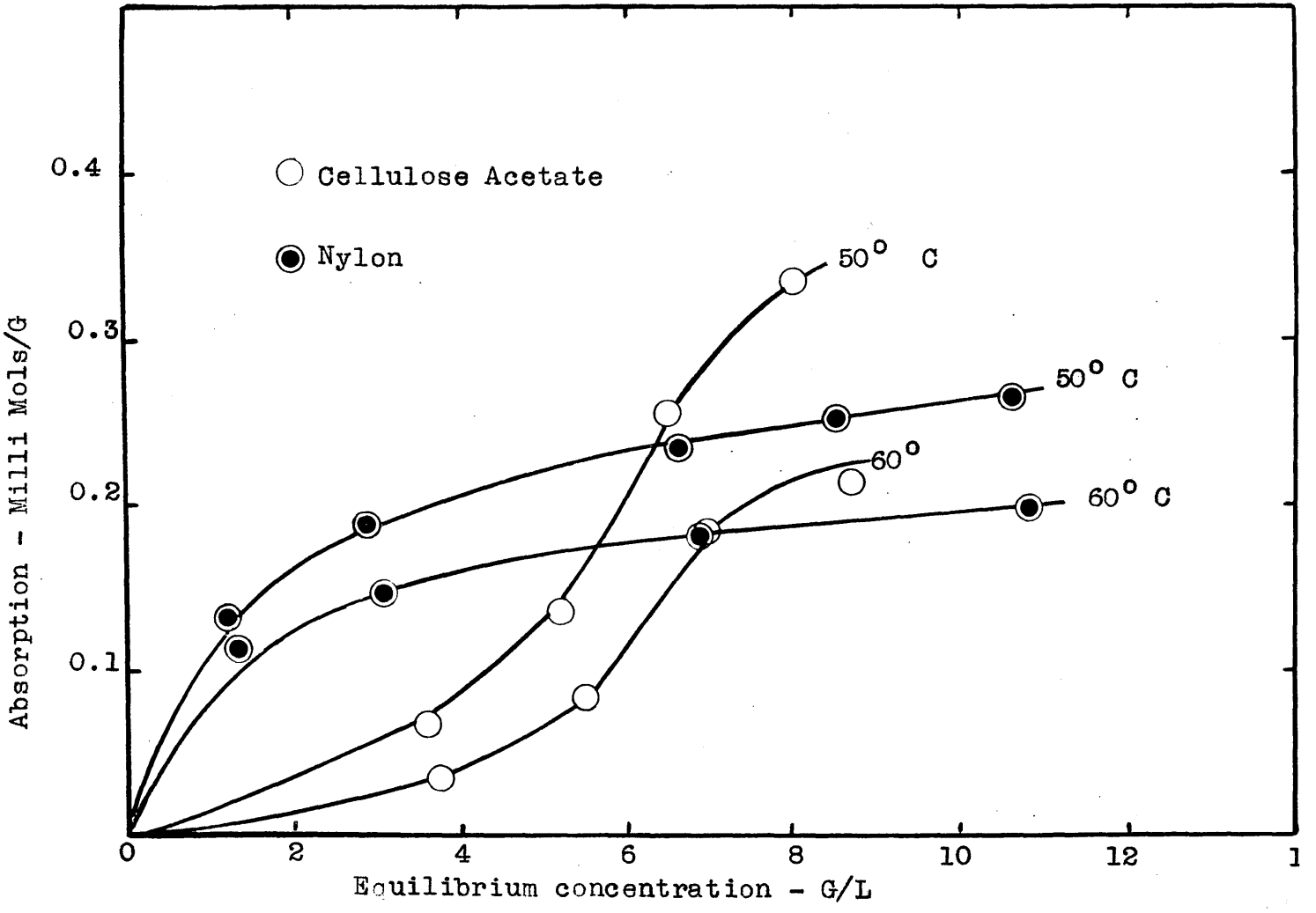


Fig. 2B. Absorption isotherms of haematoxylin on wool.

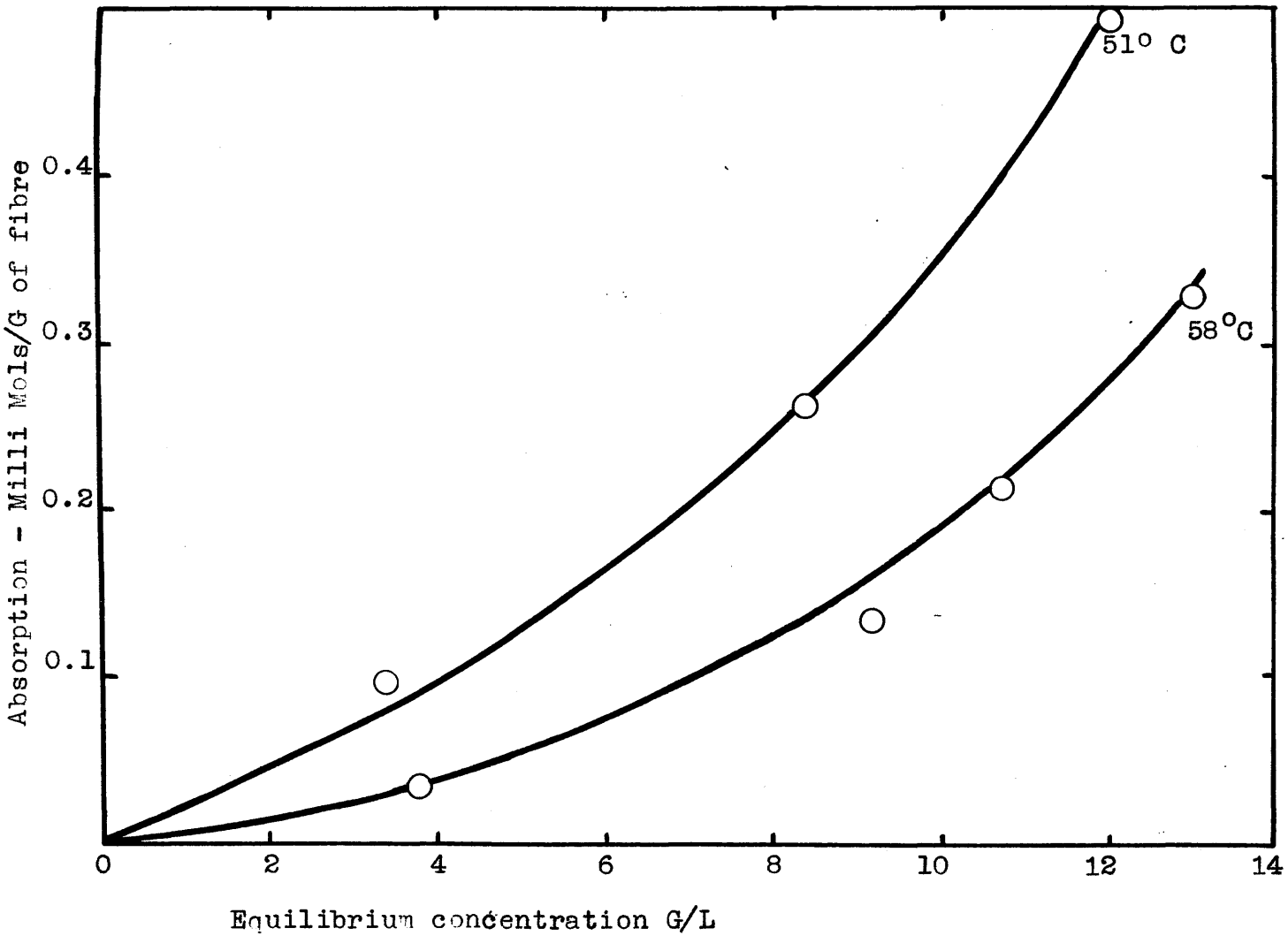


Fig. 3B . Relation between dielectric constant and component ratio in binary solutions.

