STUDIES IN LIQUID-PHASE ADSORPTION AT ORGANIC AND INORGANIC SURFACES

BY

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SUMMARY

The first section of the thesis is concerned with adsorption by chitin. Lobster-shell chitin, prepared from the carapace of Nephrops norvegicus, has been used in quantitative adsorption studies with mineral and organic acids and sulphonated azo-dyes in aqueous solutions.

In the case of acids the hydrogen ions are adsorbed initially on the acetylamino-groups in the substrate with a consequent swelling and breakage of inter-chain bonds owing to the pressure of solvated water around the resultant cationic centres. The actual amount of acid adsorbed is determined however by the ability of the anion to penetrate the structure. The hydrogen ion can penetrate it readily, but to preserve neutrality each adsorbed hydrogen ion must be accompanied by an anion, and owing to the high crystallinity of chitin the entry of anions is restricted, and in fact the amount adsorbed decreases linearly with the volume of the anion in any given series of acids with similar basic structure. Superimposed on this volume effect, however, is the effect of increased van der Waals attraction of the anion for chitin, with increase in the number of aromatic nuclei in the anion. Generally the affinity rises with increase in length of the conjugated system of the dye molecule. The ion-exchange adsorption process between the chitin and sulphonate groups of the dye has a negligible apparent heat change,

but the non-polar attraction of the remainder of the dye molecule does produce a heat change which increases with the non-polar affinity. Affinity measurements show that one sulphonate group in an adsorbed dye becomes associated with one of the cationic centres in chitin and that additional groups after the first are not so combined and remain dissolved in water, hence decreasing the affinity of the anion for the substrate. Hydrogen-bonding is also operative where there are potential hydrogen-bonding groups in the substrate, but seems to decrease with increasing acidity of the bath.

The results of full elementary analyses suggest that chitin does not consist entirely of poly-N-acetylglucosamine, but that about one eighth of the amino-groups are unacetylated.

The next section of the thesis describes an investigation made to study and compare the adsorption mechanism of a variety of aromatic compounds, with and without hydrogen-bonding groups, by cellulose and by chitin from water and from non-aqueous solvents. In absence of water polar non-ionic compounds are adsorbed by both cellulose and chitin principally by hydrogen-bonding. In aqueous solution chitin adsorbs anionic solutes with potential hydrogen-bonding-groups principally by ion-exchange and hydrogen-bond formation. Non-polar attraction is also operative in

the case of large molecules. Cellulose seems to adsorb these compounds by non-polar attraction only, the affinity increasing with the size of the solute molecule and being independent of the presence therein of hydrogen-bonding-groups.

Planar non-hydrogen-bonding anionic compounds are not adsorbed on chitin from alkaline solutions. Cellulose however does adsorb such compounds from either neutral or alkaline solution, because its attraction is non-polar and dependent not on hydrogen-bonding forces, but only on the presence of a highly conjugated system in the solute molecule

This work was followed by a study of the adsorptive properties of graphite for organic solutes, mainly dyes, from aqueous and non-aqueous solvents.

Rate measurements demonstrate a rapid adsorption and the short period required to reach equilibrium suggests that adsorption is entirely superficial. Basic dyes are quickly adsorbed, by electrostatic attraction. Anionic dyes appear to be adsorbed by physical attraction and the rate of adsorption is higher in the case of dyes which dissociate easily into single molecules.

The surface area of graphite was determined by electron microscopy and the orientation of adsorbed molecules studied. At low concentration it seems that most of the compounds used

form condensed monolayers. Sulphonated compounds appear to be so oriented that the sulphonate groups are as far away as possible from the graphite surface and non-ionic compounds lie flat so that they present a maximum surface area to the graphite.

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PART III ADSORPTION STUDIES ON GRAPHITE

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PREFACE

Dyeing has been practised empirically for thousands of years, but it is only in the last fifty years that it has been subjected to precise scientific investigation. In particular during the past two decades a considerable volume of research has been directed towards a better understanding of the dyeing process. This research has followed, broadly, three main paths, viz., (a) kinetic studies, mainly of the diffusion rate of dyes in water alone and in fibres in presence of water; (b) thermodynamic studies in which attempts have been made to consider the dyeing process as a normal chemical reaction, and methods of evaluating changes in free energy, entropy and the heat changes which occur during dyeing, have been worked out; and (c) studies of the mechanism by which dyes are adsorbed to the surface of fibres, i.e., of the nature of the chemical or physical forces which contribute to the thermodynamic affinity of a dye for a fibre. Of these three, it can be said that the adsorption mechanisms of dyeing are probably still much less understood than the kinetics or thermodynamics of the processes involved.

The present thesis is a record of an investigation designed to lead to a better understanding of these mechanisms, in particular, those on chitin, cellulose and

carbon itself, in the form of graphite.

Chitin has some of the characteristics of the chemical constitution of both cellulose and proteins, and it was hoped that its use might help to elucidate some points in the understanding of dyeing mechanisms on these classes of substance.

Graphite was used as a substrate because the absence of polar groups in its structure simplifies the interpretation of its surface adsorption effects. Further, very little was previously known of its reactions with dyes. Its behaviour should also throw light on the important subject of clarification of solutions by charcoal, because basically both materials have the same constitution, the difference being their physical form: graphite is an impermeable solid, but charcoal a very porous one.

The first part of this thesis deals with adsorption studies on chitin, the second with adsorption on cellulose and chitin, in direct comparison with each other, and the third with adsorption on graphite. Each is discussed separately, with the survey of relevant literature.

PART I

MECHANISM OF ADSORPTION ON CHITIN

INTRODUCTION

Chitin is one of the most important natural structural materials (see, e.g. Richards). In the animal kingdom it occurs mainly as protective cuticles in invertebrates and in the vegetable kingdom it forms part of the cell walls of some fungi and micro-organisms. Its constitution has been fairly well established, and its chemical properties have been frequently studied, but when the present work was commenced there was little or no record of systematic investigations of its adsorptive properties. Since then, however, Hackman has published the results of adsorption tests on chitin with aqueous solutions of proteins.

The constitution assigned to chitin is that of a polymer composed of acetylglucosamine units linked in the 1:4 positions (Meyer and Mark,1928; Meyer and Pankov, 1935; Meyer and Wehrli,1937; Fraenkel and Rudall,1940; Darmon and Rudall,1950). In its natural state it occurs in intimate association with many other substances, including protein and, in crustacea, with calcium carbonate and colouring matters, and its separation usually requires rather lengthy treatments with aqueous solutions of acid or alkali. Chitin is relatively stable towards acids, alkalis and oxidising agents. However, under drastic acid

conditions, it can be completely hydrolysed, yielding equimolar portions of D-glucosamine and acetic acid (Purchase and Braun).

Adsorption of dyes by textile fibres has been extensively studied (see e.g. Vickerstaff, 1954), yet the mechanism of adsorption has not been completely explained. In particular, the relative importance of polar (hydrogen bond) and non-polar forces has not been satisfactorily elucidated in adsorption by cellulosic or protein fibres, nor has the precise mechanism of adsorption of acids and other anionic compounds by proteins, especially wool. The chemical structure of chitin occupies an intermediate position between cellulose and proteins and it was thought that the results of these studies might help in interpreting the nature of adsorption by these substances.

Hydrogen bonding:

Hydrogen bonding has in recent years been considered to be one of the principal forces contributing to dye adsorption on cellulose, cellulose acetate and proteins.

In this laboratory the methods of detecting hydrogen bonding between pairs of solutes in solution, by measurement of dielectric constant or refractive index, have been extensively used. In particular the refractive index method has proved very useful in investigating bonding in

aqueous solutions, which cannot readily be done by the more usual procedures. This method, supplemented by studies on monolayers on water, has been used to investigate the nature of bonds between model compounds representing fibres and dyes.

The author and co-workers (Arshid, Giles et al.,1956) used the refractive index method to detect intermolecular and chelate complexes involving a variety of nitrogen-containing compounds, with a view to elucidating the mechanism by which certain polymers, especially proteins, adsorb organic solutes, including dyes. Various amido- and amino-compounds were used as models of these polymers. The reactions of some substituted and unsubstituted simple aliphatic amides with a variety of second solutes were tentatively interpreted as indicating that the enol-tautomer of the unsubstituted and N-monosubstituted compounds predominates in most non-aqueous solutions, and the keto form in aqueous solutions. Also, the behaviour of some sulphonated ortho-hydroxyazo dyes indicates that their azo groups do not interact in water with alcoholic groups in a second solute.

Using the same method for investigating the hydrogen bonding activity of N-acetylglucosamine, the model used for chitin, it appeared to be a monofunctional proton donor in water (Arshid, Giles, and Jain, 1956). This is probably

due to the acetyl group at the nitrogen atom or the carbon atom in the methyl residue, the hydroxy-groups being solvated and the molecule acting in the ring form. In ethylene glycol solutions 1:1 and 1:4 complexes are detected between this compound and alcohols or phenols, and in these cases three of the hydroxyl groups must also be reactive; the fourth is probably chelated. Darmon and Rudall have suggested this type of chelate bond as existing (together with free amino groups) in chitin, on evidence of studies with polarised infra-red and X-radiation. It has been shown that the esters examined can act as hydrogen donors in forming intermolecular hydrogen bonds in non-polar solvents and in water. This may take place through a -C-H....O or a -C-H....N bridge facilitated by the enhanced lability of the carbon-hydrogen bond adjacent to a carbonyl group. Chitin consists largely of poly-N-acetylglucosamine and adsorbs non-ionic solutes. This adsorption might take place through hydrogen-bonding at the hydroxy or the acetamido groups. The behaviour of N-acetylglucosamine 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 types of group may be reactive.

PRESENT WORK

This work is a quantitative study of the mechanism by which some mineral and organic acids and a variety of azo dyes are adsorbed from water by chitin.

Hardly any quantitative work on the adsorption properties of chitin has previously been published, yet these are of undoubted biological importance, and their study might be expected to help in interpreting the adsorption behaviour of other related natural polymers.

EXPERIMENTAL

Preparation of Chitin.

This was prepared by Thor's method from the carapace of *Nephrops norvegicus*. The shells, broken to about ¼ in., were successively treated with:

(a) cold 5% aqueous hydrochloric acid solution for 10-20 hr.; (b) water; (c) 1% aqueous sodium carbonate solution containing 0.02% of an anionic detergent (Lissapol C, I.C.I.) at b.p. for 8 hr.; (d) water; (e) cold 5% aqueous hydrochloric acid solution for 1-2 hr.; (f) water; (g) sodium carbonate solution (treatment as before); finally the product was well rinsed with water, dried in air at 105°, then allowed to condition 24 hr. in air and stored in a stoppered bottle. The material at this stage was colourless.

