STUDIES IN HYDROGEN-BOND FORMATION

AND

ADSORPTION OF ORGANIC SUBSTANCES

BY

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Publications

Part I of this thesis has already been published in three papers in the Journal of the Chemical Society entitled "Studies in Hydrogen Bond Formation Parts III, IV and V". (J.C.S., 1956, 14, 72-75; 1956, 114, 559-569; 1956, 260, 1272-1277.)

Section I of Part II is also published in the Journal of the Society of Dyers and Colourists as a portion of a paper entitled "A Study of Natural Colouring Matters. Part I" (J.Soc.Dyers and Col., 1954, 70, 392.)

The contents of Section II of Part II have been submitted as a paper to the Journal of Applied Chemistry.

Some of the conclusions of the refractive index work were incorporated in a Communication to the Editor of Chemistry and Industry (1955, 629) entitled "The Nature of Adsorption on Cellulose from Aqueous Solutions".

Preface

The general aim of the work carried out in this laboratory is to investigate various aspects of the chemistry of surfaces, especially the mechanism of adsorption of dyes by fibres and other related substrates. A number of methods have been used to study the latter phenomena, e.g. investigation of the photo-degradation of dyes, of adsorption of dyes and other simple organic compounds on various solid substrates from solution or vapour phase, measurements on monolayers.

It is generally accepted that both polar and non-polar attractions are responsible for adsorption. Amongst the polar forces the importance of hydrogen bonds is well recognised, yet hardly any attempt has previously been made to study the most likely conditions for their formation in adsorption, particularly from aqueous solution.

This thesis describes an investigation of hydrogen-bonding properties of simple organic compounds made to establish the relationship between hydrogen bonds and adsorption. The technique for detecting hydrogen bonds between pairs of solutes by the refractive index method has been described by Arshid et al. (1955). In the first part of the present thesis, this method is reviewed, and work on a

large number of pairs of solutes is described, in aqueous and non-aqueous solutions, and their relationship with adsorption phenomena is discussed.

In the second part of the thesis, the adsorption of the logwood colouring matter, haematoxylin, is described and the results are interpreted in terms of hydrogen bonding and van der Waals attraction. This dye was chosen because of its interesting molecular structure and because it exhibits the property, very unusual in a single substance, of substantivity for cellulose as well as for cellulose acetate, nylon and wool. It had also been used in earlier investigations here, into the structure of its metallic lakes.

To complete the studies in adsorption, the part played by ionic forces was also examined, the substrate chosen being silica. The adsorption of basic dyes by silica, studied earlier in this laboratory, had appeared to show several interesting features meriting further investigation and therefore a more exhaustive study of its adsorption properties was undertaken.

The general abbreviations used in this thesis are those current in the Journal of the Chemical Society.

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Summary.

A study is presented of the forces involved in adsorption from solution with particular reference to hydrogen bonds and electrostatic attraction.

In the first part, the refractive index method is used to detect intra- as well as inter-molecular complexes, particularly of hydrogen bond type, between simple organic compounds in aqueous and non-aqueous solution. The reality of the existence of such complexes is demonstrated by infra-red spectrophotometry, molecular weight determinations, and by various comparisons of physical properties. The mechanism of adsorption of dyes by various fibres has been considered in the light of the results obtained. The following are some of the conclusions reached: (i) Water has a protective effect on certain groups, e.g., on the carbonyl group, on hydroxyl groups in some alcohols, etc. so that certain types of hydrogen bond do not form in aqueous solution. (ii) The hydroxyl group in alcohols is monofunctional and when present on vicinal carbon atoms forms weak five-membered chelate rings, e.g. in ethylene glycol or glycerol. (iii) The aldehyde group can act both as hydrogen-acceptor and hydrogen-donor. (iv) Carbohydrates normally exist in the ring form in aqueous solution and the hydroxy-groups are then protected by the solvent. The open-chain form reacts with pyridine or triethylamine. (v) In ethylene

glycol, as a solvent, all the hydroxy-groups of the carbohydrates are reactive. (vi) The keto-group behaves bifunctionally as a hydrogen-acceptor though it is unreactive in water, ether or benzene. (vii) The reactivity of nitrogen-containing compounds suggests that the unsubstituted or N-monosubstituted amides exist in an enol-form in non-aqueous solution, but in aqueous solution the keto-form predominates. (viii) In sulphonated azo-compounds the azo-group is inactive towards alcoholic groups in aqueous solution. (ix) Esters, besides being hydrogen-acceptors, also act as hydrogen-donors, probably the hydrogen atom on the α-carbon being that involved in the complex formation. This is considered to show that adsorption by cellulose acetate and Terylene fibre may depend on this form of bonding. (x) The reactions of N-acetylglucosamine show that the adsorption on chitin is influenced by the hydrogen-bond formation. (xi) It has been concluded from the non-reactivity of the hydroxy-groups of carbohydrates in water that adsorption on cellulosic fibres from aqueous solution cannot be due to hydrogen-bonding.

The refractive index method was also used to determine the importance of hydrogen-bonding by phenoxyacetic acids, in their activity as plant hormones. Unfortunately time did not permit this work to be completed. However, it was noticed that a hydrogen atom on the α-carbon atom adjacent to the carboxylic group is reactive and its absence in e.g.

phenoxyisobutyric acid may be the cause of its inactivity as a growth-promoting agent.

A study of the adsorptive properties of haematoxylin, a natural colouring matter has also been made. This dye is adsorbed by many different types of fibre. The apparent heats of adsorption and affinities for different fibres are reported. Adsorption on cellulose is probably due to van der Waal's attraction, while on wool, nylon, and cellulose acetate it is due to hydrogen bond formation.

The adsorption of basic dyes and other compounds on varieties of silica has also been studied. Basic dyes are readily adsorbed, to a much greater extent than expected if they formed a monolayer of single molecules. It is suggested that cationic micelles, instead of single ions or molecules, are adsorbed. This is confirmed by a study of spectral absorption curves of solutions of Methylene Blue and pseudo-cyanine chloride before and after treatment with silica. The heat of adsorption of basic dyes is very low and the rates of adsorption are very high.

Two acid dyes, viz. Orange I and II, are adsorbed by silica of high specific surface area. The reaction appears to be endothermic and rates of adsorption are very low. The adsorption of Orange I is probably due to hydrogen-bonding, and that of Orange II to an ion-exchange or physical process.

GENERAL DISCUSSION

General Discussion

Adsorption, the process by which bombarding molecules are retained on a surface, is the basis of many technical operations and is of great scientific interest. Dyeing is a special case of adsorption from solution and the studies of its mechanism have helped a great deal to elucidate the structure of textile fibres, to reveal the nature of dye solutions and to further the understanding of the forces involved in adsorption as a whole. As the present investigation is mainly concerned with the forces of adsorption with particular reference to dyeing, a brief review of the existing knowledge of this subject is thought to be desirable here.

The process of dyeing consists in the transference of the dye from one phase, to another, i.e. from solution to substrate, and the rôles of substrate, dye, and their mutual forces of attraction are now very briefly outlined.

Influence of the Substrate.

The pore size of a fibre plays an important part in dyeing. All fibres are known to be comprised of crystalline regions, where the fibre chains are packed in a highly oriented fashion, and amorphous regions where they are distributed more at random. All fibres undergo

swelling to a varying degree in water and it is in this state that the rather larger dye molecules can penetrate the fibre; e.g. Morton has found that it is very difficult for dye to pass through the pores of cellulose in its unswollen state.

The pore size of cellulose has been found by many workers to be of the order of 5 Å in the dry state and 20 Å in the water-swollen condition. Cellulose acetate, on the other hand, does not swell much in aqueous solution and therefore the intermicellar canals are narrow and the entry of rather bulky dye molecules and their diffusion into the fibre is very difficult. Nylon is even more hydrophobic than cellulose acetate and hardly swells at all in aqueous solution, whereas the pore size of wool in the swollen state is about 40 Å.

The chemical nature of the substrate may also influence dye adsorption in one or other of three ways: (a) by virtue of ion-exchange processes, which can occur with fibres e.g. proteins or nylon, which in water contain charged basic or acidic groups, (b) by hydrogen bonding; all fibres contain potential hydrogen-bonding groups, and it was one of the purposes of this research to discover how far these are likely to be reactive in dyeing; (c) by affecting the sign of the charge in water (zeta-potential); this effect is particularly noticeable with minerals, e.g.

alumina and silica. Part of this research was to investigate the effect of the charge on silica upon its adsorptive properties.

Influence of Dye Structure and Properties.

It is found empirically that anionic dyes (in practice most anionic dyes are sulphonates) have high affinity for nylon and protein fibres, in acid solutions, and if they have certain well-defined structural qualities, namely, a long planar molecule and an extended conjugate system, then they have affinity for cellulosic fibres in solutions containing sodium chloride or other simple salts. Dyes which have polar, but no ionic groups, and are only very slightly soluble in water, have the ability to colour cellulose acetate and the newer synthetic hydrophobic fibres.

Dyes of high molecular weight are known to be highly aggregated in solution, and their degree of aggregation has been studied e.g. by Valkó and by Morton, but the precise relationship between aggregation and adsorption properties has not been well defined. Some early theories of dyeing postulated the building-up of aggregated dye in fibre as the source of affinity. This idea has apparently become discredited in the last two decades, but the results of recent investigations in this laboratory lend some

support to it.

Forces of Attraction between Dye and Fibre.

These forces may be summarised as follows.

Physical forces: (i) Van der Waal attraction
(ii) Electrostatic attraction

Chemical forces: (i) Hydrogen bond formation
(ii) Electrovalent bond formation
(iii) Covalent bond formation

Van der Waals attraction.

Though not much work has been done to prove its importance in adsorption from solution, it has been recognised that this force plays an important part in dyeing. To be substantive to cellulose, a dye must possess a large and planar molecule. This was first suggested by Hodgson and later confirmed by many other workers. Very recently Hassan in this laboratory has studied the adsorption of various dyes on cellulose and chitin and has come to the conclusion that adsorption by cellulose is entirely due to van der Waals forces.

The adsorption of dyes on wool and nylon, though primarily due to salt-formation (see below), is also influenced to some extent by van der Waals forces. Lemin (quoted by Vickerstaff) has shown that the affinity for

wool of a series of acid dyes and of certain organic acids rises almost linearly with increase in molecular weight. Chipalkatti et al. have found that dry wool and nylon under certain conditions can adsorb appreciable amounts of certain aromatic compounds from dry solvents which they considered must be attracted to the fibre by van der Waals forces.

Recently, Derbyshire and Peters have suggested that polar forces are of secondary importance in adsorption, and that the principal contribution to the free energy of dyeing is from non-polar van der Waals forces.

Electrostatic Attraction.

Fibres acquire negative potential when in contact with aqueous solutions. Gee and Harrison have suggested that fibres attract or repel dye ions according to the nature of this charge. This theory has been elaborated by Neale, who has stated that there are two types of electrical forces, short range ones, with a range of less than 5 Å which are mainly responsible for hydrogen bond or covalent bond formation; and long range ones, effective over a distance of 100 Å, which may be considered as an electrical attraction or repulsion between the dye and the fibre. This theory has been supported by dyeing wool, cotton and silk under neutral conditions.

Paneth and Radu have studied the adsorption of basic

dyes by cellulose acetate. They have attributed this adsorption to the electrostatic attraction between the negatively charged cellulose acetate and the positively charged dyes. The adsorption of sulphato-ester dyes by the film of alumina on anodised aluminium has been suggested by Giles et al. to be due to a similar effect. The adsorption of basic dyes by graphite (Macaulay), and amino acids by silica (Watson), is probably also due to electrostatic attraction.

Hydrogen bond Formation.

In recent years the operation of hydrogen bond forces in the dyeing process has frequently been suggested, e.g. in cellulose dyeing (see Vickerstaff for a survey), but it appears, from work carried out here, that hydrogen bonds are operative only when dyeing cellulose from non-aqueous solutions (Giles, Jain, and Hassan, 1955). In aqueous solutions the cellulose hydroxy groups are probably protected by water.

The formation of hydrogen bonds in the adsorption of phenol by cellulose acetate is generally accepted and therefore the adsorption of disperse dyes by this fibre and also by nylon has been attributed to the same effect.

In the dyeing of wool from neutral solutions, Valkó has suggested that hydrogen bonds are formed between dye

and fibre. This would account for the small and varying residual affinity of deaminated wool for acid dyes, since no electrovalent bond formation can occur with this material.

Salt Formation.

The nature of salt linkages between dye and fibre has been studied fairly intensively. Wool contains both acidic and basic groups and the combination of acid or basic dyes with the fibre takes place through these groups. This theory, in its simple form, was first suggested by Knecht and later developed by Speakman, Speakman and Stott, and Elöd.

The dyeing of wool from acid solutions may be visualised as taking place in two stages. Firstly, there is combination of wool with the acid, followed by replacement of acid anions by dye anions -

$$-\overset{+}{N}H_3.\overset{-}{O}OC- \quad + \quad HCl \rightleftharpoons -\overset{+}{N}H_3 \quad \overset{-}{Cl} \quad + \quad HOOC-$$

$$-\overset{+}{N}H_3 \quad \overset{-}{Cl} \quad + \quad \overset{+}{Na}\overset{-}{D} \rightleftharpoons -\overset{+}{N}H_3.\overset{-}{D} \quad + \quad NaCl$$

Elöd explained this reaction on the basis of Donnan theory. He stated that hydrogen ions are adsorbed at the specific sites i.e. combine with the carboxylic groups, whereas the acid anions are taken up only to maintain the electrical neutrality.

Gilbert and Rideal's later treatment differs from this in that they assume that the anions, in addition to the cations, are adsorbed on specific sites in the substrate. Oloffson, who studied the adsorption of acid by wool in the light of these two theories has come to the conclusion that the experimental results fit more closely to the Gilbert and Rideal conception.

Subramanian has suggested an electrovalent linkage in the adsorption of acid dyes by chitin, which in acid solution contains a cationic amido-group.

Covalent Bond Formation.

This type of bond formation in dyeing is encountered when a dye is applied to a fibre containing a mordant, the covalent bond being formed between the dye and the mordant. The direct combination between dye and substrate by covalent bonding is, however, found only in the dyeing of anodised aluminium with mordanting dyes and sulphonated acid dyes (Giles *et al.*), and in the case of the very recently introduced Procion dyes (I.C.I.), which are said to combine directly with the fibre, but their constitutions have not been disclosed.

The thermodynamical aspects of dyeing will now be very briefly discussed.

The Kinetics of Dyeing.

The dyeing process may be visualised as taking place in three stages.

(i) Diffusion of the dye through the aqueous dye solution to the surface of the fibre.

(ii) Adsorption of the dye on the outer surface of the fibre.

(iii) Diffusion of the dye into the fibre.

The diffusion of the dye through the aqueous solution must be faster than the diffusion of the dye within the fibre as the dye molecules are subject to much less mechanical obstruction to movement in solution than within a fibre. Since operation (ii) is supposed to be very rapid the factor determining the dyeing rate must therefore be (iii).

Diffusion within the fibre, with particular reference to cellulose, has been studied in much detail by Neale, who regards the diffusion process as governed by Fick's Law. The rate of diffusion, $\frac{ds}{dt}$, of a dye across a unit area at a given point in the substrate is proportional to the concentration gradient $\frac{dc}{dx}$ i.e.

$$\frac{ds}{dt} = -D.\frac{dc}{dx}$$

where D is the diffusion constant.

Neale and Stringfellow have applied McBain's equation for diffusion through plane slabs to the adsorption of dyes by cellophane discs and have found that the calculated and the observed values are in good agreement. Further, Neale and Garvie have shown that the experimental data fit well to the equation

$$\frac{ds}{dt} = -D' . c^{0.5} . \frac{dc}{dx}$$

where D' is a new constant and c the concentration of the dye. This might be due to a variation of the 'apparent' diffusion constant of the dye from the surface to the centre of the fibre.

The rate of adsorption is also affected by the presence of foreign electrolytes. The course of diffusion in such cases may be predicted by Donnan's equations. Here, the substrate may be considered to be a membrane through which the diffused dye ions may be regarded as non-permeable.

Much further study of rates of diffusion of dyes has been made by Crank and co-workers, some of this being summarised in Vickerstaff's monograph.

Dyeing Equilibria.

In any reacting system, the equilibrium conditions are governed by free energy change accompanying the reaction.

Equilibrium dyeing measurements are expressed in the form of adsorption isotherms i.e. the plot of concentration of dye in the fibre with change in concentration of solution, and the properties of dyeing systems in thermodynamical terms i.e. affinity, heat of dyeing and entropy change, may be calculated from these and other data.

Most dyeing isotherms comply with Langmuir's equation (Vickerstaff)

$$\frac{1}{c_1} = \frac{1}{kS.c_2} + \frac{1}{S}$$

where c_1 and c_2 are the concentrations (more correctly, activities) of the dye in the fibre and in the dyebath respectively, S is the concentration of the dye at maximum adsorption and k is a constant. This equation has been derived on the assumptions that adsorption takes place at specific sites, that it is uninfluenced by the presence of dye molecules on adjacent sites, and that a site, once occupied, is incapable of further adsorption. There are, however, a number of objections to these premises and a number of authors have put forward alternative theories. Nevertheless the Langmuir equation is still widely used.

The affinity, or the tendency of a dye molecule to pass from solution to substrate, may be defined as the difference between the standard chemical potential of the

dye in the two phases. Mathematically it may be expressed as

$$-\Delta\mu^{o} = RT \ln x_1 - RT \ln x_2$$

where $\Delta\mu^{o}$ is the difference between the standard chemical potential of the dye in two phases and x_1 and x_2 are the activities. Hence the affinity can be calculated if the activities of the dyes are known. In the case of dilute ideal solutions this is simple, because activities can be replaced by concentration as a first approximation.

Adsorption is an exothermic process. The heat changes are very small and difficult to measure by calorimetric methods, although Derbyshire has determined a value for a sulphonated acid dye on wool. However, the heat of adsorption can be determined from adsorption isotherms making use of the Clausius-Clapeyron equation

$$\Delta H = \left[R\, T_2T_1/(T_1-T_2)\right] \ln c_1/c_2$$

where c_1 and c_2 are the concentrations of the dye in solution at temperatures T_1 and T_2 in equilibrium with the same concentration of the dye in the fibre under both sets of conditions.

Δ H values thus obtained from adsorption isotherms are, in fact, only "apparent" heats of adsorption, since the adsorption process is the result of two successive

operations viz., the removal of the solute from the solvent and its attachment to the fibre. For absolute values, a knowledge of heat of solution is required. However, these values are useful as a comparative measure of the strength of bond between fibre and dye when the adsorption system is varied in one component only.

The entropy change can be calculated from a knowledge of the heat change and the affinity, according to the following equation -

$$\Delta\mu = \Delta H - T\Delta S$$

The use of entropy values in studying dyeing appears to be of limited interest, because, either two dyes are compared on a common fibre, or the same dye on two fibres. Entropy may be regarded as a measure of the degree of orientation and restraint achieved on fibres as compared with solution. If two dyes are applied to the same fibre and one is found to have a greater entropy change, then it may be concluded that it is more rigidly attached than the other. A general comparison of various dyes on different fibres, however, cannot be made.

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Part I.

Studies in Hydrogen-bond Formation

Part I. Studies in Hydrogen-bond Formation

The Hydrogen Bond.

The importance of hydrogen bonding has been increasingly recognised in the last two or three decades. It serves an important function in many technical operations, it is the basis of existence of many natural products and it is of great biological significance. Its importance in adsorption, with particular reference to dyeing, has already been pointed out. The structures of fibres e.g. wool, silk, nylon etc., the reactions of much living matter, e.g. of antibiotics in presence of protein or antigen, the tanning of leather, chromatographic adsorption, all these, and many others are phenomena which depend upon hydrogen bonding. Methods of study of its operation, however, have been in many cases tedious and complex, and in particular most of them are unsuitable for studying aqueous systems, of which the bulk of technically and biologically important processes involving the bond are comprised. Arshid *et al*. have described a simple method of examining hydrogen bond formation in aqueous solutions by measurement of their refractive index, and this has been used in the present investigation.

The hydrogen bond results when the positive hydrogen atom is situated between, and sufficiently close to two

electro-negative atoms, so that it may be considered to be acting as a bond or bridge between them. For example, in a system XH + Y two structures are possible under certain conditions -

$$X - H \cdots Y \rightleftharpoons X \cdots H - Y.$$

It was at one time thought that the bond was symmetrical but with the development of quantum-mechanical theory this has been disproved. A hydrogen atom cannot form more than one covalent bond and therefore hydrogen-bond formation must be due to ionic forces. It is formed between the most electronegative atoms, and by referring to the electronegativity scale, it has been found that the strength of the bond, in fact, increases with the increase in electronegativity of the two bonded atoms. For example, fluorine forms very strong hydrogen bonds, oxygen weaker ones and nitrogen still weaker ones.

The formation of the hydrogen bond also depends upon the interatomic distances between the bonded atoms. The values for interatomic distances for certain intramolecular hydrogen bonds are given by Pauling; these lie between 2.26 and 3.5 $\mathring{A}$. The hydrogen bond is a weak bond having an energy of 4-8 kcal./mole. It has also been pointed out by Pauling that intramolecular hydrogen bonds are favoured when they form part of a six- or seven-membered chelate

ring, thus following the normal rule of ring stability.

The first suggestion of the hydrogen bond was made by Moore and Winmill in order to account for the weakness of trimethylammonium hydroxide as a base. Later Pfeiffer used it to explain the diminished combining power of the hydroxyl-group when ortho- to the carbonyl-group, as compared with its reactivity in the meta-position. Other effects, like abnormally high boiling point and dielectric constant, as, e.g. in water and hydrogen fluoride, the low ionization constant of ammonium hydroxide, the lower water solubility of ortho-nitrophenol than the meta- and para-isomers, the association of acetic acid etc., have been attributed to hydrogen bond formation. The solubility of certain solutes is probably due to hydrogen bond formation between them and the solvent.

Much less is known about the bonding power of hydrogen between atoms other than fluorine, oxygen, nitrogen, and chlorine. The high dielectric constant value of hydrogen cyanide however, together with its high melting point and boiling point as compared with analogous compounds, has been attributed to hydrogen bond formation (Pauling). Pauling states that the electronegativity of the carbon atom increases, because of the resonating structures of hydrogen cyanide and hence it is capable of forming a hydrogen bond (----H - C $\equiv$ N). Other hydrogen bonds formed through

hydrogen attached to carbon atom in halogenated hydrocarbons e.g. chloroform, have also been reported frequently (see, e.g. Glasstone).

Detection of the Hydrogen Bond.

Infra-red spectrophotometry, electron diffraction and X-ray diffraction methods have been widely used for detecting hydrogen bonds (Hunter). Indirect methods involving the studies of various physical and chemical properties e.g. freezing point, boiling point, solubility determinations, or dielectric constant, which are known to be affected by hydrogen bond formation, have also been used.

The detection of intermolecular complex formation by the "method of constant variations" using some physical property of the reacting substances, studied at constant total molarity, was first used by Ostromisslensky and later, independently, was fully discussed in its theoretical aspects by Dension. Ostromisslensky used the method for spectroscopic detection of the formation of coloured organic complexes. The refractive index has also been used in a similar manner by Pushin and co-workers for detecting inter-molecular complexes in binary mixtures of certain organic liquids. Spacu and Popper also measured refractive index values for binary aqueous solutions of certain inorganic salts and similarly detected complex

formation. More recently, the general method has been used in this laboratory for dielectric constant measurements and both intramolecular and intermolecular complex formation has been detected, particularly of hydrogen bond type, in non-aqueous solutions (Giles, Rose, and Vallance). Since by the Maxwell law, the dielectric constant is equal to the square of refractive index, Arshid et al. (1955) in this laboratory later used this latter parameter for detecting complexes. They demonstrated its great utility over other methods and used it with success for the detection of complexes formed by pairs of solutes in aqueous as well as non-aqueous solution. They also showed that in most cases the complexes formed are due to hydrogen bond formation. This method is very quick, requires only a small amount of solution and complexes can be detected in solutions of as low a concentration as 0.01 M.

Present Work.

The exact role of hydrogen bonding in the mechanism of dyeing has remained largely speculative up to now for two main reasons.

(i) All the auxochrome groups necessary to produce the intense colour required in a dye are also potential hydrogen bonding groups, so that it is hardly possible to discover a dye without at least one hydrogen-bonding centre.

This makes it difficult to carry out decisive control tests.

(ii) Hitherto most of our knowledge of hydrogen bonding has been obtained by the study of non-aqueous systems, e.g., crystals, pure liquids, or solutions in non-aqueous solvents, and little has been known of the behaviour of hydrogen-bonding systems in water. Dyeing is of course nearly always carried out in water.