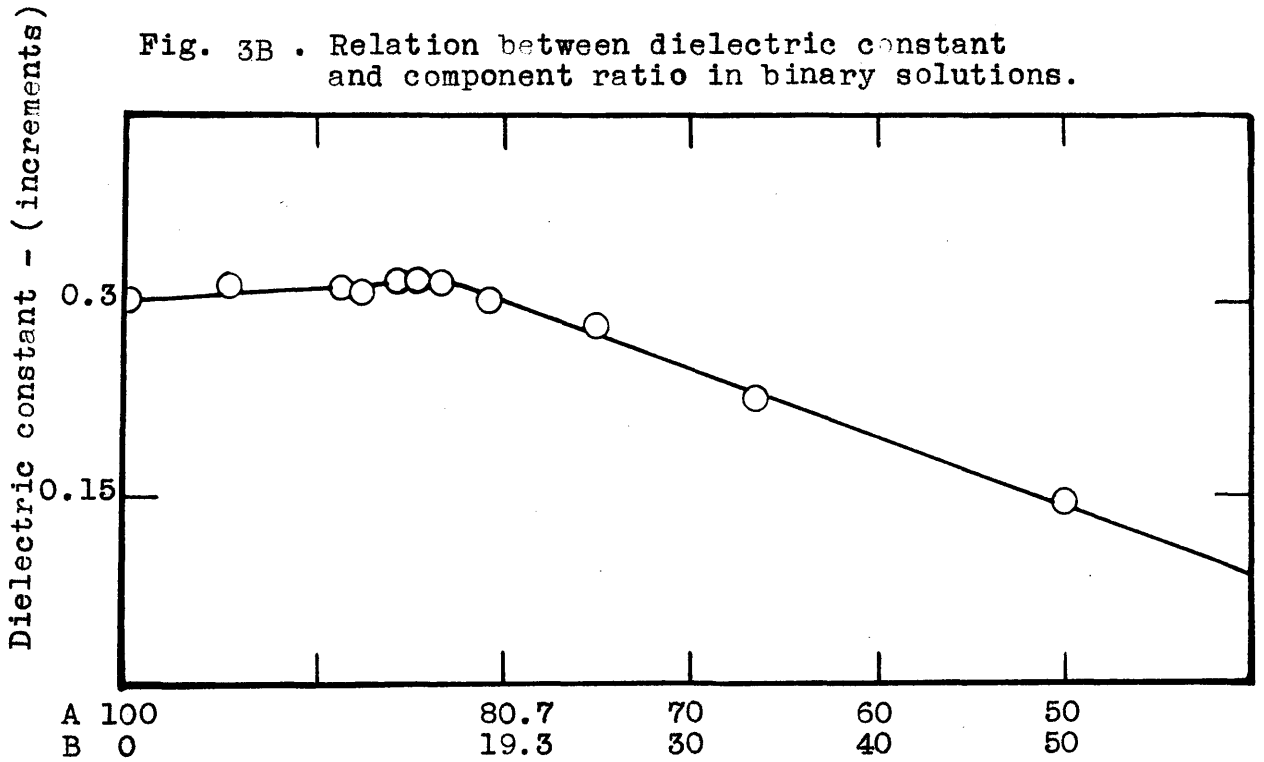


Fig. 4B . Absorption isotherms of phenol on Cellulose Acetate

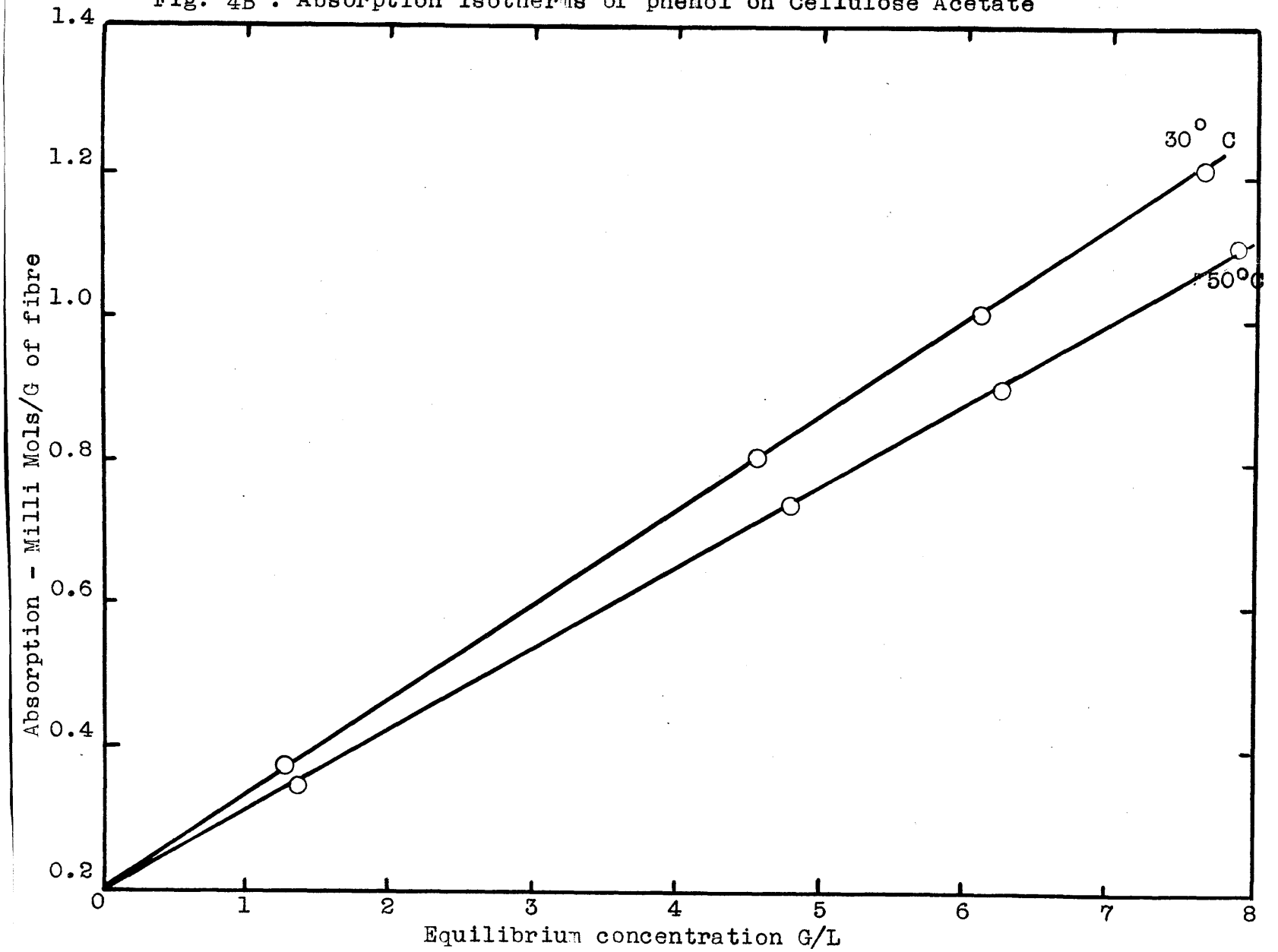


Fig. 5B . Absorption of haematein and haematoxylin by wool at different pH values.

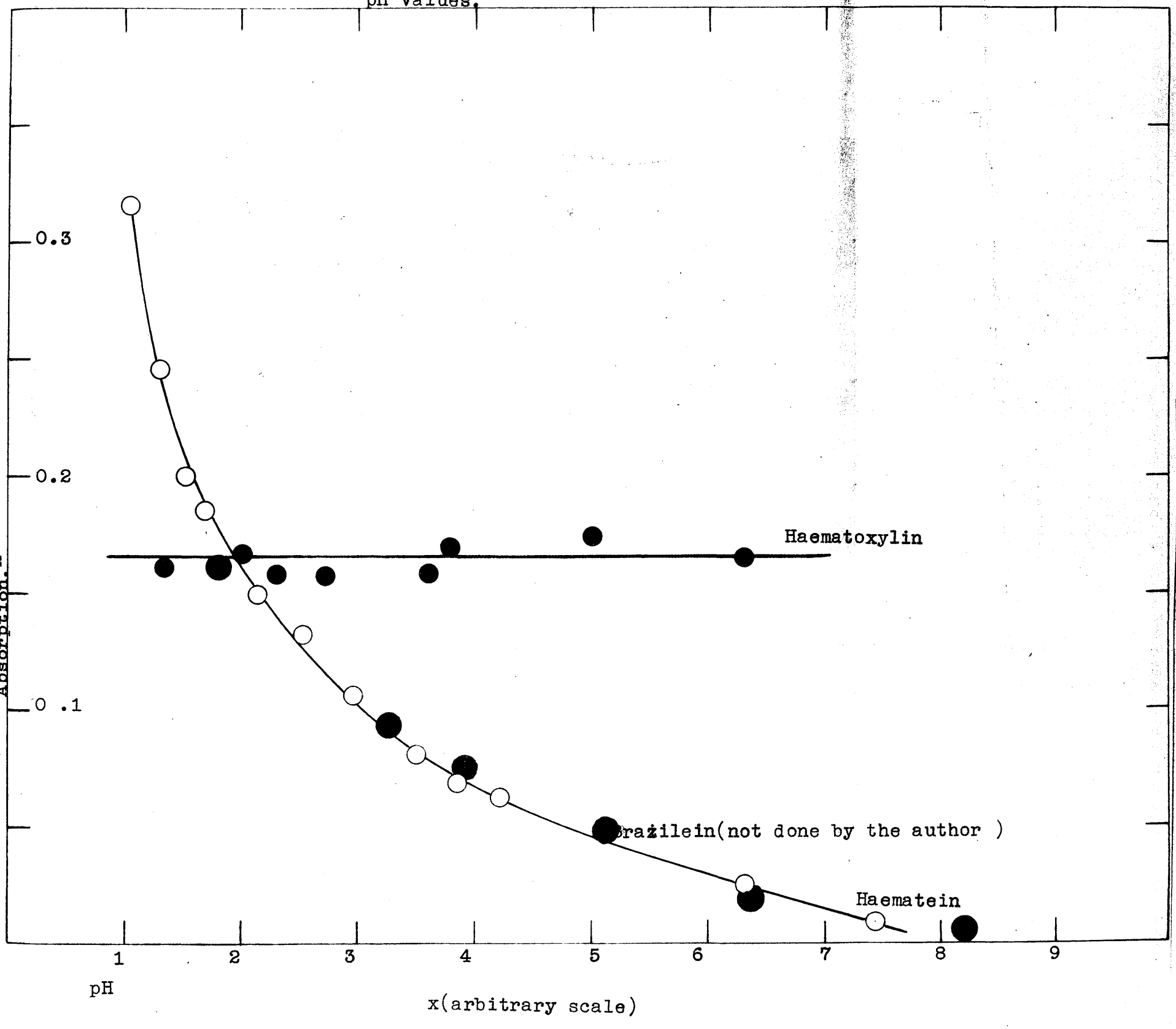
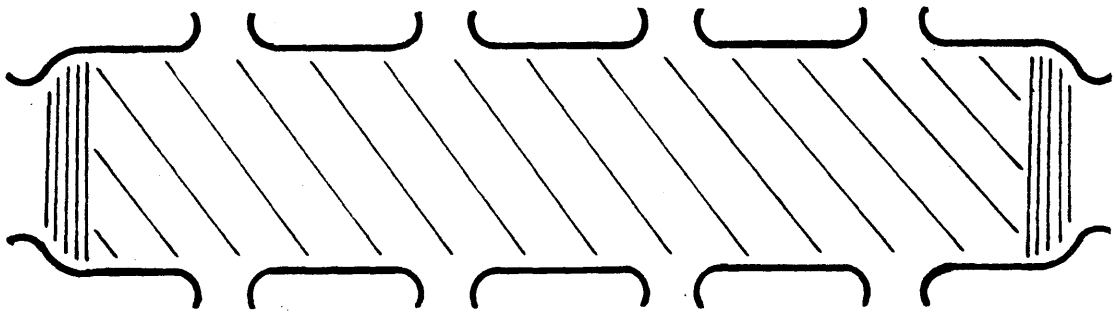


Fig. 6B . Apparatus to ease absorption.