For analysis, the material was dehydrated, first by soaking in ethanol and then in ether, then dried at 50° in air, and finally dried *in vacuo* over phosphorus pentoxide at 110° for 36 hr. The normal moisture content (calculated by drying to constant weight at 105°) is about 7-8%, varying with the atmospheric conditions. All data for chitin given in this thesis are corrected for the weight of the adsorbed moisture.

For removal of protein the enzyme treatment, used by

Burgess (1934) for degrading wool by trypsin and pepsin, was used. The shells, broken to ca. ¼ in., were incubated for periods up to eight days at 37° with 0.5% pepsin solution and added buffer solution (pH 1.4), then washed well in hot water, treated with cold 5% hydrochloric acid solution, again well washed in water, decolourised by acetone extraction, washed with ether and dried.

Preparation, purification and estimation of solutes.

Purified commercial or laboratory prepared materials were used, dissolved in distilled water or analytical quality solvents. Some of the azo dyes were obtained in an already purified state, others were prepared by customary methods from recrystallised intermediates and were themselves recrystallised from water to 90-100% purity. Organic and inorganic acids were obtained as analytical quality reagents. The free acids of simpler compounds were prepared by ion exchange methods (Richardson). Free acids of less soluble azo dyes were obtained by precipitation of the solutions of their sodium salts by dilute hydrochloric acid. The tetrasulphonated direct cotton dye was supplied in pure form by the manufacturers (I.C.I.) who disclosed its constitution confidentially.

Colourless acids were determined volumetrically by titrating them against suitable strengths of standard

sodium hydroxide using phenolphthalein as indicator. Phenol was estimated by the bromide-bromate method (Koppeschaar, 1876). Coloured solutes were estimated absorptiometrically on either a Hilger Spekker photoelectric absorptiometer of a Unicam S.P.500 Spectrophotometer. Some of the dyes used changed colour with change of pH. In this case the pH of all the solutions was brought to the same value before analysis. The pH values were measured on a glass electrode.

Purities of the dyes were determined by titanous chloride titration method (Knecht and Hibbert, 1925) and the adsorption data corrected according to the respective purity figures. It is assumed that the impurities are inactive, since they are likely to consist largely of sodium chloride or firmly bound water.

Normally the amounts adsorbed were determined by difference from the initial and final solution concentrations. The plot of optical density against concentration is linear, and from difference in optical densities before and after adsorption the amount of solute adsorbed can be calculated. For those azo-compounds in which adsorption took place from highly concentrated solutions, the measurements were made on solutions of the substrate and dye in 80% (v/v) sulphuric acid, as used by Rowe and Levin for dissolving dyed cellulose. The dyed chitin was removed

from the test solution, rinsed, dried at 105° for 2 hr., then placed in the acid mixture and kept in a refrigerator for 12 hr., when complete solution of the material was seen to have taken place without charring. The dye could not otherwise be completely extracted from the dyed chitin, even by sodium hydroxide solution, followed by pyridine.

Types of Isotherm.

The adsorption was studied by determination of four different types of isotherm (cf. the methods used for wool, Vickerstaff, 1954). The methods are:-

(a) High constant concentration baths, in a range of pH values.

In this method, solutions were prepared in concentrations equal to the saturation values for the free dye-acids and then adjusted to a range of higher pH values by addition of sodium hydroxide. This was found to be the best method for studying the effect of pH on adsorption, but it was used for only a few dyes because it required more solute than was in many cases available, and because several dyes are not sufficiently soluble in acid solutions to be applied in this way.

(b) Low constant concentration baths in a range of pH values.

This method was used with a wide range of azo-dyes as a substitute for method (a).

Solutions of constant azo-compound concentration (0.0001 M) are applied after adjustment to a range of pH values by addition of sulphuric acid or sodium hydroxide. This method enables a wider range of pH values to be used than does method (a), but the results are of course affected by the competition for the substrate between the acid anion and the dye anion.

(c) Variable concentration baths of constant pH.

A series of solutions covering a range of initial dye concentrations was used, each adjusted by addition of sulphuric acid to the initial pH value found to give maximum adsorption by method (b). This method is also affected by competition of the acid anion. Results are quoted in Table 1 which shows the maximum adsorption, determined by direct inspection of the isotherm or by a "Langmuir" plot.

(d) Variable concentration baths, pH not adjusted.

This method was employed for a few dyes to determine apparent heats of adsorption. The tests were continued

for a period which preliminary rate measurements had shown to be sufficient to achieve equilibrium. This varied from about 30 min. for some of the azo-dyes with smaller molecules, to about 5 hr. for some of the direct cotton dyes.

Experimental procedure.

The adsorption tests were made in sealed tubes containing the required weight of the chitin and the appropriate solution. The tubes were tumbled in a water thermostat (Clunie and Giles) for the necessary period in each case. A Sunvic thermostatic control unit maintained the temperature in the thermostat to an accuracy of $\pm$ 0.5°C. of the desired temperature.

For the azo-compounds tested by methods (b) and (c) 0.01g. chitin and 20 c.c. solution were used and for those tested by method (a) and (d) 0.02g. chitin and 20 c.c. solution.

Nature of compounds studied.

The following table gives a list of the compounds used, and the procedures employed with them.

	Temp. (C°.)	Method
Mineral acids.		
Sulphuric	50	a
Hydrochloric	50	a
Aliphatic acids.		
Formic	50	a
Acetic	50	a
Monochloroacetic	50	a
Benzene derivatives.		
Benzene sulphonic acid	50	a
Picric acid	50	a
Aniline 2:5-disulphonic acid	50	a
Phenol	50 , 60	d
Naphthalene derivatives.		
Naphthalene 2-sulphonic acid	50	a
G-acid (2-naphthol-6:8-disulphonic acid)	50	a
Benzeneazobenzene derivatives.		
Azobenzene 4-sulphonic acid	50	b
4-Hydroxyazobenzene-4'-sulphonic acid	50	b
do	50	c
4-Aminoazobenzene-4'-sulphonic acid	50	a

	Temp. (C^{o}.)	Method
Benzeneazonaphthalene derivatives.		
Orange I (Sulphanilic acid ⟶ 1-naphthol)	50	a
Orange II (Sulphanilic acid ⟶ 2-naphthol)	50	a
Sulphanilic acid ⟶ 2-naphthol-6-sulphonic acid)	50	b
Naphthaleneazonaphthalene derivatives.		
Naphthalene Red J (naphthionic acid ⟶ 2-naphthol)	50	a
Direct cotton dyes.		
Congo Red (Benzidine ⟶ (naphthionic acid)$_2$)	50 , 60	d
Chlorazol Azurine G (3:3'- dianisidine ⟶ (1-naphthol-4-sulphonic acid)$_2$)	50 , 60	c
do	50 , 60	d
do	50 , 60	b
Tetrasulphonated direct cotton dye (I.C.I.)	50 , 60	c

Other substrates used.

Phenol was adsorbed on cetyl alcohol at two temperatures in order to study the apparent heat of adsorption.

RESULTS AND DISCUSSION

Preparation of Raw Material and its Constitution:-

The starting materials used here were the shells of the Norwegian lobster (Nephrops norvegicus)* and also the lining of the shell of the common lobster. The latter, which forms a thin colourless transparent film, containing little or no calcium carbonate and over 50 percent chitin, would be the preferred material, were it not difficult to obtain in sufficient quantity. Nephrops shells were the next in order of preference, because they are more readily broken up. The previous work, by Subramanian, was made on ground chitin and in order to ensure that impurities from grinding did not interfere with the tests, silica balls were used, since silica does not adsorb anionic compounds from aqueous solution. Reference to differences in adsorption properties between ground and unground material is mentioned later.

In previous work three methods of purification have been examined, viz. Clark and Smith's (1936) process, Thor's process, and a new process using enzyme hydrolysis.

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* Knecht and Hibbert (1926) give a useful survey of the general properties and occurrence of chitin, with a review of early work. For a more recent, and very full survey, see Richards' monograph.

Clark and Smith removed calcium carbonate by cold dilute nitric acid, and protein by hydrolysis with 20% aqueous sodium hydroxide at b.p. for 4 hr. Thor's method is milder, sodium carbonate solution being used as the hydrolysing agent. Analysis of products prepared by these methods are given in Tables 5 and 6.

Enzymatic treatment was examined in this laboratory (Miss M. Laidlaw, 1949, unpublished) as a possible method of removing protein without causing hydrolysis of the acetylamino-group, since the attack should be specific for the peptide linkages in the protein molecule. The protein in crustacean shells has a high proportion of tyrosine (Fraenkel and Rudall, 1946) and thus should be hydrolysed by treatment with pepsin. Examination of the product by the biuret test showed that this procedure did not completely remove protein (Table 5) from broken shell fragments, probably owing to incomplete penetration by the enzyme. The experiment when repeated using finely ground (ball-milled) starting material appeared to remove the protein completely. Unfortunately not only did the product contain silica, but some natural colouring matter also, which could not be fully extracted from it, though it could be destroyed by bleaching with potassium permanganate solution, followed by sodium bisulphite.

The analytical data and the adsorption results, however,

do not show that enzymatic treatment of shells offers any substantial advantage over the shorter process of Thor, which was therefore used for preparing most of the chitin used in this research.

It has been assumed in recent years that chitin consists entirely of poly-N-acetylglucosamine as suggested by Meyer and Mark (1928). Irvine (1909) however, had suggested, following polarimetric experiments, that chitin consists of one molecule of aminoglucose condensed with three molecules of acetylaminoglucose with the elimination of four molecules of water, and Margulis (1916) noticed that not all the nitrogen is equally reactive. Darmon and Rudall (1950) state that chitin isolated by them from insect cuticles gives a value for nitrogen content corresponding to about 93% pure chitin. They also state that purified lobster chitin has shown a still nearer approach to the theoretical nitrogen content.

The elementary analyses (Table 6) of samples prepared by different methods and analysed at different times are consistent, but do not correspond with the theoretical value for polyacetylglucosamine. The titration curve for acids, however (Fig.1 and 5) and the isotherms for azo dyes suggest that some 10-15% of the amino-groups are unacetylated, and a hypothetical mixture of 82.5% poly-N-acetylglucosamine and 12.5% poly-glucosamine with 5% bound

water, gives a theoretical analysis (see Table 6) very close to the experimental value. This seems at first sight a high quantity of water to be retained even under severe drying conditions, but it is not unreasonable in a substance of such very high crystallinity as this.