A detailed study of hydrogen bond complex formation between pairs of solutes representing dyes and fibres, by this method has therefore been undertaken and the results form a large part of the present thesis. Over 300 pairs of compounds have been examined by the present author and his colleagues. For simplicity, the results and their discussion have been divided into three sections. The first section deals with water (in non-aqueous solution), alcohols, aldehydes, carbohydrates, ketones, phenols and quinones, the second section with amines, amides and azo-compounds, and the third section with esters and acids in aqueous and non-aqueous solution. The reality of existence of the complexes so detected has been demonstrated by a variety of procedures, including molecular weight determination, comparison with complexes previously reported, and the use of infra-red spectrophotometry.

Experimental

Materials.

All the compounds used were either of analytical reagent quality or were purified in the laboratory, from commercial or laboratory-prepared products.

Anilidoacetylglycine was kindly prepared by the author's colleague, Mr. A. S. A. Hassan, by condensation of acetylated glycine with aniline (Granacher et al.). It was recrystallised from hot water, forming colourless flakes, m.p.189°.

Diacetamidohexane was prepared by treating hexamethylene diamine with acetic anhydride in the cold. It formed colourless needles, m.p.125°.

N-n-Butylpropionamide was prepared by the method described by Giles, Rose, and Vallance. 37g. of propionyl chloride were slowly added to 58.4g. of n-butylamine, cooled in a bath of ethanol and solid carbon dioxide. After the addition the mixture was heated to 80° , kept thereat for 15 minutes and allowed to cool overnight. The liquor was then shaken with equal volume of water, and the oily layer thus separated was extracted with ether. Colourless liquid, b.p.236°/760 mm.

Formaldehyde was prepared by heating paraformaldehyde.

The gas was collected in water and its concentration was determined volumetrically by oxidation with hydrogen peroxide in presence of sodium hydroxide.

Quinol diacetate was obtained by treating quinol with acetic anhydride, in the cold, in presence of a drop or two of sulphuric acid. The product thus obtained was recrystallised from ethanol, forming plates, m.p.121°.

Catechol diacetate was prepared by mixing acetyl chloride and catechol in the cold, followed by addition of water, and recrystallisation from ethanol. Needles, m.p.63.5°.

Pentane-1:5-diol diacetate. Pentamethylene glycol (pentane-1:5-diol) was refluxed with excess of acetic anhydride and dry pyridine for 2 hr. The mixture was then washed successively with water, dilute acetic acid, and sodium carbonate solution. The oily layer was extracted with ether and redistilled, and the distillate kept over sodium to ensure removal of all traces of unesterified diol; b.p.240°, f.p.6°.

All the solvents were completely dried before use. 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 to remove all traces of water.

Instruments.

In the earlier part of the work, the refractometers used were the Bellingham and Stanley Abbe type (reading to 10^{-4} unit) and the Zeiss Pulfrich type (reading to 10^{-5} unit). These require respectively ca 0.1 and 1.0 c.c. of the liquid for each determination. In the later part of the work, however, a new model Bellingham and Stanley Pulfrich refractometer was mainly employed. The source of monochromatic light used for most of the work was a sodium lamp, except where the solutions were too densely coloured, in which case mercury or cadmium light was used. The Pulfrich type of instrument, particularly the new Bellingham and Stanley model, is preferred because of its high precision, especially for aqueous solutions in which the variation in refractive index often occurs only in the fourth decimal place. In all cases a mean of at least two or three independent readings was taken for each solution.

Infra-red spectra were recorded in 1 mm. cells (solutions) on a Perkin-Elmer model 13 instrument or in 0.05 and 0.025 mm. cells (pure liquids) on a Grubb-Parsons instrument, both with sodium chloride prism.

Procedure.

The solutions of the two solutes to be examined were prepared, then mixed in different proportions giving 8 - 12 separate binary solutions of different molar ratios, and then stored in ground-glass-stoppered tubes. These solutions were then measured in quick succession in the instrument at room temperature. The thermostatic temperature control of the test liquid was found unnecessary because a complete series of readings can be made within 30 minutes and any slight variation of temperature during that time does not affect the results. A concentration of 0.1 M or 0.25 M was normally used, but in special cases where very little material has been available 0.01 M solutions have been employed quite satisfactorily.

It has been found in some cases that the results show less random error if the solutions are either warmed and then cooled again or left overnight before measurement, probably because the solutes have a low reaction or solution rate.

Over certain temperature ranges certain curves pass from convex to concave, relative to the x-axis, and thus at some intermediate temperature the curve is linear and there is no evidence of complex formation. Therefore, to establish the reality of negative results, the determinations were made either at more than one temperature, or a

variety of second solutes were used, or different solvents were employed.

Determination of "Apparent Molecular Weight".

The Beckmann freezing point method was used for a series of binary solutions. The 'apparent' molecular weight is the value calculated on the assumption that only one compound is present, and is equal to the sum of the products of the true molecular weights of each solute and their respective molar fractions. The results are each the mean of two or three separate determinations. The ebulliometric method for the determination of molecular weight, with the aid of foaming substances, using a Beckmann thermometer (Polydoropoulos) was also tried. Unfortunately, this method did not prove very satisfactory for the precise measurements required for this work and hence it was abandoned.

Results and Discussion

For ease of explanation the results of the present work and their discussion, which follows immediately, are presented here in three sections.

Section I.

The Hydrogen bonding Properties of Water in Non-aqueous Solution and of Alcohols, Aldehydes, Carbohydrates, Ketones and Phenols in Aqueous and Non-aqueous Solutions.

In the present investigation it is assumed that most of the complexes detected are attributable to hydrogen bonds, although other forms of intermolecular complexes have sometimes been detected. The results are summarised in Table 1 and some of the typical curves are shown in Figs.1-7. Some of the results in Table 1, particularly those obtained by the dielectric constant method, are included by courtesy of Dr. F. M. Arshid. These are suitably differentiated from those obtained by the writer. A number of the tests made by Arshid have also been repeated by the writer, in confirmation.

Water.

Water enters so intimately into almost all reactions involving fibres that its bonding properties towards a

Table 1.

Solutes a	Solutes b	Solution Solv.*	Solution Total mol. concn.	Solution Method† and temp.	Mol. ratio of complex (a:b) ‡
Alcohols					
Methanol	Phenol	D	0.1	n 20°	1:1
		W	0.25	n 20	1:1
Ethanol	Water	D	0.1	ε, n 20	1:1
"	Phenol	T	0.25	ε, n 19	1:1
		W	0.25	n 20	1:1
n-Pentanol	"	D	0.1	n 21	1:1
Ethylene glycol	Methanol	D	0.1	n 20	1:1
"	Phenol	D	0.1	n 19	1:1;1:2
"	Triethylamine	W	0.2	n 19.7	1:1
		W	0.25	n 20	1:1;(1:2)
Glycerol	Methanol	D	0.1	n 20	(1:1)
		W	0.25	n 20	§
"	Phenol	W	0.25	n 20	1:1;1:3
"	Triethylamine	W	0.1	n 20	1:1
"	Water	D	0.1	n 20	1:1
Erythritol	Methanol	W	0.25	n 21	§ xx
"	"	Cs	0.05	n 18	1:1 xx
"	Phenol	W	0.25	n 19	1:1;1:4 xx
Mannitol	"	W	0.25	n 19	1:6 xx
"	"	EG	0.1	n 22	(1:1);1:6xx
"	Water	EG	0.1	n 18	1:1 xx
Butane-1:4-diol	Methanol	D	0.1	n 15.5	§
"	Phenol	D	0.1	n 16.5	§
Pentane-1:5-diol	Methanol	D	0.1	n 18	1:2
"	Triethylamine	W	0.2	n 19.7	1:2

Table 1 (Cont'd)

Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method† and temp.	Mol.ratio of complex (a:b) ‡
Aldehydes					
Acetaldehyde	Azobenzene	T	0.1	n 20	2:1 xx
"	Diethylamine	W	0.25	n 20	1:1 xx
"	Phenol	W	0.25	n 20	(§)
Formaldehyde	"	W	0.2	n 20	§
"	Triethylamine	W	0.2	n 20	1:1
m-Nitrobenz-aldehyde	Phenol	T	0.2	n 21	1:1;1:3
"	Pyridine	T	0.1	n 21	1:1
"	Triethylamine	T	0.2	n 21	1:1
o-Nitrobenz-aldehyde	Phenol	T	0.1	n 19	1:2
"	Pyridine	T	0.1	n 21	§
"	Triethylamine	T	0.1	n 19	§
Propionaldehyde	Diethylamine	B	0.2	n 15	1:1;(1:2)
"	Dimethyl-formamide	C	0.2	n 18	1:1
"	"	W	0.2	n 18	1:1
"	Ethanol	C	0.2	n 17.5	1:1
"	"	W	0.2	n 17.5	(§)
"	Phenol	C	0.1	n 17	(1:1)
"	"	EG	0.2	n 18	1:1
"	"	W	0.2	n 17.5	§
"	Pyridine	D	0.2	m.w.	1:1
"	"	W	0.2	n 17.5	1:1
"	Triethylamine	W	0.2	n 17.5	1:1
Carbohydrates					
D-Cellobiose	Diethylamine	W	0.25	n 19	(1:1)
"	Dimethyl-formamide	W	0.25	n 15	1:1 xx
"	Pyridine	W	0.1	n 18	1:1
"	Quinol	W	0.25	n 16	(§) xx

Table 1 (Cont'd)

Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method† and temp.	Mol.ratio of complex (a:b) ‡
Carbohydrates (cont'd)					
D-Cellobiose	Triethylamine	W	0.25	n 15	(1:1)
D-Fructose	Ethanol	W	0.25	n 20	(§) xx
"	Phenol	W	0.25	n 21	(§) xx
"	Triethylamine	W	0.25	n 20	(§)
D-Glucose	Aniline	W	0.25	n 18	2:1
"	Diethylamine	W	0.25	n 19	1:1
"	Ethanol	W	0.25	n 20	§ xx
"	Methanol	W	0.25	n 20	§
"	p-Nitrophenol	W	0.10	n 18	1:1 xx
"	Phenol	W	0.25	n 20 m.w.	§
"	"	Buffer pH 8.4	0.2	n 17.5	§
"	"	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
"	Urea	W	0.2	n 15	§
"	"	W	2.0	n 16	§
"	Water	EG	0.1	n 14	1:6;(2:1)
Sucrose	Triethylamine	W	0.25	n 20	§ xx
Solutions of ternary mixtures					
D-Glucose (1 mol) + Pyridine (1 mol)	Phenol	W	0.1	n 19	1:6
		W	0.2	m.w.	1:6
D-Glucose (1 mol) + Triethylamine (1 mol)	"	W	0.1	n 13	1:1;1:6
Ketones					
Acetone	Phenol	E	0.25	n 20	§ xx
"	"	W	0.1	n 20	§
"	Methanol	C	0.25	n 20	(1:2)

Table 1 (Cont'd)

Solutes a	Solutes b	Solv.*	Solution: Total mol. concn.	Method† and temp.	Mol. ratio of complex (a:b) ‡
Ketones (cont'd)					
Acetone	Methanol	D	0.05	n 17	1:2
"	Propion-aldehyde	T	0.2	n 20	1:1
"	Triethylamine	W	0.25	n 21	§
"	Quinol	E	0.25	n 18	§ xx
Benzophenone	Phenol	B	0.25	n 18	§
Diisobutyl ketone	"	D	0.25	ε,n 20	1:2
Phenols					
Catechol	Methanol	D	0.1	n 15.5	1:1
"	Phenol	D	0.2	n 16	(1:1;1:2)
Pyrogallol	"	W	0.25	n 20	(1:1);1:3 xx
Quinol	Methanol	D	0.1	n 20	(1:2)
"	Phenol	W	0.25	n 19	1:2
Water					
Water	Acetone	D	0.2	n 20	1:1;2:1
"	Aniline	D	0.25	ε,n 20	(2:1) xx
"	Aniline ⟶ 2-naphthol	D	0.1	ε,n 20	1:2
"	Azobenzene	D	0.1	ε,n 20	1:1;2:1
"	Benzophenone	D	0.2	ε,n 20	(1:2) xx
				n 17	1:2
"	N-n-Butylpropionamide	D	0.2	ε,n 20	1:2 //
"	Diisobutyl ketone	D	0.1	ε,n 20	1:1
				n 17	1:1 //
"	Phenol	D	0.2	n 20	1:1;1:2 xx
"	Propion-aldehyde	EG	0.2	n 17	1:1

* Solvents: B = benzene; C = carbon tetrachloride; Cs = "Cellosolve" (2-ethoxyethanol); D = dioxan; E = diethyl ether; EG = ethylene glycol; T = toluene; W = water.

† Methods: ε = dielectric constant; n = refractive index; m.w. = apparent molecular weight.

Table 1 (Cont'd)

‡ Data in parentheses denote uncertain indications.

§ No evidence of complex formation.

// These curves show particularly pronounced change of slope.

xx This result reported by Arshid.

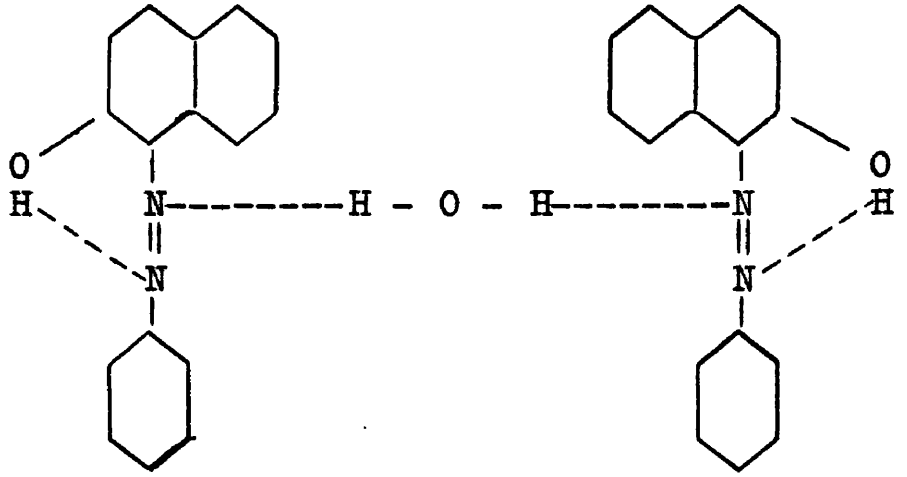
number of the model compounds which represent fibres are of special interest and for the first time the present method has provided an opportunity of studying these properties.

From a study of Table 1, and also of Table 4 (Section II), it will be noticed that water as a solvent plays an important part in determining the hydrogen-bonding properties of other solutes. For example, in spite of the potential proton-accepting group i.e. carbonyl-group, in acetone, acetaldehyde or propionaldehyde, they do not form any complex with phenol in water but do so in dioxan. From these and other examples it appears that water is inhibiting complex formation by protecting the carbonyl-group. Again, a similar protective effect is noticed in the case of carbohydrates. Unsulphonated azo-compounds can form intermolecular bonds between the azo-group and (i) amide groups in non-aqueous solvents (Table 4), (ii) alcoholic groups in solutes in the water sub-phase when an azo-compound is spread as a monolayer thereon (Giles and Neustädter), but sulphonated azo-compounds do not appear to interact in water either with alcoholic groups (Table 4) or with the amide groups of amino-acids (Derbyshire and Marshall). These facts show that the sulphonic acid may be preventing interaction of the azo-group 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 of the azo-nitrogen atoms. Phenols, however, have enough affinity to interact with the sulphonated compounds.

Apart from the above evidence of the protective effect of water, the results demonstrate that the molar ratio of the complexes between given solutes is sometimes not the same in water as in non-aqueous solvents. For example, in non-aqueous solution diethylamine combines with two molecules of phenol but in aqueous solution with one molecule only.

Water as a solute, in non-aqueous solvents, acts either monofunctionally or bifunctionally (Fig.1) as a cross-linking agent, both hydrogen atoms being involved in bonds, e.g., water acts as a cross-link between two molecules of 1-phenylazo-2-naphthol thus -



Brode et al. have attributed the appearance of a new band in the light absorption spectra of alcoholic solutions of certain azo-compounds, on addition of water, to a hydrogen bond between the azo-group and water.

Protective Influence of Other Solvents.

It was reported by Giles, Rose and Vallance that no evidence could be obtained of intermolecular bonding involving the ketone group in benzene solution although Badger and Bauer detected bonding between acetone and methanol by infra-red spectrophotometry of binary mixtures, or solutions in carbon tetrachloride. In the present investigation, it has been noted that benzene, and also diethyl ether, do prevent complex formation of phenol with ketones. The exact nature of this preventive effect is however not very clear. A study of the Tables 1, 4 (Section II) and 5 (Section III) reveals a number of other examples of the protective effect of a solvent preventing hydrogen bonding between various individual groups. These are summarised in Table 2 below.

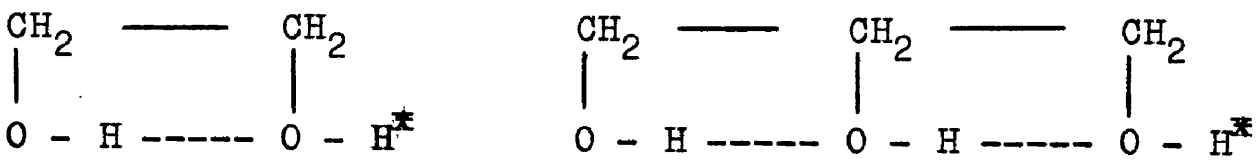
Table 2.

Solvation effects in intermolecular hydrogen bonding.

Groups		Solvent (see Table 1)	
a	b	a Reactive with b in	Inactive in
OH (alk)	OH (alk)	Cs,D	W
"	OH (ar)	T,W	None
OH (ar)	OH (ar)	D,T,W	None
CHO (alk; ar)	OH (alk,ar)	C,T	W
"	$:N_2\cdot$, $\cdot NR_3$, etc.	All	None
C=O (keto)	All	C,D,T	B,E,W

Alcohols and Phenols.

Monohydric alcohols would be expected to form only one complex and, in fact, methanol, ethanol, n-butanol etc. do form only 1:1 complexes with phenol (Fig.2). Poly-hydric alcohols however form additional complexes, corresponding with the number of hydroxy-groups, with phenol but with methanol, triethylamine, or water, no other complex but that of 1:1 ratio is evident (Fig.2). The most reasonable interpretation of these observations is that pairs of vicinal hydroxy-groups interact to form weak five-membered chelate rings, e.g. in ethylene glycol or glycerol -



thus only one hydrogen atom (*) is left free to form intermolecular bonds with a weak second solute like triethylamine. Phenol, being a more powerful hydrogen bonding agent, can disrupt these rings in a suitable solvent and so unite with each hydroxyl-group.

The above interpretation is supported by the work of Bastiansen, who detected this form of intramolecular bond in ethylene glycol and glycerol by the electron diffraction sector method, and pointed out that published heats of combustion lend further support to the hypothesis, being for these compounds respectively 5.4 and 10.3 kcal/mole. lower than required by theory, i.e., less by about the values for one and two hydrogen bonds.

Further confirmation of the existence of this intramolecular bond was obtained by the examination of a diol in which the pairs of alcoholic groups are too widely separated to form such bonds. Thus, in pentane-1:5-diol (Fig.2) both groups are free to react and so it forms a 1:2-complex with methanol. In butane-1:4-diol, probably, a seven membered ring exists, but even so it is difficult to account for the complete unreactivity of this compound in the tests made here.

A similar intramolecular bond has been detected in poly-hydric phenols as well. For example, Wulf, Liddel and Henricks have shown the existence of chelation in the ortho-hydroxy groups of catechol, by infra-red spectroscopic examination of its carbon tetrachloride solution. In the present work the existence of this link is evident in the 1:1-complex between catechol and methanol in comparison to the 1:2-complex between quinol and methanol.

As mentioned earlier the presence of hydrogen bonds affects the melting or boiling points of substances. The melting and boiling points of certain diols shown in Table 3 thus give evidence of chelation since the compounds with vicinal groups, i.e. those where the formation of intramolecular hydrogen bonds is expected, have lower values than the corresponding isomers with more widely separated groups.

Table 3.

Physical Constants of Certain Chelated and Unchelated Compounds.

Chelated	M.p.	B.p.	Unchelated	M.p.	B.p.
Alcohols and Phenols					
Catechol	104°	-	Quinol	169°	-
Butane-1:2-diol	-	191°	Butane-1:3-diol	-	203°
Butane-2:3-diol	-	183°	Pentane-1:4-diol	-	219°
Pentane-2:3-diol	188°	-	Pentane-1:5-diol	-	238°
			Pentane-2:4-diol	-	197°
Nitro-compounds					
o-Nitrophenol	44°	-	p-Nitrophenol	114°	-
o-Nitrobenzoic acid	144°	-	p-Nitrobenzoic acid	241°	-
o-Nitrobenzaldehyde	44°	-	p-Nitrobenzaldehyde	106°	-

Aldehydes and Ketones.

Aldehydes form 1:1-complexes with almost all the hydrogen-donor solutes used, except ethanol or phenol in water, where, as discussed elsewhere, the solvent is probably protecting the carbonyl-group. Rather unexpectedly aldehydes also form 1:1-complexes with hydrogen-acceptors, e.g. triethylamine or pyridine (Fig.3). The reality of existence of such complexes was further obtained by molecular-weight experiments (Fig.3). The most likely interpretation of the results is that the interaction is by bonding with the hydrogen atom of the aldehyde-group, which is activated by the adjacent carbonyl-group. This bond is comparable to that in the hydrogen cyanide crystal (Pauling) -

$$Et_3N \text{ ----- } H - \underset{\underset{R}{|}}{C} = O \quad \text{--- } H - C \equiv N \text{ --- } H - C \equiv N \text{ ---}$$

Dipole-interaction effects produced by hyperconjugation of the attached alkyl group (Coulson) might be thought perhaps to account for these results. Formaldehyde was therefore examined which cannot exhibit such effects, yet it behaves like its higher homologues, so the suggested hydrogen bond mechanism is confirmed.

The nature of the complexes formed by phenol or pyridine with ortho- and meta-nitrobenzaldehyde (Fig.4)

also indicates that the hydrogen atom of the aldehyde-group must be capable of forming intra- as well as inter-molecular bonds. Lundgren and Binkley have noticed that Rhodamine B (Colour Index No.749) gives a red colour only in presence of hydrogen-donors e.g. phenol or water; it is colourless in hydrocarbons, but they have found that o-nitrobenzaldehyde exhibits little activity towards the dye, compared with the activity of the meta-isomer, and this difference they attributed to chelation in the ortho compound. Therefore, in the present work also, Rhodamine B was used as a hydrogen-donor indicator and it was noticed that propionaldehyde in dry toluene imparted a red colouration to Rhodamine B.

From Table 3 also it is evident that o-nitrobenz-aldehyde, like o-nitrobenzoic acid and o-nitrophenol, has a lower melting point than its meta-isomer, further evidence of chelation.

In order to obtain further evidence of hydrogen bond formation through hydrogen attached to a carbon atom, infra-red spectroscopic examination of solutions of (i) phenol (0.05 M) and propionaldehyde (0.05 M) and (ii) pyridine (0.05 M) and propionaldehyde (0.05 M) in carbon tetrachloride solution were made and their spectra were compared with the spectra of 0.1 M phenol, 0.1 M pyridine and 0.1 M propionaldehyde respectively, all in

carbon tetrachloride solution. Also, the spectra of iso-butyraldehyde (pure) and its equimolar mixture with pyridine, were recorded. No conclusive information could be drawn from the results however because the propionaldehyde (0.1 M) reference curve gave indication of the presence of propionic acid resulting from aerial oxidation of the aldehyde, though little or no acid was evident in the pyridine-propionaldehyde solutions. There also appeared traces of carboxylic acid in the iso-butyraldehyde-pyridine mixture which interfered with examination of the aldehyde bands. However, there is some evidence of a small increase in hydrogen bonding of the phenolic group in presence of propionaldehyde, the optical densities of the free and bonded OH-stretching frequencies of phenol alone (0.1 M) being 0.505 and 0.097 respectively, and of phenol (0.05 M) in presence of propionaldehyde 0.0315 and 0.105, respectively. The bonded OH band also broadened and shifted slightly from 3460 $cm.^{-1}$ to 3440 $cm.^{-1}$ Yet in spite of the fact that there is some evidence of interaction between phenol and propionaldehyde, there were no changes in the characteristic bands of the aldehyde groups in this system. All that can be said therefore is that the spectroscopic results give no evidence either for or against the hypothesis of bonding by the hydrogen of the aldehyde group.