Caterpillar

Fig. 7B . Sorption Isotherms of aniline → R-acid on anodised aluminium

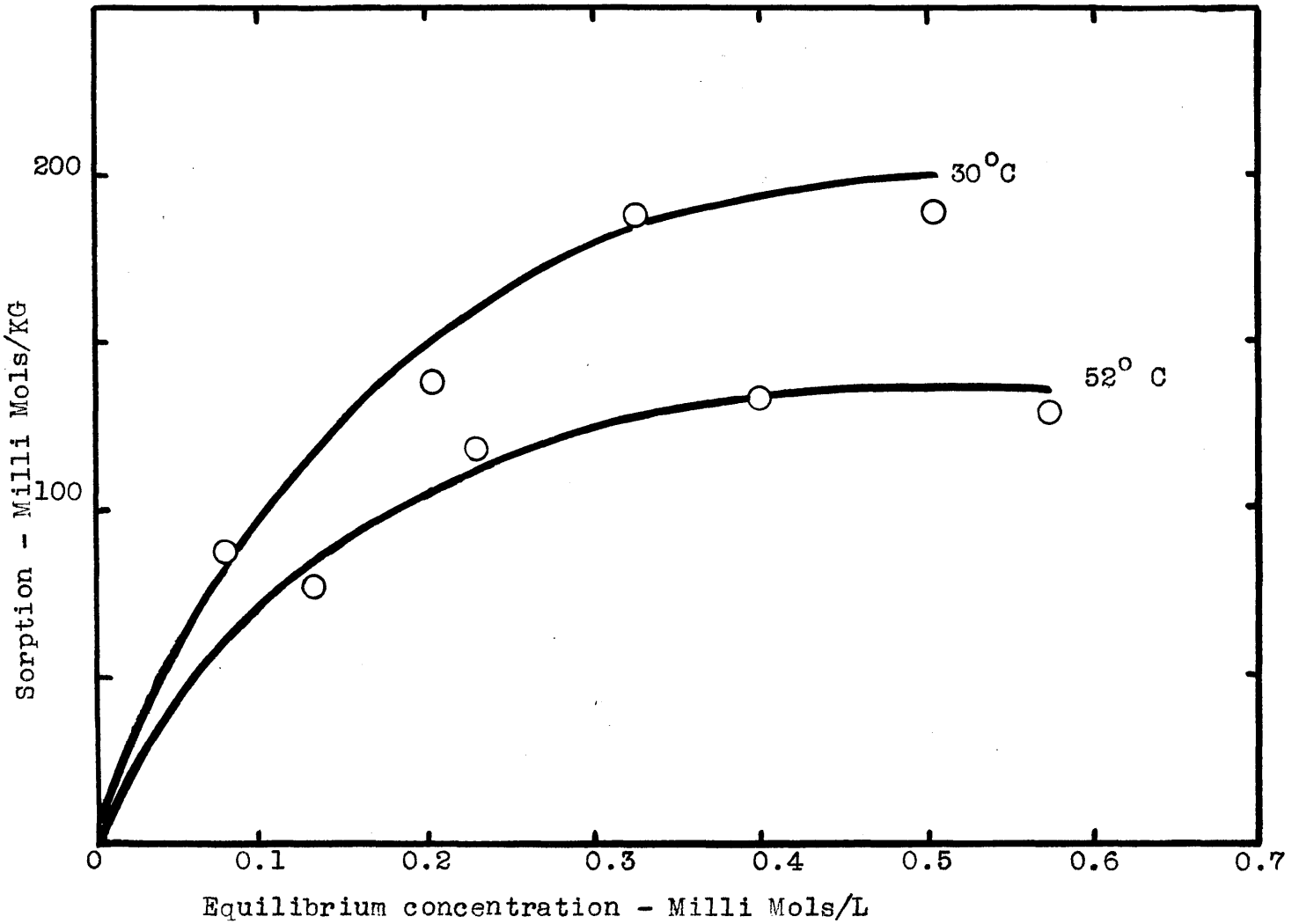


Fig. 8B .Sorption Isotherms on anodised aluminium

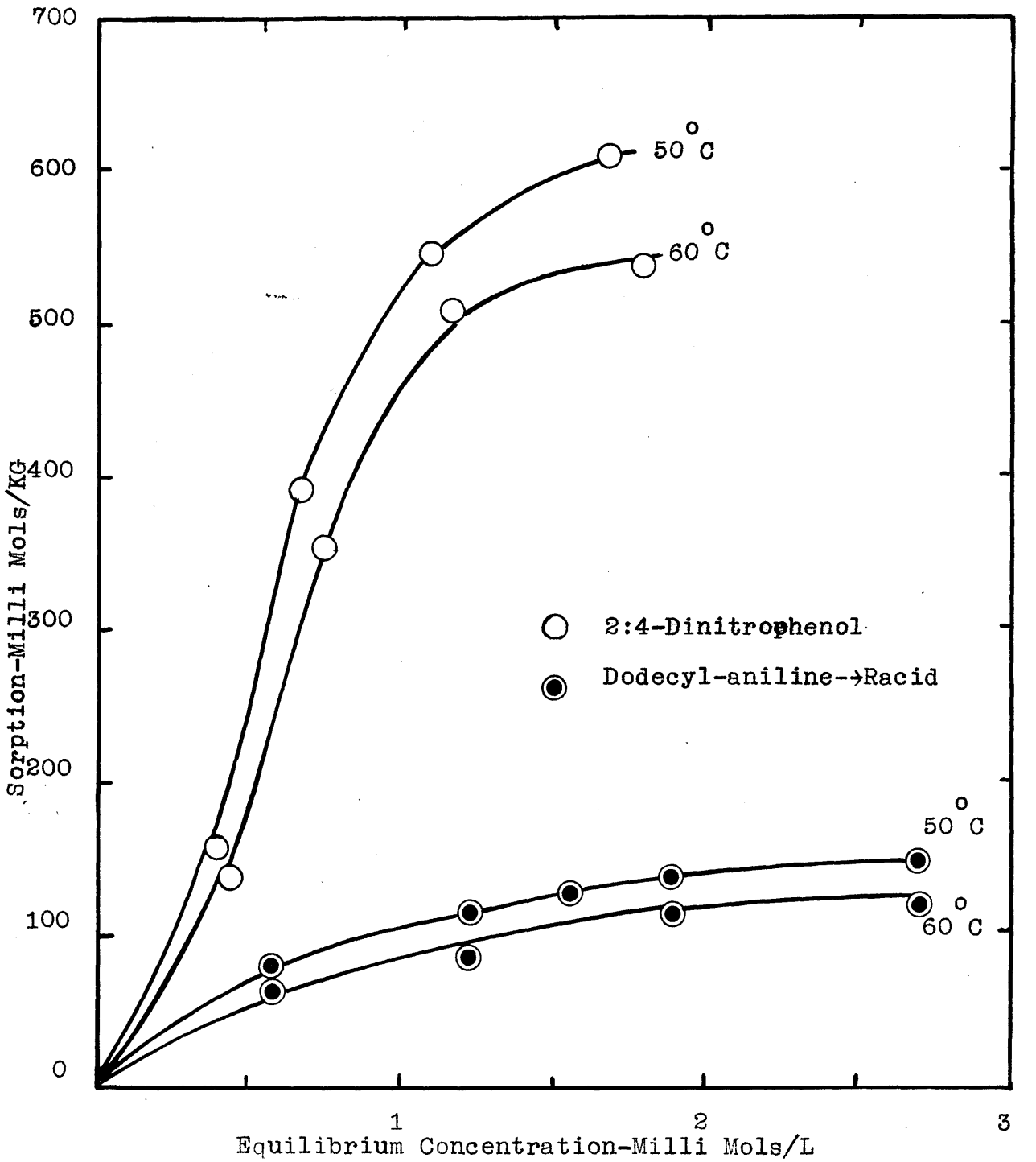


Fig. 9B . Sorption Isotherms Phenol on anodised aluminium.

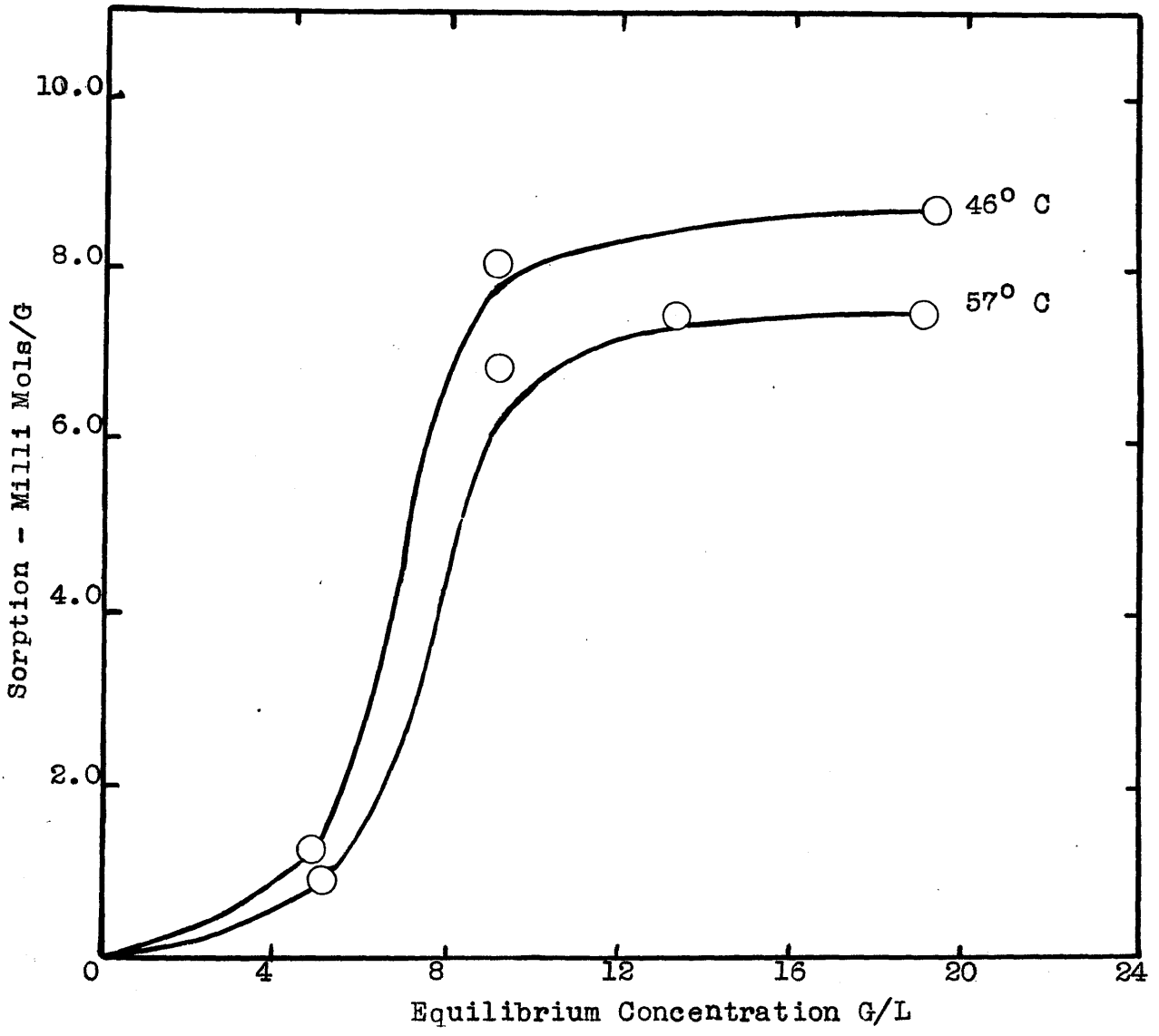


Fig. 10B . Sorption Isotherms

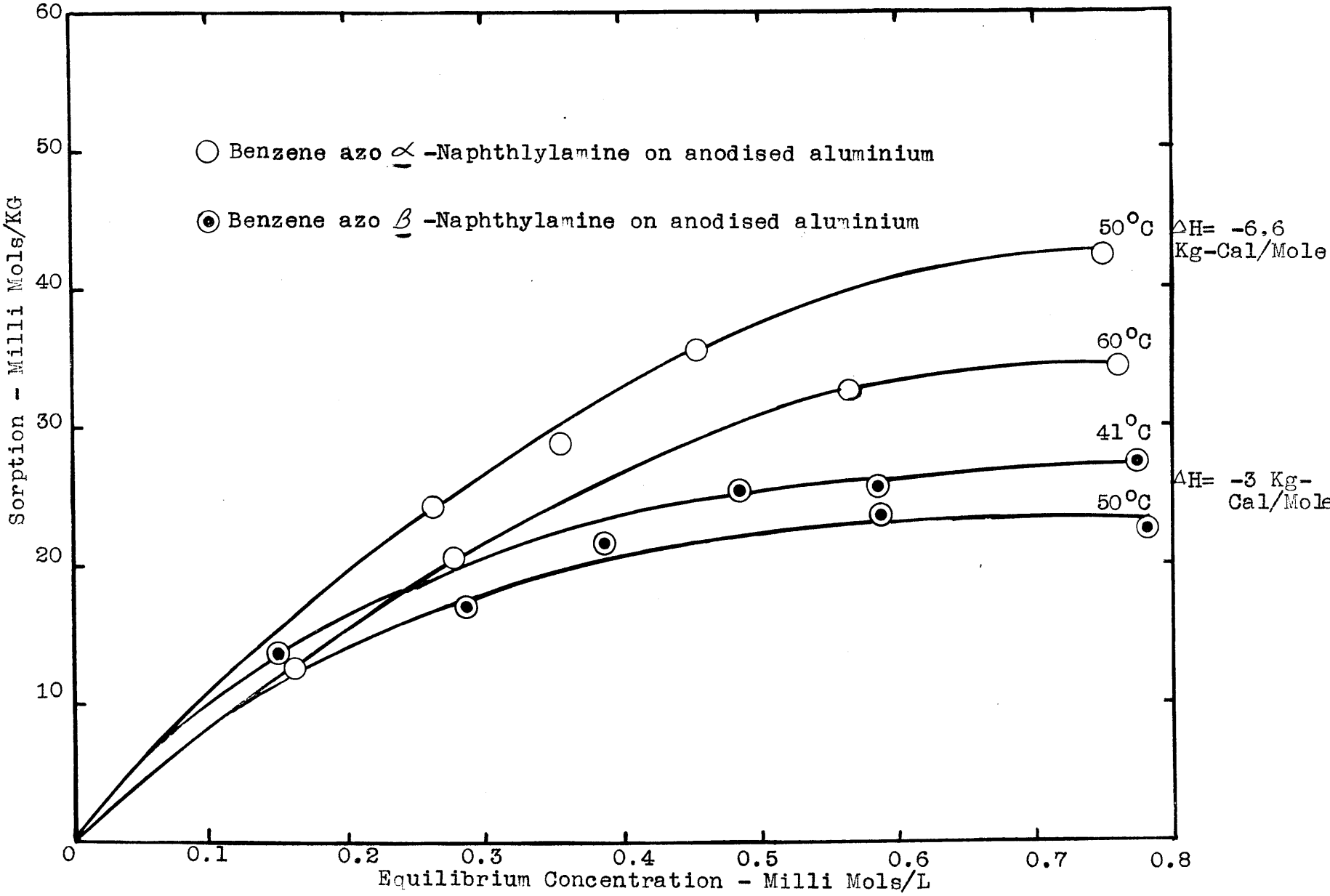


Fig. 11B . Sorption Isotherms of Benzene-azo-α-Naphthylamine + Quinol on anodised aluminium.