The adsorption data suggest that a very high proportion, perhaps even 80%, of chitin is crystalline. Wool, which has low crystallinity (about 10-15 % inaccessible to deuterium oxide (Burley, Nicholls, and Speakman, 1955)), retains about 0.5-1 % of bound water after drying, so that a five per cent bound water content for chitin is not unlikely. In air dry chitin there is also of course a proportion of labile adsorbed water which varies with the state of the atmosphere; this is normally 7-9 % by weight. In all the adsorption data shown by the figures correction has been made for this moisture but not for the postulated bound water. The low value for carbon analysis cannot be reproduced e.g. by any hypothetical mixture containing a preportion of polyglucose, on the assumption that some acetylamino-groups are removed entirely in the preparation, because the carbon content of polyglucose is itself almost the same as that of the product.

It seems unlikely that a proportion of free amino-groups in the material is formed during the purification

process, because (a) if this occurred in the acid treatment the nitrogen content would be much lower than it is and (b) if it occurred in the alkaline treatment, the analysis for the pepsin-treated sample (which has not been subjected to alkali) would be significantly different from that of others, which it is not.

Further, the dye adsorption isotherms give indications of the presence of the same proportion of free amino-groups in the amorphous regions as in the whole structure, and it therefore appears that the molecular chains in chitin may contain one glucosamine residue to about each eight N-acetylglucosamine residues. It may be mentioned that the infra-red spectra of chitin and its deacetylation product (chitosan) shown by Darmon and Rudall are not inconsistent with the presence of some free amino-groups in chitin.

Difference in adsorptive properties of ground and unground chitin:-

Two samples of chitin, both prepared by Thor's method, one being merely broken into $\frac{1}{4}$ in. flakes, and the other finely ground 6 hr. in an agate mortar, showed a considerable difference in adsorptive properties (Fig.1), for whereas both adsorbed hydrochloric acid to the same extent, their adsorption of sulphuric acid was different. The two acids had the same adsorption on powdered chitin, but

on flakes sulphuric acid was adsorbed much less than hydrochloric acid. These differences appeared to be quite real and reproducible. They must be attributed to physical disturbances of the crystalline structure of chitin caused by the heat or mechanical action of grinding, which appears to reduce the crystallinity of the substrate.

In the present work all the remaining adsorption tests were made on flaked chitin.

Deacetylation by acid:-

A previous investigator (Subramanian, 1955) made tests to discover whether deacetylation is liable to occur in treating chitin with mineral acid for prolonged periods. The nitrogen content of the material (N = 7.1% originally) immersed at 60° for 24 hr. in aqueous hydrochloric acid fell to 6.8, 4.9 and 3.7% when the final pH values were 2.5 and 2.0, or the initial concentration 2 N, respectively.

Thus it appears that on the acid side of pH 2.5 the acetylamino-group is removed and ammonia and acetic acid must be lost. The partial deacetylation in the initial preparation of the raw material probably occurs in the hot alkaline solution with the amine group remaining unaffected.

Adsorption of mineral acid*:-

Titration curves of finely ground chitin were determined with hydrochloric acid in presence and absence of sodium or potassium chloride of constant molarity, and with sulphuric acid. (Some of this work was cafried out by R. V. R. Subramanian (1955)). These curves are shown in Fig.1. Material of the composition corresponding to the elementary analysis (Table 6) would have a theoretical maximum acid binding capacity of 4.80 equiv.per kg., of which 0.62 equiv. would be contributed by the free amino-groups. There is, in fact, a trace of inflection in the titration curve for hydrochloric acid alone at about 0.6 equiv. per kg. and the Langmuir plot of the data (Fig.2) gave evidence of a maximum close to the value predicted, with a slight trend towards a still higher maximum at pH values less than about 3.5.

No explanation can be given for the exceedingly high adsorption values at very low pH and the absence of any maximum. (cf. The unaccountably high adsorption values of glucose and sucrose on graphite, reported elsewhere in this thesis). The amount of acid bound appears to exceed

* Most of this discussion on mineral acid adsorption is based on that given by Subramanian(1955), but it is included here to complete the evidence on anionic adsorption and because the present author repeated some of the tests to check the uniformity of the chitin used.

the theoretical limit by a considerable margin; even if it is supposed that some acid is taken up at the ether oxygen atoms by oxonium salt formation this could not account for the high values obtained, which are beyond any possible stoichiometric quantities. Certainly there must be considerable degradation of the substrate, because it becomes gelatinous in strongly acid solutions. The excess acid must be taken up by the gel by some unidentified physical action. It should be emphasised that the effect is not due to occlusion of some of the external liquid phase in the gel, in addition to adsorption. The amount adsorbed is determined by difference from the titration values of aliquots of the external solution at equilibrium. A little consideration will show that mere occlusion of liquor would not be shown by the method, which returns only the amount that is removed from the solution by actual adsorption in the solid phase.

The inter-chain -NH....O=C- bonds must be broken when the nitrogen atoms take up hydrogen ions. This allows adsorption of water by these cationic groups so formed, and by the hydroxy-groups throughout the structure, leading to pronounced swelling.

The adsorption reaction of mineral acid by chitin has some resemblance to its reaction with wool. This is seen from a consideration of the simple equations (1) and (ii)

for combination of an acid HX with these two materials respectively.

$$Wl.\overset{+}{N}H_3.\overset{-}{O}OC.Wl \xrightarrow{H^+} Wl.\overset{+}{N}H_3 + HOOC.Wl \xrightarrow{X^-}$$

$$(Wl.\overset{+}{N}H_3)\ \overset{-}{X} + HOOC.Wl \qquad .....(i)$$

$$Ch.NH.CO.CH_3 + H^+ \longrightarrow Ch.\overset{+}{N}H_2.CO.CH_3 + X^- \longrightarrow$$

$$(Ch.\overset{+}{N}H_2.CO.CH_3)\ X^- \qquad .....(ii)$$

(Wl, Ch = residues of wool and chitin molecular chains)

Until broken by combination with the entering hydrogen ions nearly all the basic amino- and acidic groups in wool are combined as salt links (Peters and Lister, 1954) and thus probably do not act as separate ionic entities. When the fibre is saturated with acid no salt links are present and the only ionic centres are the charged amino-groups. Thus in wool and in chitin, after adsorption of the hydrogen ion, the anion is adsorbed at a surface whose only effective ionic sites are singly charged cations, and thus the two systems may be compared by similar quantitative means.

The quantitative treatment of the adsorption of acids by wool has been the subject of much attention: thus Gilbert and Rideal (1944), and some later investigators, have assumed that adsorbed anions are located at specific

sites, the occupation of any site not interfering with that of an adjacent one, whilst Peters and Speakman (1949) and others assume that the wool-acid system has Donnan membrane properties and that adsorbed anions are dissolved in the water inside the fibre and are not located at sites. Since each treatment satisfies some, but not all, of the experimental facts, there is room for considerable discussion on their relative merits.

In the Gilbert-Rideal treatment, the activity of the hydrogen ions in the wool fibre is equated with $\theta/1-\theta$, where θ is the fraction of the available sites occupied, the affinity of hydrochloric acid thus being given by the expression -

$$-\frac{(\Delta\mu_{H^o} + \Delta\mu_{Cl^o})}{2} = 2.3\ RT\ \log(\theta/1-\theta) + \underline{p}H + \underline{p}Cl \quad \ldots(i)$$

(Vickerstaff, 1954)

The plots of log $(\theta/1-\theta)$ against $\underline{p}H$ (Fig.3) for chitin are linear, with slopes of -1.0 (acid alone), and -0.46 (0.1 N. NaCl), and -0.48 (N. NaCl) in good agreement with the theoretical values of -1.0 and -0.5, and -0.5 respectively, required by this equation (cf. the corresponding values for wool, Vickerstaff, 1954, viz., -0.88, -0.50, -0.50). The affinity values for hydrochloric acid calculated from eq.(i) for wool, however, are virtually constant at all the acid or chloride concentrations (Vickerstaff,

1954), whereas here they show a downward trend with increase either in acid or chloride concentration*.

The theory, however, takes no account of the physical accessibility of sites to the anions. In wool the proportion of total sites available for reaction is determined solely by their degree of ionisation, which in turn is a function of the pH of the solution. Accessibility in chitin, however, as will be demonstrated below, is restricted by the mechanical difficulty of penetration of the structure, and at any given pH large anions, which would be expected to have higher affinity than the chloride ion, are adsorbed much less than the latter, because they cannot reach as many sites. It is thus possible that the chloride anion also has not access to as high a proportion of the theoretically possible sites as has the hydrogen ion, and thus with added chloride the increase in adsorption is less than theoretically predicted.

The expression for the affinity of hydrochloric acid for wool considered as a Donnan membrane is

$$-\Delta\mu_{H^o} = 2.3\ RT \log(S_H)/V + \log \theta^2/1-\theta + pH + pCl \quad \ldots(ii)$$

(Vickerstaff, 1954)

where (S_H) is the saturation adsorption value, and V is the

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* This trend is much greater than can apparently be accounted for by neglect of activity coefficients (cf. Vickerstaff, 1954).

volume of internal solution in the substrate. Plots of log ($\theta^2/1-\theta$) against pH (Fig.4) are linear, as required by this equation, but the slopes for adsorption from solutions containing acid alone, and those with constant chloride ion concentration (0.1 N. and 1.0 N.), are respectively -1.6 and -0.72, compared with the theoretical values of -2.0 and -1.0 (cf. the corresponding value of -1.4 for acid alone on wool). The affinity values for chitin cannot be calculated from equation (ii) in absence of a value for V. On general considerations the actual state of the ions in any substrate may be considered to lie between the two suggested extremes of complete fixation at cationic sites or completely unlocalised solvation, so that the more highly crystalline the substrate the more restricted should be the mobility of the anions in the internal aqueous phase, and the nearer should the conditions approach those assumed in the localised site theory.

Adsorption of Organic Acids:-

Adsorption tests were made with a variety of organic acids, titration curves (Fig.5) being plotted showing the amount adsorbed from solutions over a range of pH values, obtained by variation of the concentration of the acid. Table 8 gives some comparative data showing the variation in amounts of several organic and two inorganic acids,

adsorbed at two equilibrium pH values, and some of the data are plotted in Fig.6 in comparison with corresponding data for a protein fibre, wool, the only natural polymer on which acid adsorption has been extensively studied.

There is a striking difference between the two sets of values shown in Fig.6*. In chitin the amount of acid (expressed as molecules) decreases with molecular size; in wool it increases markedly.

As already mentioned, wool is largely non-crystalline (Burley et al., 1955), the proportion inaccessible to deuterium oxide being as low as 11-17%. Thus, in water, anions have free access to most of the wool substance and the actual amount adsorbed will be determined mainly, by (a) the pH of the solution, on which depends the degree of ionisation of the active sites and by (b) the affinity of the anion itself, on which depends the proportion of these active sites which can be occupied by anions.