Very few tests were made with ketones, though it was noticed that these can react bifunctionally with alcohols or phenols. However, they are unreactive with other solutes in benzene, water or ether (discussed elsewhere). There is no evidence that any symmetrical ketones can act as hydrogen-donor (also see Section III).

Carbohydrates.

Normally, the carbohydrates possess the pyranose ring-structures in water, only a small percentage of open-chain compound being present. Therefore, it would be expected that cellobiose will react with twice as many molecules of a second solute as glucose does. On the other hand, it was found (Table 1) that these carbohydrates behave mono-functionally with most of the second solutes and do not react at all with phenol in water (Fig.5).

These observations can be best interpreted if it is assumed that the hydroxy-groups of carbohydrates are chelated or solvated by water and that the second solute, e.g. triethylamine or pyridine, reacts with the aldehyde group of the open-chain structure, which is present in small quantity, in equilibrium with the pyranose ring-form. As this reaction proceeds with, say pyridine, the equilibrium shifts in favour of the open-chain structure and therefore a 1:1-complex is obtained, the aldehyde group acting as a

hydrogen-donor*. With phenol no such complex is evident because, firstly, the aldehyde group is unreactive with phenol (see aldehydes) and, secondly, in the ring-form the water-attracting power of the hydroxy-groups may be greater than in open-chain form, and reaction with phenol will thus be prevented.

In the open-chain form the hydroxy-groups are not so strongly solvated by water as they are in the ring-form, and their apparent unreactivity with, e.g. triethylamine, must be attributed to the form of chelation observed here with the open-chain alcohols, note e.g. that glycerol and triethylamine form only a 1:1-complex. In the glucose open-chain chelation restricts the number of free hydrogen atoms to one, at the aldehyde group.

These conclusions are further confirmed by the examination of solutions of ternary mixtures. If the open-chain structure is thus favoured or stabilized by the presence of pyridine, it would be expected that phenol with its high potentiality for forming hydrogen bonds, will penetrate through the solvated hydroxy-group of the open-structure of the carbohydrate and will react with all the hydroxy-groups. In fact, the results in Table 1 show that phenol does form a 6:1-complex with glucose in presence of either triethylamine or pyridine (Fig.6). Apparent

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* If this is so, triethylamine in water should be unable to form complexes with ketoses and in fact none is detected with either fructose or sucrose.

molecular weights determinations were also made to confirm the reality of existence of these complexes (Fig.6).

In confirmation that these complexes are not formed merely by an increased reactivity of phenol produced by the alkalinity of the added base, the solutions of binary mixtures of glucose and phenol buffered at pH 8.4 were also examined and no complexes were detected.

It was also noticed that mannitol forms a 1:6-complex with phenol in ethylene glycol but only a 1:1-complex with water, because phenol can disrupt the chelate rings, but water cannot. When phenol or water are used with glucose in ethylene glycol solution both give 6:1-complexes. Therefore the reactions here must be with the ring-structure of glucose, which is unchelated*, so that even water is free to bond with all the hydroxy-groups. Even though there may still be an equilibrium mixture of (chelated) chains and (unchelated) ring-forms of glucose in this solvent, this would clearly not prevent the ring-form from reacting in the manner suggested.

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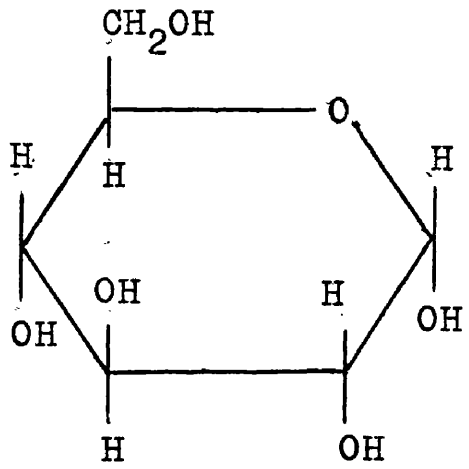
* Molecular models show that chelation is not possible in the ring-structure.

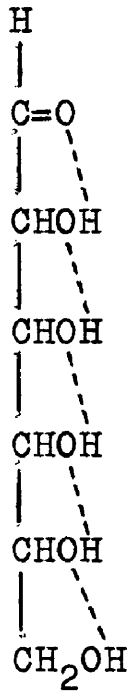
These reactions of the carbohydrates are best summarised as follows -



Ring structure
(unchelated)

Unreactive in <u>water</u> because of strong solvation of all -OH groups.

In <u>ethylene glycol</u> solution all -OH groups and -O- react with phenol or with water.



Open-chain structure
(chelated)

All -OH groups are chelated and unreactive. CH --- bond on aldehyde group reacts in water with a N-atom, but not with an alcoholic or phenolic group, in any second solute.

Mechanism of Adsorption by Cellulose.

From a study of the reactions of carbohydrates just discussed, explanations can be advanced to account for the adsorbtive properties of cellulose. Preston and Nimkar, by studying freezing-point curves of adsorbed moisture in cellulose fibres, have shown that the non-crystalline parts of the fibre are in a state resembling solution in the water. Since adsorption on cellulose takes place on molecular chains in non-crystalline regions consisting of chains of cellobiose residues, it is very likely that these are also surrounded by water molecules and bound so firmly that other solutes cannot normally penetrate.

This explains why phenol is not adsorbed on cellulose (Hassan, Marsden and Urquhart) from aqueous solution, whereas other substrates, e.g. alumina, nylon, wool, cellulose acetate etc. which are capable of forming hydrogen bonds, readily adsorb phenol from dilute aqueous solution.

Section II.

The Reactivity of Amines, Amides and Azo-compounds in Aqueous and Non-Aqueous Solutions.

A study of the reactivity of the amino- and amido-compounds used as models of proteins and certain synthetic materials, e.g. nylon, with azo-compounds, used as models of dyes,is of great interest in helping towards an understanding of the mechanism of adsorption of dyes by these fibres. The results of the present investigation have been summarised in Table 4 and some typical curves are shown in Figs.8-12. Some of the results were obtained by the author's colleagues and these are suitably differentiated from those obtained by the author.

Reactivity of Amides.

The alkylamide group reacts bifunctionally, both as hydrogen donor and hydrogen acceptor i.e. reacts both with phenol and triethylamine (Fig.8). The present results can be most satisfactorily explained if it is assumed that the unsubstituted and mono-substituted amides usually react in the enol form (.C(OH):N.) in non-aqueous solvents, and in the keto form in water. The carbonyl group should thus be present in water but may be protected by the solvent (see Section I). Consider, e.g. quinol, which forms a

Table 4

Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method† and temp	Mol. ratio of complex (a:b) ‡
Amides					
Acetamide	Benzoquinone	T,El	0.04	n 20°	1:1 xx
"	"	W	0.1	n 20	2:1
"	Ethanol	D	0.2	n 21	(1:1)
"	Haematoxylin	Ac	0.3	ϵ —	(2:1)xx
"	Phenol	W	0.25	n 22	1:1
"	"	D	0.2	n 21	1:1
"	Pyridine	W	0.2	n 19	1:1
"	Quinol	W	0.25	n 20	2:1
"	"	D	0.2	n 19	1:1
"	Triethylamine	W	0.2	n 19	1:1
N-n-Butylpropion-amide	Diethylamine	T	0.2	ϵ,n 20	(1:2)xx
	Ethanol	T	0.2	ϵ,n 20	1:1//
"	Urea	El	0.1	n 20	1:1
"	Quinol	E	0.15	ϵ —	1:1
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	Acetone	B	0.25		§
"	Aniline	B	0.25	ϵ,n 20	2:1
"	Diethylamine	B	0.25		1:1
"	Diphenylamine	C	0.05	n 17	§ xx
"	Haematoxylin	W	0.05	n 20	4:1 xx
"	Phenol	B	0.25		1:1
"	"	W	0.25	n 19,35	1:1
"	"	C	0.1	n 22	1:1;1:2

Table 4 (Cont'd)

Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method† and temp	Mol. ratio of complex (a:b) ‡
Diamides					
Diacetamidomethane	Diethylamine	W	0.1	n 17	§
"	"	El	0.1	n 17	1:1
"	Phenol	El	0.1	n 21	1:1
"	"	W	0.1	n 17	1:1
"	Pyridine	W	0.2	n 22	§
"	Triethylamine	W	0.1	n 17	§
"	"	El	0.1	n 16.5	1:1
Anilidoglycine-acetyl	Phenol	El	0.1	n 17	1:2 xx
	Triethylamine	An	0.05	n 17	§ xx
"	"	El	0.05	n 21	(1:2)xx
Diacetamidohexane	n-Pentanol	W	0.1	n 19	(1:2)
"	Phenol	El	0.1	n 21	1:2
"	Triethylamine	El	0.1	n 21	§
Amines					
Aniline	Anisole	B	0.25	¢—	§ xx
"	Diethylamine	W	0.25	n 18	1:1
"	Triethylamine	W	0.25	n 19	(1:1)
Diethylamine	Azobenzene	B	0.25	n 19	1:1
"	o-Nitrophenol	B	0.25	n 18	1:1 xx
"	Phenol	B	0.25	n 19	1:1
"	"	D	0.1	n 20	1:1;(1:2)
"	"	T	0.05	n 17	1:1;(1:2)
"	"	W	0.25	n 18,20	1:1 //
"	Triethylamine	D	0.2	n 22	§
"	"	W	0.1	n 17	(§)
"	"	El	0.1	n 17	§

Table 4 (Cont'd)

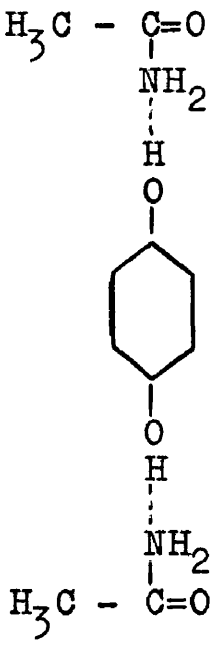
Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method† and temp.	Mol. ratio of complex (a:b) ‡
Triethylamine	Ethanol	W	0.25	n 21	§
"	Resorcinol	T	0.25	ε,n 20	2:1
Azo-compounds					
$PhNH_2 \longrightarrow$ 2:3:6- $C_{10}H_5(OH)(SO_3Na)$	Diethylamine	W	0.05	n 20	1:2
	Ethanol	W	0.05	n 20	§
"	Glycol	W	0.05	n 20	§
"	Phenol	W	0.05	n 20	1:1
$PhNH_2 \longrightarrow$ 1- $C_{10}H_7.NH_2$	Phenol	T	0.1	ε,n 20	(1:3;1:4)
$PhNH_2 \longrightarrow$ 2- $C_{10}H_7.NH_2$	Phenol	T	0.1	ε,n 20	1:2
$PhNH_2 \longrightarrow$ 2- $C_{10}H_7.OH$	Aniline	B	0.25	ε —	2:1 xx
	Phenol	B	0.25	ε —	1:1;(1:2)
"	Quinol	D	0.1	n 20	1:1;(2:1)
"	Resorcinol	E	0.25	ε —	2:1;1:1xx
"	CCl_2:CHCl	T	0.1	ε,n 20	1:2 xx
Azobenzene	Aniline	B	0.25	n 19	2:1
"	Benzoquinone	T	0.1	n 19	§
"	$PhCH_2.OH$	C	0.1	n 20	1:1 xx
"	Diethylamine	B	0.25	n 19	1:1
"	Phenol	B	0.25	n 19	1:1;1:2
"	Triethylamine	D	0.1	n 18	§

* Ac = acetone; An = aniline; B = benzene; C = carbon tetrachloride; D = dioxan; E = diethyl ether; El = ethanol T = toluene. † ε = dielectric constant; n = refractive index.

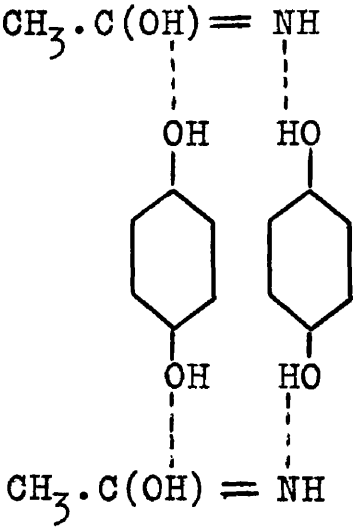
‡ Data in parentheses denote uncertain indications.

§ No evidence of complex formation. // Curves show particularly pronounced change of slope. xx Results reported by Arshid and Hassan.

1:1-complex with acetamide in non-aqueous solution but a 1:2-complex in water (Fig.9). Since quinol is bifunctional and in water it is assumed that the carbonyl group is inactive, quinol may here be complexing with one acetamide molecule at each end thus forming a 1:2-complex (I). In non-aqueous solution i.e. in the enolic form, a 2:2-complex will be formed as shown in II, but by the present method this would be registered as a 1:1-complex.



I (in water)



II (in non-aqueous solvents)

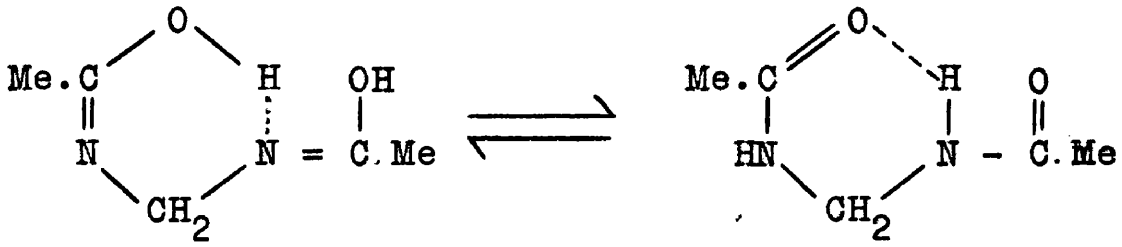
Complexes of Quinol and Acetamide

Similar results have been obtained by Giles, Rose and Vallance on their studies of interaction of the amido-group by the dielectric constant method; these authors suggested

the tautomeric change in the two types of solvent as an explanation of the complexes they observed. Buswell, Rodebusch and Roy observed (by infra-red spectrophotometry) that N-ethylacetamide enolises in carbon tetrachloride solution.

The disubstituted amides as expected, exist only in the keto form. It is interesting to note that these disubstituted forms seem to give 4:1-complexes with azobenzene and benzoquinone (Fig.10). If it is assumed that this combination is due to hydrogen-bond formation, the hydrogen atom must be denated by the $-CO.CH_3$ group (cf. Section III) and each nitrogen atom of azobenzene must be accepting two hydrogen atoms, which is rather unusual and has apparently not been reported before, although two hydrogen atoms are readily taken up by oxygen, e.g. 1:8-dihydroxyanthraquinone has two chelate rings, both hydroxy-groups combining with the same quinone oxygen (Pauling).

The reactivity of the amido-group in diamides is similar to that in amides in general. Diacetamidomethane, however probably exists in the chelated forms:



and thus reacts as a monoamide (Fig.11). Similar stable ring structures are not possible in the other two diamides, anilidoacetylglycine (Ph.NH.CO.CH_2.NHAC) and diacetamidohexamine (CH_3CO.NH.(CH_2)$_6$.NH.CO CH_3), examined and thus they behave as normal diamides.

The behaviour of amides may thus be summarised -

(a) The reactivity of the nitrogen in amides is similar to its reactivity in amines.

(b) In non-aqueous solution the unsubstituted and mono-substituted amides exist probably in the enol-form but in water in the keto-form only.

(c) The reactivity of the carbonyl group in the keto-form, and its effect on the adjacent methyl group, is similar to its reactivity in aldehydes and esters.

Reactivity of Azo-compounds:-

Azo-dyes are in terms of volume of output much the most important class of dyes, and they are used for dyeing all types of fibres. Amongst the various forces that cause adsorption of azo-dyes by fibres, the formation of hydrogen bonds has frequently been suggested. Therefore a knowledge of the hydrogen bond reactivity of azo-compounds in aqueous solution should help in interpreting its importance in dyeing. Direct examination of many dyes by the

refractive index method was not possible because of the difficulties arising from their intense colour even in very dilute solutions, and in spite of the fact that different sources of light were used.

From Table 4, however, it is clear that both the nitrogen atoms in the azo-group form hydrogen bonds, unless of course one of them is previously chelated. For example, the presence of a chelate ring is obvious in aniline ⟶ 2-naphthylamine when its combination with phenol is compared with that of aniline ⟶ 1-naphthyl-amine and phenol. A similar chelate ring has also been observed in Orange II (Arshid et al. 1955).

The free nitrogen atom in sulphonated o-hydroxyazo-compounds forms a 1:1-complex with phenol but no combination is evident with ethanol (Fig.12). This may be because of the protective effect of the solvent, the bond with the alcoholic group being a weak one (cf. Section I). The 1:2-complex with diethylamine is probably due to salt-formation with the sulphonic acid groups.

Mechanism of Adsorption of Dyes by Wool and Nylon:-

It is now fairly well established (see, e.g. Speakman, Elod, Gilbert and Rideal) that salt-formation between the basic amino-groups of these fibres and acid dyes is of

primary importance in adsorption. However, Valkó; Steinhardt, Fuggitt, and Harris; and Vickerstaff have suggested that hydrogen bonds may also be formed between dye and fibre. The present work, also, reveals that the amido-groups is further capable of attracting dyes by hydrogen-bond formation and thus explains the very high adsorption of acid dyes observed which is unaccountable on the basis of salt-formation.

Section IIIa

Reactivity of Esters

In the present work the hydrogen-bonding reactivity of esters has been investigated with a view to determining its importance in adsorption of solutes by chitin, cellulose acetate, Terylene fibre, and other polymeric esters. Amongst the model compounds used were aliphatic esters (for cellulose acetate), N-acetyl-D-glucosamine (for chitin), and dimethyl-terephthalate and ethylene glycol dibenzoate (for Terylene).

From Table 5 it is clear that esters, besides being hydrogen-acceptors, also donate hydrogen to form complexes with hydrogen-acceptors, e.g. pyridine, triethylamine or azobenzene (Fig.13). It has already been pointed out in Section I that in aldehydes the hydrogen attached to the carbonyl group is activated and rendered capable of forming hydrogen bonds. The reactions of the esters show that this effect can apparently occur also at a hydrogen atom attached to the α-carbon atom. In ethylene glycol dibenzoate, e.g., the active -CH group appears to be that attached α to the -O-C=O group.

The effect of a carbonyl group on adjacent atoms may be seen readily by comparing the ionisability of the hydrogen atom in the carboxyl group and in the alcoholic group respectively. The reactivity of the hydrogen attached to carbon is of course even more increased if this group is

Table 5.

Results of complex-detection tests.

Solutes		Solution				
a	b	Solv.*	Total mol. concn.	Method(s)† and temp.	Mol. ratio of complex (a:b) ‡
Acetyl chloride	Acetone	C	0.2	n 19°	1:1
"	Azobenzene	D	0.1	n 22	2:1
Benzyl acetate	Acetone	T	0.1	n 22.5	§
"	Dioxan	T	0.1	n 22.5	§
"	Pyridine	T	0.1	n 24	§
N-Acetyl-D-glucosamine	Methanol	W	0.25	n 19	1:1 xx
	"	EG	0.1	n 18	1:1;(1:4)xx
"	ß-Naphthol	EG	0.05	n 18	(1:1);1:4
"	Phenol	EG	0.05	n 16,18	1:1;1:4
"	"	W	0.25	n 18	1:1
"	Triethylamine	W	0.25	n 20	1:1
"	Quinol	W	0.25	n 20	2:1
"	Alizarin-3-sulphonic acid(sodium salt)	pH 9	0.01	n 20	1:2
"	Anthraquinone-2-sulphonic acid(sodium salt)	pH 9	0.012	n 20	1:2
"	2-Hydroxyanthraquinone	pH 9	0.01	n 20	1:3;1:1
2-Acetylpyridine	Acetone	T	0.1	n 21	(§)
"	Triethylamine	T	0.1	n 21	1:1

Table 5 (Cont'd)

Solutes a	b	Solv.*	Solution Total mol. concn.	Method(s)† and temp.	Mol. ratio of complex (a:b) ‡
3-Acetylpyridine	Acetone	T	0.1	n 21.5	§
"	Pentyl alcohol	T	0.1	n 22	1:1
"	Azobenzene	T	0.1	n 19.5	(§)
"	Diisobutyl ketone	C	0.1	n 21	§
"	Diethylamine	T	0.1	n 21	1:1
"	Pyridine	T	0.1	n 19.5	(§)
"	Triethylamine	T	0.1	n 21.5	§
Catechol diacetate	Acetone	D	0.1	n 21	§
	Diisobutyl ketone	C	0.05	n 21	1:1
"	"	T	0.1	n 22.5	1:1;1:2
"	Triethylamine	C	0.05	n 20.5	1:1
"	"	D	0.1	n 21	1:1
"	"	T	0.1	n 22.5	(1:1)
Dimethyl terephthalate	Phenol	T	0.1	n 18	1:4
	Triethylamine	T	0.1	n 18	1:4
Ethylene glycol diacetate	Acetone	D	0.2	n 21	(1:1)
	Diisobutyl ketone	D	0.2	n 21	1:1
"	Triethylamine	T	0.2	n 21	1:1
Ethylene glycol dibenzoate	Phenol	T	0.1	n 22	1:4 xx
	Triethylamine	T	0.1	n 20	1:4
Ethyl acetate	Acetone	T	0.2	n 21	1:1
"	Azobenzene	T	0.1	n 17,21.9	4:1
"	1-Naphthol-5-sulphonic acid (oxy-L-acid)	W	0.04	n 24	§

Table 5 (Cont'd)

Solutes a	b	Solv.*	Total mol. concn.	Method(s)† and temp.	Mol. ratio of complex (a:b) ‡
			Solution		
Ethyl acetate	o-Nitrophenol	P	0.1	n 20	(1:1)
"	"	T	0.1	n 14	1:1
"	p-Nitrophenol sulphuric ester	W	0.04	n 24	1:1
Ethyl trichloroacetate	Acetone	T	0.2	n 20	1:1
	Azobenzene	C	0.2	n 20	1;1;2:1
"	Triethylamine	T	0.2	n 20	(1:1)
α-D-Glucose pentaacetate	Acetone	T	0.1	n 21	1:1;1:3;1:5
	Aniline	T	0.1	ϵ,n 20	(1:1)
"	Anisole	T	0.1	ϵ,n 20	(1:1) xx
"	Azobenzene	T	0.1	ϵ,n 20,21	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 xx
"	Phenol	D	0.1	n 20	1:1;1:6 xx
"	Triethylamine	T	0.1	n 20,21	1:1
"	"	D	0.1	n 20	1:1;1:6
Glycerol triacetate	Azobenzene	T	0.1	n 20.5	2:1
	Diisobutyl ketone	T	0.1	n 21	1:1;(1:2 or 1:3)
"	Diethylamine	D	0.1	n 15	(1:3)
"	"	T	0.1	n 12	1:1
"	Dioxan	T	0.1	n 21.5	1:3
"	2:2'-Dipyridyl	W	0.025	n 18.8	(2:1)
"	4-Hydroxyazobenzene-4'-sulphonic acid	W	0.025	n 20.8	§ xx
"	1-Naphthol-5-sulphonic acid	W	0.05	n 21	(§)

Table 5 (Cont'd)

Solution

Solutes a	b	Solv.*	Total mol. concn.	Method(s)† and temp.	Mol. ratio of complex (a:b) ‡
Glycerol triacetate	2-Naphthol-6-sulphonic acid	W	0.05	n 24	(§)
"	o-Nitrophenol	T	0.1	n 21.5	1:1 xx
"	p-Nitrophenyl sulphuric ester	W	0.04	n 17.5,23	1:1
"	Pyridine	T	0.1	n 20.5	1:1
"	Sulphanilic acid ⟶ 1-naphthol	W	0.01	n 22	(§) xx
"	Triethylamine	W	0.2	n 20.8	1:1;1:3
Methyl oxalate	Acetone	C	0.2	n 20.5	1:1;1:2
"	Phenol	D	0.05	n 16.5	1:2
"	Triethylamine	C	0.2	n 20.5	1:1;1:2
Pentane-1:5-diol diacetate	Diisobutyl ketone	T	0.1	n 21	1:2
"	Triethylamine	T	0.1	n 21	1:2
isoPropyl acetate	Anisole	D	0.1	n 20	1:1 xx
	Azobenzene	D	0.1	n 19	4:1
"	Benzoquinone	T	0.2	ϵ,n 20	2:1
"	3-Methoxy-benzanthrone	D	0.01	n 20	(2:1) xx
"	o-Nitrophenol	D	0.1	n 19	1:1
"	"	T	0.1	n 20	1:1;(1:2)
"	Phenol	T	0.2	ϵ,n 20	1:1
Quinol diacetate	Acetone	D	0.1	n 21	§
"	Diisobutyl ketone	C	0.05	n 21	(1:1);1:2
"	Triethylamine	C	0.05	n 20.5	(1:2)
"	"	D	0.1	n 21	1:2

Table 5 (Cont'd)

Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method(s)† and temp.	Mol. ratio of complex (a:b) ‡
Trichloro-acetyl chloride	Acetone	C	0.1	n 22.5	1:1
	Azobenzene	D	0.1	n 22	(§)
"	Diisobutyl ketone	T	0.1	n 21	(1:1 or 1:2)

* Solvents: B = benzene; C = carbon tetrachloride; D = dioxan; EG = ethylene glycol; P = light petroleum (b.p. 80-100°); T = toluene; W = water.