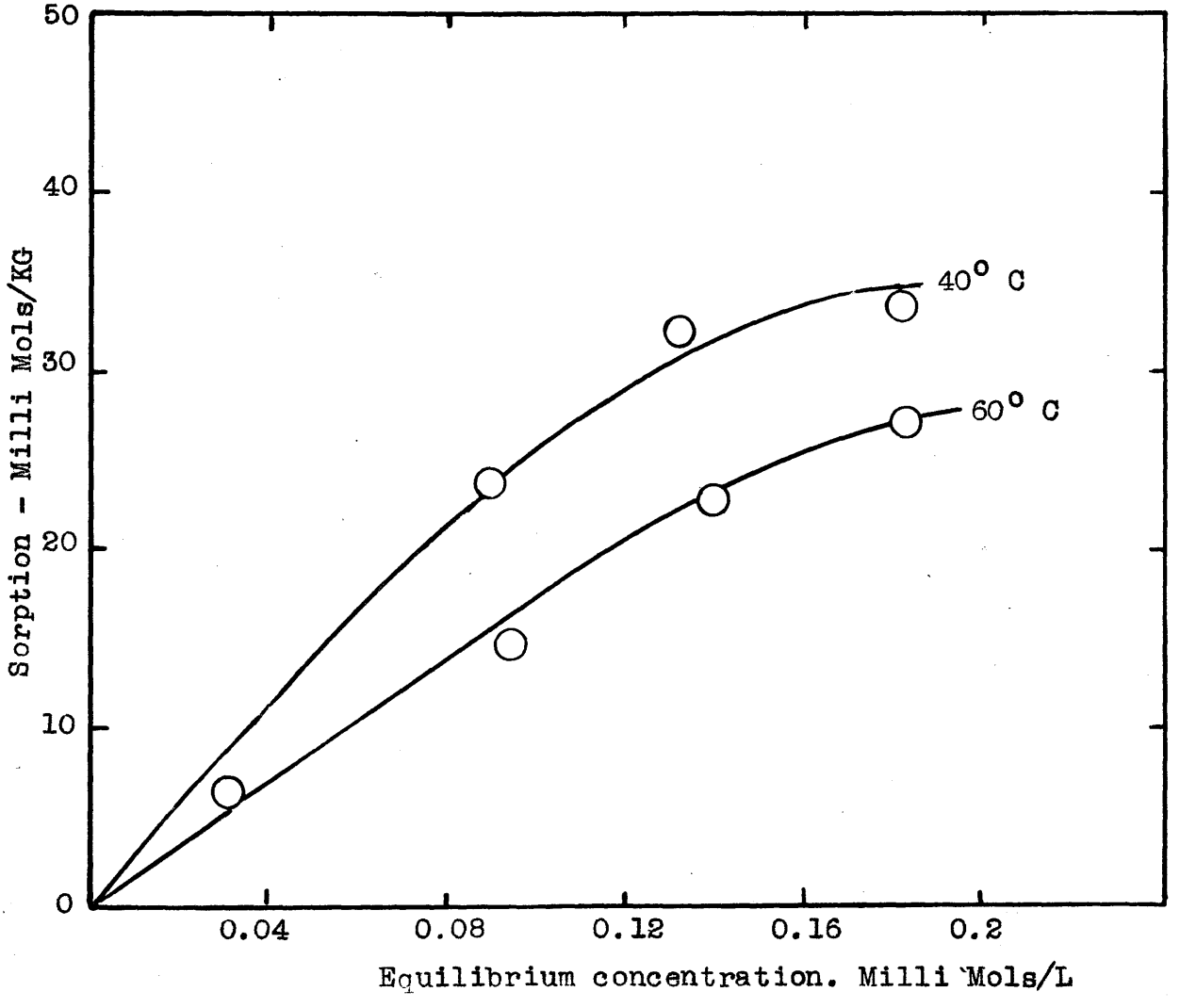


Fig.12B . Absorption isotherms of
p-Nitro-aniline → R-acid on cotton.

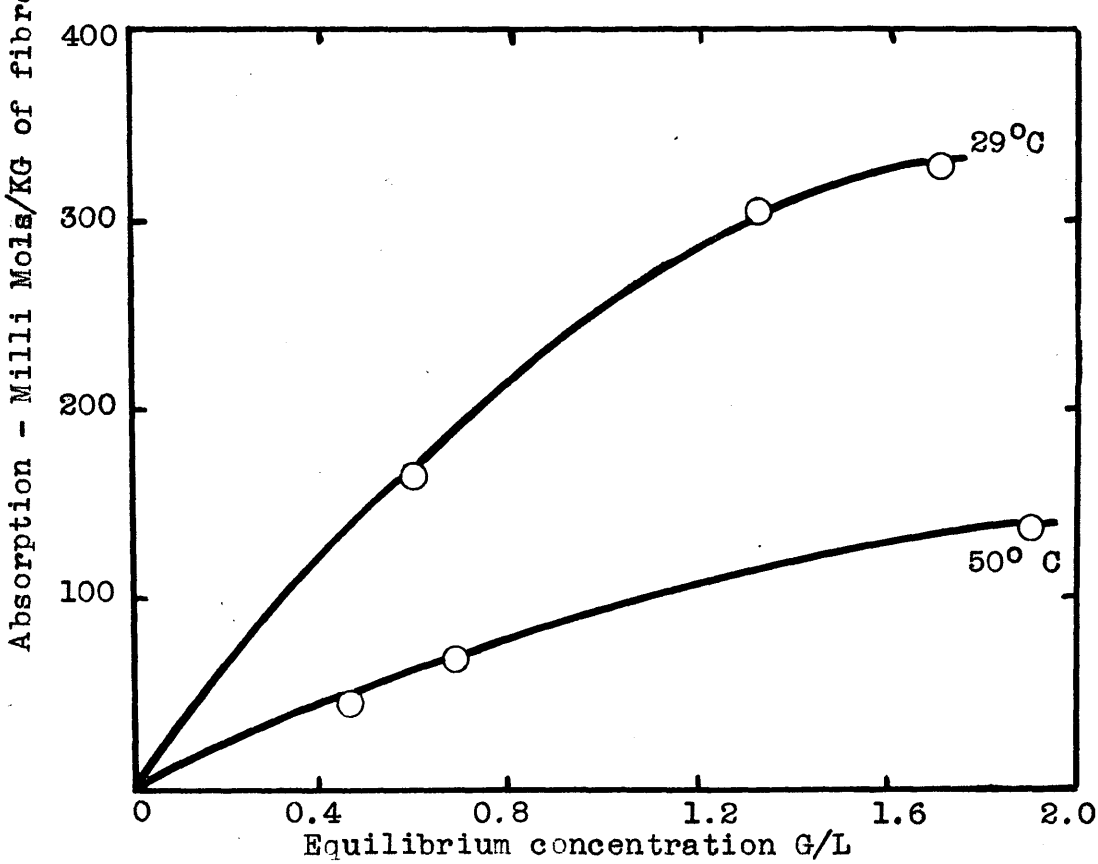
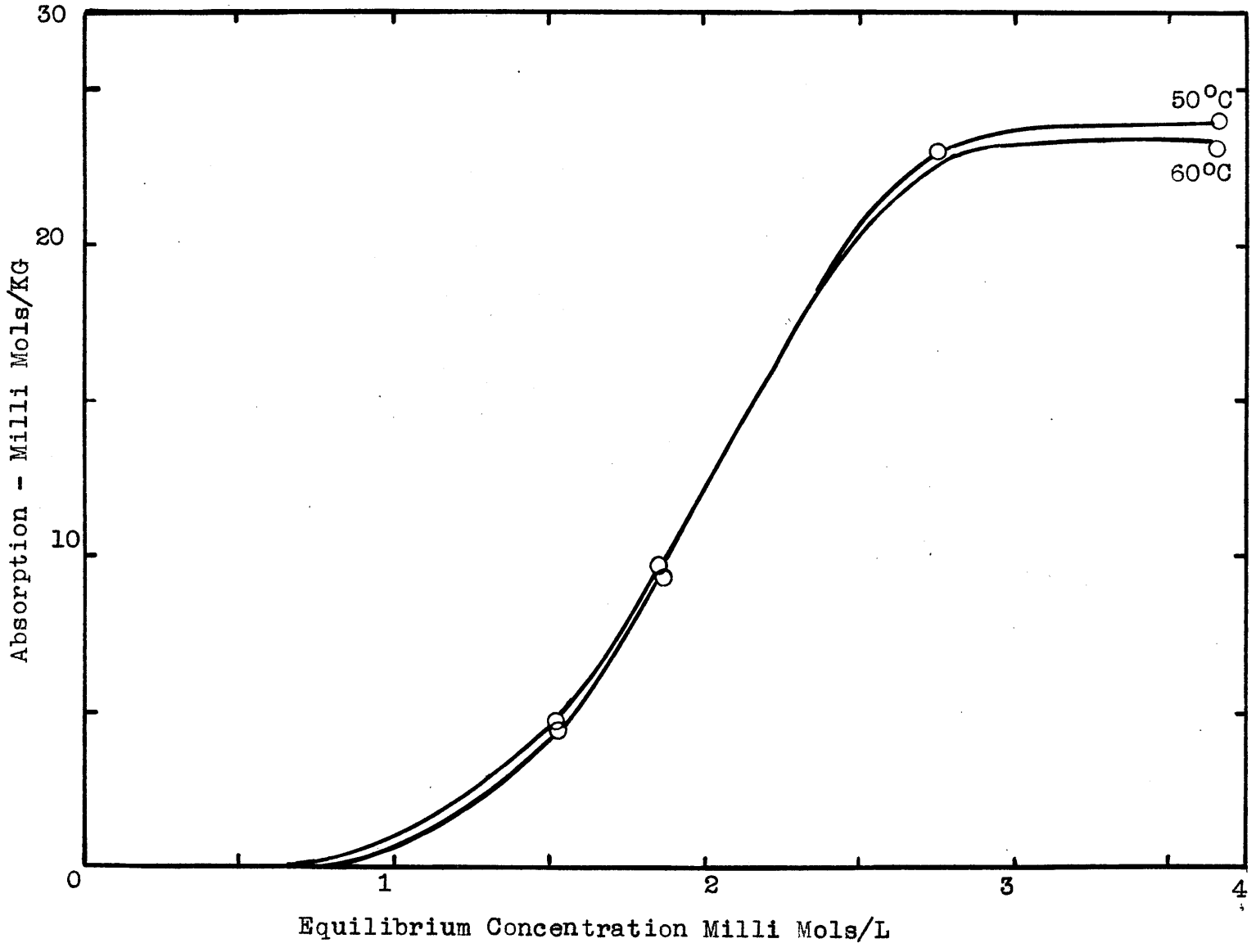


Fig. 13B Absorption Isotherms; Anthracene-1-Sulphonic Acid on Cotton.



GENERAL DISCUSSION.

Analysis of dyes, etc.