The increase in adsorption on wool with increase in molecular size is usually now attributed to enhanced van der Waals attraction of the acid anion for wool protein (Vickerstaff, 1954). The opposite effect observed with chitin must be attributed to the restraint imposed on

---

* The pH 4.5 data for chitin show the same trend as those at pH 3 but the linearity is not so good; HCl is seen to have an anomalously high adsorption value.

penetration of the anions by the highly crystalline structure of the substrate.

The data for chitin at pH 3, in fact, show that in a particular series of acids the number of molecules adsorbed decreases linearly with increase in volume of the anion. It will be observed that the six acids of the simple aliphatic or benzenoid series fall on one line (a)* and the two naphthalene acids on another (b) which apparently has the same origin; these latter acids clearly have the higher affinity. If the points for the free acids of certain azo-dyes (determined by a slightly different procedure (isotherm a, see below)) are added, and lines drawn through them also to meet at the origin of curves a and b , it will be seen that there are apparently two opposing factors, one chemical, and the other mechanical, which determine the amount adsorbed:-

(i) The chemical effect is seen in the rise in amount of acid adsorbed with enhancement of conjugation in the molecule, thus the following series of compounds are in order of increasing affinity: (a) simple fatty acids and benzenoid compounds, (b) naphthalene compounds, (c) benzeneazobenzene derivatives, (d) benzeneazonaphthalene

* It is possible that the aliphatic acids may lie on yet another line, further to the left, but on account of the difficulty in deciding the effective volumes of these small anions, this cannot be stated with certainty.

derivatives, (e) naphthaleneazonaphthalene derivatives.

This shows that an increase in the area of planar molecules raises their non-polar attraction for the chitin molecular chains. A single benzene ring apparently has negligible affinity, because the benzenoid acids fall in the same affinity class as the simplest fatty acid, but the affinity rises steadily with increase in the planar area of the molecule. The results show that the direct cotton dyes, which have very large planar molecules, have an affinity high enough to affect the temperature coefficient of adsorption appreciably (Fig.7).

(ii) The mechanical effect depends upon molecular volume.

Apparently in any series of acids having similar areas for their aromatic nuclei the amount adsorbed decreases linearly with increase in molecular volume. This is clearly a purely mechanical effect, caused by the chitin structure being highly crystalline*. By a simple calculation from the intercept of the curves in the y-axis of Fig.6 it can be shown that only about 8% of the chitin structure is accessible to the smallest anions, in water. Moreover, the pores in this material appear to cover a range of sizes, the largest being able normally to accommodate a non-swelling anion of volume about 550 A^3. Anions

* Darmon and Rudall (1950) found that the chains in lobster tendons are <u>very</u> highly oriented (their italics).

having high affinity, by virtue of their larger size and conjugation, are however able to swell the substrate, so that it can then apparently accommodate anions as large as 1000 A^3 or perhaps even larger.

The curves for the three aliphatic acids and picric acid have not attained a maximum at the lowest pH values tested (ca. pH 2.0), whereas those of the aromatic acids do reach a maximum, and it appears that at low pH values the molecular sieve action of the substrate becomes especially marked.

Hydrogen Bonding:-

The weak acids do not appear to have increased affinity for chitin as they do, by virtue of the hydrogen-bond adsorption of their undissociated molecules, for wool. Nor is there any evidence in the present tests of increased affinity for chitin caused either by the presence of the amino-group in aniline-2:5-disulphonic acid or by the strongly hydrogen-bonding phenolic group in G-acid. These tests were, however, made under acid conditions, where hydrogen-bonding by the chitin is least likely to occur for the following reason. Chitin in presence of water probably forms hydrogen bonds by electron-donation by its nitrogen atom, a large proportion of its carbonyl oxygen atoms being chelated, each with one hydroxy-group,

and the remaining hydroxy-groups being strongly solvated (Arshid, Giles et al., 1956 c). Under acid conditions the amino-nitrogen atom accepts a hydrogen ion thus losing its electron-donating power, so that no hydrogen-bonding sites remain. It will be shown later that the apparent heat of adsorption of certain azo-dyes is a little more under neutral conditions than under acid conditions, and this may be evidence of hydrogen-bonding (Fig.11 insert).

Adsorption of Azo-dyes:-

Using method a , four dyes were examined (Fig.8), and the results show clearly that the apparent affinity rises markedly with the size of the aromatic portion of the molecule, which is evidence of non-polar attraction between dye and chitin. Over the range of pH values used there is no evidence that the free hydroxy-group in Orange I contributes to its affinity. Indeed this dye has somewhat lower affinity than its analogue, Orange II; perhaps the o-hydroxyazo-chelate ring in the latter raises the affinity a little by increasing the planar area of the molecule.

The method b isotherms all have certain characteristics viz: a maximum lying between pH 4.7 and 1.8, the curve falling on either side of this (Fig.9 and 10). This maximum must represent adsorption at the acetylamido-

groups, and the fall in adsorption when the acidity is increased beyond this point must be due to competition by the anion of the added sulphonic acid or the removal of the acetamido-groups by acid hydrolysis, with a resultant fall in cationic sites. A similar phenomenon is observed in the adsorption of some anionic dyes on wool (Vickerstaff, 1954). Besides this principal maximum, each curve has a rather poorly defined subsidiary maximum lying in the region between pH 6 and 4, which is attributed to adsorption at the free amino-groups.

Effect of Structural Changes on Dye Affinity:-

A qualitative comparison of affinities of the dyes studied during the present work (Fig. 9) together with those used by Subramanian (Fig.10) was made by estimating the volumes of dye anion adsorbed (method b) at a pH value (5.0) at which both competition from sulphate ions and loss of acetylamido- (or amino-) groups by hydrolysis can be disregarded. The results are shown in Table 1 and a summary arranged to illustrate the relationship between constitution and affinity is given in Table 2. Certain general tendencies are evident in these data: (a) the affinity rises markedly with increase in the number of benzene nuclei*, i.e., with the planar area of the anion.

* Except with dye VI Table 1, which is unexpectedly out of order in this affinity sequence.

This agrees with the results of the isotherm a tests and with the adsorption of organic acids (b) the affinity falls with increase in the degree of sulphonation of the dye*.

Thus each sulphonate group, at least each one after the first, has a negative affinity for chitin. This must mean that the second, and subsequent sulphonate groups in an anion are not located at cationic sites, owing to steric effects, but remain dissolved in the water, thus tending to desorb the anion from the substrate. It is not perhaps surprising that the cationic sites are not correctly spaced to accommodate each anionic group in a poly-basic anion. In anodic alumina, however, where the sites (aluminium atoms) for attachment of sulphonate groups are closely packed, each such group in poly-basic dyes does combine with the substrate, and what may be termed the "partial affinities" of the groups are additive (Stewart, 1956).

The possibility must of course be considered, that even a single sulphonate group has negative affinity, i.e., that the anions are not located at cationic sites at all, but are adsorbed entirely by non-polar attraction, the presence of the sulphonate group merely enabling the compound to dissolve in water and enter the fibre. This

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* On wool the introduction of a second sulphonate group into a monosulphonated dye also decreases the affinity (Vickerstaff, 1954; Gilbert, 1944).

however seems unlikely, because if it were so, cellulose, which has no cationic centres, would adsorb these simple monoazo-dyes as readily as chitin does, which is not the case.

The introduction of a p-hydroxy-group into azobenzene sulphonic acid raises the affinity and the apparent heat of adsorption (Table 3). It is not clear whether this is due to hydrogen bonding by the hydroxy-group or to stronger non-polar attraction following the increase in conjugation of the molecule.

Among dyes with the same number of sulphonate groups, the affinity is higher when one component of the dye is unsulphonated than when both are sulphonated (cf. VII and VIII with V and VI (Table 1)). This is no doubt the result of a more ready formation of a condensed monolayer of dye, by intermolecular attraction when there are large planar unsulphonated aromatic nuclei.

There is a general tendency for the pH of maximum adsorption to fall with increase in degree of sulphonation or with decrease in anionic size. The lower is the pH at which maximum adsorption is reached the higher is that adsorption (see Table 4). This is a result of the increase in number of cationic sites with increase in acidity. Its effect is seen in a reverse manner in the data for monosulphonates (Table 1), which though having

highest affinity, reach only low saturation values at their optimum pH because this occurs in regions of low activity.

Anionic Adsorption on Chitin Considered as an Ion-exchange Mechanism.

The adsorption of acids and sulphonated dyes by chitin may be considered as an ion-exchange process at cationic sites. Thus for adsorption of dye in presence of sulphuric acid the following reaction sequence may be formulated:-

$$(Ch.\overset{+}{N}H_2.CO.CH_3)(\tfrac{1}{2}SO_4)^- + Na\ Dy \longrightarrow (Ch.\overset{+}{N}H_2.CO.CH_3)\ Dy^- + \tfrac{1}{2}Na_2SO_4$$

(Ch = chitin residue, Dy = dye anion)

Little appears to be known regarding heat changes in ion-exchange adsorption mechanisms, but in the four types of such adsorption for which data are available, i.e., sulphate esters on γ-alumina (Giles, Mehta, et al., 1954), basic dyes on silica, Jain (1956), and on graphite, Macaulay (1951), and some adsorption on resins (quoted by Giles, Mehta et al) there is a very low apparent heat of adsorption. It will also be seen (Fig.7 and 11 Table 3) that the monoazo-dyes have very low apparent heats of adsorption, their isotherms showing almost no change with

change in temperature, which is thus consistent with ion-exchange*.

The first adsorption of hydrochloric acid (40 m.mole/kg.) from water by wool at 25°, has been found by Derbyshire and Peters (1955), by direct colorimetric measurement, to occur with negligible heat evolution. They ascribe the reaction to back titration of free carboxylate ion sites, which are present in small amount accompanied by a corresponding quantity of free cationic histidine groups, with which the chloride ion will then become associated, presumably also with negligible heat evolution. With increase in uptake of acid beyond this amount the heat change is constant at about -2.8 kcal/mole of acid bound, attributed to breakdown of amino-carboxylic acid salt links in the protein by back titration of the carboxylate groups following adsorption of hydrogen ions.

The apparent heats of adsorption of the disulphonated direct cotton dyes on chitin in neutral solution, however, are quite appreciable (Table 3), having values of about 9.0 kcal/mole (calculated in the usual manner from the data of Fig.7). Apparent heats of adsorption of the anions of dyes and organic acids by wool are also quite appreciably larger than the value for hydrochloric acid, figures between

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* Derbyshire and Marshall loc.cit. suggest that the low heat value (for Orange II on wool may be a result of the large heat of dilution of the dye.