† ϵ = dielectric constant; n = refractive index.

‡ Data in parentheses denote uncertain indications.

§ No evidence of complex formation.

xx This result reported by Arshid.

adjacent to two carbonyl groups, as in acetoacetic ester.

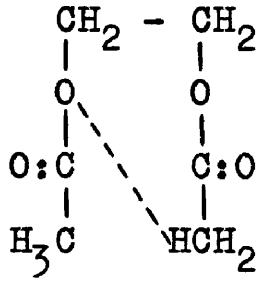
Further confirmation of the reactivity of hydrogen in such cases was obtained by Rhodamine B test (cf. Section I). It was found that in toluene solutions of glycerol triacetate or pentane-1:5-diol diacetate, a red colouration was obtained on addition of Rhodamine B, indicative of the presence of a hydrogen available for bonding. Ethyl acetate however, though it seems to form complexes with hydrogen-acceptors, fails to give this test.

Trichloroacetyl chloride forms complexes with acetone and diisobutyl ketone. These complexes seem unlikely to be due to hydrogen-bonding, because there is no evidence that normal ketones can act as hydrogen donors; they are probably due to dipole-dipole interaction at the C=O bond, strongly activated by the trichloro-group. With bases in non-aqueous solution trichloroacetyl chloride gives copious precipitates of "Lewis salts". Similar bonds with hydrogen attached to carbon, have also been detected by other workers. For example, Earp and Glasstone detected bonding between ethers and alkyl halides. The high solubility of alkyl halides of the type CH_2X_2, CHX_3, in solvents possessing hydrogen-acceptor groups compared with that predicted from Raoult's law, is also attributable to the same effect. To explain the unusual behaviour of n-butyric acid compared with its analogous compounds, Dippy has suggested that even the hydrogen

attached to the γ - or δ -carbon atom can form hydrogen bonds. Recently, Jones and Badger have given evidence from infra-red spectrophotometry, of intermolecular bonding between methanol and the hydrogen of aromatic rings. The present investigation, however, gives no evidence that the effect of an adjacent carbonyl group or other electron-attracting groups can be propagated beyond the α-carbon atom.

Chelation in Esters.

The evidence for the existence of chelation in adjacent hydroxy groups of polyhydric alcohols has been presented in Section I. Since esters can act as hydrogen donors, similar chelation in adjacent ester groups might be expected and therefore a number of diacetates have been examined to find out if chelation can be detected. Ethylene glycol diacetate, like ethylene glycol, forms only a 1:1-complex with proton-acceptors e.g., with triethylamine, diisobutyl ketone or acetone. With glycerol triacetate, however, in addition to the 1:1-complex, a 1:3-complex is also detectable (Fig.14). This shows that chelate rings of very low energy exist in 1:2-diesters, which can be formulated thus -



Similarly catechol diacetate forms a 1:1-complex with

triethylamine whereas a 1:2-complex is formed between quinol diacetate and triethylamine (Fig.15).

Infra-red spectra were also recorded in further confirmation of the existence of such chelate rings. The characteristic absorption frequencies of various groups in catechol diacetate and quinol diacetate (1.5% CCl_4 solutions, 0.8 mm. cells) are shown in Table 6.

Table 6.

Characteristic Absorption Frequencies

	Catechol diacetate	Quinol diacetate
>C = O	1776 cm.$^{-1}$ and 1727 cm.$^{-1}$	1776 cm.$^{-1}$
$-CH_3$ (Symmetrical deformation)	1443 cm.$^{-1}$ and 1468 cm.$^{-1}$	1439 cm.$^{-1}$
-C-O stretching peak	1190 cm.$^{-1}$ (very broad)	1175 cm.$^{-1}$ and 1205 cm.$^{-1}$

Both catechol diacetate and quinol diacetate show a carbonyl peak at 1776 cm.$^{-1}$, but the appearance of an additional peak at 1727 cm.$^{-1}$ in the former only, indicates some interaction involving this group. At the same time, the slight differences in the CH_3 symmetrical deformation band and the -C-O stretching peak appear to show that some form of hydrogen bond may be affecting both these groups.

The solutions of ethylene glycol diacetate and pentane-1:5-diol diacetate (1.5% CCl_4, 0.8 mm. cells), and the two pure liquids, were also examined. There were no significant

differences in the C=O band of the two compounds, but the centre of the broad C-O acetate band at 1070 cm.$^{-1}$ in ethylene glycol diacetate shifted to 1050 cm.$^{-1}$ in pentane-1:5-diol diacetate; also the C-O stretching frequency at 1247 cm.$^{-1}$ in the former shifted to 1258 cm.$^{-1}$ in the latter. In the CCl_4 solutions the CH_3 symmetrical deformation band occurs at 1381 cm.$^{-1}$ in both spectra but in addition to this another band at 1403 cm.$^{-1}$, probably also a CH_3 symmetrical deformation, appears only in the spectrum of pentane-1:5-diol diacetate. These small differences do not give conclusive evidence of hydrogen-bonding, but indicate that some interaction occurs only when the two acetate groups are sufficiently close to each other.

The physical constants of some of the diacetates are shown in Table 7 below. The melting or boiling points of the diacetates having adjacent substituent groups are consistently lower than the corresponding ones with the substituent group more widely separated, which is again confirmatory evidence of chelation in the former.

Table 7.

Physical constants of diacetates of dihydric alcohols and phenols.

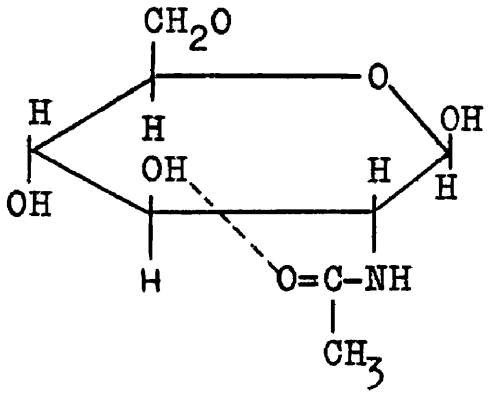
Diacetate of	M.p.	B.p.	Diacetate of	M.p.	B.p.
Catechol	63.5°	-	Quinol	121°	-
Butane-1: 2-diol	-	196-199°	Butane-1: 3-diol	-	208°
Butane-2: 3-diol	-	190(200)	Butane-1: 4-diol	-	230
Pentane-1: 2-diol	-	216-217(219)	Pentane-1: 5-diol	-	241
Hexane-2: 3-diol	-	215-220	Hexane-1: 6-diol	-	260
			Hexane-2: 5-diol		225-230

Another interesting feature of the reactivity of the esters is that they do not combine with hydrogen-bonding groups in highly ionic compounds, e.g. glycerol triacetate does not form any complex with either 1-naphthol-5-sulphonic acid or 2-naphthol-6-sulphonic acid, but it does combine with the less highly ionised p-nitrophenyl sulphuric ester (Fig.16). This fact may have some bearing on the adsorbtion properties of acetate fibres. Experiments

with monolayers on water (Allingham et al; Cameron), however, do appear to indicate the possibility of interaction between acetate groups and hydrogen-bonding centres in sulphonated dyes, so that the negative evidence reported here is not conclusive.

Reactivity of N-acetyl-D-glucosamine.

A knowledge of the reactivity of this substance is of special interest in interpreting the adsorption phenomenon of the natural polymer, chitin, of which it is the principal building unit. From Table 5 it is clear that it is monofunctional in water, whereas in ethylene glycol solution it forms a 1:4-complex with phenol or β-naphthol (Fig.17). These reactions are comparable with those of glucose (Section I). It may be concluded therefore that, like glucose, this compound has its hydroxy-groups protected by water and the 1:1-complex with phenol or alcohols is formed at the nitrogen atom. The 1:4-complex with phenol in ethylene glycol solution could be explained if it is assumed that three of the hydroxy-groups combine with three molecules of phenol and the fourth phenol molecule combines with the nitrogen atom. The fourth hydroxy-group of N-acetyl-D-glucosamine is probably chelated thus -



This type of chelate bond has been suggested by Darmon and Rudall as existing, together with free >NH groups, in chitin, on the evidence of studies with polarised infra-red and X-radiation.

The complex formed with alizarin-3-sulphonic acid in alkaline solution (pH 9), where salt-formation between the acid and the basic amide group is suppressed, further shows that this dye must be combining with N-acetyl-D-glucosamine through hydrogen bonds.

Mechanism of Adsorption by Cellulose Acetate, Chitin and Terylene.

Cellulose Acetate.

This fibre, unlike cellulose, is hydrophobic, it does not swell much in aqueous solution and is almost undyed by the normal sulphonated dyes used for cotton and wool. "Disperse" dyes, i.e. non-ionic dyes of very low water solubility are almost exclusively used for it. Various ideas have been put forward as to the nature of adsorption of dyes by cellulose acetate. Thus the adsorption of basic dyes has been attributed to the negative charge on the fibre (Paneth and Radu); Knoevenagel, who found a constant partition ratio for the distribution of simple organic compounds between cellulose acetate and water, was among many authors who have suggested adsorption by "solid solution". Marsden and Urquhart, however, have shown that the very high swelling action of phenol on the fibre is due to the formation of hydrogen bonds with the hydroxy-group of phenol. They suggested the carbonyl oxygen atom as the reactive centre. Allingham *et al.*, on the evidence of their studies on monolayers, have suggested that the hydrogen of the methyl residue might be the bond-forming centre in dyeing the fibre. This would explain why many compounds containing no active hydrogen, e.g., azobenzene, nitroazobenzenes,

etc. are adsorbed.

The present investigation indicates that esters are able to form hydrogen bonds even with hydrogen-acceptors and that the carbonyl group is ineffective in water, being solvated. These observations support the view put forward by Allingham et al. The lower energy of the -C-H--- bond is consistent with the general low affinity of solutes for cellulose acetate. (Also see Section I, Part II).

Chitin.

The chitin molecular chain consists mainly of N-acetyl-glucosamine units. A large amount of work on its adsorbtion properties has been carried out in this laboratory by Subramanian (Ph.D. thesis, Glasgow, 1955) and by Hassan (private communication). They have found that sulphonic acids are adsorbed by salt-formation with the N-acetyl groups of chitin, but in solutions of alkaline pH values, the adsorption of these acids is apparently assisted by the presence of hydrogen-bonding groups, and that the adsorption of simple hydroxy-compounds in non-aqueous solution is due to hydrogen-bonding. These results appear to be consistent with the hydrogen-bond reactions of N-acetylglucosamine in solution. The behaviour of this compound suggests that in water the hydroxy-groups of chitin are solvent-protected and adsorption takes place by bonding at the acetamido-group.

In organic solvents both may be reactive.

Polyethylene terephthalate fibre ("Terylene").

It appears that the model compounds representing this fibre can act as proton-donors and the adsorption of non-ionic compounds could therefore be due to hydrogen-bond formation by this fibre, the mechanism being somewhat the same as for cellulose acetate. In Terylene however the molecular chain has repeating benzene nuclei and these may well exert considerable van der Waals attraction on the aromatic nuclei of dyes oriented parallel to them, so that physical attraction may well be more important here than in the case of cellulose acetate.

Section IIIb

Reactivity of Carboxylic Acids.

The refractive index method has also been used for an entirely different and novel purpose, viz. to investigate the reasons for the activity of certain carboxylic acids as hormones in plant growth promotion, and the inactivity of others. Many of these hormones are substituted acetic acid derivatives and slight changes in the nature and position of substituents may have a considerable effect on their activity. (For a useful survey of the subject, see Wain). It appeared from an inspection of formulae that

there might be some connection between hormone activity and ability to form intermolecular hydrogen-bond complexes, and the present section of the work is concerned with tests made to check this hypothesis. Some of these tests were made earlier by Arshid (Ph.D. thesis, Glasgow, 1954) and Watson.

It is known (Wain, loc.cit.) that a compound to be active must possess an unsaturated ring, a carboxylic group, and a hydrogen atom on the carbon adjacent to the carboxyl group. The aim of the present investigation was to determine the bonding activity of this hydrogen atom, which is supposed to play an important role in the growth-regulating properties of the plants.

The results of the present investigation have been summarised in Table 8 and the typical curve is shown in Fig.18.

A few of these acids were kindly supplied by Professor R. L. Wain of Wye College and were examined (Table 8). The results are very difficult to interpret because of the presence of the carboxylic group. However, the interaction ratio with diisobutyl ketone or triethylamine (Fig.18), could in some cases be interpreted as due to a reaction with a hydrogen atom on the carbon adjacent to the carboxylic group, thus supporting the view that this hydrogen is of some importance in the growth-regulating

Table 8

Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method(s)† and temp.	Mol. ratio of complex (a:b)‡
Acetic acid	Triethylamine	D	0.1	n 20	1:1
Phenoxy acetic acid	Diisobutyl ketone	D	0.1	n 22	1:1
"	Triethylamine	D	0.1	n 22	1:2
4-Chlorophenoxy acetic acid	Diisobutyl ketone	D	0.1	n 19.5	1:1
"	Triethylamine	D	0.1	n 19.5	1:3
2:4:5-Trichlorophenoxy acetic acid	Diisobutyl ketone	D	0.1	n 22.5	(1:1)
	Triethylamine	D	0.1	n 19.5	1:1
2:4:6-Trichlorophenoxy acetic acid	Diisobutyl ketone	D	0.1	n 21	(1:1)
	Triethylamine	D	0.1	n 21	(1:1)
α-(4-Chlorophenoxy)propionic acid	Diisobutyl ketone	D	0.1	n 21.7	(§)
	Phenol	D	0.05	n 21	1:1
"	Triethylamine	D	0.1	n 22	1:2
α-(2:4-Dichlorophenoxy) propionic acid	Diisobutyl ketone	D	0.05	n 19	1:1
α-(2:6-Dichlorophenoxy) propionic acid	Diisobutyl ketone	D	0.05	n 19	1:1
α-(2:4:5-Trichlorophenoxy) propionic acid	Diisobutyl ketone	D	0.1	n 21	1:1
	Triethylamine	D	0.1	n 20	1:1

Table 8 (Cont'd)

Solutes		Solution			
a	b	Solv.*	Total mol. concn.	Method(s) and temp.	†Mol. ratio of complex (a:b)‡
α-(2:4:6-Trichlorophenoxy) propionic acid	Diisobutyl ketone	D	0.1	n 21.5	1:1
	Triethylamine	D	0.1	n 21.5	1:2
α-(4-Chlorophenoxy) butyric acid	Diisobutyl ketone	D	0.1	n 19	(§)
	Phenol	D	0.05	n 23	1:1
"	Triethylamine	D	0.1	n 20	1:2
α-(4-Chlorophenoxy) isobutyric acid	Diisobutyl ketone	D	0.05	n 19	(1:1)
	Triethylamine	D	0.05	n 23	1:1

---

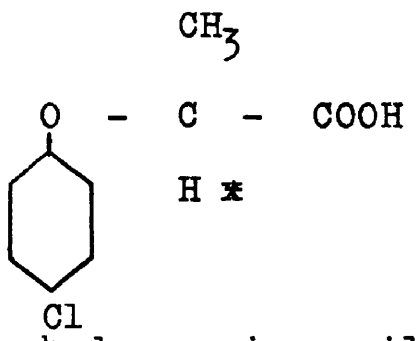
* Solvent: D = dioxan;

† n = refractive index;

‡ Data in parentheses denote uncertain indications;

§ No evidence of complex formation.

properties of plant hormones. For example, triethylamine forms 1:1-complexes with acetic acid and 4-chlorophenoxy-*iso*butyric acid, but with 4-chlorophenoxypropionic or 4-chlorophenoxyacetic acid an additional 2:1-complex is also evident (Fig.18). If the first triethylamine molecule reacts with the carboxylic group then the second molecule in the case of the latter two compounds must be reacting with a hydrogen (*) atom *α* to the carboxyl group.



Since no free hydrogen is available in the *iso*butyric acid derivative, no complexes other than the 1:1-complex can be formed. Presumably acetic acid is not reactive at the *α* -CH group because of the absence of the phenoxy substituent. Wain states that both 4-chlorophenoxyacetic and 4-chlorophenoxypropionic acids are active as growth-promoting substances whereas 4-chlorophenoxy*iso*butyric acid is almost inactive; thus there appears to be some parallelism between hormone activity and the availability of a hydrogen atom.

Unfortunately, time did not permit further investigations to be made on this series of compounds.

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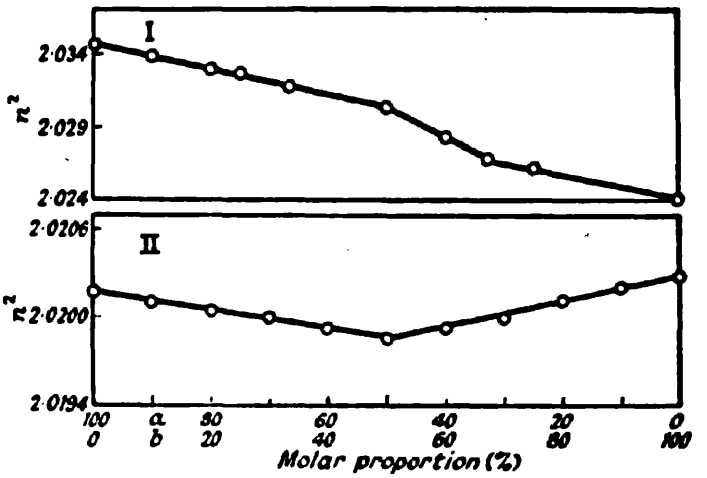


FIG. 1. *Relation between the square of the refractive index and the component ratio in solutions of binary mixtures containing water.*

I: *a*, Azobenzene; *b*, water. Solvent: dioxan.

II: *a*, Diisobutyl ketone; *b*, water. Solvent: dioxan.

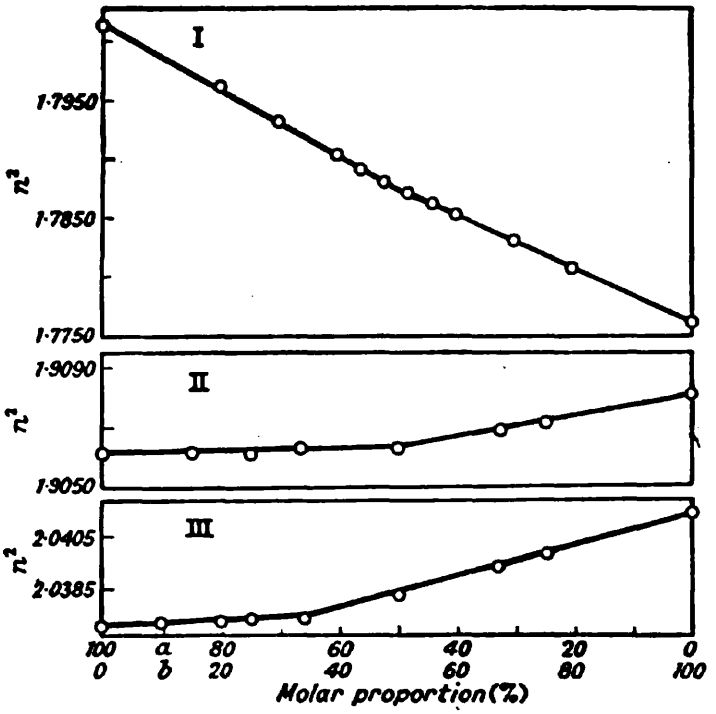


FIG. 2. *Relation between the square of the refractive index and the component ratio in solutions of binary mixtures containing methanol.*

I: *a*, Phenol; *b*, methanol. Solvent: water.

II: *a*, Methanol; *b*, erythritol. Solvent: 2-ethoxyethanol.

III: *a*, Methanol; *b*, pentane-1:5-diol. Solvent: dioxan.

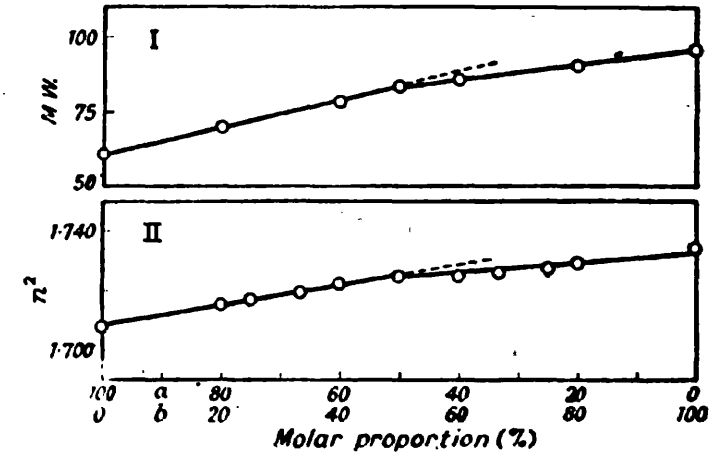


FIG. 3. *Relation between the molar ratio, square of the refractive index, and apparent molecular weight in solutions of binary mixtures containing propionaldehyde.*

a, Propionaldehyde; *b*, pyridine. Solvent: I, dioxan; II, water.

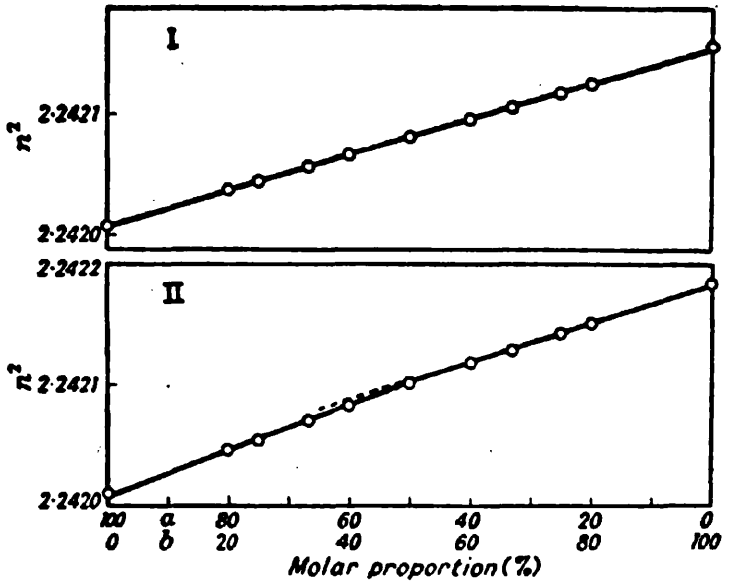


FIG. 4. *Relation between molar ratio and the square of the refractive indexes in solutions of binary mixtures containing nitrobenzaldehydes.*

I : *a*, Pyridine ; *b*, *o*-nitrobenzaldehyde. Solvent : toluene.

II : *a*, Pyridine ; *b*, *m*-nitrobenzaldehyde. Solvent : toluene.

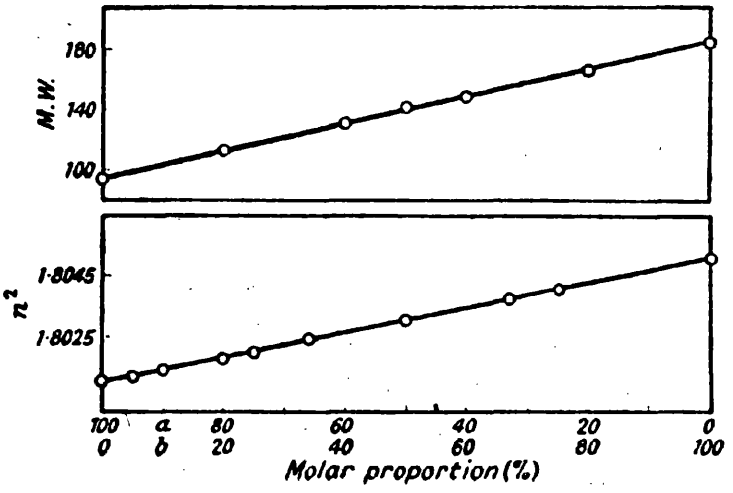


FIG. 5. *Relation between molar ratio, square of refractive index at 20°, and apparent molecular weight of solutions of binary mixtures*

a, Phenol; *b*, glucose. Solvent : water.