The new dichromate oxidation method described in Part I of this thesis appears to be suitable for all azo dyes except the small number which contain neither a sulphonic acid group nor a hydroxy group, and also for some nitrogen-containing dyes of other classes, e.g., the triphenyl methane and anthraquinone classes. The method is simpler, robust and in most cases more rapid than the titanous salt reduction method.

The method is unsuitable for nitrogen-containing intermediates, but many of these may be determined readily by the colorimetric method also described in the same part of the thesis.

The ceric sulphate oxidation method can conveniently be employed where a large number of routine purity determinations are required.

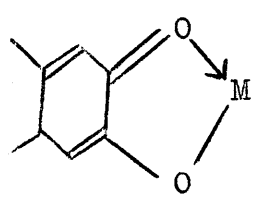
The oxidative procedure for the analysis of dyes does not give reliable results if nitrogen containing impurities, e.g., uncoupled diazo compound or its decomposition products, are present in the dye sample. The presence of such substances is believed to account for abnormally high nitrogen yields obtained from some laboratory preparations of azo dyes in the crude state, e.g., some dyes prepared from chloroanilines. After recrystallisation the analyses by dichromate and titanous chloride were in agreement.

Lakes from logwood, etc.

The oxidised forms, brazilein and haematein, rather than the leuco-compounds appear to be the lake forming agents. Lakes can be formed from the latter, but the reactions almost certainly involve prior oxidation of the leuco-compound by air and/or the metal salt used.

Further, the anions of the colouring matters, rather than the neutral molecules, must be the reactive species, because lake formation is promoted by alkaline conditions and retarded in acid solutions. The retardation in acid must be due to competition for the colour anion between the metal cation and the hydrogen ion of the acid. Moreover, in aqueous solution, all the 6-covalent metals examined form 2:1- (dye:metal) complexes (copper, the only 4-covalent metal examined, appears to form 1:1-complexes in water), but in organic solvents, e.g., ethanol, in which, of course, the degree of ionisation will be less than in water, the reaction appears to be retarded, so that mainly 1:1 complexes are formed.

Each colouring matter molecule must therefore form a chelate ring with a metal atom thus:-



From the water-soluble haematein lakes, it appears that the ratios tend towards 2:1 (dye:metal) in every case. The chromate or dichromate ion must first be reduced to the chromic

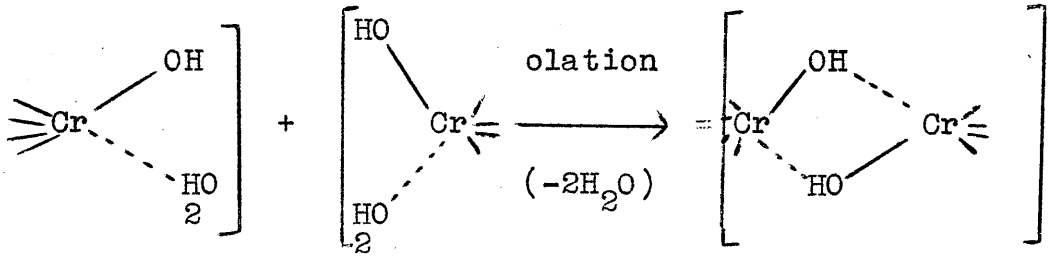
salt state, and this means that some colouring matter must be oxidised and destroyed before the remainder can enter into complex formation.

The lakes once prepared in substance and dried, have become virtually insoluble in all solvents, except by destruction in concentrated mineral acids and alkalies. Their insolubilisation is attributed to the operation of one or more of these processes:

(a) the formation of neutral, unionised complexes,

(b) the formation of complex salts between cationic lakes and anions of colouring matter,

(c) "olation", which takes place in aqueous chromic salt solutions on standing, or by heating:-



If this occurs when the lake solutions are concentrated and evaporated to dryness it could account for the insolubility of the final products of reaction of the colouring matters with chromate, dichromate, and iron salts.

Copper lakes are probably 1:1-complexes of 4-covalent copper in which some of the free phenolic groups are additionally substituted by the metal and they may contain some cuprous ion stabilised by chelation, a possible formula for the haematein lake can be shown as:

$$\left[Cu(aq_2) = \underline{hn} \overline{\cdots} Cu(aq_2)\right]\left[\underline{hn}\right]^{-} 2aq$$

The composition of iron lakes appears to be very similar to the products from potassium-dichromate, i.e., it is an olated anionic complex associated with hydrated ferric cations.

Hydrogen bond reactions.

Part II deals with hydrogen-bonding studied by refractive index and dielectric constant measurements.

Intra- as well as inter-molecular bonds can be detected by these means, and a qualitative estimate of their relative stability may be made. Alcoholic and phenolic hydroxy-aldehyde, amino-, amido-, azo-, carbonylic and sulphonic acid, ester, keto-, nitro-, and quinone groups are amongst those examined.

The protective influence of solvents has been examined by studying the reaction of different compounds in various solvents. For instance, benzene as a solvent prevents the keto group from forming bonds, and so do both ether and water, but not either carbon tetrachloride or dioxan. A number of other examples are revealed in Table 4A (Part II). By the use of the refractive index method, hydrogen-bonding can be readily detected between water (as a solute) and various other compounds. Water appears to act either as monomer or dimer, or bifunctionally as a cross-linking agent.

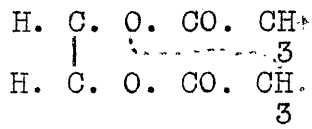
Hydrogen attached to carbon forms bonds less readily than when attached to nitrogen or oxygen, and a neighbouring group of powerful electron-attracting nature is usually required

to facilitate the reaction.

Water appears to form a bond with hydrogen of an ethylene linkage in styrene. A bond between a hydrogen atom of trichlorethylene and the azo group in 1- benzene-azo-2-naphthol is also detected, which could account for the high solubility of unsulphonated azo-compounds in this solvent.

It was desired, if possible, to detect the reactivity of the hydroxy- and ether groups in glucose. Both water and phenol were found to form 6:1- complexes with glucose in ethylene glycol as a solvent, from which it is inferred that protection by the solvent is indeed the cause of the non-reactivity of the hydroxy- and ether groups of glucose in water and no chelate rings are present, since in the same solvent the chelate rings persist in mannitol. This must mean that the ring-form of glucose is the form reacting in ethylene glycol.

Penta-acetyl glucose, like glucose, appears to react in the open-chain aldehyde form. In toluene solution the acetyl groups are unreactive, yet they are reactive when dioxan is a solvent and the acetyl group in ethyl or isopropyl acetate can form complexes in both dioxan and toluene. It appears that there are weak chelate rings, which are stable in toluene but are broken even by the weakly polar solvent, dioxan. It is demonstratable by scale models that a series of 7-membered rings can be formed in this compound, leaving one free hydrogen atom at the end-group, thus:



(A fuller discussion on hydrogen-bonding is given in Part II of this thesis).

The knowledge thus gained of hydrogen-bonding reactions led the author to investigate the mechanism of bonding between fibres and dyes. Firstly, haematoxylin (a tetrahydric phenol) was chosen and its sorption examined on cellulose acetate, nylon, wool and viscose. The apparent heat of sorption on cellulose acetate varies within the range of -4.5 - 8 Kcal/mol. according to the amount bound. By refractive index and dielectric constant measurements, the possibility of this compound forming four hydrogen bonds arises. The apparent heat of sorption of phenol on cellulose acetate is -2.5 Kcal/mol. It is thus just possible that four bonds are formed when haematoxylin is sorbed. The apparent heat of sorption of phenol from aqueous solutions by nylon is about -3 $\pm$ 0.5 Kcal per mol. (Chipalkatti, private communication), so that if a nylon molecule behaves like the amide group in dimethyl-formamide which can unite as a 4:1 complex with haematoxylin, one should expect a value for haematoxylin lying between -10 and -14 Kcal. per mol. Actually the isotherms (Fig. 1B, Part III) give a value of $\underline{Ca}$ -13 $\pm$ 1 Kcal. The corresponding value for wool is -13 Kcal per mol.

Sorption on aluminium.- Benzene-azo-α-naphthylamine and benzene-azo-β-naphthylamine show very little sorption on anodised aluminium in benzene as a solvent, but on using carbon tetrachloride a fair amount of sorption occurs. This fact agrees well with the facts discovered regarding the relative protective effects in hydrogen bonding, of these solvents. Unfortunately,

no time was available to pursue the subject of hydrogen bonding on this substrate, and its relation to the other results of this work.

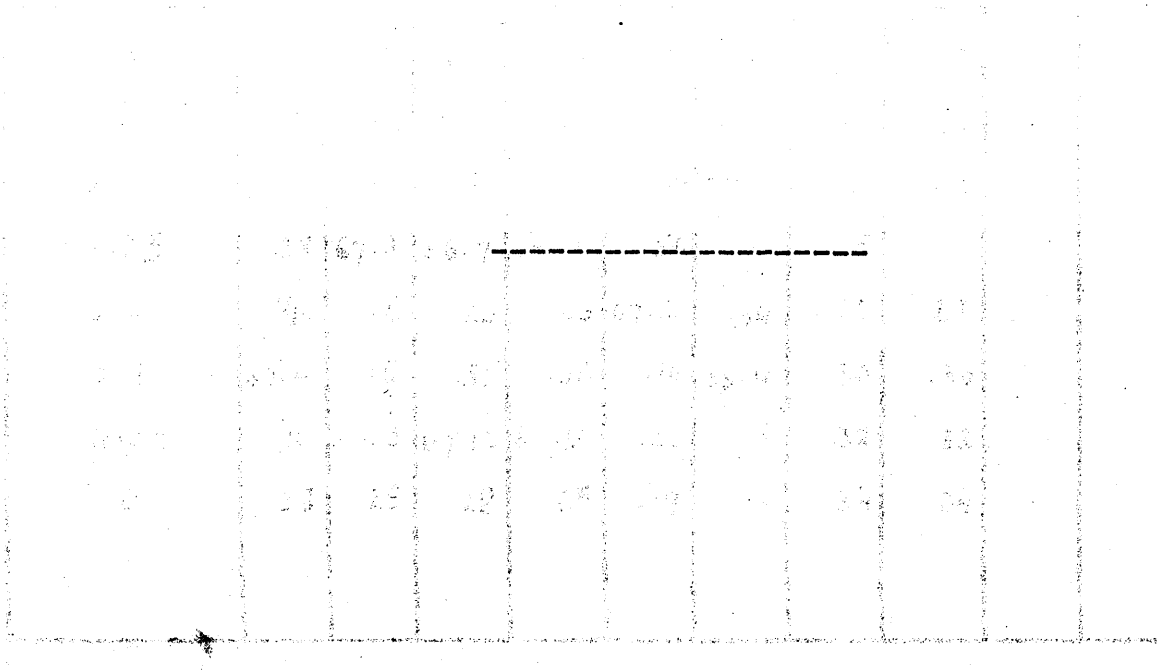


TABLE 8A

Molar Concentration	Angles of Emergence (deg; min) for Compounds 1a to 8a											
	1a	2a	3a	4a	5a	6a	7a	8a				
0.5	65·28	66·34	64·49	64·49	66·23	35·55	38·16	38·18				
0.4	·52	·45	65·20	65·20	·36	36·32	·20	·21				
0·3	66·16	·56	·51	·51	·49	37·2	·23	·24				
0·25	·28	67·1	66·7	66·7	·56		·25					
0·2	·40	·6	·23	·23	67·2	·34	·27	·27				
0·1	67·4	·18	·55	·56	·16	38·4	·30	·30				
0·05	·16	·23	67·12	67·13	·22	·18	·32	·32				
0	·28	·28	·28	·29	·29	·34	·34	·34				