-3 and -11 kcal/mole being given in the few recorded cases (Vickerstaff (1954); Steinhardt, Fugitt, and Harris (1941); Peters and Lister (1956); Derbyshire (1955); Derbyshire and Marshall (1954)). In all these cases, therefore, the inference is that the heat change represents some reaction, in addition to ion-exchange, taking place between the anion and the substrate. This reaction could be either polar or non-polar in nature, and a non-polar reaction between the molecular chain of chitin, and the planar highly conjugated anions of the dyes is highly probable. Similar attraction is believed to be responsible for adsorption, from water, of the same type of dyes by cellulose, (Giles, Jain and Hassan, 1955) for which apparent heats of adsorption between about -10 and -30 kcal/mole are reported (Marshall and Peters, R.H., 1947).

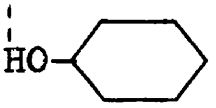
The apparent heat values become less in magnitude with increase in acidity of the solution (Fig.11 and Table 3). The reason for this is not very clear and it may be, as mentioned before, that the amino nitrogen atom accepts hydrogen ions under acid conditions thus losing its electron donating power.

Hackman (1955) has studied the adsorption of water-soluble proteins by chitin. The adsorption is nil on the alkaline side of pH 9 and rises steadily to a maximum at about pH 5. Temperature change has very little effect on

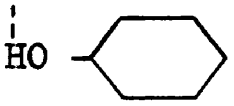
the adsorption, which thus appears to resemble the ion-exchange adsorption of the smaller azo-dyes.

Apparent Heat of Adsorption of Phenol.

The apparent heat of adsorption data (Table 9) show that the phenol-chitin bond is stronger than the -OH...HO- bond between phenol and cetyl alcohol. It is in fact comparable in strength with bonds formed by phenol with wool and nylon, which are believed to be -NH - C - bonds.



This agrees with the deduction made from a study of hydrogen-bonding properties of N-acetylglucosamine, that in chitin in aqueous solutions the hydroxy-groups are protected by water and hydrogen-bonding is most likely to take place at the acetylamino group. The bond with phenol would thus be -C - NH - CO - CH_3



The apparent heat of adsorption was calculated in the usual manner from the isotherms by the Clausius-Clapeyron equation -

$$H_a = \frac{R\,T_1\,T_2}{T_1 - T_2} \ln \frac{C_1}{C_2}$$

where C_1 , C_2 are the respective concentrations of the

baths at equilibrium at two temperatures T_1 , T_2 with the same concentration in the fibre.

Appearance of dyed Chitin under the Microscope:-

From microscopic investigations it was found that dyes do not stain the interior of the raw shell substance at all, even after treatment for 24 hr. at 50° in acid solutions. When a microscopic examination is made of the shell, after immersion in the dye solution, a thin dyed layer, presumably of protein, is seen on the inner surface and an almost regular pattern of minute round holes containing a stainable substance, also presumably protein, is seen covering the whole outer surface. When the protein and mineral matter have been removed, the dye appears to penetrate the whole of the shell substance fairly evenly.

CONCLUSIONS

The following general conclusions may be drawn:-

(i) Chitin is highly crystalline (about 90%). It appears to contain about one residue of glucosamine to every eight of N-acetylglucosamine, and also a high proportion (about 5% by weight) of very firmly bound water located in the crystalline structure.

(ii) When chitin is placed in an acid solution, adsorption of hydrogen ions takes place at the acetylamido- (and amino-) groups, and the accompanying anions are then taken up at the cationic sites so formed.

(iii) The association of hydrogen ions with the acetamido-groups causes the interchain hydrogen bonds between them to be broken; this allows water to enter and to become adsorbed at these and at hydroxy-groups, thus swelling the substrate.

(iv) The swelling process is limited, however, first by the pH of the external solution, which determines the maximum number of acetamido-groups which could become charged, and secondly by the size of the anion. The latter determines the proportion of these groups that is actually charged, because a group can only adsorb a hydrogen ion if the anion can accompany it to preserve electrical neutrality,

and its ability to accompany the hydrogen ion is limited by the highly crystalline character of the substrate. The substrate acts as a molecular sieve; the larger is the anion the smaller is the amount which can enter, and so the smaller is the quantity of the acid which can be adsorbed at any given pH. Only the smallest mineral acids are able to penetrate the whole structure.

(v) Yet another factor, however, influences the amount of an organic acid adsorbed, viz. the planar area of the aromatic nuclei of its anion; for with increase in this area, the anion acquires enhanced powers of penetration by virtue of a rise in its non-polar attraction for the substrate.

(vi) Adsorption of anionic dyes by chitin appears to take place through a mechanism similar to that applying to organic acids but van der Waals attractive forces seem to play a more important part, because of their larger sized molecules and the increase in size of their conjugate system. The apparent heat of adsorption is largely due to the non-polar attraction process; it is very small for small anions, but becomes appreciable with large anions e.g. those of direct cotton dyes. The possible role of hydrogen bonds in increasing the affinity of dyes is not clearly revealed by the present work.

(vii) The ion-exchange process operates only with one

sulphonate group in the dye; if more than one are present, the others appear to remain dissolved in the aqueous phase, presumably because they are prevented by steric hindrance from approaching other cationic centres. The very high crystallinity of chitin severely limits the total amount of any dye which can possibly be taken up.

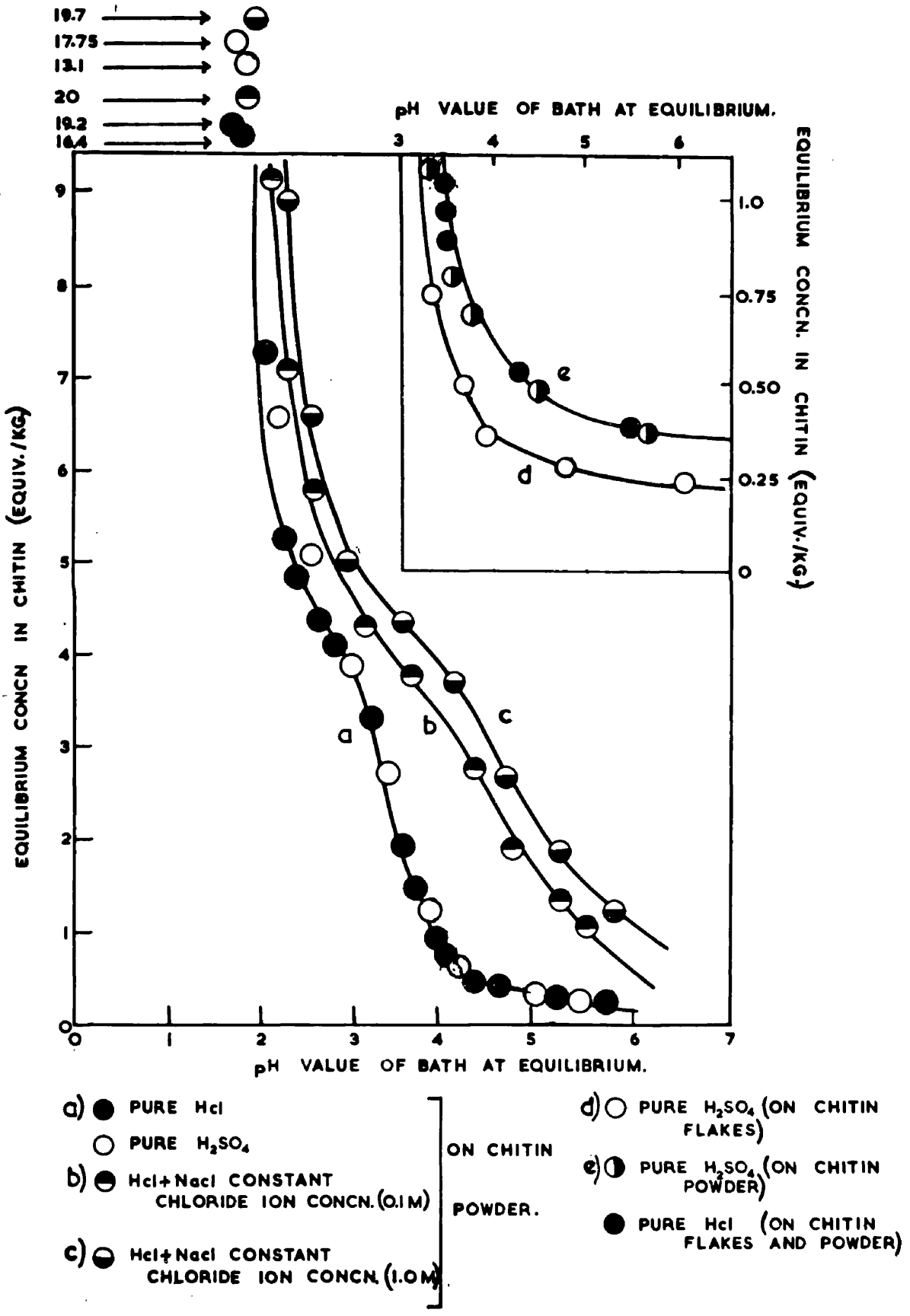
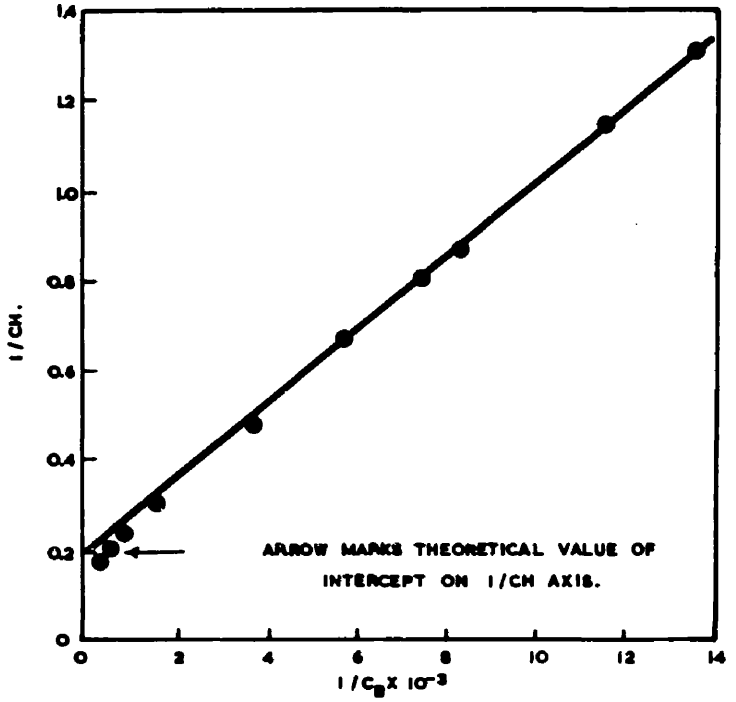


FIG.1 ADSORPTION OF MINERAL ACIDS BY CHITIN AT 50°.