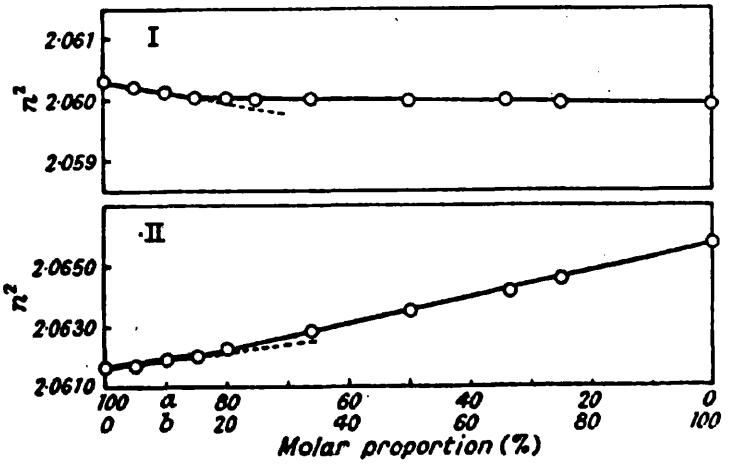


FIG. 6. *Relation between square of refractive index and component ratio in solutions of binary mixtures.*

I : *a*, Phenol; *b*, glucose. Solvent : ethylene glycol.

II : *a*, Water; *b*, glucose. Solvent : ethylene glycol.

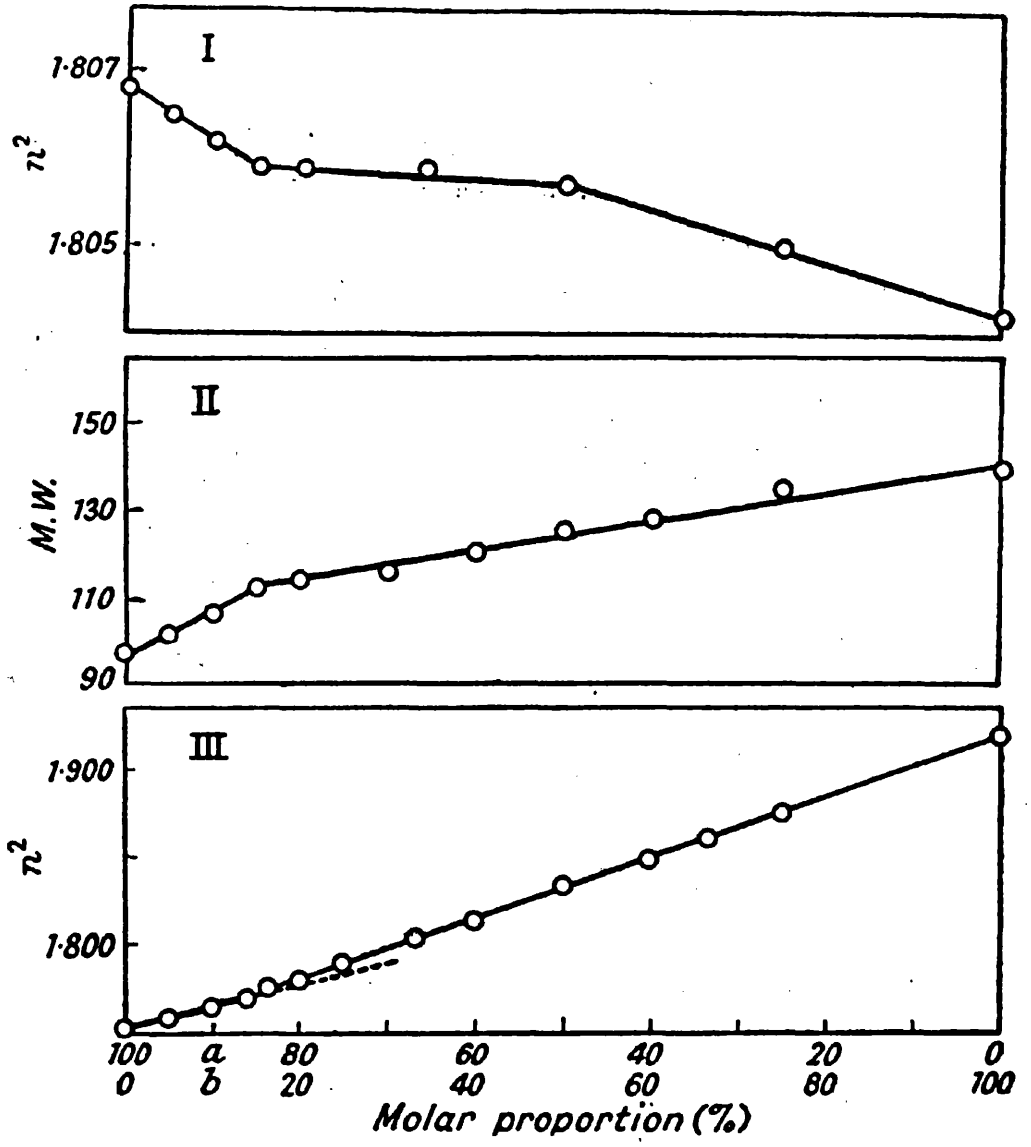


FIG. 7. *Relation between molar ratio, square of refractive index, and apparent molecular weight in solutions of ternary mixtures containing glucose.*

I : *a*, Phenol; *b*, glucose–triethylamine (1 : 1 molar ratio). Solvent : water.

II and III : *a*, Phenol; *b*, glucose–pyridine (1 : 1 molar ratio). Solvent : water.

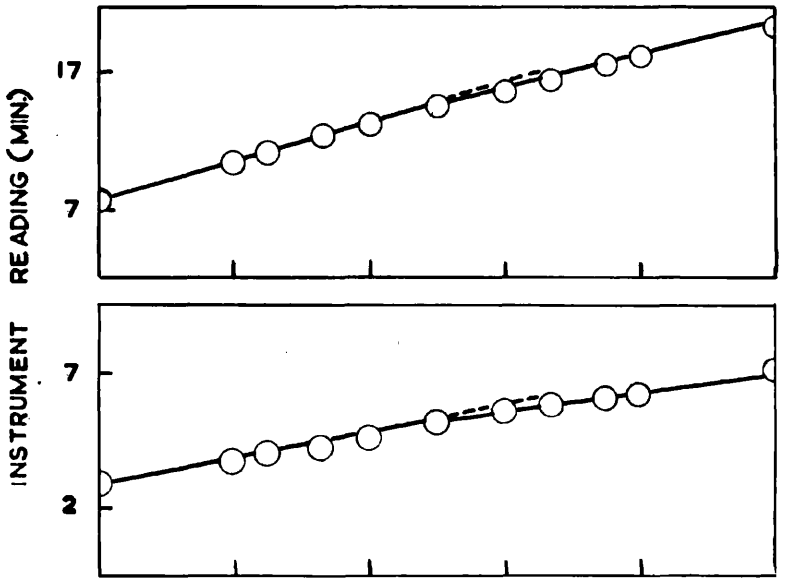


FIG. 8—

a, ACETAMIDE

b, PHENOL

SOLVENT : DIOXAN.

a, ACETAMIDE

b, TRIETHYLAMINE

SOLVENT : WATER.

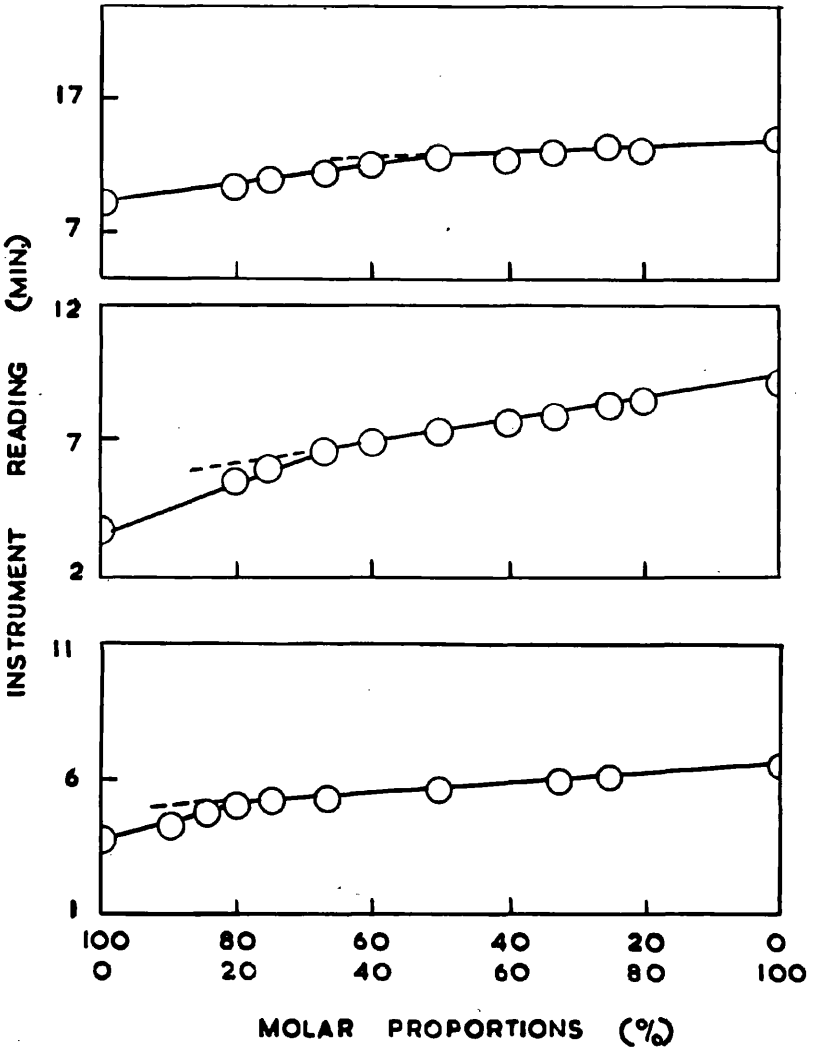


FIG. 9—

a, ACETAMIDE

b, QUINOL

SOLVENT : DIOXAN.

a, ACETAMIDE

b, QUINOL

SOLVENT : WATER.

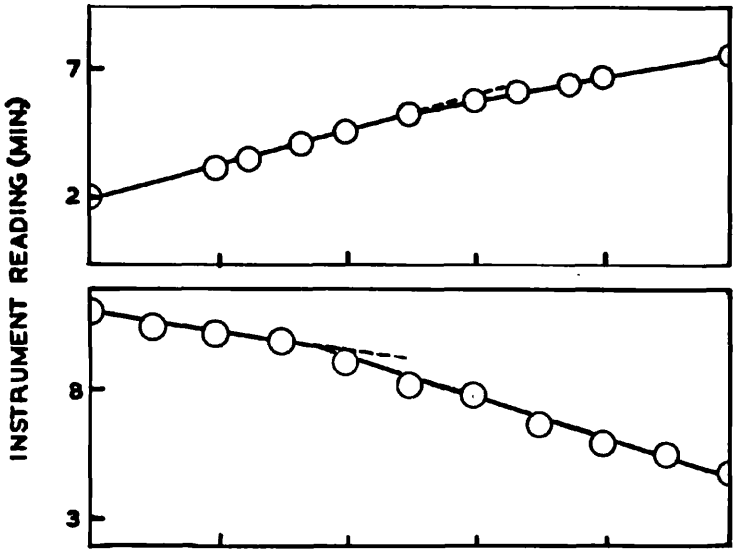
FIG. 10—

a, DIMETHYL ACETAMIDE

b, QUINONE

SOLVENT : TOLUENE.

FIG. 11—



a, PHENOL

b, DIACETAMIDOMETHANE

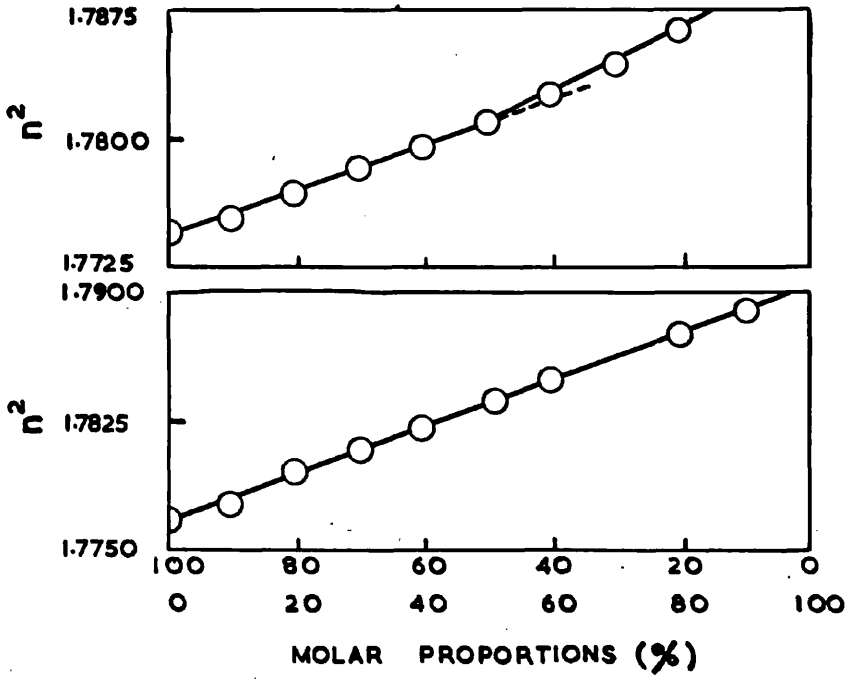
SOLVENT: ETHANOL

a, PHENOL

b, DIACETAMIDOHEXANE

SOLVENT: ETHANOL

FIG. 12—



a. PHENOL

b, ANILINE→RACID

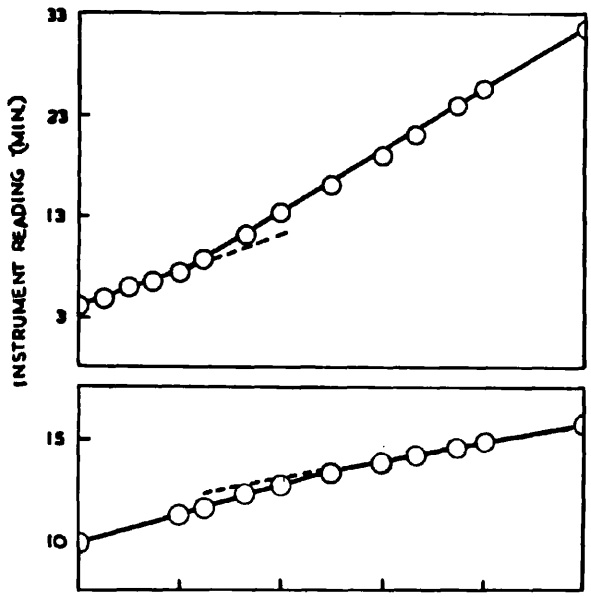
SOLVENT: WATER

a, ETHANOL

b, ANILINE→RACID

SOLVENT: WATER

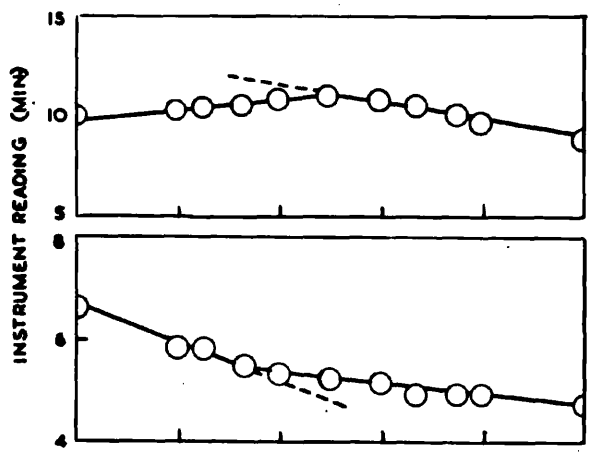
FIG. 13 —



a, ETHYL ACETATE
b, AZOBENZENE
SOLVENT : TOLUENE

a, ETHYL ACETATE
b, ACETONE
SOLVENT : TOLUENE

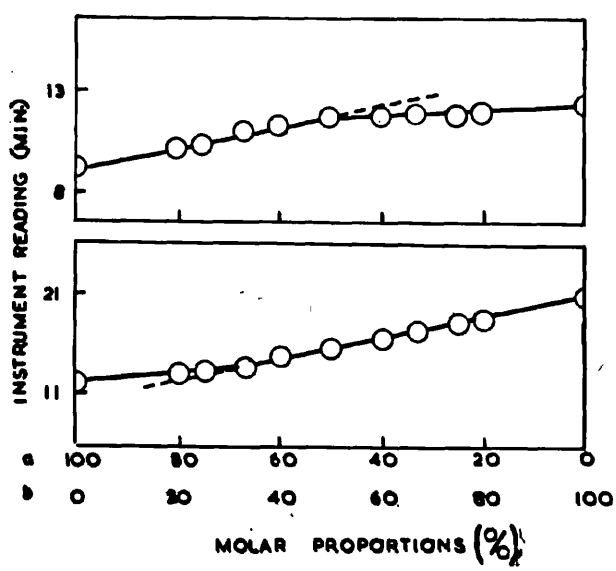
FIG. 14 —



a, TRIETHYLAMINE
b, ETHYLENE GLYCOL DIACETATE
SOLVENT : TOLUENE

a, TRIETHYLAMINE
b, PENTANE-1:5-DIOL DIACETATE
SOLVENT : TOLUENE

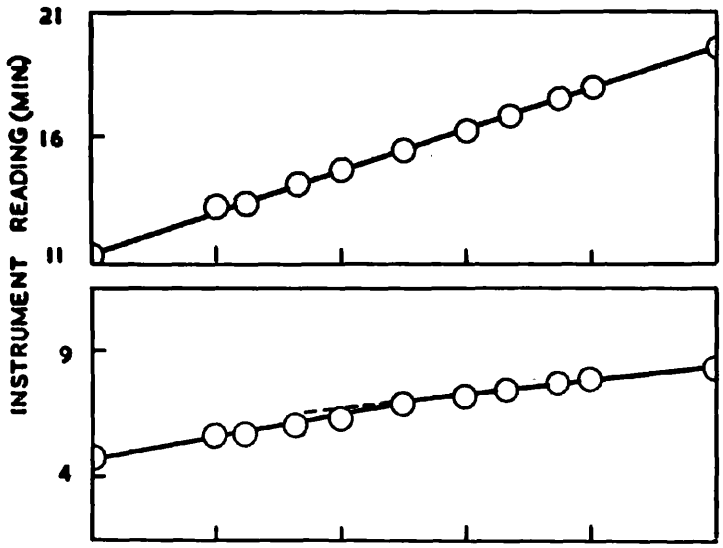
FIG. 15 —



a, TRIETHYLAMINE
b, CATECHOL DIACETATE
SOLVENT : DIOXAN

a, TRIETHYLAMINE
b, QUINOL DIACETATE
SOLVENT : CARBON TETRACHLORIDE

FIG. 16 —



a, GLYCEROL TRIACETATE

b, 2-NAPHTHOL-6-SULPHONIC ACID

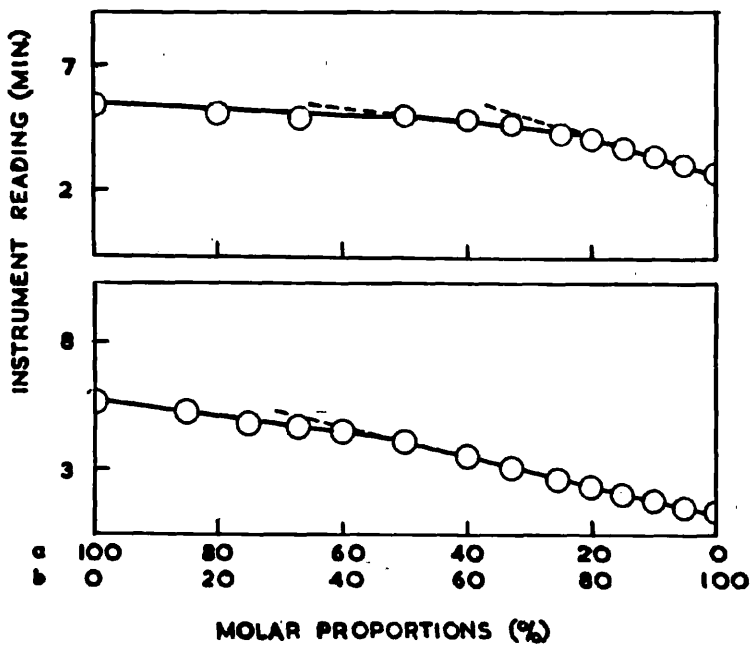
SOLVENT: WATER.

a, GLYCEROL TRIACETATE

b, NITROPHENYL SULPHURIC ESTER

SOLVENT: WATER.

FIG. 17 —



a, N-ACETYL-D-GLUCOSAMINE

b, PHENOL

SOLVENT : ETHYLENE GLYCOL.

a, N-ACETYL-D-GLUCOSAMINE

b, PHENOL

SOLVENT: WATER.

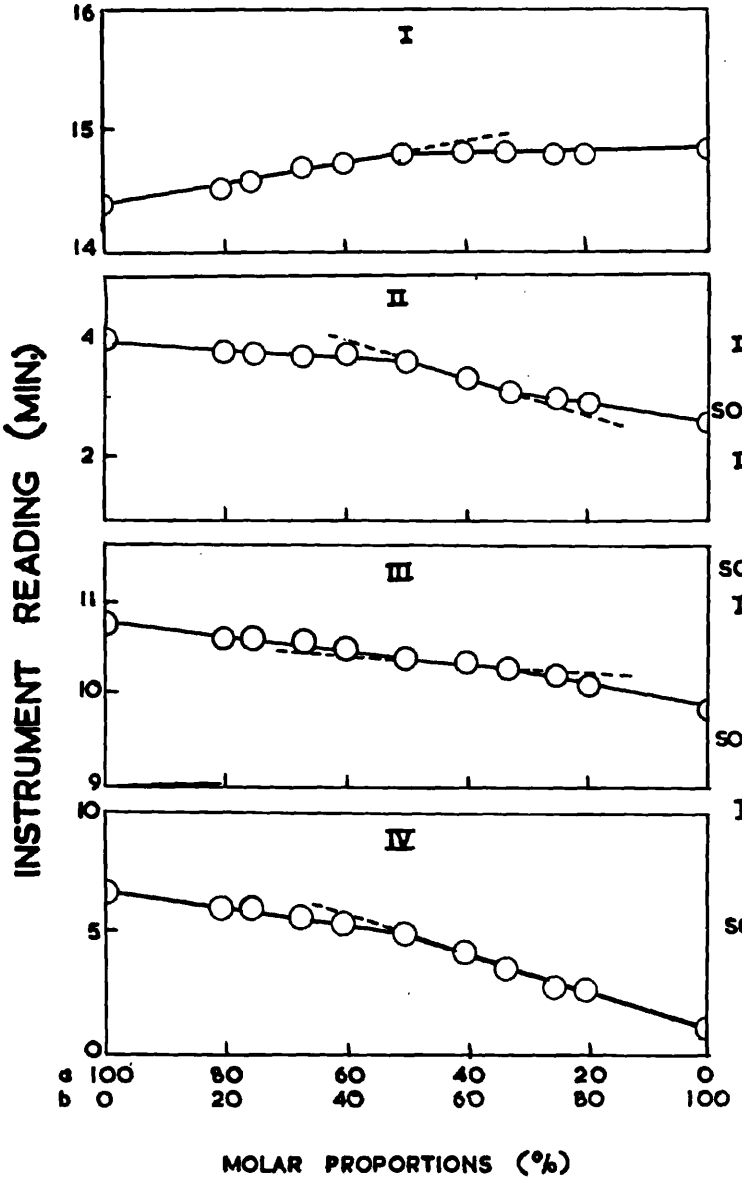


FIG. 18—

I a ACETIC ACID
b TRIETHYLAMINE
SOLVENT : DIOXAN

II a, 4 CHLORO PHENOXY ACETIC ACID
b, TRIETHYLAMINE
SOLVENT : DIOXAN

III a, 4 CHLORO PHENOXY PROPIONIC ACID
b, TRIETHYLAMINE
SOLVENT : DIOXAN

IV a, CHLORO PHENOXY ISO BUTYRIC ACID.
b, TRIETHYLAMINE
SOLVENT : DIOXAN

Part II.