TABLE 9A

Molar proportion of a	Angles of Emergence (deg., min.) for mixtures 1 to 12											
(a + b = 100)	1	2	3	4	5	6	7	8	9	10	11	12
100	65.38	65.38	65.37	65.37	65.41	65.41	66.45	67.27	67.14	67.14	67.14	67.22
85	.49	.50	.46	.50	.49	.48	.43	.25	.8	.16	.8	.16
75	.57	.57	.50	66.0	.54	.55	.41	.23	.4	.16	.8	.11
66.67	66.5	66.4	.54	.5	.59	.56	.39	.22	.0	.17	.9	.6
50	.17	.16	66.3	.20	66.7	66.1	.36	.20	66.52	.19	.3	66.58
40	.24	.26	.7	.29	.12	.6	.34	.20	.49	.20	.3	.53
33.33	.31	.32	.11	.33	.17	.10	.33	.20	.46	.20	.4	.50
25	.39	.39	.15	.40	.20	.13	.22	.19	.41	.20	.4	.47
0	67.5	67.7	.29	67.2	.34	.24	.25	.16	.30	.21	.0	.33

Molar proportion of a	Angles of Emergence (deg., min) for mixtures 13 to 24											
(a + b = 100)	13	14	15	16	17	18	19	20	21	22	23	24
100	67.22	67.22	38.30	38.33	67.12	38.27	38.23	51.12	51.13	51.12	66.40	44.55
85	.23	.18	.36	.33	66.50	.27	38.29	.4	.13	.13	.45	.53
75	.24	.14	.41	.34	.39	.27	.33	.2	.12	.15	.47	.49
66.67	.24	.14	.43	.33	.30	.24	.36	50.58	.13	.16	.49	.49
60			.46	.33		.24	.39	50.54	.13			
50	.24	.11	.51	.33	.13	.23	.42	.49	.14	.17	.53	.47
40	.23	.10	.56	.34	.4	.25	.47	.46	.13	.17	.56	.46
33.37	.24	.8	.57	.35	65.58	.25	.50	.43	.13	.16	.57	.44
25	.24	.7	39.0	.34	.50	.25	.52	.39	.13	.16	.54	.44
15											67.2	.43
0	.24	.4	.8	.34	.30	.25	39.1	.28	.13	.17	.6	.42

TABLE 10A

Molar proportion of a	angles of Emergence (deg ; min) for mixtures 25 to 36											
(a + b = 100)	25	26	27	28	29	30	31	32	33	34	35	36
100	51·7	39·13	39·13	50·53	50·50	50·33	66·20	51·15	51·0	51·15	51·20	51·20
90				·49	·54	·36	·25	·14	50·58	·3	·17	·18
85	·2	·3	·0									
80				·49	·57	·39	·30	·13	·58	50·54	·14	·14
75	50·58	38·56	38·52	·49	·59	·40	·32	·12	·56	·50	·13	·14
66·67	·55	·50	·44	·47	51·3	·43	·36	·11	·55	·47	·13	·13
50	·50	·45	·37	·57	·3	·48	·45	·10	·54	·40	·6	·14
40	·47	·43	·32	51·4	·7	·55	·50	·9	·54	·33	·2	·15
33·37	·45	·42	·32	51·9	·10	51·0	·54	·8	·54		50·59	·16
25	·41	·40	·32		·13	·3	·58	·7	·52	·30	·57	·14
15	·37	·37	·30									
0	·30	·34	·25	·26	·22	·10	67·13	·6	·46	·15	·45	·9

Molar proportion of a	angles of Emergence (deg ; min) for mixtures 37 to 48											
(a + b = 100)	37	38	39	40	41	42	43	44	45	46	47	48
100	51·20	50·38	50·57	50·30	51·1	51·17	37·0	61·24	51·8	38·27	50·59	49·55
90	·18	·40	·53	·34	·0	·14			·3	·31	·57	50·2
80	·16	·39	·50	·35	50·59		·23	·21	50·58	·34	·55	·9
75	·14	·38	·49	·37	·58	·10	·28	·19		·37	·55	·12
66·67	·13	·41	·47	·39	·57	·8	·38	·19	·56	·39	·53	·20
50	·8	·48	·44	·43	·59	·6	·49	·22	·56	·45	·54	·31
40	·7	·50	·45	·46	51·0		38·0	·24	·53	·47	·57	·39
33·33	·6	·53	·42	·47	·1	·4	·7	·26	·57	·49	·55	·42
25	·5	·56	·42	·49	·2	·3	·15	·28	51·0	·55	·58	·47
15			·42	·52				·30				
0	·1	51·4	·42	·56	·5	50·59	·35	·34	·4	39·6	51·3	51·4

TABLE 11A

Molar proportion of a	angles of Emergence (deg ; min) for mixtures 49 to 60											
(a + b = 100)	49	50	51	52	53	54	55	56	57	58	59	60
100	38·27	38·27	39·7	39·7	39·7	39·7	39·7	39·7	49·22	49·22	39·13	39·13
95	·21	·22										
90	·16	·19	·4	·3	·2	·13	·10				·11	·7
85			·1	·3	·0	·12	·6	·10	·30	·35	·10	·5
80	·7	·9	·1	·5	38·58	·10		·9		·40		
75	·1	·5	·1	·1	·53	·7	·5	·10	·36	·44	·11	·1
66·67	37·55	·0	38·58	·1	·50	·9	·5	·8	·40	·53	·10	·0
60	·48	37·55							·46	50·2		
50	·38	·43	·53	38·57	·40	·10	·3	·8	·53	50·12	·8	·0
40											·8	38·57
33·33	·26	·28	·50	·56	·33	·6	·0	·8	50·9	·32	·8	·56
25	·18	·22	·49	·54	·29	·8	38·59	·8	·19	·41	·8	·54
0	36·52	36·58	·42	·49	·19	·5	·53	·5	·40	51·9	·9	·30

Molar proportion of a	angles of Emergence (deg ; min) for mixtures 61 to 72											
(a + b = 100)	61	62	63	64	65	66	67	68	69	70	71	72
100	39·13	66·14	66·14	66·14	51·20	66·30	66·30	38·52	61·2	54·55	52·23	38·57
90	·13				51·17							
85		·20	·17	·23		·37	·35	39·0	·6	55·1		·50
80	·12				51·14							
75	·15	·24	·19	·30	·13	·42	·39	·3	·9	·5	·29	·44
66·67	·13	·30	·20	·36	·13	·47	·43	·8	·11	·13	·31	·42
60	·14						-					
50	·14	·38	·22	·49	·6	·54	·52		·17	·19	·35	·36
40	·11	·44	·25	·55	·2	·58	·58	·28		·28	·37	·33
33·33	·13	·47	·26	67·0	50·59	67·2	67·1	·34	·21	·31	·37	·35
25	·13	·52	·28	·5	·57	·5	·8	·41	·23	·33	·38	·37
0	·11	67·4	·32	·24	·45	·16	·19	·56	·31	·51	·43	·28

TABLE 12A

Molar proportion of a	angles of emergence (deg ., min.) for mixtures 73 to 84											
(a + b = 100)	73	74	75	76	77	78	79	80	81	82	83	84
100	39.4	51.17	51.1	51.8	50.40		51.21	51.21	66.9	66.10	65.0	66.29
95			50.56						.14	.14		
90	38.56		.52	.3	.43				.18	.17		
85		.15	.48	50.58	.40	51.20	.23	.27	.21	.20	.17	.29
80	.49		.53						.26			
75		.14	.54	.57	.40	.13	.24	.29	.30	.27	.29	.31
66.67	.43	.14	.53	51.0	.41	.6	.25	.28	.35	.33	.40	.29
60									.40	.38		
50	.36	.14		50.54	.40	.2	.27	.29	.48	.46	66.1	.28
40	.31	.12		.54		.2	.27	.31	.56	.53	66.14	.27
33.37	.27	.8	.52	.54	.42	50.59	.27	.32	67.1	.58	.24	.29
25	.25	.3	.50	.54	.44	.59	.27	.33	.7	67.4	.34	.27
15									.15	.11		
0	.11	.6	.48	.52	.48	.57	.27	.36	.28	.21	67.7	.25

Molar proportion of a	angles of emergence (deg., min) for mixtures 85 to 88			
(a + b = 100)	85	86	87	88
100	64.54	66.9	66.20	61.24
90				.17
85	65.11	.16	.27	
80				.14
75	.23	.20	.32	.11
66.67	.35	.24	.36	.7
50	.53	.33	.45	.6
40	66.4	.37	.49	.2
33.33	.15	.40	.52	.2
25	.25	.47	.55	.1
15				60.56
0	67.0	67.0	67.7	.50

TABLE 13A

Molar proportion of a	Refractive Index for mixtures 89 to 100											
(a + b = 100)	89	90	91	92	93	94	95	96	97	98	99	100
100	1.4381	1.4357	1.3440	1.5013	1.4978	1.4991	1.4993	1.3390	1.4373	1.4359	1.3443	1.3444
90	.4376	.4355		.5016	.4989	.4999	.5002	.3399	.4376	.4361	.3441	
85	.4373	.4354	.3439	.5018	.4997	.5004	.5006		.4377	.4363	.3438	.3442
80	.4371	.4353		.5019	.5001	.5009	.5009	.3409	4378	.4363	.3439	
75	.4375	.4353	.3438	.5020		.5010	.5011	.3411	.4378	.4366	.3437	.3440
66.67		.4352	.3438	.5018	.5005	.5012	.5013	.3419	.4378	.4366		.3438
50	.4378	.4352	.3436	.5019	.5008	.5016	.5019	.3431	.4377	4366	.3428	.3432
33.37	.4378	.4352	.3429		.5011	.5019	.5021	.3444	.4378	.4368	3423	.3427
25	.4378	.4352	.3427	.5018	.5013	.5021	.5022	.3452	.4378	.4368	.3422	
15									.4378	.4369	.3420	
0	.4378	.4352	.3416	.5018	.5018	.5029	.5032	.3473	.4378	.4371	.3414	.3416

Molar proportion of a	Refractive Index for mixtures 101 to 112											
(a + b = 100)	101	102	103	104	105	106	107	108	109	110	111	112
100	1.3446	1.4341	1.4359	1.3422	1.3416	1.4278	1.5031	1.4294	1.3436	1.3440	1.3440	1.5021
95		.4343		.3423							3439	
90		.4344	.4361	.3423					.3432	.3440	.3440	
85	.3449	.4346	.4362	.3423		.4281	.5031	.4296			.3440	.5033
80		.4347	.4363	.3423	.3412				.3429	.3440	3442	
75	.3452		.4363	.3422	.3411	.4283	.5031	.4296	.3427	.3440	3443	.5039
66.67	.3455	.4349	.4363	.3422	.3409	.4285	.5031	.4294	.3423	.3438	3445	.5042
50	.3460	.4356	.4363	.3422	.3406	.4287	.5030	.4298	.3417	.3437	.3448	.5049
33.37	.3465	.4360	.4363	.3422	.3403	.4289	.5028	.4297	.3410	.3438	.3452	.5055
25	.3468	.4362	.4363	.3421	.3402	.4290	.5026	.4299	.3406	.34375	.3454	.5059
15			.4363								.3456	
0	.3476	.4370	.4363	.3419	.3399	.4294	.5022	.4300	.3393	.3436	.3460	.5069