C_B = EQUILIBRIUM CONCN. IN BATH (MEQUIV./L.)

C_{CH} = EQUILIBRIUM CONCN. IN CHITIN (MEQUIV./GM)

FIG.2 LANGMUIR PLOT OF HYDROCHLORIC ACID ADSORPTION DATA FOR CHITIN (ACID ALONE).

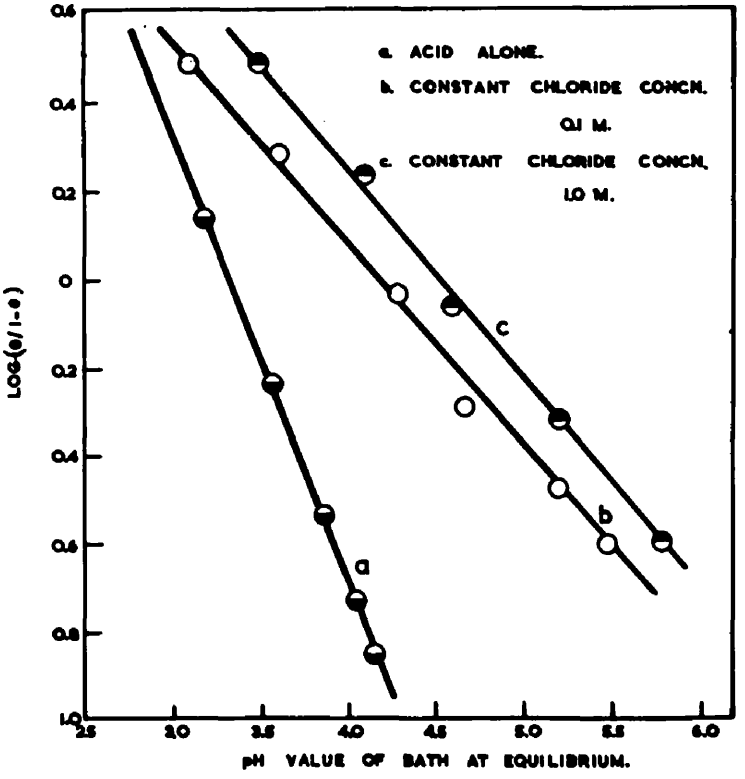


FIG.3 HYDROCHLORIC ACID ADSORPTION DATA (SPECIFIC SITE INTERACTION HYPOTHESIS).

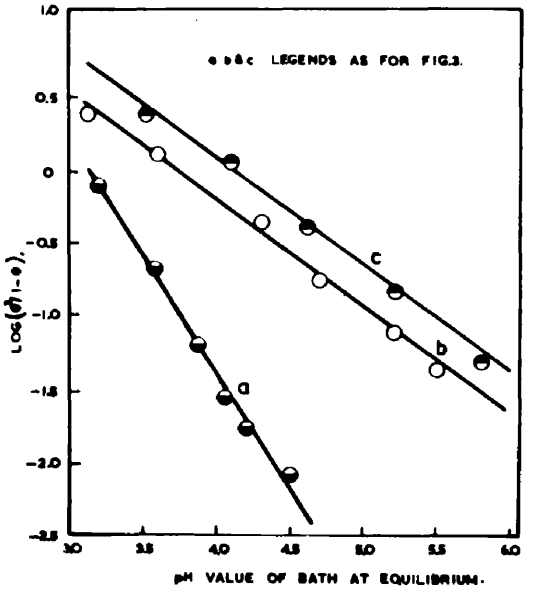


FIG.4 HYDROCHLORIC ACID ADSORPTION DATA FOR CHITIN.
(DONNAN MEMBRANE ADSORPTION HYPOTHESIS)

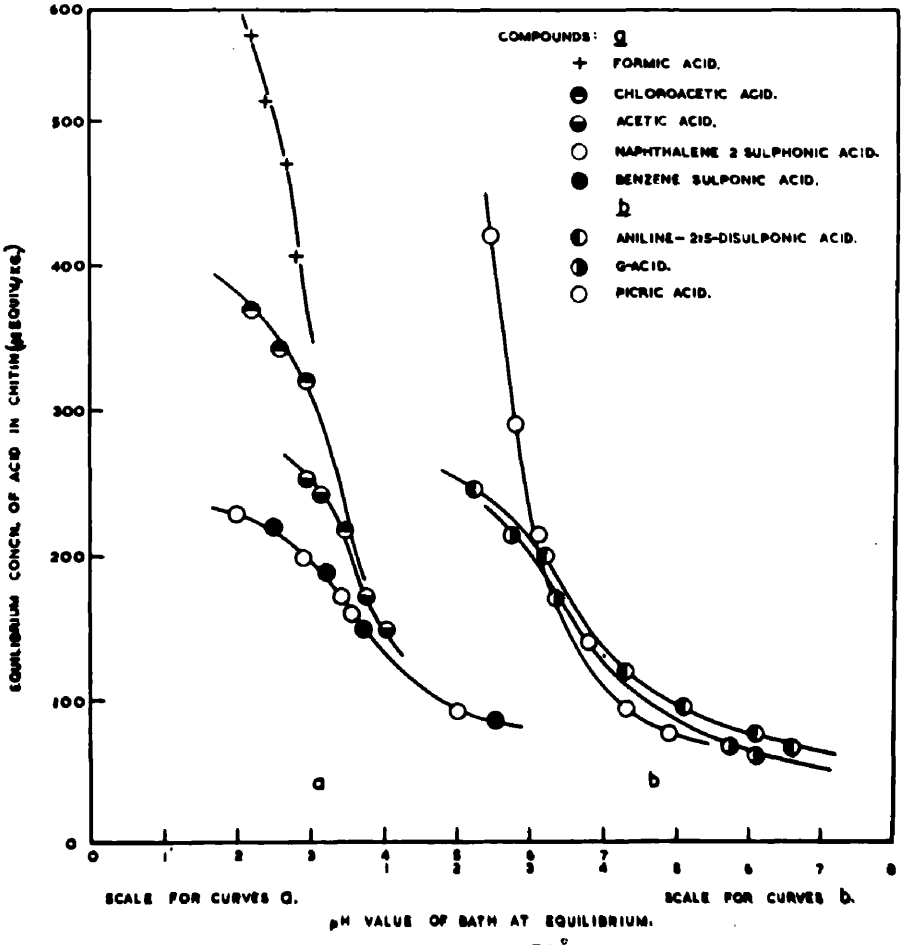
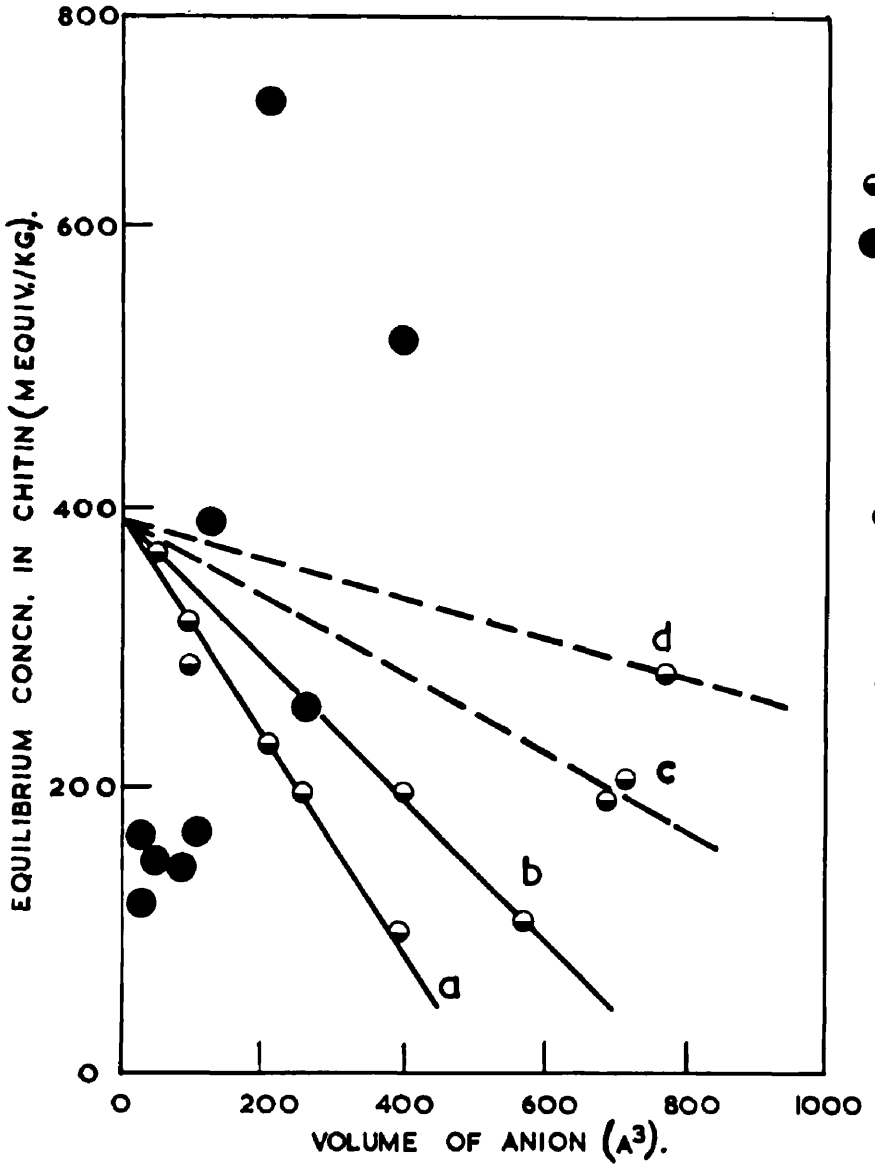


FIG.5 ISOTHERMS FOR ACIDS ON CHITIN. AT 50°.



◒ : DATA FOR CHITIN (SEE TABLE 8).

● : DATA FOR WOOL.

[STEINHARDT FUGITT AND HARRIS (1941) ; SPEAKMAN AND STOTT (1935)]

a : ALIPHATIC AND BENZENE COMPOUNDS.

b : NAPHTHALENE COMPOUNDS.

c : BENZENE AZO NAPHTHALENE COMPOUNDS.

d : NAPHTHALENE AZO NAPHTHALENE COMPOUNDS.

FIG.6 RELATION BETWEEN VOLUME OF ANION AND ADSORPTION ON CHITIN AND WOOL.