Adsorption Studies

Section Ia The Adsorption of Logwood Colouring Matters by Fibres.

Section Ib Adsorption Studies on Cellulose Triacetate.

Section II Studies of the Adsorption of Dyes and Related Compounds by Silica.

Part II

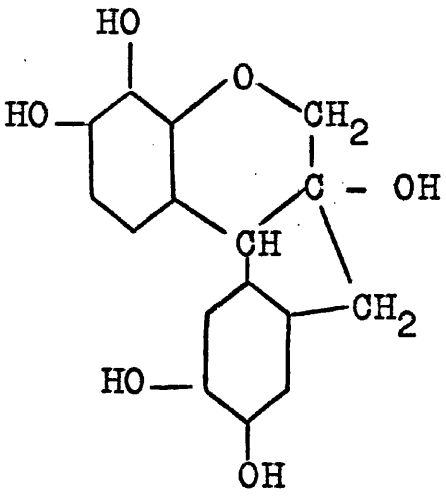
Section Ia.

The Adsorption of Logwood Colouring Matters by Fibres.

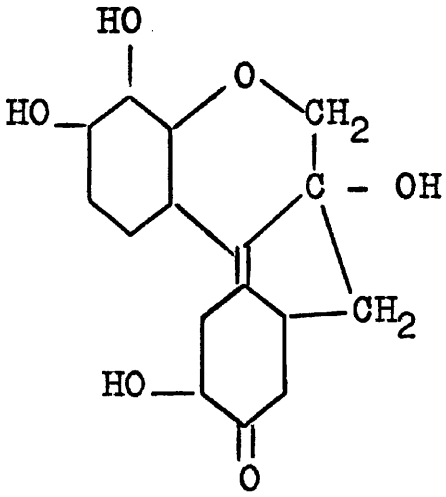
Synthetic dyes have been used for all the hitherto reported detailed studies of the chemistry of dyeing, but little or no attention has been paid to natural colouring matters. A study of the dyeing process of a natural colouring matter, logwood, has therefore been undertaken, because of its interesting structural features which differ markedly from those of most synthetic dyes, and also because it is the only natural dye still widely used. Its molecular structure bears some resemblance to tannins and when used with chromium, iron, copper, tin or aluminium as mordant, it gives a variety of dark blue and black shades, some of which have not been surpassed for quality by any of the synthetic dyes. Chromium produces very attractive deep blue-black shades which are very fast to washing, but, unfortunately, not as fast to light as those of the best synthetic products.

Logwood is the heartwood of the tree Haematoxylon campechianum and the colouring principle of logwood is haematoxylin (I_a) (C.I.No.1246) which is itself colourless but is readily oxidised to the dark brown haematein (I_b). It was first isolated by Chevreul who had, earlier, also

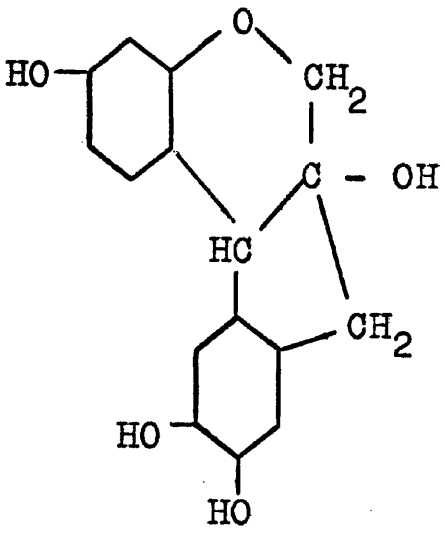
isolated brazilin from brazilwood. Subsequent studies by other authors especially Perkin and Robinson have established the close relationship between logwood (I_a and I_b) and Brazilwood colouring matters (II_a and II_b) although these compounds have never been synthesised.



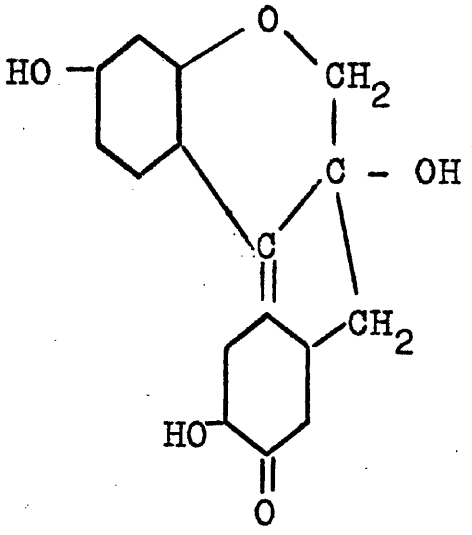
Haematoxylin - I_a



Haematein - I_b



Brazilin - II_a



Brazilein - II_b

The present work describes the adsorption properties of haematoxylin on wool, nylon, cellulose and cellulose triacetate. Adsorption of haematein by these fibres was studied by J. N. Desai (1948) and the structures of the metallic lakes were determined by Arshid *et al*. (1954).

Experimental

Purification of Materials.

Cellulose Acetate. Powdered cellulose acetate (acetyl value as acetic acid 62.2%) was kindly supplied by British Celanese Ltd., Derby and was used as such.

Wool. The raw material was Lincoln Fleece. Root ends, about 1.5 in. to 2 in. in length were cut off. This material was thoroughly combed to remove dirt and extraneous matter and was treated with methylene chloride in a Soxhlet apparatus for 24 hours and after being steeped overnight in running water, it was rinsed in distilled water and dried.

Nylon. The fibre was lightly scoured at 60°C. for about 30 minutes in a 0.5% solution of the non-ionic detergent Lissapol N (I.C.I.), thoroughly washed in running water, rinsed in distilled water and dried.

Viscose Rayon. Courtalds "Fibro" staple fibre was used. It was scoured in weak Lissapol N solution, and then well rinsed in distilled water and dried.

All the fibres were first oven-dried at 100-110°C., then allowed to condition in air for 24 hours and stored in stoppered bottles. Before use they were again (Soxhlet) extracted with the solvent used in the particular adsorption test to be made, and dried overnight.

Haematoxylin. The commercial product, a buff-coloured powder, was supplied by the British Dyewood Company Ltd., Glasgow and one crystallisation was sufficient to prepare it in its pure form.

A 50g. sample of the commercial product was dissolved in 500 c.c. of boiling water containing two or three crystals of sodium hydrosulphite; 20g. of activated charcoal was then added and the solution was stirred well, then filtered, cooled and left overnight to crystallise. The long thin colourless needles were filtered off, washed with water and dried in a vacuum desiccator. The product thus obtained is a monohydrate, which loses water on heating and melts at 140°C. On slow heating an anhydrous form is obtained, which melts with decomposition at 240°C.

Adsorption Experiments.

For most of these experiments, a 1.0% solution of haematoxylin was prepared, which was further diluted to make five or six different concentrations; the fibre samples (0.5 - 1.0g.), were then treated with 20 c.c. of each solution in sealed test tubes, fixed by phosphor-bronze spring clips to a shaft mechanically rotated at 35 r.p.m. under water in a thermostat tank in order to give a constant and regular end-over-end agitation (Clunie and Giles, 1957). For loose fibres, which tend to stick as a lump on

the side of the test tubes, a perforated glass tube fibre-holder, of 'caterpillar' shape, was used, devised by Arshid (Arshid et al., 1954a).

It was noticed that haematoxylin undergoes oxidation during adsorption experiments, particularly in the presence of wool or nylon, up to the extent of ca 5%. Therefore all the tests were also made in the presence of a reducing agent, hydroxylamine sulphate (2.5g./litre).

Estimation of Haematoxylin.

The following two methods were used.

(i) Colorimetric Method. Haematoxylin forms a deep blue water-soluble lake when treated with the theoretical amount of potassium chromate at 60°C. On dilution the solutions were estimated on a Hilger Spekker photoelectric absorptiometer, using Ilford Spectrum filter No.607 (orange). This method which gave in most cases consistently reliable results, sometimes proved unsatisfactory, perhaps because the traces of fibre decomposition products interfered with lake formation. Where different ranges of pH values were used, it was necessary to adjust the solutions to pH 5.9, which is the optimum pH for lake formation, by cautious addition of ammonia. pH measurements were made on a Marconi glass electrode.

(ii) Refractometric Method.

This method proved more satisfactory. The square of the refractive index, when plotted against concentration gives a straight line calibration curve, which can be used to determine the concentrations of the solutions after test. The results are quite reproducible and do not seem to be affected either by the presence of traces of haematin or reducing agent. The measurements were made on a Zeiss Pulfrich refractometer.

Load Extension Tests.

These tests were made on a Cambridge Instrument Co. extensometer maintained in a controlled atmosphere at 20°C. and 65% R.H. Single fibres, 2 in. in length, from the purified Lincoln Fleece were used. Untreated fibres were soaked in distilled water before use, and a drop of water was run on to them when they were clamped in the apparatus. Similarly, treated fibres were taken straight from adsorption experiments where they had been treated with the required solutions for 24 hours at 60°C. They contained 280 mmol. of haematoxylin and 850 mmol. of phenol respectively per kilogram, and before extension tests, the fibres were wetted by pipette with the respective solutions.

The Apparent Heat of Adsorption.

This has been calculated by a derivation of the Van't Hoff equation, which relates the change of heat of a reaction with temperature to the equilibrium constant $\underline{k}$ of a reversible reaction:

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

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

$$\Delta H/_{RT_2} - \Delta H/_{RT_1} = - \ln {C_{F2}}/{C_{B2}} \cdot F + \ln {C_{F1}}/{C_{B1}} \cdot F$$

where C_{F1}, C_{B2} etc. are the concentrations (strictly the activities) of the solute in the fibre and the bath, and F is the activity of the fibre itself. If dilute solutions are used and the two values of bath concentration are selected from the isotherms such that the concentration of the solute in the fibre in both cases is identical, then we have:

$$\Delta H = \left[RT_2T_1/(T_1 - T_2) \right] \ln {C_{B2}}/{C_{B1}}$$

Calculation of Affinities.

Direct calculations of the affinities were made using the following formula

$$-\Delta\mu = RT \ln {}^{C_F}/_{C_B} \cdot V$$

where $\Delta\mu$ is the difference between the standard chemical potential of the solute in the two phases and, in the present case, is the quantitative measure of the affinity of the dye for the fibre, V is the "volume" term, representing the effective volume of water in the fibres (in litres/kg.). For viscose rayon the value of 0.45 for V, as employed by Marshall and Peters, was used; for cellulose triacetate, 0.1, as used by Fowler and Michie for cellulose diacetate, though it is not certain that it is correct for triacetate; and 0.3 for wool. No value for nylon is available but the arbitrary figure of 0.05 has been used because this fibre has a regain about half that of cellulose acetate.

Results and Discussion.

The attraction responsible for adsorption of dyes by fibres consists of both polar and non-polar forces. The operation of non-polar forces i.e. van der Waals attraction and the hydrogen bond polar forces are not as clearly identified as is the operation of ionic forces. Haematoxylin is a useful material with which to study non-ionic attractions, because the molecule itself is neutral, has four (phenolic) groups, which are potentially strong hydrogen-bonding centres, and is fairly large so that it may exhibit appreciable van der Waals attraction for the fibres. The adsorption of haematoxylin by the several fibres is discussed under the following headings.

a. Nature of isotherms
b. Affinity and apparent heats of adsorption
c. Effect of pH
d. Nature of bonds.

a. Nature of Isotherms.

The adsorption isotherms of haematoxylin on wool, nylon, cellulose acetate and cellulose are shown in Fig.1 and Fig.2. It will be seen that cellulose and cellulose acetate give quite reproducible results whereas the isotherms for wool and nylon were not determinable with any

high precision, perhaps because both these substrates are more active in promoting oxidation.

The isotherms for cellulose are S-shaped which is characteristic of high affinity of the solvent for the substrate and comparatively low affinity of the solute (Giles and McEwan). On the other hand, the isotherms for the other three substrates i.e. nylon, wool and cellulose triacetate are of type 'L' (Giles and McEwan), which are very common and represent high affinity of the solute for the substrate.

The isotherms for cellulose triacetate, wool and nylon after having once attained the maxima rise again steeply. This shows that haematoxylin, besides being able to combine with the favourable groups in the amorphous regions of these fibres may even act as a powerful swelling agent, thus resulting in very high adsorption.

The reducing agent affects adsorption in the case of nylon only, which is probably due to its swelling action on this fibre.

b. Affinity and Apparent Heats of Adsorption.

The results of affinity and apparent heats of adsorption measurements for haematoxylin calculated from the adsorption isotherms are shown in Table 1. The apparent

heats of adsorption of phenol, from water, on cellulose triacetate (Cameron), nylon and wool (Chipalkatti et al.) are -3.0, -4.5, and -4.0 kcal/mole respectively, which are comparable to those of haematoxylin (Table 1).

The affinity of haematoxylin decreases markedly in ethanol-water (50:50) as solvent: cellulose loses almost all its adsorptive power and the adsorption by other fibres is much lower than from water (Table 2).

Table 1.

Apparent Heats of Adsorption and Affinities of Haematoxylin

Substrate	C_F (mmole/kg.)	ΔHa (kcal/mole) 50 - 60°C.	$\Delta\mu$ (kcal/mole) 60°C.
Viscose rayon	25	-3.5	-1.25
	50	-3	-1.3
	70	-2.5	-
Cellulose triacetate	25	-7.5	-2.6
	35	-7.5	-2.6
Nylon*	25	(-10)	-3.3
	45	-	-3.3
	60	(-10)	-
Wool	25	-	-2.7
	50	-11	-
	100	-11	-2.4
	150	-8	-

* No addition of reducing agent to bath

Table 2.

Adsorption of Haematoxylin from 50% Aqueous Ethanol

C_B = Equilibrium bath concn. (mmole/l)

C_F = Equilibrium concn. in fibre (mmole/kg.)

Temp. 60°C.; time 24 hr.; 0.5g. fibre in 10 c.c. soln.

Fibre	C_B	C_F
Cellulose (Viscose rayon	6.7-26.5	Nil
Cellulose triacetate	1.0	ca.1.0
	2.5	25
Nylon	0.9	40
	2.5	40
Wool*	0.9	45
	2.0	33
	2.6	25

* The fall in adsorption on wool with increase in bath concentration is an effect attributable to associati0n in the solvent.

c. Effect of pH.

Fig.3 shows the effect of pH on the adsorption of haematoxylin, haematein and brazilein on wool. The adsorption of haematoxylin is almost independent of the acidity because of its neutral character and is markedly different from that of haematein and brazilein. Haematein is weakly

acidic, the pKa value being 6.5 and pKb 10.3 (Arshid et al. 1954) and the effect of pH is very similar to that found by Steinhardt et al. for other weak acids.

d. Nature of Bonds.

(a) With cellulose.

Preston and Nimkar by studying the freezing-point curves of adsorbed moisture in cellulose fibres, have shown that the non-crystalline parts of the fibre, where adsorption probably takes place, are in a state resembling solution in the water. They probably therefore behave rather like glucose with regard to hydrogen-bonding affinity. The studies on the hydrogen-bonding properties of carbohydrates show (see Part I, Section I) that water is firmly held by glucose hydroxy groups, which are thus rendered inactive and incapable of forming hydrogen bonds with other hydrogen-bonding agents.

Further, phenol, a very powerful hydrogen-bonding agent, is not adsorbed by cellulose (Hassan, Marsden and Urquhart). From this it may be concluded that hydrogen bonds play little part in the adsorption of haematoxylin by cellulose, in spite of its having four hydrogen bonding groups. Therefore, probably the only force which takes part in adsorption of haematoxylin by cellulose is van der Waals attraction. This fact is further supported

by referring to the regression line of the affinity values for cellulose of a series of aminoanthraquinone vat dyes on their molecular weight, given by Vickerstaff (1953), which shows that the value obtained here for haematoxylin (mol. wt. 302; affinity -1.25 kcal/mole.) falls almost exactly on this line. Vickerstaff states that in the case of these and other vat dyes the affinity for cellulose must be largely attributable to van der Waals forces proportional to the molecular area, and the conformity of haematoxylin with the same relation suggests that its affinity also arises from the same cause.

(b) Cellulose Acetate.

Cellulose acetate, though derived from cellulose, differs from it markedly in its dyeing behaviour. There seems no reason to doubt that it can adsorb solutes by hydrogen bonds. Phenol is adsorbed readily by this fibre and it has been suggested (Marsden and Urquhart) that it forms O---H---O bonds with the carbonyl oxygen atom of the acetyl group. It does not necessarily follow from this that a similar mechanism is involved in the adsorption of all the non-ionic dyes which dye this fibre, because a number of such dyes have no hydrogen atom free to form a hydrogen bond with the carbonyl group. Further, studies on the hydrogen bonding properties of acetates (Part I, Section III) and the solvation effect of water in inter-

molecular hydrogen bonding (Part I, Section I) show that the carbonyl group is more or less protected by water and is incapable of accepting a hydrogen atom from proton donors in water.

Recently however, Campbell et al. have shown that an ether oxygen atom can form an intermolecular hydrogen bond with a hydroxy group, in water, and it seems likely therefore that it is the ether oxygen adjacent to the acetyl group that operates in adsorbing haematoxylin and other phenols. This is probably a weak bond, in agreement with the low value for the affinity of haematoxylin for cellulose acetate (-2.6 kcal/mole)(Table 1).

The -CH--- bond on the methyl residue of the acetyl group, suggested by Allingham et al. is thought now to operate only with a nitrogen atom in the adsorbed solute, and not with a hydroxy-group.

(c) Nylon and Wool.

Haematoxylin is a neutral molecule, therefore its adsorption by nylon or wool will be uninfluenced by the charge on the fibres. Only van der Waals forces and hydrogen bonds, will be responsible for its adsorption.

Haematoxylin forms a 1:5-complex with phenol (in dioxan, by dielectric measurements) and a 1:4-complex with dimethylformamide (in water, by refractive index measure-

ment). It is expected, therefore, that it is capable of acting as a cross-linking agent for wool by combination with sets of peptide linkages in the fibre. In that case it will replace rather weaker aliphatic interchain bonds, thus increasing the tensile strength of the fibre. Also, by the introduction of the rather bulky haematoxylin molecule, the rigidity of the fibre will be much reduced, giving greater longitudinal freedom of movement, which means that the stretching of the fibre will be facilitated. To verify this a few load-extension tests were made on wool fibre containing (i) adsorbed haematoxylin in equilibrium with the adsorption liquid, (ii) adsorbed phenol in equilibrium with its solution in the bath and (iii) wetted in water alone.

The results are shown in Table 3. The measurements are insufficient for any precise quantitative conclusion, yet the trend is in the anticipated direction. The tensile strength as well as the extensibility are markedly increased in both the phenol-treated and the haematoxylin-treated samples. The lesser effect of phenol on extensibility may be because of its inability to break the interchain links as readily as haematoxylin, since it is monofunctional. The increase in tensile strength, however, is difficult to understand although it may be suggested that the restraining force against longitudinal breakage due to the cohesion of adjacent phenol molecules is greater than the strength of the cross-

links normally present.

Table 3.

Mechanical Characteristics of Treated and Untreated Single Wool Fibres.

(20^{o}C. and 65% R.H.)

Original fibre length 50.5 mm. Rate of loading 43.5g./min.

Untreated								
								Mean
Breaking load, g.	12.7	9.8	14.2	11.9	11.3	12.1		12.1
Extension at break, %	17	12	10	8	6	6		9.8
Treated with Phenol								
Breaking load, g.	19.8	18.4	17.0	22.5	14.2	18.4	19.8	18.6
Extension at break, %	30	25	20	30	22	22	26	25
Treated with Haematoxylin								
Breaking load, g.	24.0	25.5	31.0	28.4	24.0	25.5		26.4
Extension at break, %	34	31	37	37	26	28		32.2

Conclusions.

1. Haematoxylin is adsorbed by strong hydrogen bonds on nylon and wool, and perhaps acts as a cross-linking agent by replacing interchain bonds, thus increasing the tensile strength and extensibility of wool fibres.

2. Its adsorption on cellulose acetate is due to weak hydrogen bonds probably through the ether oxygen atom adjacent to the acetyl group.

3. Adsorption on cellulose is due to van der Waals forces and not to hydrogen bonding.

4. The adsorption of haematoxylin on wool is unaffected by the change in pH on the acid side of neutrality because it is then an unionised molecule.

Section Ib.

Adsorption Studies on Cellulose Triacetate.

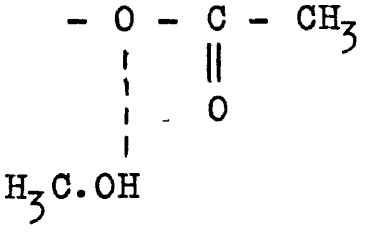
Following the examination of hydrogen-bonding properties of the acetates, it was desired to correlate the results with adsorption tests on cellulose acetate in substance. Since it is known that phenol is strongly adsorbed by this fibre, probably through hydrogen-bond formation (Marsden and Urquhart), and that even the hydrogen atom in the methyl residue of esters is available for bonding, it was at first proposed to examine the adsorption of alcohols, followed by some phenols and later some hydrogen-acceptor compounds. Unfortunately, little time was available and only preliminary tests were made. Adsorption of methanol, ethanol, and n-propanol by cellulose triacetate was studied from benzene solution and of quinol and ethylene glycol from aqueous solution.

Cellulose triacetate was used both in powder and fibre form (acetyl value as acetic acid 62.2%), supplied by British Celanese Ltd., Derby. It differs from secondary cellulose acetate in being more hydrophobic and it swells very little in aqueous solution. The powder form was used for experiments in aqueous solution and the fibre form in benzene solution. All the reagents used were of analytical reagent quality and the estimation of the solutes was carried

out by the refractive index method (for details see Section Ia).

The results are shown in Tables 4, 5, and 6. The work done is too limited for any precise generalisation, but the following points are clear.

(i) Methanol is strongly adsorbed (Table 4), and this must almost certainly be due solely to hydrogen bond formation. The bond is probably formed thus -



because the C=O group appears to be protected in benzene (see Section I, Part I, above).

(ii) From water, ethylene glycol is unadsorbed, but quinol (and phenol) are both strongly adsorbed (Table 5). Therefore the $>O\text{----}HO-$ bond must be much weaker when the hydroxyl group is alcoholic than when it is phenolic, and in the former case the competition of the water-alcohol bond prevents adsorption.

(iii) Only methanol and not the other two alcohols is adsorbed by this substrate from benzene solution. This shows that in dry conditions the pore size of the fibre is large enough to admit the methanol molecule and not those

Table 4.

Adsorption of Methanol on Cellulose Triacetate from Benzene Solution

Temperature 23.5°; Time 24 hr.; 0.4g. fibre in 5 c.c.

Initial Concn. g.mole/l.	Equil. Concn. g.mole/l.	Adsorption g.mole/kg.
0.2476	0.1463	1.265
0.4952	0.2872	2.581
0.7328	0.4548	3.458
0.9904	0.6364	4.40
1.238	0.824	5.15
Temperature 59°		
0.2476	0.208	0.487
0.4952	0.4310	0.800
0.7328	0.651	1.012
0.9904	0.8940	1.200
1.2380	1.210	0.4(?)

No measurable adsorption of ethanol or n-propanol from benzene.

Table 5.

Adsorption of Quinol on Cellulose Triacetate from Water

Temperature 60°; Time 24 hr.; 0.4g. fibre in 10 c.c.

Initial Concn. g.mole/l.	Equil. Concn. g.mole/l	Adsorption g.mol/kg.
0.05	0.0268	0.58
0.10	0.074	0.65
0.15	0.116	0.85
0.20	0.158	1.05
0.25	0.200	1.25

of ethanol or n-propanol.

(iv) The apparent heat of adsorption calculated from the isotherms using the Clausius-Clapeyron equation for methyl alcohol is -10.5 ± 0.5 k.cal/mole. It is interesting to compare this result with others obtained in this laboratory (Chipalkatti et al.) (Table 6). The consistency of the ratios of the heats of adsorption between the two substrates, wool and cellulose triacetate, for phenol and methyl alcohol, suggests that both the solutes are adsorbed on similar sites in the respective substrates.