TABLE 14A

Molar proportion of a	Refractive Index for mixtures 113 to 124											
(a + b = 100)	113	114	115	116	117	118	119	120	121	122	123	124
100	1·4139	1·5021	1·4359	1·3416	1·3392	1·4282	1·4283	1·4275	1·3438	1·3421	1·3374	1·3438
95			·4359									
90			·4360		·3396			·4275				
85	·4139	·5026	·4360	·3412		·4290	·4291		·3434	·3416	·3377	·3439
80			·4361		·3400			·4276				
75	·4139	·5028		·3409	·3402	·4296	·4296	·4276	·3432	·3413	·3379	·3439
66·67	·4140	·5029	·4363	·3407	·3405	·4301	·4301	·4276	·3430	·3410	·3381	·3440
50	·4140	·5031	·4365	·3407	·3412	·4308	·4309	·4279	·3426	·3405	·3386	·3442
33·37	·4142	·5033	·4367	·3406	·3419	·4317	·4317	·4282	·3421	·3402	·3391	·3442
25	·4143	·5034	·4364	·3402	·3421	·4321	·4321	·4283	·3419	·3401	·3393	·3442
0	·4140	·5037	·4373	·3401	·3431	·4334	·4334	·4288	·3412	·3395	·3399	·3444

Molar proportion of a	Refractive Index for mixtures 125 to 136											
(a + b = 100)	125	126	127	128	129	130	131	132	133	134	135	136
100	1·3421	1·3438	1·3420	1·3446	1·3446	1·4289	1·4289	1·3466	1·3468	1·3468	1·3466	1·3407
95		·3439	·3420									
90		·3440	·3422									
85	·3421	·3441	·3422	·3437	·3434	·4297	·4286	·3453	·3454	·3459	·3448	·3399
80		·3442	·3423									
75	·3422	·3443	·3424	·3432	·3432	·4301		·3447	·3446	·3449	·3437	·3394
66·67	·3422	·3444	·3425	·3432	·3429	·4305	·4292	·3441	·3439	·3442	·3430	·3389
50	·3423	·3448	·3428	·3431	·3423		·4300	·3430	·3421	·3430	·3414	·3387
40				·3428	·3421	·4303	·4300	·3422	·3408	·3426	·3403	·3379
33·37	·3424	·3449	·3431	·3428	·3420	·4303	·4300	·3418	·3404	·3417	·3395	·3377
25	·3424	·3456	·3432	·3426	·3418	·4305	·4300	·3411	·3397	·3413	·3387	·3373
0	·3427	·3458	·3436	·3421	·3412	·4303	·4305	·3388	·3367	·3388	·3357	·3354

Table 15A

Molar proportion of a	Refractive Index for mixtures 137 to 148											
(a+b = 100)	137	138	139	140	141	142	143	144	145	146	147	148
100	1·3407	1·3406	1·3408	1·3361	1·3404	1·3401	1·3442	1·4998	1·5023	1·3312	1·3308	1·4222
95							·3441					
90				·3367			·3440	·5008		·3322	·3308	·4219
85	·3402	·3399	·3404	·3368	·3398		·3439	·5014	·5026		·3309	
80				·3370			·3439	·5019		·3332	·3309	·4214
75	·3400	·3396	·3402	·3371	·3396	·3399			·5028	·3337	·3310	
66·67	·3401	·3392	·3401	·3370	·3396	·3397	·3439	·5029	·5030	·3347	·3312	·4210
60						·3397						
50	·3395	·3385	·3400	·3373	·3389	·3397	·34385	·5039	·5033	·3362		·4202
40	·3394	·3380	·3399									
33·37	·3393	·3378	·3398	·3381	·3386	·3398		·5050	·5039	·3379	·3316	·4201
25	·3389	·3375	·3398	·3382	·3384	·3395	·3436	·5056	·5042	·3387	·3322	·4200
15												·4199
0	·3375	·3363	·3394	·3386	·3377	·3399	3432	·5071	·5050	·3412	·3329	·4197

Molar proportion of a	Refractive Index for mixtures 149 and 158 to 167										
(a + b = 100)	149	158	159	160	161	162	163	164	165	166	167
100	1·4222	1·4221	1·4221	1·4221	1·4221	1·4221	1·4221	1·4232	1·4219	1·3358	1·4958
90	·4220	·4221	·4222	·4220	·4224	·4223	·4222	·4234	·4221	·3368	·4961
80	·4218	·4223	·4223	·4219	·4229	·4225	·4223	·4237	·4222	·3378	·4964
75								·4238			
66·67	·4216	·4225	·4223	·4220	·4233	·4225	·4225	·4240	·4224	·3391	·4968
60											·4970
50	·4211	·4228	·4225	·4220	·4239	·4226	·4228	·4241	·4228	·3407	·4972
33·37	·4208	·4229	·4226	·4222	·4241	·4228	·4230	·4242	·4229	·3422	·4978
25	·4204	·4229	·4227	·4222	·4242	·4229	·4232	·4242	·4229	·3428	·4981
15	·4202									·3439	
10										·3447	
0	·4197	·4231	·4229	·4223	·4247	·4233	·4236	·4242	·4231	·3457	·4989

Table 16A

Molar proportion of a	Angles of Emergence (deg, min) for mixtures 150 to 157											
(a + b = 100)	150	151	152	153	154	155	156	157				
100	66·52	66·23	50·59	38·30	44·38	51·5	51·5	66·23				
90	·51	·25	51·0	·27	·34	·4	·5	·26				
80	·51	·27	50·58	·24	·30	·3	·4	·29				
66·67	·52	·30	·57	·20	·25	·3	·5	·33				
50	·54	·33	·57	·16	·17	·4	·6	·37				
40												
33·33	67·1	·39	·55	·13	·10	·7	·11	·43				
25	·5	·44	·54	·11	·8	·9	·14	·47				
15		·51						·54				
0	·20	67·3	·51	·4	43·58	·13	·21	67·3				

Table 17A

Molar proportion of a	Scale Readings (D/C meter) for mixtures 1 to 24											
(a + b = 100)	1	2	3	4	5	6	7	8	9	10	11	12
100	125·28	125·05	125·44	125·46	125·02	124·64	125·39	125·36	125·01	125·24	125·61	125·58
85	·14	·02	·47	·37	124·96	·46	·40	·34	124·97	·18	·58	·54
75	·09	·0	·47	·31	·85	·54	·39	·31	·96	·14	·56	·53
66·67	·04	·0	·46	·28	·72	·52	·39	125·28	·89	·12	·47	·53
60	124·99	124·98	·46	·23	·63		·39	·36	·94	·07	·53	·50
50	·90	·89	·46	·17	·64	·59	·39	·31	·90	·12	·51	·44
40	·84	·95	·46	·12	·66		·40	·34	·96	·12	·47	·50
33·37	·79		·47	·04	·63	·62	·41	·32		·11	·49	·51
25	·67	·97	·48	124·99	·53	·61	·41	·34	·94	·10	·48	·49
0	·52	·99	·49	·81	·53	·67	·41	·36	·92	·08	·44	·40

Molar proportion of a												
(a + b = 100)	13	14	15	16	17	18	19	20	21	22	23	24
100	124·52	125·36	125·31	125·35	125·34	125·34	125·72	125·72	123·85	123·57	123·89	124·56
90		·36	·28	·36		·31			·79	·61	·94	·55
85	·49	·35	·28	·35		·31	·62	·76	·77	·60	·90	
80		·33	·26	·35	·35	·31		·73				·57
75	·47	·29	·32	·34	·35	·31	·53	·71	·86	·68	·95	·57
66 67	·44	·23	·32	·35	·35	·34	·53	·71	·96	·74	124·02	·58
60	41						·51	·70				
50	·41	·21	·35	·40	·38	·36	·45	·73	124·18	·94	·24	·68
40	·44				·40				·24	124·03	·29	·72
33·37	·47	·25	·38	·43	·41	·39	·45	·74	·28	·08	·34	·76
25	·44	·29	·40	·43	·42	·40	·39	·74	·38	·13	·39	·79
0	·43	·37	·43	·47	·46	·44	·29	·76	·62	·36	·60	·91

Table 18A

Molar proportion of a	Scale Readings (D/C meter) for mixtures 25 to 31											
(a + b = 100)	25	26	27	28	29	30	31					
100	124.72	125.28	125.24	124.90	124.90	125.89	125.89					
90	.73											
85		.23	.13	.84	.81							
80	.70											
75	.70	.18	.04	.77	.75	.59	.96					
66.67	.70	.12	124.93	.72	.65	.49	.92					
50	.72	.08	.90	.62	.57	.40	.94					
40	.72	.02	.87	.57	.54							
33.37	.74	.0	.87	.58	.52	.38	.96					
25	.75	124.94	.81	.59	.50	.29	.98					
15		.94	.77				.96					
0	.78	.93	.71	.46	.44	.18	.92					

Prisma I^{b} u. IV^{b}

i	n_D	Δ_n	Korrektionswerte für C	F	G'
30° 0	1.54238	82	517	1301	2411
10	216	82	7	2	2
20	134	82	8	3	4
30	052	83	8	3	5
40	1.53969	83	6	4	6
50	886	83	9	5	8
31° 0	1.53803	83	519	1303	2419
10	719	84	9	6	20
20	635	84	9	7	2
30	551	85	20	1	3
40	466	85	0	8	4
50	381	85	0	9	5
32° 0	1.53296	85	520	1310	2427
10	211	86	1	[illegible]	8
20	125	86	[illegible]	[illegible]	30
30	039	86	[illegible]	[illegible]	[illegible]
40	1.52953	86	2	3	3
50	866	87	2	4	4
33° 0	1.52779	87	522	1315	2436
10	692	87	2	6	7
20	605	88	3	6	9
30	517	88	3	7	40
40	429	88	3	8	1
50	341	88	4	9	3
34° 0	1.52253	89	524	1319	2444
10	164	89	4	20	5
20	075	89	4	1	7
30	1.51986	90	5	2	8
40	896	90	5	2	30
50	806	90	5	3	1
35° 0	1.51716	90	526	1324	2452
10	625	90	6	5	4
20	536	91	7	6	5
30	445	91	7	6	7
40	354	91	7	7	8
50	263	91	6	8	9
36° 0	1.51172	92	528	1329	2461
10	080	92	8	5	2
20	1.50987	93	8	30	4
30	895	92	9	1	5
40	803	92	9	2	7
50	710	93	9	3	8
37° 0	1.50619	92	530	1333	2470

i	n_D	Δ_n	Korrektionswerte für C	F	G'
37° 0	1.50618	92	530	1333	2470
10	526	93	0	4	1
20	433	94	0	5	3
30	339	93	1	6	4
40	246	94	1	7	6
50	152	94	1	7	7
38° 0	1.50058	94	532	1338	2479
10	1.49964	94	2	9	80
20	870	95	2	40	2
30	773	95	3	1	3
40	680	95	3	2	5
50	585	95	3	2	6
39° 0	1.49490	95	534	1343	2486
10	395	96	4	4	9
20	299	95	4	5	91
30	204	96	5	6	2
40	108	95	5	7	4
50	013	96	5	7	6
40° 0	1.48917	97	536	1348	2496
10	820	96	6	9	300
20	724	97	6	50	1
30	627	96	7	1	3
40	531	97	7	2	4
50	434	97	7	3	6
41° 0	1.48337	97	538	1353	2508
10	240	98	8	4	9
20	142	97	8	5	11
30	045	98	9	6	2
40	1.47947	98	9	7	4
50	849	98	40	8	5
42° 0	1.47751	98	540	1358	2517
10	653	98	0	60	8
20	555	98	1	1	21
30	457	98	1	1	2
40	359	98	1	2	4
50	261	98	2	3	5
43° 0	1.47163	98	542	1364	2527
10	064	98	2	5	9
20	1.46966	98	3	6	30
30	867	99	3	7	2
40	768	99	3	8	4
50	669	99	4	9	5
44° 0	1.46569	100	544	1370	2537

i	n_D	Δ_n
44° 0	1.46569	99
10	470	100
20	370	100
30	270	99
40	171	99
50	071	100
45° 0	1.45972	99
10	873	99
20	773	100
30	673	100
40	573	100
50	473	100
46° 0	1.45373	100
10	273	100
20	173	100
30	073	100
40	1.44973	100
50	873	100
47° 0	1.44773	101
10	672	100
20	572	100
30	472	101
40	371	100
50	271	100
48° 0	1.44171	101
10	070	101
20	1.43969	101
30	868	100
40	768	100
50	668	100
49° 0	1.43566	101
10	467	100
20	367	100
30	267	100
40	167	100
50	067	100
50° 0	1.42967	100