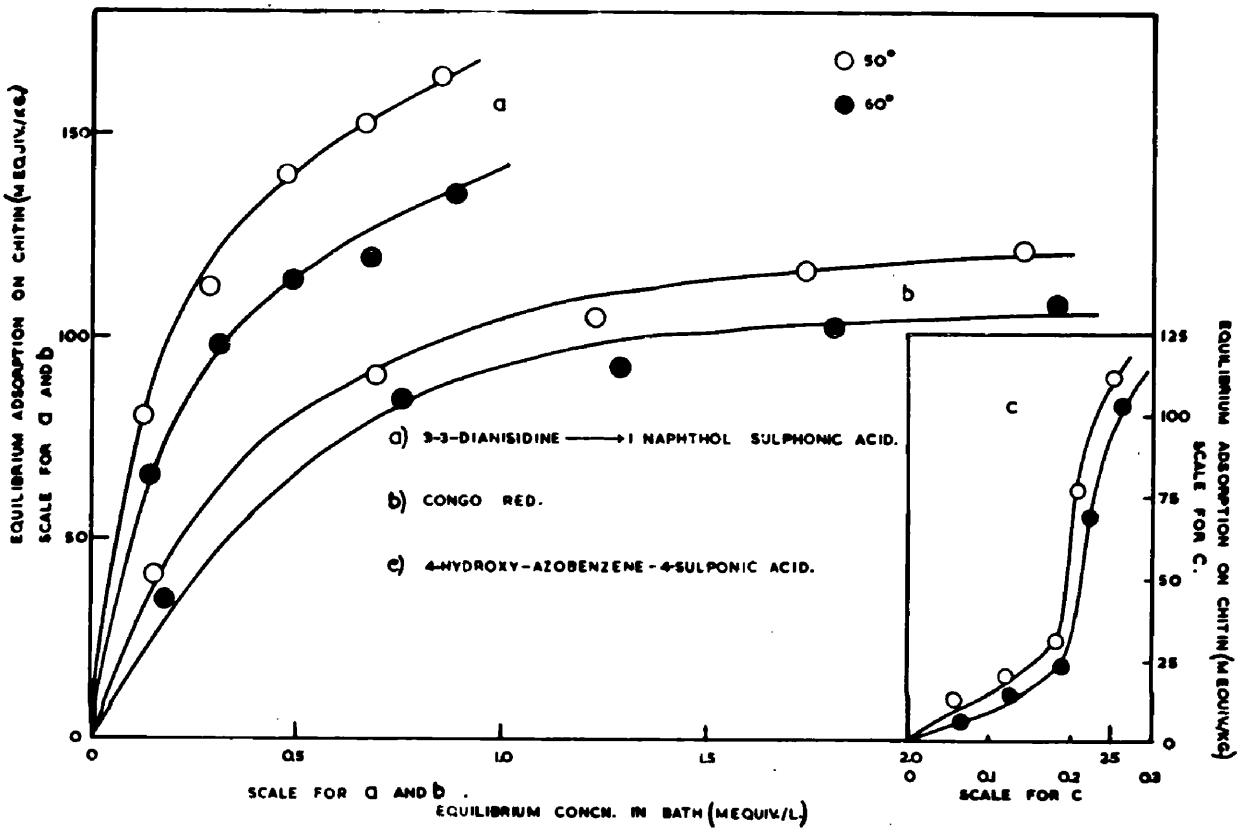


FIG.7 ISOTHERMS FOR AZO COMPOUNDS ON CHITIN (METHOD d)

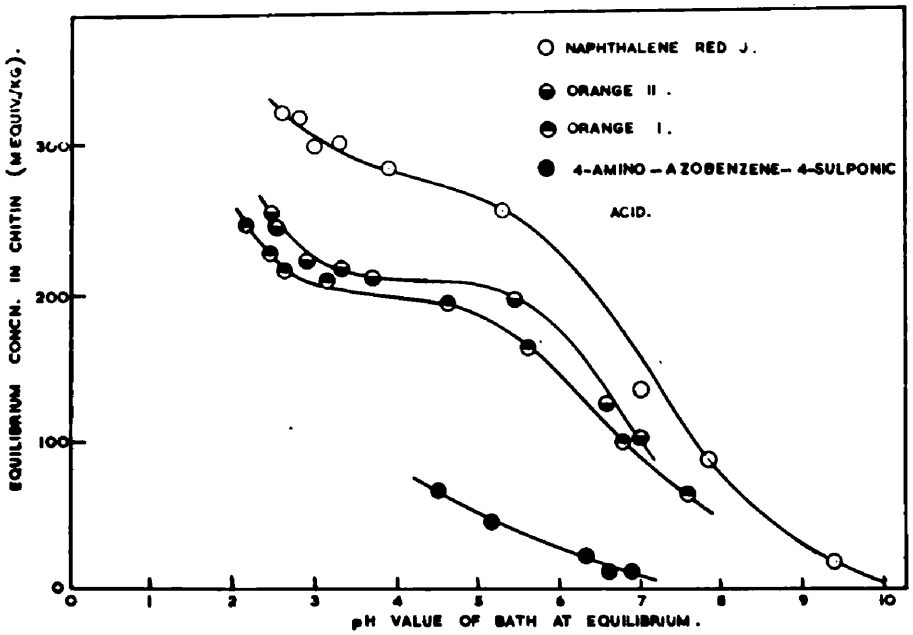
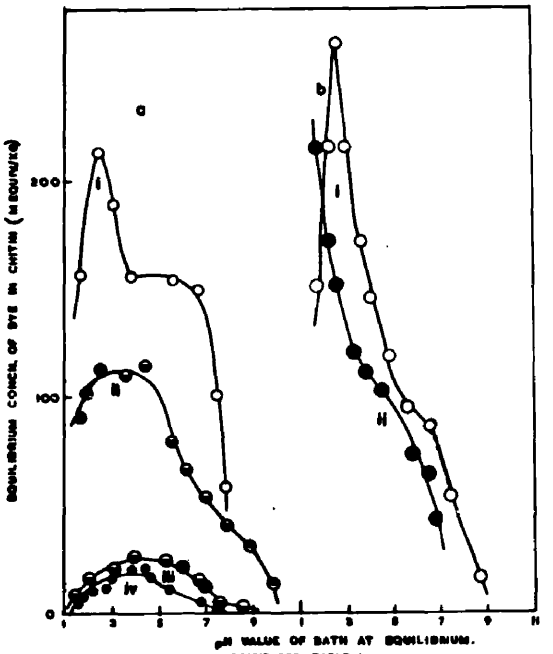


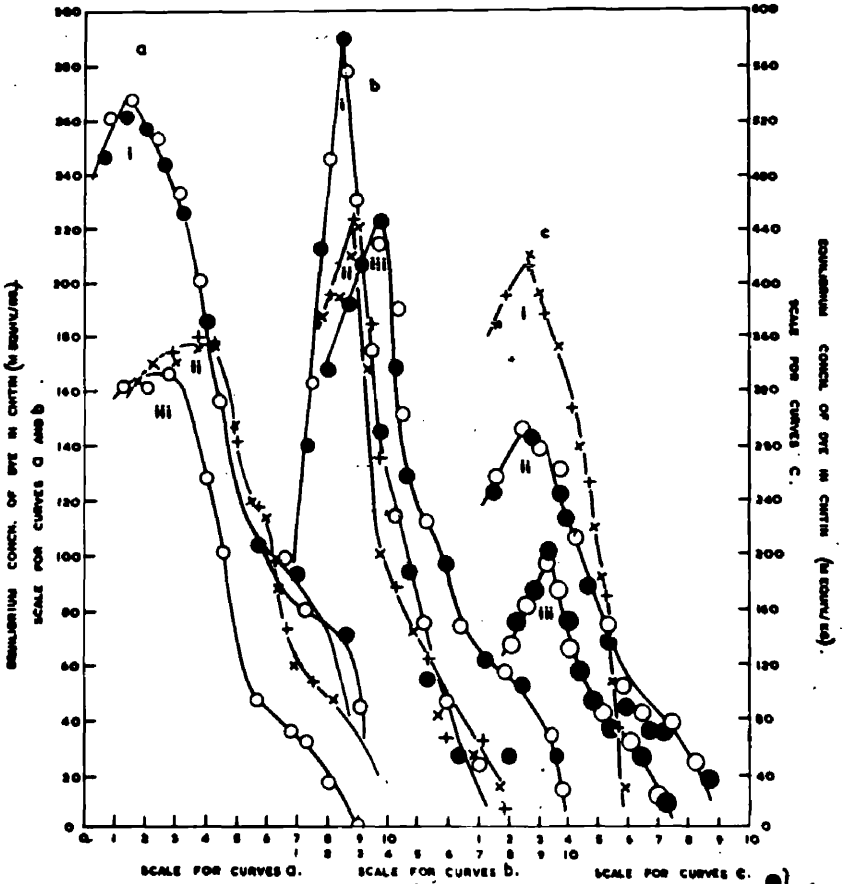
FIG.8 ISOTHRMS FOR AZO COMPOUNDS ON CHITIN (METHOD d) AT 50°.



FOR NAMES OF COMPOUNDS SEE TABLE I.

a) I-III I-II III-III I-IV b) I-III II-TETRASULFONATED DIRECT COTTON DYE (SEE EXPERIMENTAL SECTION)

FIG. 9 ISOTHERMS FOR AZO COMPOUNDS ON CHITIN (METHOD b) AT 90°.

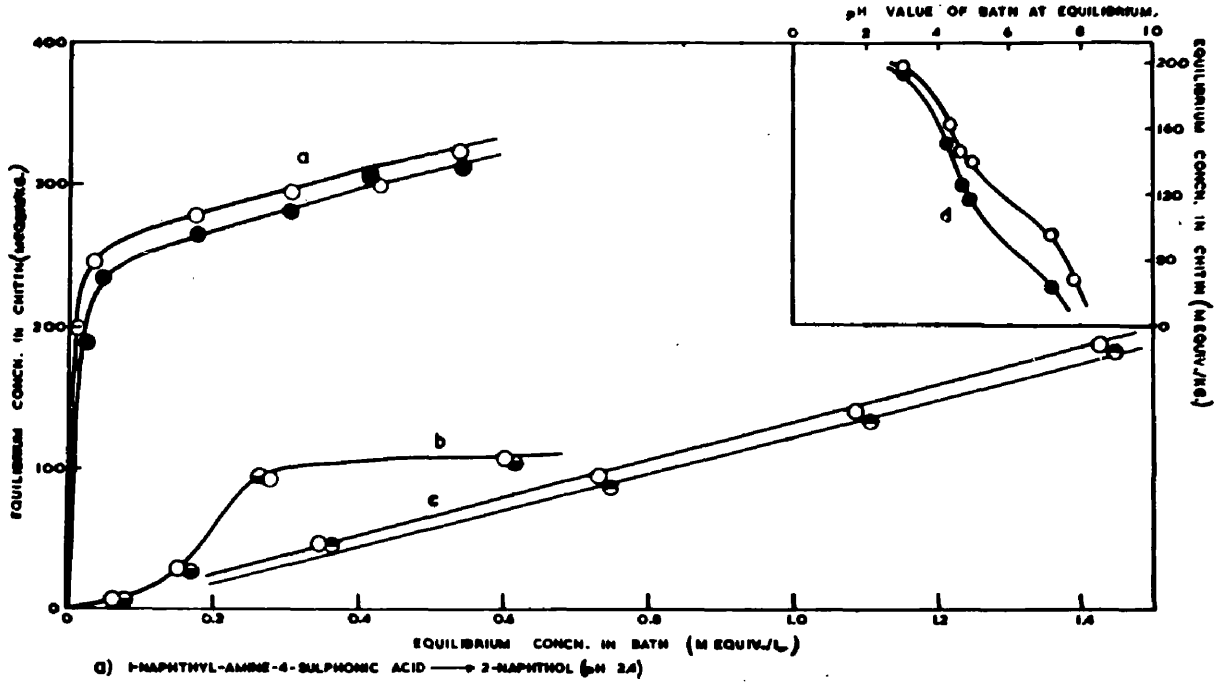


FOR NAMES OF COMPOUNDS SEE TABLE I.

a I-IV I-II II-IV b I-III II-II II-VII I-II c II-VII I-IV

60°. 90°.