It may be mentioned that the isotherms for methanol and quinol are of the normal ('L') shape, the quinol curve showing a second rising portion after an initial maximum, but phenol gives a linear ('LN') isotherm (Cameron, private communication). These facts suggest (cf. Giles and McEwan): (a) that quinol in dilute solution in water has rather less ability to swell cellulose triacetate than phenol has, probably because its higher ratio of hydrophilic to hydrophobic groups give it more affinity for water; and (b) that methanol swells the substrate less than benzene; this is another indication of the weakness of the alcoholic-ether bond formed in this adsorption.

Table 6.

Apparent Heats of Adsorption (K.cal/mole.)

	Wool	Cellulose Triacetate
Phenol from water	ca - 4	- 2.5*
Methanol from benzene	ca -15	-10.5

* Cameron, private communication.

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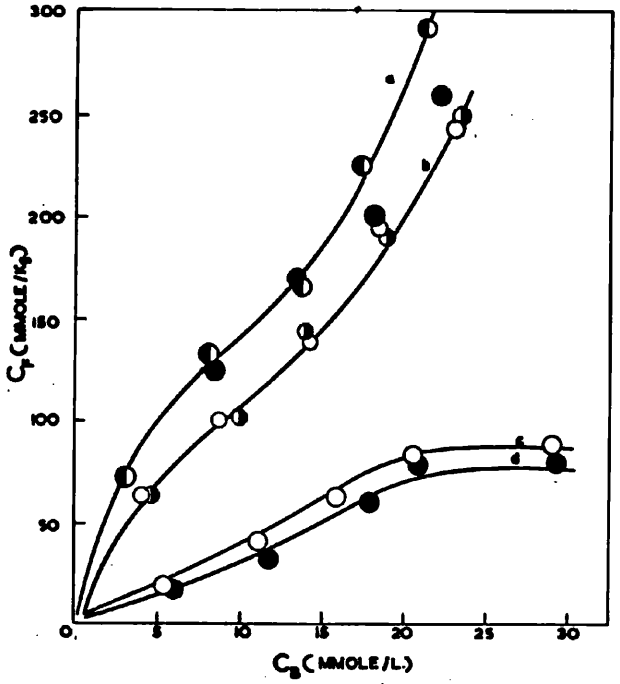
FIG-1——HAEMATOXYLIN ADSORPTION ISOTHERMS.



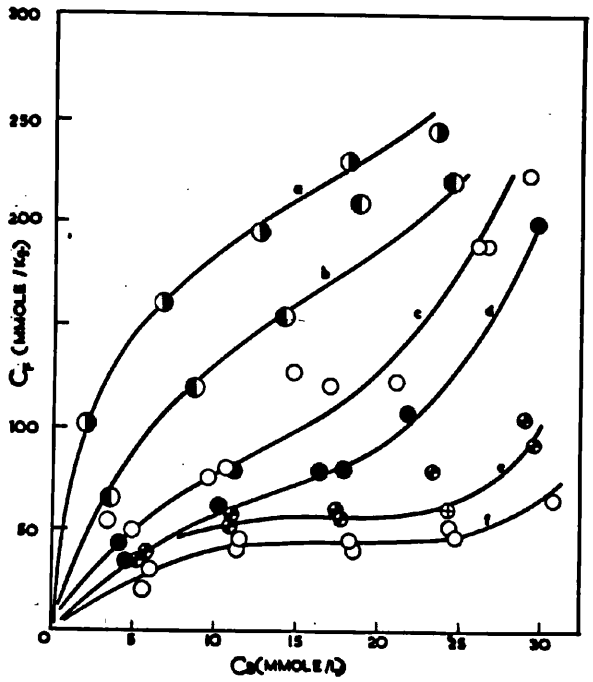
a, ● WOOL AT 50° ◐ HYDROXYLAMINE SULPHATE (2.5 g/L.) ADDED

b, ○ WOOL AT 60° ◑ HYDROXYLAMINE SULPHATE (2.5 g/L.) ADDED

c, ○ VISCOSE RAYON AT 60°

d, ● VISCOSE RAYON AT 90°

FIG-2— HAEMATOXYLIN ADSORPTION ISOTHERMS.

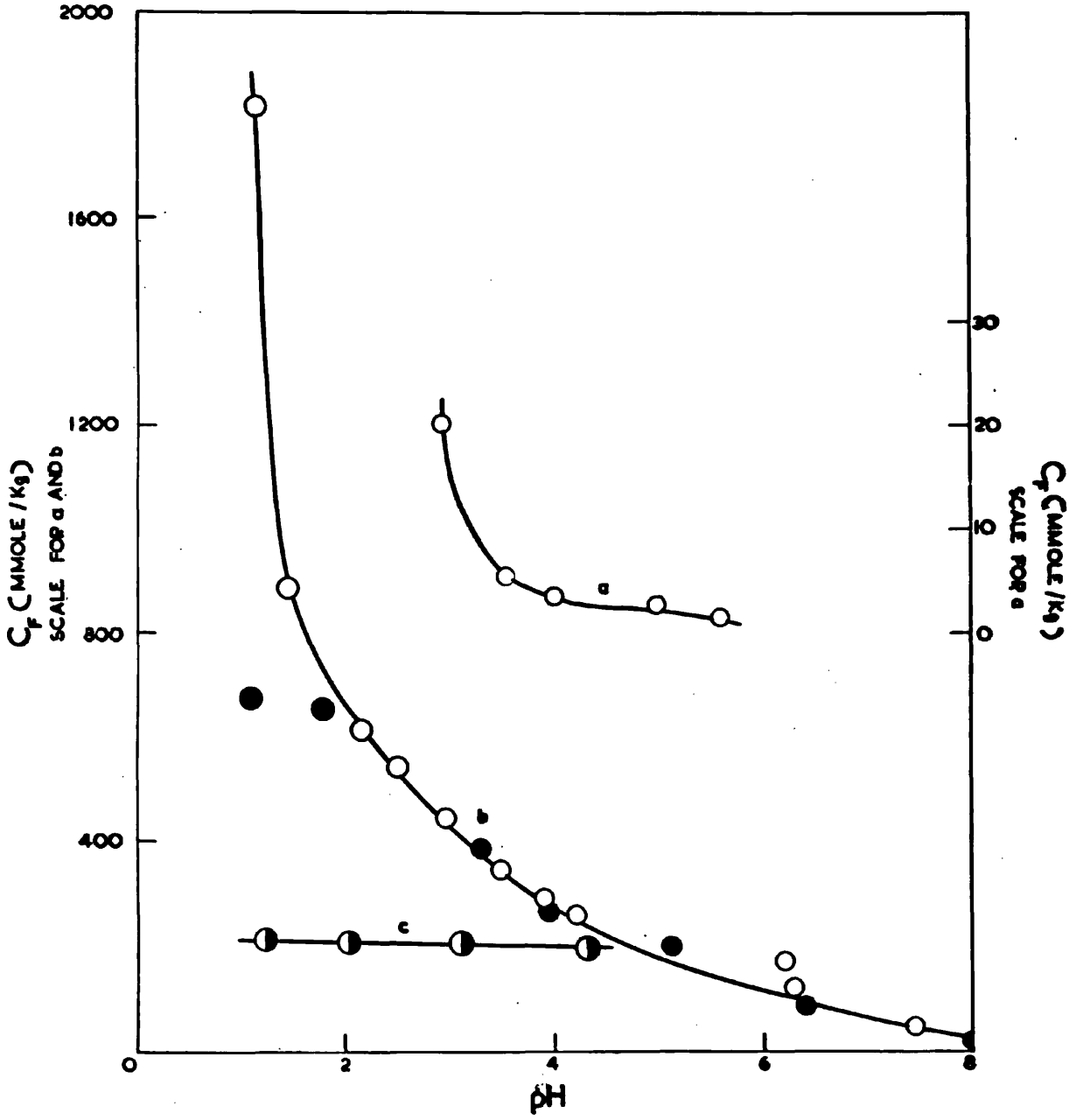


a, NYLON, 50° } HYDROXYLAMINE SULPHATE (2.5 g/L.) ADDED
b, NYLON, 60° }

c, NYLON, 50° } NO ADDITION
d, NYLON, 60° }

e, CELLULOSE TRIACETATE, 50° } NO ADDITION
f, CELLULOSE TRIACETATE, 60° }

FIG 3—— ADSORPTION OF HAEMATOXYLIN, HAEMATEIN, AND BRAZILEIN BY WOOL UNDER VARIOUS CONDITIONS OF ACIDITY.



a, HAEMATEIN, pH ADJUSTMENT BY CHANGE IN CONCN. 1·0–0·1 g./L., 60°, 12 Hr.

b, HAEMATEIN ⊙ AND BRAZILEIN ● pH ADJUSTMENT BY MINERAL ACID ADDITION 2·0 g./L., 85°, 8 Hr.

c, HAEMATOXYLIN, pH ADJUSTMENT BY ACID ADDITION 8·0 g./L., 60°, 12 Hr.

Part II.

Section II.

Studies of the Adsorption of Dyes and Related Compounds by Silica.

Introduction.

Adsorption studies on inorganic surfaces, e.g. carborundum, sulphur, carbon, glass, and varieties of silica, have been made fairly extensively, although little is reported upon the actual mechanism of adsorption from solution. In the present investigation, the mechanism of adsorption of aromatic solutes, especially dyes, by silica has been studied.

The influence of the charge which a surface possesses in a particular solvent is of great importance in adsorption. It is now well recognised that, at a liquid/solid interface, there is a layer of firmly held positively or negatively charged ions at the solid surface and also there is a diffuse layer of such ions extending into the bulk of the solution. The potential across these two layers, known as the Zeta-potential, plays an important part in adsorption.

Silica in contact with water possesses a negative charge. It is now generally believed that the silica surface is covered with acidic -SiOH groups (see e.g. Jones and Wood; Iler; Greenberg; Shapiro and Weiss) in aqueous

solution, which dissociate thus -

$$SiOH \rightleftharpoons SiO^- + H^+$$

O'Connor and Buchanan have determined the zeta-potential of varieties of silica under different conditions and have come to the conclusion that though the potential can be reduced considerably in presence of multivalent electrolytes it cannot be made to change its sign.

The adsorption of cationic dyes on silica is almost certainly due to this negative charge. Plesch and Robertson believe that the adsorption of basic dyes on montmorillonite takes place in two stages. First there is irreversible ion-exchange, and then physical adsorption. O'Connor and Buchanan, following a study of changes in surface charge, considered that inorganic or organic anions are adsorbed by quartz by a process of physical adsorption, the accompanying cations being adsorbed by ion-exchange. Freundlich, Euslin and Lindau observed that after adsorbing the basic dye Crystal Violet the surface of quartz became much more hydrophobic than before. Also, Haller and Duecker detected an irreversible reaction of p-nitrobenzyl bromide with glass, to produce a permanent hydrophobic surface, which they attributed to reaction of the bromine atom with hydrogen of the hydroxyl groups in the glass surface. Imamura and Koizumi have found that the amount of the dye, Rhodamine 6G, adsorbed by silica gel is less from a bath which was

illuminated than from one kept in the dark, which may indicate some difference in the arrangement of charges on the adsorbed species. Gibb and Ritchie examined the rate of adsorption of Methylene Blue on Loch Aline sand, powdered quartz, and powdered Vitreosil, both before and after removal of the disturbed (amorphous) surface layer, and found that the disturbed layer adsorbs more dye for a given surface area than does the underlying core. Watson has studied the adsorption of amino-acids on silica and finds that ionic attraction is of first importance in adsorption, followed by hydrogen-bond formation. In this laboratory preliminary tests were carried out by Cullen, Allingham and Wood on adsorption of dyes by different varieties of silica.

Several authors have observed that silica has little or no adsorptive properties for anionic dyes (Dale and King), though Haldeman and Emmett have recently prepared silica gels with adsorption properties for specific azo-dyes. Kayser and Bloch in their studies on adsorption of basic and azo-dyes by montmorillonite found that azo-dyes are adsorbed much less than basic dyes. They suggested that the positive nature of the azo-group dominates the negativity of the sulphonic acid group.

Adsorption studies have also been utilised by many authors to determine the surface area of the adsorbent. Paneth suggested that in the adsorption of dyestuffs by

charcoal and other finely divided substances a single layer of adsorbed molecules is not exceeded and on this basis determined the surface areas of crystalline powders. Difficulties were, however, encountered when it was found that different dyes covered different portions of the total surface area, which may be explained by different orientations of the dye molecule on the surface. Jopling has determined the surface area of barium sulphate powders by different methods and has found that there is good agreement between dye adsorption and air permeability methods. Suito, Arakawa and Arakawa have calculated the specific surface areas of calcium carbonate powders from the adsorption data of stearic acid from different solvents; they found that the results obtained from benzene solution are in good agreement with those obtained by other physical methods. However, it may be pointed out that the solubility of the solute in the solvent and also the effect of the solvent on the surface must be considered before any attempt is made to determine absolute values of surface area by adsorption studies from solution.

Present Work.

The adsorption has been studied of a number of aromatic compounds, mainly dyes, by varieties of silica. Specific surface areas have been calculated assuming that a monolayer is formed and the results have been compared with those obtained by physical means.

Experimental.

The substrates used were -

(a) Loch Aline sand (99.8% SiO_2) (specific surface area, 0.009 x 10^5 cm.^{2} per g.);

(b) Pure ground quartz (specific surface area, 0.008 x 10^5 cm.^{2} per g.);

(c) Ground Vitreous silica ("Vitreosil"), (specific surface area, 0.005 x 10^5 cm.^{2} per g.);

(d) A commercial silica dust "MSC", 98% SiO_2, (specific surface area, 0.11 x 10^5 cm.^{2} per g.).

The specific surface areas of a, b, and c, were estimated from counts of particles and measurement of dimensions by microscope; the value for (d), as supplied by the manufacturers, was obtained by air permeability measurement.

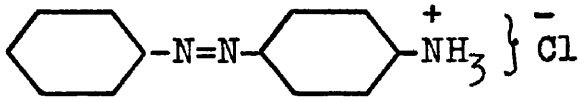
Dyes, etc.

The dyes used, except two, were pure samples, either obtained in this state or recrystallised from ethanol or dilute hydrochloric acid. Rhodamine B and Malachite Green were used in the form of commercial products supplied without adjuvants. All other reagents were purified by normal methods; distilled water was used for the adsorption tests.

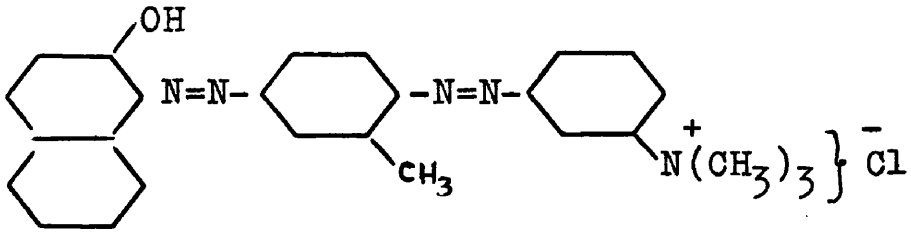
The names of the dyes used and their constitutions are shown below.

Molecular sizes were estimated by use of Stuart-type models (Catalin Ltd.) and the figures quoted in Table 1 refer in each case to the dimensions of the smallest enclosing rectangles.

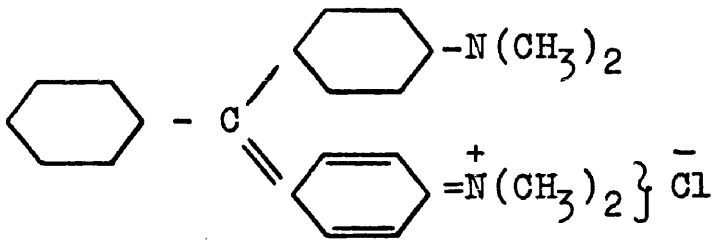
I p-aminoazobenzene hydrochloride



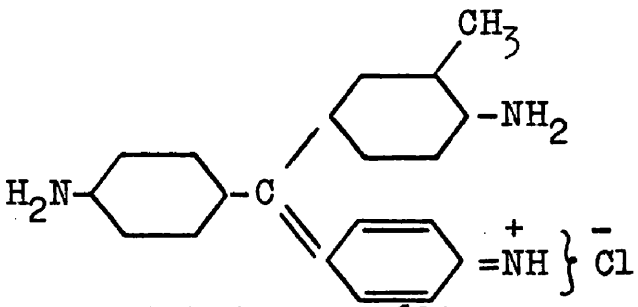
II Janus Red B. C.I.266.



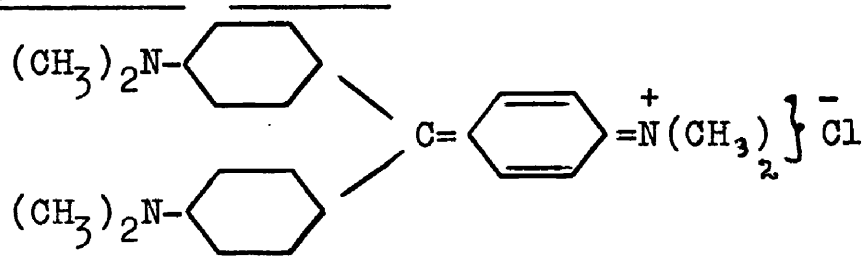
III Malachite Green. C.I.657.



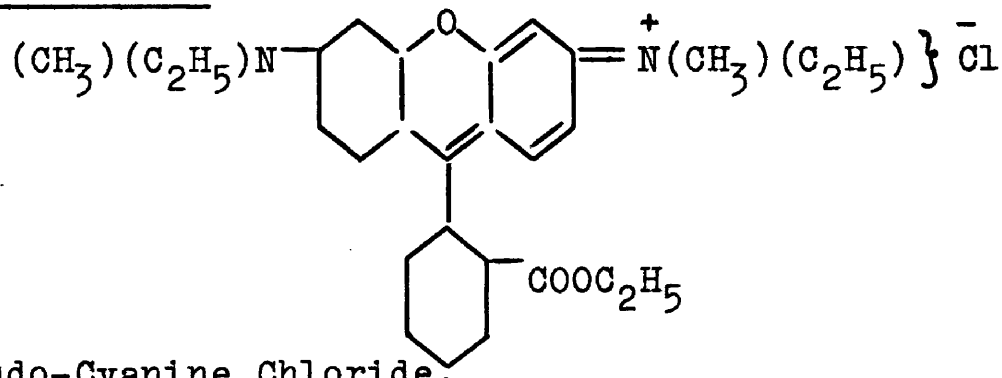
IV Magenta P. C.I.677.



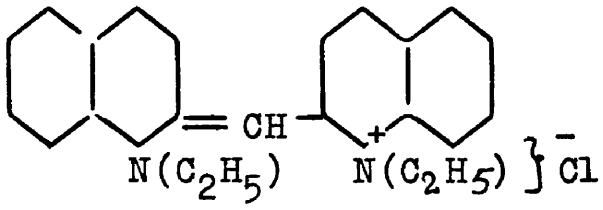
V Crystal Violet. C.I.681.



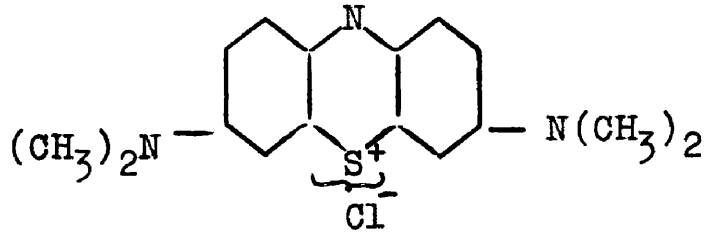
VI Rhodamine 6GB.



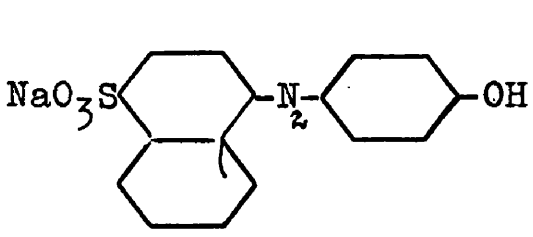
VII Pseudo-Cyanine Chloride.



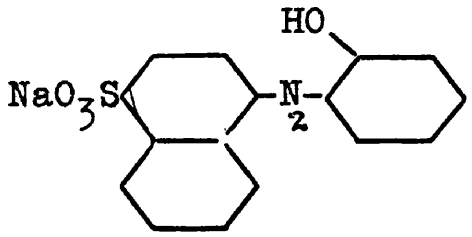
VIII Methylene Blue B. C.I.922



IX,X Orange I and II.



Orange I



Orange II

Adsorption and analytical procedure.

Weighed quantities of silica (0.1-1.0g.) and 10 c.c. of the test solutions were placed in glass tubes which were completely sealed by fusion and tumbled end-over-end in a thermostat (Clunie and Giles).

Normally the amount of solute adsorbed was calculated from the difference in initial and final solution concentration, measured absorptiometrically on one or other of three instruments, viz. a Hilger Spekker absorptiometer, an EEL colorimeter, or a Unicam SP500 photoelectric spectrophotometer. In order to avoid errors due to loss of dyes by staining of the glass apparatus during analysis, all items of volumetric apparatus and the optical cells of the spectrophotometer were first filled with a dilute solution of a cationic surface-active agent (Lissolamine A (I.C.I.) and then rinsed once with cold water before use with basic dye solutions. This procedure was found to be unnecessary, however, for tests with the silica of greatest specific surface area.

Results and Discussion.

Experiments with all types of silica show that all basic dyes are readily adsorbed from aqueous solution but the amount of acid dyes adsorbed is hardly detectable for all types of silica except silica MSC, which has a large specific surface area.

The present tests show that the adsorption of basic dyes has three marked characteristics, viz. rapid attainment of equilibrium, very high adsorption values, and low apparent heat changes. On the other hand, the adsorption of acid dyes has an entirely different nature, the adsorption values are low, the reaction endothermic, and rate of adsorption very low.

Some of the preliminary experiments were carried out by earlier workers in this laboratory. The results have been included in the present investigation and suitably differentiated from those obtained by the author.

Rates of Adsorption.

The study of the rate curves, though it does not lead to any precise description of the nature of adsorption, gives some useful general indications. When adsorption takes place in the internal amorphous region of a solid (e.g. in fibres) or in micro-pores, e.g. in the anodic film of aluminium (cf. Stewart), the process is very slow and in most

cases requires many hours or even days for its completion. In the present experiments, adsorption of basic dyes was found to reach equilibrium in a few minutes, even at room temperature. This is an indication that adsorption is taking place on the external surface of the silica. It may be noted here that temperature has hardly any effect either on the rate or on the amount of adsorption (see Fig.1).

Initial rates could not be determined accurately for the very fine silica dust because of the time required to separate it centrifugally from the liquid, but an inspection of Fig.1 shows that a very rapid initial adsorption probably occurs also with this material.

The adsorption of an acid dye, Orange I, however, (Fig.7) takes almost 48 hours to reach equilibrium probably because the adsorbed anion has to penetrate a barrier at the silica surface, with the same sign of charge as the anion; thus only a small proportion of high energy anions may get through to the surface.

Isotherms for Basic Dyes.

Typical isotherms for the adsorption of various basic dyes by the several varieties of silica are shown in Fig.4 and 5. These isotherms are of the 'Langmuir' shape, normally associated with monolayer adsorption. The specific surface areas of different varieties of silica has been

calculated on the assumption that a monolayer is formed. In Table 1 the ratio of the calculated specific surface area to the surface area determined by physical means (microscope, air permeability or Nitrogen adsorption) is given. It is evident from the data that the amount of the dye adsorbed is far too high for a monolayer and cannot be accounted for by any errors in surface area measurements. Also it seems impossible that successive deposition of layers could occur to such an extent.

Table 1.

Coverage of Silica Surfaces by Dyes.