Prisma I^{b} u. IV^{b}.

i		n_D	Δn	Korrektionswerte für C	F	G'
50°	0	1,42967	100	538	1404	2600
	10	867	100	8	5	2
	20	767	100	9	6	4
	30	667	100	9	7	5
	40	567	100	60	8	7
	50	467	100	0	9	9
51°	0	1,42367	100	560	1410	2611
	10	267	100	1	1	2
	20	167	100	1	2	4
	30	067	100	2	3	6
	40	1,41967	100	2	4	8
	50	867	99	2	5	20
52°	0	1,41768	99	563	1416	2622
	10	668	100	3	7	3
	20	569	99	3	8	5
	30	469	100	4	9	7
	40	370	99	4	20	9
	50	271	99	5	1	50
53°	0	1,41172	99	565	1422	2632
	10	073	99	5	3	4
	20	1,40974	98	5	4	6
	30	875	99	6	5	8
	40	777	98	7	6	40
	50	679	98	7	7	1
54°	0	1,40580	99	567	1428	2643
	10	482	98	8	9	3
	20	384	98	8	30	1
	30	286	98	9	1	3
	40	188	98	9	2	50
	50	090	98	70	3	2
55°	0	1,39992	98	570	1434	2654
	10	894	98	0	5	6
	20	791	97	1	6	7
	30	700	97	1	7	9
	40	603	97	1	8	51
	50	506	97	2	9	1
56°	0	1,39409	97	572	1441	2665
	10	312	97	3	2	7
	20	215	97	4	3	9
	30	119	96	4	4	71
	40	023	96	5	5	3
	50	1,38927	96	5	6	4
57°	0	1,38831	96	575	1447	2676
	10	736	95	6	8	8
	20	641	95	6	9	80
	30	546	95	7	50	2
	40	451	95	7	0	4
	50	356	95	8	1	5
58°	0	1,38261		578	1452	2687

i		n_D	Δn	Korrektionswerte für C	F	G'
58°	0	1,38261	94	578	1452	2687
	10	167	95	8	3	9
	20	072	94	9	4	91
	30	1,37978	94	9	5	2
	40	884	94	9	6	4
	50	790	93	80	7	6
59°	0	1,37697	93	580	1458	2698
	10	604	93	1	9	9
	20	511	92	1	60	701
	30	419	93	1	1	3
	40	326	92	2	2	5
	50	234	92	2	3	6
60°	0	1,37142	92	583	1464	2708
	10	050	91	3	5	10
	20	1,36959	91	4	6	2
	30	868	91	4	7	3
	40	777	91	4	8	5
	50	686	91	5	9	7
61°	0	1,36595	90	585	1470	2719
	10	505	90	6	1	20
	20	415	89	6	2	2
	30	326	89	6	2	4
	40	237	89	7	3	6
	50	148	89	7	4	7
62°	0	1,36059	89	587	1475	2729
	10	1,35970	88	8	6	31
	20	882	88	8	7	2
	30	794	88	8	8	4
	40	706	87	9	9	6
	50	619	87	9	80	7
63°	0	1,35532	87	589	1481	2739
	10	445	86	90	2	41
	20	360	86	0	3	3
	30	274	86	1	4	4
	40	188	85	1	4	6
	50	103	85	1	5	8
64°	0	1,35019	84	592	1486	2750
	10	1,34935	84	2	7	2
	20	848	84	2	8	4
	30	764	83	3	9	5
	40	681	84	3	90	7
	50	597	83	4	1	9
65°	0	1,34514	83	594	1492	2761
	10	431	82	4	3	2
	20	349	82	5	4	4
	30	267	82	5	5	5
	40	185	81	6	6	7
	50	104	81	6	8	9
66°	0	1,34023		596	1497	2773

i		n_D	Δn	Korrektionswerte für C	F	G'
66°	0	1,34023	80			
	10	1,33943	80			
	20	863	80			
	30	783	79			
	40	704	79			
	50	625	79			
67°	0	1,33546	78			
	10	468	78			
	20	390	77			
	30	313	77			
	40	236	77			
	50	159	76			
68°	0	1,33083	75			
	10	008	76			
	20	1,32932	75			
	30	857	75			
	40	782	74			
	50	708	73			
69°	0	1,32635	73			
	10	562	73			
	20	489	72			
	30	417	72			
	40	345	71			
	50	274	71			
70°	0	1,32203	71			
	10	132	70			
	20	062	69			
	30	1,31993	69			
	40	924	69			
	50	855	68			
71°	0	1,31787	68			
	10	719	67			
	20	652	67			
	30	585	67			
	40	518	66			
	50	452	65			
72°	0	1,31387	65			
	10	322	65			
	20	257	64			
	30	193	63			
	40	130	63			
	50	067	62			
73°	0	1,31005	61			
	10	1,30944	61			
	20	883	61			
	30	822	60			
	40	762	60			
	50	702	59			
74°	0	1,30643				

INDEX TO REFRACTIVE INDEX TABLES.

No.	(a)	(b)
1	n-Acetyl-D-glucosamine	Diethylamine
2		Triethylamine
3		Phenol
4		Dimethylformamide
5		Aniline
6		Quinol
7		Azobenzene 4-sulphonic-acid
8		Aniline 2 - naphthol-3:6 -disulphonic acid
9	Benzaldehyde	Phenol
10		Ethanol
11		Diethylamine
12	Acetaldehyde	Phenol
13		Ethanol
14		Diethylamine
15	Phenol	Acetic acid
16		Benzoic acid
17	Glycine	Sulphanilic acid B-Naphthol
18	Phenol	Benzoquinone
19		Ethanol
20	Water	Aniline
21		Di-isobutyl ketone
22		Ethanol
23	Naphthalene 1-sulphonic acid	Phenol
24	Acetone	Methanol
25	Di-isobutyl- ketone	Phenol
26	iso Propyl Acetate	Benzoquinone
27		Phenol
28	Styrene	Water
29	Phenol	Water
30	Azobenzene	
31	2- Naphthol- 3:6- disulphonic--acid	Phenol
32	iso Propyl Acetate	3-Methoxybenzanthrone
33	2:3:4:6 Tetramethyl Glucopyranose	Water
34	iso Propyl Acetate	Azobenzene
35		o- Nitrophenol (D)
36		Water
37		Anisole
38	Benzaldehyde	Di-isobutyl-ketone
39	Phenol	2:3- Benz-9-anthrone
40		Dimethylformamide (20°)
41	Anisole	Benzoquinone
42	Water	Dioxan
43	Benzene-azo-B-Naphthol	Trichlorethylene
44	Urea	Water
45	Cetyl alcohol	Water
46	Azobenzene	Ethyl Acetate (20°)

continued/...

No.	(a)	(b)
94	Phenol	Ethylene glycol Dibenzoate
95	Triethylamine	
96	Methanol	n-Acetyl-D-glucosamine (W)
97	B-Naphthol	
98	Methanol	(Eg)
99	Aniline	Triethylamine
100		Diethylamine
101	Quinol	n-Acetyl-D-glucosamine
102	Water	Mannitol
103	Phenol	(Eg)
104	p-Nitrophenol	D-Glucose
105	Triethylamine	Ethanol
106	N-n-Butylpropionamide	2:3- Benz-9-anthrone
107	Diethylamine	Glycerol triacetate (T)
108	Diethylamine	(D)
109	Phenol	Methanol
110		Erythritol
111		Mannitol (W)
112	N-n-Dimethylacetamide	Azobenzene
113	Methanol	Erythritol (Eg)
114	N-n-Dimethylacetamide	Benzoquinone
115	Water	D-Glucose
116	Triethylamine	Acetone
117	Methanol	Erythritol (W)
118	Acetone	Azobenzene
119	Triethylamine	
120	Methanol	Pentamethylene glycol
121	Phenol	Dimethylformamide (20°C)
122		(35°C)
123	Methanol	Glycerol (W)
124	Phenol	Quinol (20°C)
125		(35°C)
126		D- Glucose (20°C,W)
127		(35°C,W)
128		Glycerol
129		Ethylene glycol
130	Methanol	Catechol
131		Quinol
132	D- Cellobiose	Aniline
133		Triethylamine
134		Pyridine
135		Dimethylformamide
136		Triethylamine
137	D- Glucose	Pyridine
138		Dimethylformamide

No.	(a)	(b)
139		Quinol
140		Azobenzene-4-Sulphonic acid
141		Aniline
142	Aniline	Phenol
143	Phenol	Triethylamine - & - Glucose
144	Ethyl Acetate	Azobenzene (17°C)
145		o-Nitrophenol
146	Ethylene glycol	Sulphanilic acid B-Naphthol
147	Dimethylformamide	Haematoxylin
148	Resorcinol	Diethylamine (D)
149	p- Nitrophenol	(D)
150	p- Nitrophenol	Diethylamine (W)
151	Resorcinol	(W)
152	Benzoquinone	Quinol
153		Azobenzene
154	Benzyl alcohol	
155	Phenol	iso- Butyl alcohol
156		n- Amyl alcohol
157	Resorcinol	Triethylamine
158	Phenol	4- chlorophenoxyacetic acid
159		∝-(4 - chlorophenoxy)-propionic acid.
160		∝-(4 - chlorophenoxy)-butyric acid
161	Di-iso butyl Ketone	∝-(4 - chlorophenoxy)-butyric acid
162		∝-(2:4-dichlorophenoxy)-propionic acid
163		∝-(2:6-dichlorophenoxy)-propionic acid
164	Triethylamine	2:6- dichlorophenoxy acetic acid
165	Di- isobutyl- ketone	Propionic acid
166	Quinol	Sulphanilic acid B- Naphthol
167	Phenol	Azobenzene

INDEX TO REFRACTIVE INDEX TABLES.

(Molar concentrations only.)

T = Toluene

W = Water

D = Dioxan

Eg = Ethelene Glycol

Pet Ether = Petroleum Ether.

INDEX TO DIELECTRIC CONSTANT TABLES.

No.	(a)	(b)
1	Phenol	Nitrobenzene
2		Anisole
3	Aniline	
4	Phenol	Aniline
5		Acetic acid
6		Benzoic acid
7		Benzoquinone
8		Ethanol
9	Water	Aniline
10		Di- isobutyl- ketone
11	Phenol	Aniline ∝-Naphthylamine
12		Aniline B-Naphthylamine
13	Water	Ethanol
14	∝-D-Glucose penta-acetate	Aniline
15		Anisole
16		Azobenzene
17		Benzoquinone
18		Diethylamine
19	Benzene-azo-B-Naphthol	Quinol
20		Water
21	N-n-Butylpropionamide	Benzoquinone
22		Ethanol
23		Diethylamine
24		Water
25	Benzophenone	Water
26	Di- isobutyl- ketone	Phenol
27	Benzene-azo-B-Naphthol	Trichlorethylene
28	iso Propyl Acetate	Benzoquinone
29		Phenol
30	1:4:5:8- Tetra-amino anthraquinone	Phenol
31		iso-Propyl Acetate