Type of Silica			Loch Aline Sand		Quartz		Vitreous Silica (Vitreosil)		Silica MSC	
Specific surface area $cm^2/g.$			900		800		500		10, 800	
No	Dye	Molecular area (A^o)	Max.*	Cov.**	Max.	Cov.	Max.	Cov.	Max.	Cov.
CATIONIC DYES										
1.	Aminoazobenzene hydrochloride								20.0	
	Flat	96	-	-	-	-	-	-		12.0
	End-on	25	-	-	-	-	-	-		3.0
2.	Janus Red B				0.171***				75.0	
	Flat	180	-	-	1.7	-	-			75
	Edge-on	100	-	-	1.0	-	-			41.5
	End-on	45	-	-	0.4	-	-			18.7
3.	Malachite Green		0.39***		0.823		0.82			
	Flat	180		2.8		10.9		17.7	-	-
	Edge-on	75		1.6		4.5		7.4	-	-
	End-on	60		1.3		3.6		5.9	-	-

Table 1. (Cont'd)

Type of Silica			Loch Aline Sand		Quartz		Vitreous Silica (Vitreosil)		Silica MSC	
Specific surface area $cm^2./g.$			900		800		500		10,800	
No	Dye	Molec^r area(A^o)	Max.*	Cov.**	Max.	Cov.	Max.	Cov.	Max.	Cov.
CATIONIC DYES (Cont'd)										
4.	Magenta P						0.18***			
	Flat		-	-	-	-		3.9	-	-
	Edge-on		-	-	-	-		1.5	-	-
5.	Crystal Violet				2.3		0.9		42.0	
	Flat	164	-	-		27.6		17.7		38.3
	Edge-on	90	-	-		15.2		9.7		21.1
6.	Rhodamine 6GB								30.0	
	Flat	160	-	-	-	-	-	-		35.9
	Edge-on	96	-	-	-	-	-	-		16.0
	End-on	60								10.0
7.	Pseudo-cyanine chloride								40.0	
	Flat	120	-	-	-	-	-	-		26.6
	Edge-on	88	-	-	-	-	-	-		19.6
8.	Methylene Blue B		0.13***		0.125		0.25		48.0	
	Flat	120		1.1		1.1		3.6		32.0
	Edge-on	88		0.8		0.8		2.6		23.4
ANIONIC DYES										
9.	Orange I								5.0	
	Flat	150	-	-	-	-	-	-		4.5
	Edge-on	80	-	-	-	-	-	-		2.4
	End-on	50	-	-	-	-	-	-		1.5
10.	Orange II								0.49	
	Flat	150	-	-	-	-	-	-		0.44
	Edge-on	80	-	-	-	-	-	-		0.24
	End-on	50	-	-	-	-	-	-		0.14

* Max. = Maximum adsorption (mmole dye/kg.SiO_2)

** Cov. = 'Coverage factor', i.e. ratio of maximum amount of dye adsorbed to calculated capacity of surface monolayer.

*** Results reported by earlier workers in this laboratory.

Moreover, an initial 'hump' in the isotherms, representing the first monolayer would be expected as e.g. in the isotherms of some cyanine dyes by silver halide (Sheppard and Crouch; West, Carroll and Whitcombe), if this were the case, but it is not observed with any of the dyes used. It is therefore suggested that the high adsorption values and the high affinity type isotherms (Giles and McEwan) indicate that a monolayer of aggregates or micelles of dye cations are adsorbed on the surface.

It is known that the mobility of small ionic micelles in aqueous solution is higher than that of the corresponding individual ions because the mobility of an ion is directly proportional to its charge but inversely proportional to its radius and with increasing aggregation number, the micellar charge increases more rapidly than the radius of the particle (McBain). Now, when silica is added to a dye solution, it is to be expected that the aggregates, because of their high mobility, will have a greater chance to reach the silica surface than single dye molecules, and thus they will be preferentially adsorbed.

This hypothesis has been checked by tests with Methylene Blue as described below.

Lemin and Vickerstaff have shown that the two light absorption peaks at 6670 Å and 6100 Å* in aqueous solutions

* In the present tests, this peak was located at 6570 Å.

of this dye correspond with monomeric and polymeric forms respectively. With increase in concentration the relative intensity of the polymer peak rises and that of the monomer peak falls. Therefore if silica is added to the solution and the absorption spectrum measured, the polymer peak at 6100 Å should fall more rapidly than that of the monomer peak at 6670 Å i.e. the ratio of the height of polymer peak to monomer peak will be lower after addition of silica than before, if solutions of the same concentration are compared. The absorption spectra of two solutions of different concentration are shown in Fig.6. It is clear from Fig.6 that the polymer peak is more affected than the monomer peak by addition of silica.

This method is subject to some experimental limitations. Thus comparatively weak solutions must be used even with a thin (1 mm.) spectrometer cell, and these will not be rich in polymer; and even if the polymer is adsorbed, it may be quickly reformed to reestablish the monomer-polymer equilibrium. Nevertheless, the result of the test is positive. (The curves are plotted on a logarithmic ordinate, so that change of concentration without change in the nature of the solute has no effect on their shape.)

Pseudo-cyanine chloride was used in a similar test; the results are summarised in Table 2. The results show a definite trend in the same direction as those for Methylene

Table 2.

Adsorption of pseudo-Cyanine Chloride

Ratio, optical density of dye solution at 5240 Å and 4920 Å *.

Without Silica	With Silica
1.535	1.452
1.476	1.420
1.473	1.396
1.470	1.420

* A lower ratio indicates that the polymer peak at 5240 Å has decreased more than the monomer peak at 4920 Å.

Blue. It is assumed therefore that other basic dyes behave in a similar fashion, which explains the very high adsorption of these dyes on silica. The reflectance spectrum of dry dyed (Methylene Blue) silica MSC was also recorded (Fig.6). The intensity of the monomer peak is low in comparison with that of the polymer peak, which also shifted to still lower wavelength. This probably slows that Methylene Blue is present on the silica surface in a much higher state of aggregation than in solution.

Effect of Solid-Liquid Ratio.

Theoretically, the amount of solute adsorbed depends upon the equilibrium concentration of the solution in contact

with the substrate, and is quite independent of either the volume of the solvent or the amount of the substrate. In the present case however it has been noted that the volume of solution used affects adsorption slightly with the increase in liquid-solid ratio (Fig.2 and 3). This may be attributed to silica surface being slightly etched by the solvent. It is known (Gibb and Ritchie) that fine silica powder has an amorphous layer which can be dissolved (Gibb and Ritchie; Alexander, Heston and Iler) away by aqueous solutions, though rather slowly. It has been noticed in the present tests that the effect of volume of solution is more pronounced in the case of adsorption of p-aminoazo-benzene hydrochloride (Fig.2) where the silica was left in contact with the solution for 24 hours, than in the case of Crystal Violet (Fig.3) where the period of contact was much shorter.

A similar effect of solution volume has also been noted in the case of adsorption of anionic dyes by the anodic oxide film on aluminium, which is also slightly soluble in water (Stewart). The data given by Greenberg for calcium hydroxide adsorption on silica from water also shows evidence of a slight increase in amount adsorbed with increase in volume of solution.

Therefore, the isotherms obtained here must represent pseudo-equilibria, because though the rate curves (Fig.1)

show an apparent maximum after a short period, the outer layer of silica is still being dissolved very slowly.

Low Apparent-heat of Adsorption.

In the present studies the heat change for adsorption of basic dyes is too small to measure. This applies also to the processes of ion exchange on resins (cf. Giles, Mehta, et al.), to the adsorption of cationic compounds by graphite (Hassan), of sulphate esters by anodic aluminium oxide (Giles et al.) and sulphonates by chromatographic alumina (Stewart). In most other cases, in the adsorption of organic solutes from solution by any type of surface, low but quite measurable apparent heats of the order of 5-10 kcal/mole, have been observed. The most likely explanation of the absence of measurable heat change in the present case is that the process of adsorption consists of the replacement of one set of water-solvated cations (H_3O^+) by another (dye cations). In such cases no bonds are broken or formed.

Nevertheless, it is difficult to account satisfactorily for the constancy of micellar adsorption over a range of temperatures, because the degree of aggregation of the dyes in the solution cannot be constant and must in fact fall with rise in temperature. The adsorption depends upon the surface charge on the silica, which is known to be almost independent of temperature (O'Connor and Buchanan), and on

the size and shape of the dye micelles, which affects their ability to pack together in the monolayer, it may be therefore that even at the highest temperature used in the present tests there are sufficient micelles of the required size in solution to form an adsorbed monolayer; or alternatively some micelles may be formed by aggregation at the silica surface during the actual adsorption process.

Effect of Aluminium Cation.

O'Connor and Buchanan have studied the electrokinetic properties and surface reaction of quartz and have come to the conclusion that the surface charge may be considerably influenced by cation exchange, but hardly ever changes its sign. Thus the zeta-potential is more affected by multivalent cations than by monovalent ones. The adsorption of a basic dye (Crystal Violet) in the presence of aluminium sulphate was therefore studied. This salt will probably reduce the surface charge of silica considerably, thus reducing the adsorption of the basic dye. Fig.2 shows that the adsorption is considerably decreased in these conditions.

The adsorption of anionic dyes would be expected to be higher in presence of aluminium sulphate. In fact its presence does increase the amount of Orange I adsorbed (Fig.8).

Adsorption of Anionic Compounds.

Silica being negatively charged in aqueous solution is not expected to adsorb anionic dyes readily, though adsorption might occur through hydrogen bond formation or van der Waals attraction. Therefore, the adsorption of the anionic dyes Azo Geranine, Benzoazurine, Solway Blue, Orange I and II from aqueous solutions, and the non-ionic polar compounds, azobenzene, ß-naphthol, anthraquinone, and ß-naphthylamine, from non-polar solvents was studied. In almost all cases the adsorption on vitreous silica, quartz and Loch Aline sand was either nil or so little that it could not be measured with sufficient accuracy. The adsorption of Orange I and Orange II on silica MSC was found however to be measurable and was studied in some detail.

The adsorption isotherms and rate curve (Fig.7 and 8) show some features different from those of basic dyes. These may be summarised thus:

(i) The rate of adsorption is low.

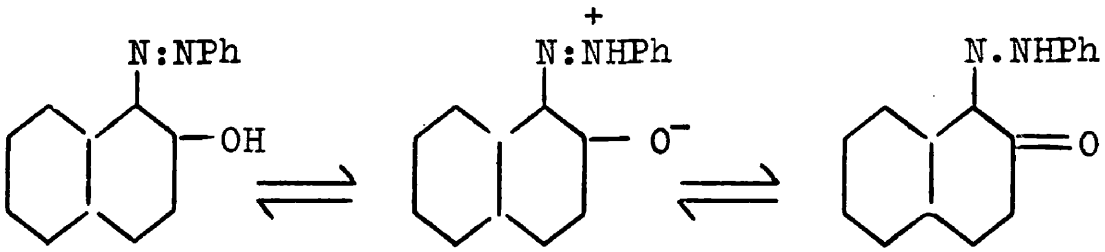
(ii) The adsorption of Orange I is greater in presence of aluminium sulphate.

(iii) The amount of Orange I adsorbed is greater than that of Orange II, although it is adsorbed much less than basic dyes.

(iv) There is higher adsorption at high temperature than at low.

The first two points have been discussed above. The lower adsorption of anionic dyes compared with basic dyes shows that micellar adsorption is very unlikely, the dyes are probably adsorbed as single ions by short range polar forces, e.g. hydrogen bonds. This explains the higher adsorption of Orange I compared with Orange II, since the former has a free hydroxyl group while the hydroxyl group in the latter is chelated (Arshid et al).

The existence of a suggested Zwitterion configuration in the resonating structure of o-hydroxyazo-compounds



(Kuhn) might also account for the adsorption of Orange II, because in the zwitterion form there is one positively charged centre which might be attracted to the silica surface, but here the attraction is less, e.g. than for basic dyes because of the closely adjacent negative charge.

The adsorption of Orange I is apparently endothermic. It has been suggested by Derbyshire that Orange II is largely dimerised in solution. Orange I may also be dimerised, but if so, its hydroxyl-group will be inactivated and the dimer must dissociate before adsorption can occur. At higher temperatures this dissociation occurs more

readily. An alternative explanation is that the disturbed layer on silica has been dissolved away causing the higher adsorption at higher temperatures. Similar results have been noted by Greenberg in the adsorption of calcium hydroxide on silica. He suggested that the chemical reaction with matrix silica begins only at the higher temperatures.

Adsorption of Janus Red B.

Preliminary experiments upon the adsorption of Janus Red B on silica revealed several interesting features meriting further study.

This dye appears to be highly colloidal, and concentrated solutions are gelatinous in the cold. Its molecule is planar, which may lead to the formation of long thin micelles in which the dye cations are arranged with their long axis at right angles to the length of the micelle. The special features of the adsorption are:

(i) An initial high rate, followed by a much lower rate; the second phase may be due to the low mobility of very large micelles.

(ii) Very high coverage (Table 1); this may be the result of a high aggregation number, and because the long thin micelles can pack tightly at the surface. The amount

of the dye adsorbed decreases in presence of pyridine-water (1:3) as solvent (Fig.9) probably because of disaggregation.

(iii) An apparently endothermic reaction; this may be the result of disaggregation.

Conclusions

(a) The adsorption of basic dyes on all types of silica takes place by electrostatic attraction. This is consistent with the tests made in presence of aluminium sulphate.

(b) The amounts of basic dye adsorbed are much higher than correspond with a normal monolayer, and the adsorption of micelles rather than single ions must be taking place.

(c) No energy changes are apparent in adsorption of basic dyes, but the reaction with anionic dyes is endothermic, probably because of increase in concentration of monomer at low temperatures, this species being preferentially adsorbed.

(d) The adsorption increases with increase in liquid-solid ratio, probably because the amorphous layer on the silica is etched away by water, thus increasing its surface area.

(e) The adsorption of the anionic dyes, Orange I and II, is probably due to ion exchange and hydrogen-bond formation.

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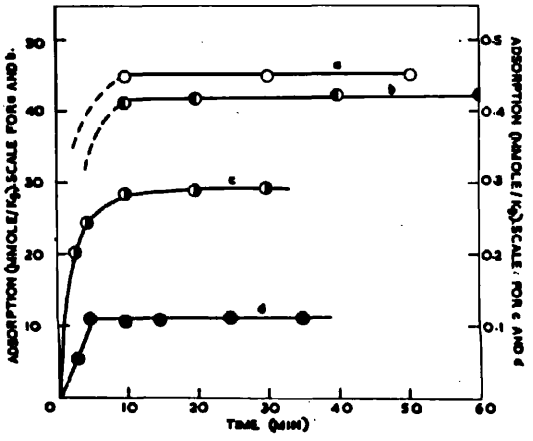
FIG.1— RATES OF ADSORPTION OF BASIC DYES ON SILICA.



a. METHYLENE BLUE ON SILICA MSC.

b. CRYSTAL VIOLET ON SILICA MSC.

c. METHYLENE BLUE ON VITREOUS SILICA.

d. MALACHITE GREEN ON QUARTZ.

FIG.2— EFFECT OF CHANGE IN SOLID-LIQUID RATIO AND OF ADDITION OF ALUMINIUM SULPHATE ON ADSORPTION OF CRYSTAL VIOLET BY SILICA MSC

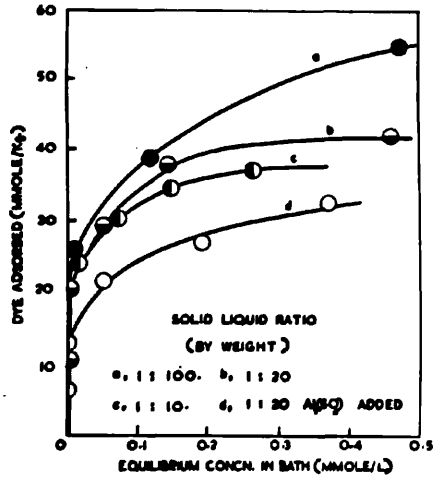


FIG.3— EFFECT OF CHANGE IN SOLID-LIQUID RATIO ON ADSORPTION OF p-AMINOAZOBENZENE HYDROCHLORIDE ON SILICA MSC.

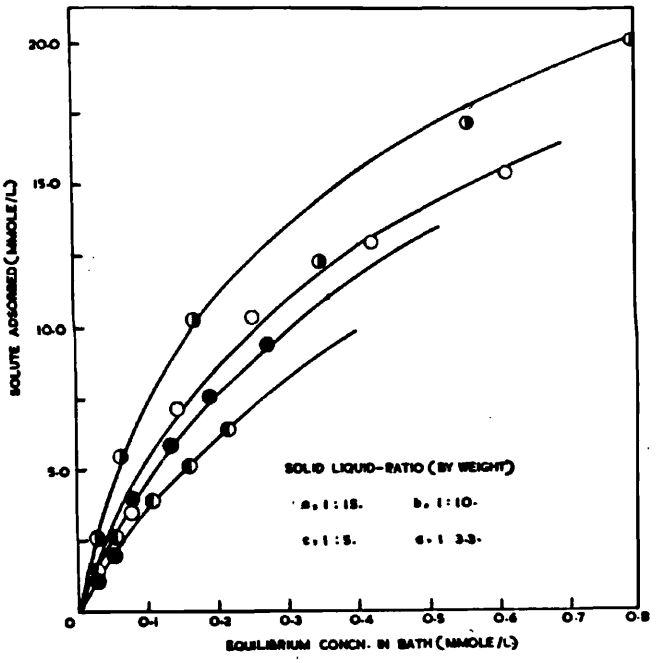


FIG.4— ADSORPTION ISOTHERMS FOR BASIC DYES ON SILICA MSC

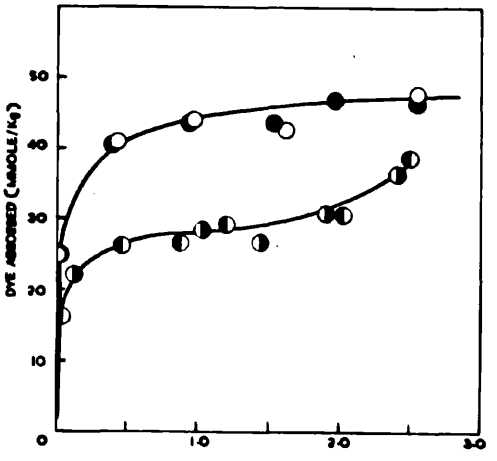


FIG. 5— ADSORPTION ISOTHERMS OF BASIC DYES ON SILICA.

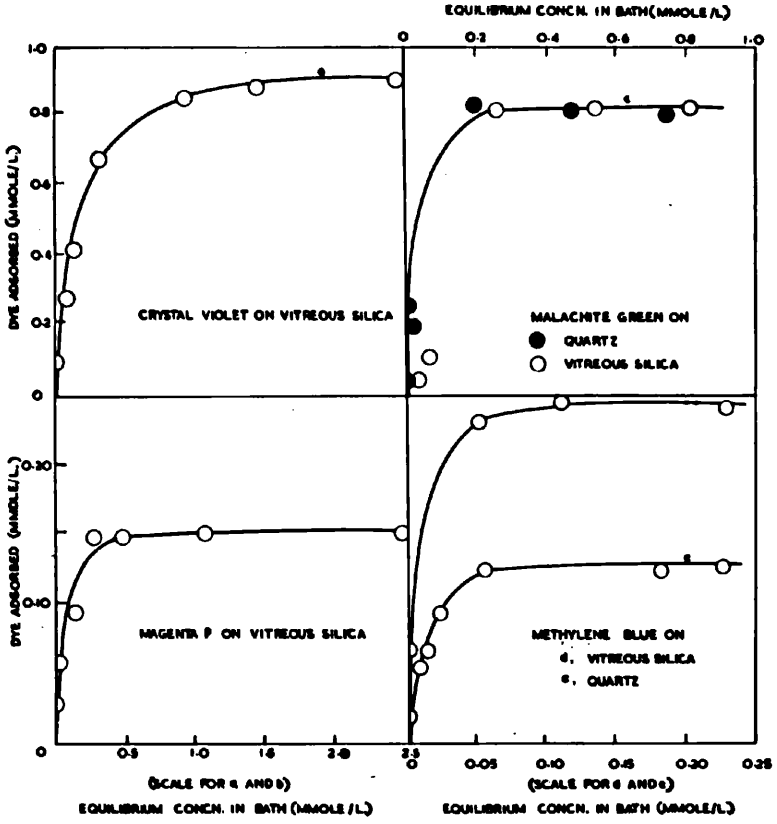
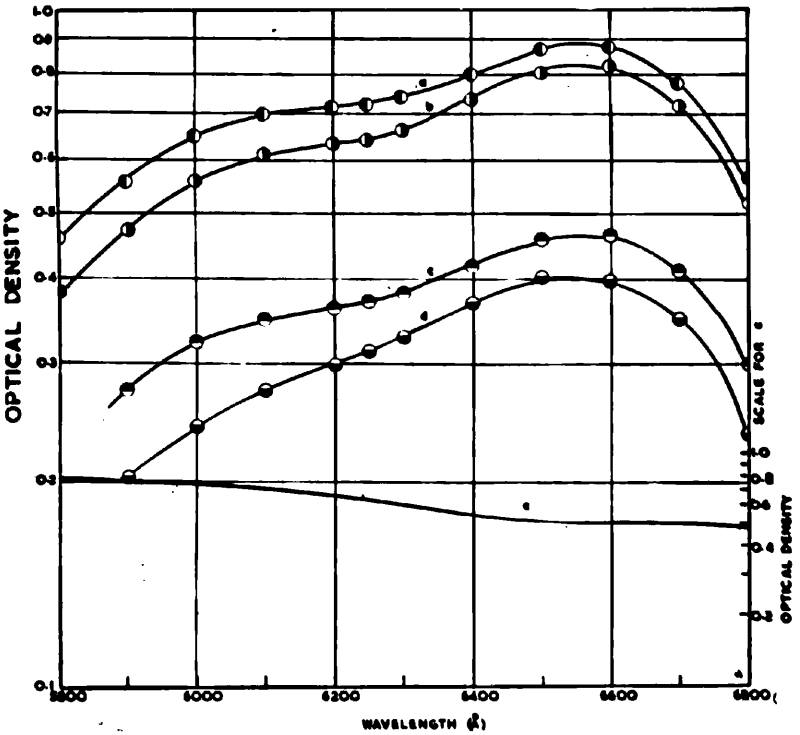


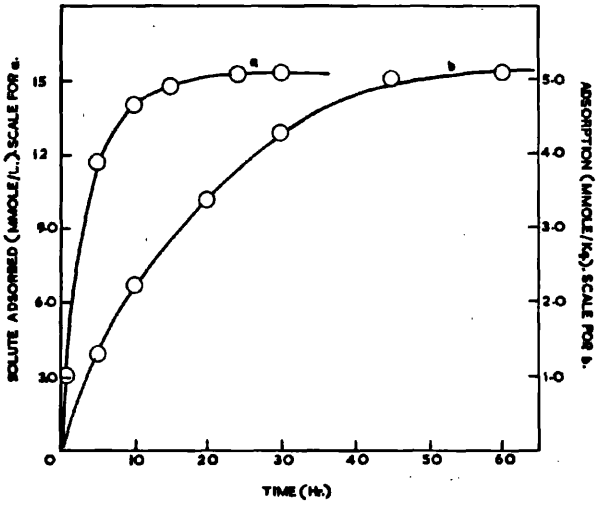
FIG. 6— LIGHT ABSORPTION CURVES OF SOLUTIONS OF METHYLENE BLUE OF TWO CONCENTRATIONS BEFORE AND AFTER TREATMENT WITH SILICA (VITREOSIL)



a AND c, BEFORE TREATMENT; b AND d, AFTER TREATMENT

e, REFLECTANCE SPECTRUM OF DRY DYED (METHYLENE BLUE) SILICA MSC.

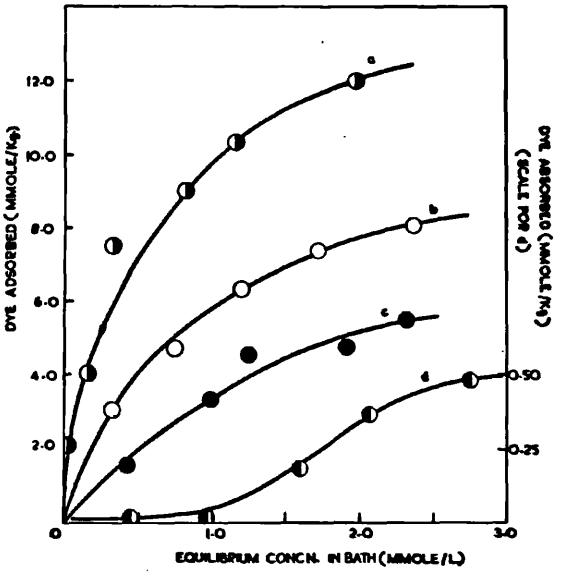
FIG.7—RATE OF ADSORPTION OF *p*-AMINOAZOBENZENE HYDROCHLORIDE AND ORANGE I BY SILICA MSC.



a, *p*-AMINOAZOBENZENE HYDROCHLORIDE (AT pH 1-2)

b, ORANGE I

FIG.8—ADSORPTION ISOTHERMS OF ORANGE I AND2 ON SILICA MSC



a, ORANGE I, 30°, WITH ALUMINIUM SULPHATE (0·4g/L)

b, ORANGE I, 50°. c, ORANGE I, 30°. d, ORANGE 2, 30°.

FIG.9—ADSORPTION ISOTHERMS OF JANUS RED B ON SILICA MSC.