FIG. 10 ISOTHERMS FOR AZO COMPOUNDS ON CHITIN (METHOD b).



a) 1-NAPHTHYL-AMINE-4-SULPHONIC ACID ⟶ 2-NAPHTHOL (pH 2.4)
b) 4-HYDROXY-AZOBENZENE-4-SULPHONIC ACID. (pH 3.5)
c) TETRASULPHONATED DIRECT COTTON DYE. (pH 2.4)
d) DYE a , METHOD b .

WHITE CIRCLES 50°.
BLACK OR HALF BLACK CIRCLES 60°.

FIG.11 ISOTHERMS FOR AZO COMPOUNDS ON CHITIN METHOD c ; INSERT METHOD b .

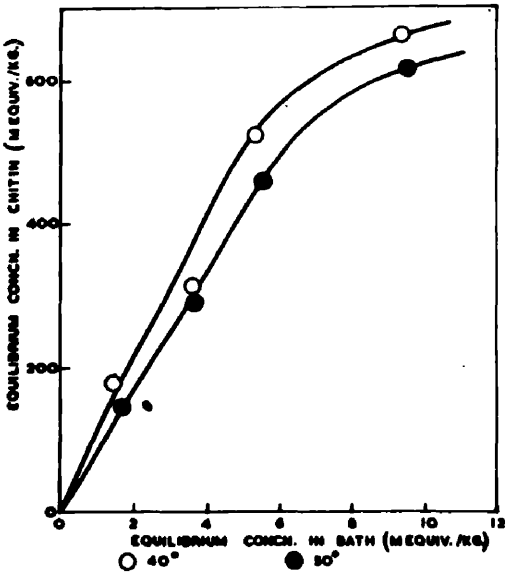


FIG.12 ISOTHERMS OF PHENOL ON CHITIN.

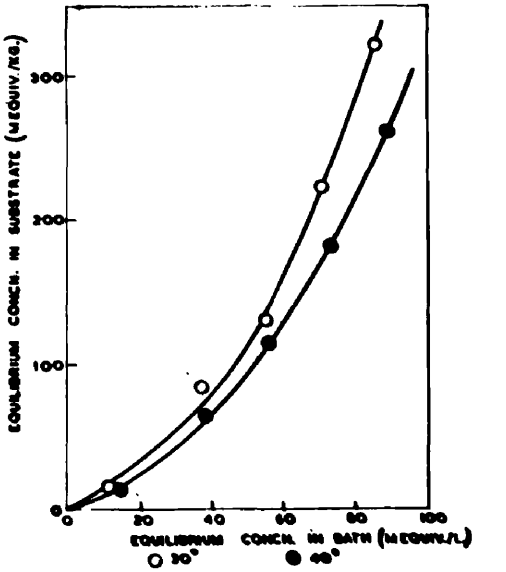


FIG.13 ISOTHERMS FOR PHENOL ON CETYL ALCOHOL.

TABLE 1.

Adsorption of Azo-dyes by Chitin

Dye Components			Approx Mol. Volume	Max. Adsorbed (**) (mequiv/ Kg.)	pH of Max. Adsorp-tion.	Adsorp-tion at pH 5.0 (mmole/ Kg.)†	‡ Vol. $A^3 \times 10^{24}$
First		Second					
Monosulphonates							
I	Sulphanilic acid	2-Naphthol	700	165	4.0	95	41
II	1-Naphthyl-amine-4-sulphonic acid	do	750	165	4.2	125	57
III	Azobenzene sulphonic acid		500	-	3.8	14	4.5
IV	4-Hydroxy-azobenzene-4'-sulphonic acid		550	120	4.2	26	8.5
Disulphonates							
V	Sulphanilic acid	2-Naphthol-6-sulphonic acid	850	185	3.3	40	21
VI	1-Naphthyl-amine-4-sulphonic acid	do	950	330	2.5	25	15
VII	Aniline	2-Naphthol-3:6-disul-phonic acid	900	330	3.8	53	29
VIII	1-Naphthyl-amine	do	900	395	2.6	70	38
IX	3:3-Dianisi-dine	1-Naphthol-4-sulphonic acid	1400	320	2.4	78	67

TABLE 1 (Cont'd.)

Trisulphonates							
X	Aniline-2:5-disulphonic acid	2-Naphthol-6-sulphonic acid	800	315	3.0	20	9.7
XI	Sulphanilic acid	2-Naphthol-3:6-disulphonic acid	1000	245	2.6	33	20
XII	1-Naphthylamine-4-sulphonic acid	do	1000	460(?)	2.6	58	35
Tetrasulphonates							
XIII	Aniline-2:5-disulphonic acid	do	950	200	2.4	17	10
XIV	2-Naphthyl-3:6-disulphonic acid	do	1250	350	1.8	31	24

(**) From method c isotherms.

(/) From method b isotherms.

TABLE 2.

Relation between Dye Structure and Volume of Dye Anions Adsorbed by Chitin at pH = 5.0 (Method b)

Number of Benzene nuclei	Volume Adsorbed ($A^3 \times 10^{-24}$) (per kg.) Number of sulphonate groups			
	One	Two	Three	Four
Two	4.5 , 8.5	-	-	-
Three	41	21 , 29**	10 , 20	10
Four	57	(15), 38	35	24
Six		67		

** First component unsulphonated.

TABLE 3.

Apparent Heats of Adsorption ($-\Delta H_{app}$) of Azo-dyes. on Chitin.*

	pH	$-\Delta H_{app}$ (K cal/mole)
4-Hydroxyazobenzene-4'-sulphonic acid	3.5	0.5
do	neutral	1.3
Congo Red (C.I.370)	neutral	9.0
Chlorazol Azurine G (C.I.502)	neutral	9.0
Tetrasulphonated direct cotton dye (I.C.I.)	2.0	1.5

* Measured at an equilibrium concentration (on the substrate) of 40 m.mole/Kg., temp. 50-60°.

TABLE 4.

Relationship between pH and Mean Maximum Adsorption of Azo-dyes (method b isotherm)

Maximum adsorption at pH -	Mean maximum adsorption (m.equiv./Kg.)
> 4.0	155
3.0 - 4.0	275
< 3.0	330

TABLE 5.

Effect of Pepsin Hydrolysis of Chitin-containing Raw Material.

Source	Incubation Period (37°)	% Nitrogen	Biuret Reaction
Lobster	Nil	7.3	Strongly +ve
shell	1 hr.	7.5	+ve
lining	2 hr.	6.9	-ve
	3 hr.	6.8	-ve
	3 days	6.6	-ve
	4 days	6.8	-ve
Nephrops	6 days	7.3	Slightly +ve
broken	7 days	7.2	do.
shells	8 days	6.6	do.
Do., Finely ground shells	8 days	6.9*	-ve

* Ash-free figure; (silica) ash content, 6.3%

TABLE 6.

Elementary Analytical Data on Chitin Samples.

Source	Treatment	Analysis % C	H	N	$COCH_3$
a. Broken shells of common lobster[x]	Clark and Smith Process	44.2	7.0	6.9	
b. Lining of shells of common lobster[x]	do	44.0	5.6(?)	6.7	
c. Broken shells of Nephrops norvegicus[x]	Thor Process	44.2	6.4	6.5	
d. do[x]	do[/]	44.6	6.3	6.7	
e. do (ball-milled)	do	45.3[//]	6.7[//]	7.1[//]	
f. do[x] (not milled)	Pepsin hydrolysis	43.7	6.5	-	17.2
g. do (ball-milled)	do	44.2[//]	6.2[//]	6.9[//]	
h. Lining of shells of common lobster[x]	do	44.5	6.7	6.5	
	Mean values	44.3	6.5[**]	6.9	
Meyer and Wehrli's product[§]	Thor Process	46.8	7.09	6.83	20.47
Substance		Calculated			
Poly-N-acetylglucosamine (I) $(C_8H_{13}O_5N)_n$		47.3	6.4	6.9	21.2
Poly-glucosamine (chitosan)(II) $(C_6H_{11}O_4N)_n$		44.7	6.8	8.7	0
82.5 pts.(by weight) of (I) + 12.5 pts.(II) + 5 pts.H_2O		44.6	6.5	6.8	17.5
Poly-glucose $(C_{10}H_{10}O_5)_n$		44.5	6.25	nil	0

x Ash-free; § Ash, 0.5%; / Product azeotropically distilled with benzene.

// Corrected for ash contents (7.5% and 6.3% respectively).

** Omitting b.

TABLE 7.

Apparent Affinity Values for Hydrochloric Acid

Acid alone			In presence of								
			0.1N.KCl (50°)			0.1N.NaCl (60°)			1.0N.NaCl (60°)		
pH	θ^{*}	$-\not$	pH	θ^{*}	$-\not$	pH	θ^{*}	$-\not$	pH	θ^{*}	$-\not$
4.50	0.09	12.2	5.80	0.23	9.3	5.50	0.02	9.0	5.80	0.20	7.9
4.17	0.12	11.5	4.55	0.41	8.0	5.18	0.24	8.7	5.20	0.32	7.5
4.06	0.15	11.5	3.52	0.68	7.2	4.68	0.33	8.2	4.60	0.46	7.0
3.87	0.22	11.0				4.3	0.48	8.0	4.10	0.63	6.6
3.56	0.36	10.5				3.60	0.63	7.4	3.50	0.75	6.1
3.18	0.57	9.9				3.10	0.75	7.0			

* Calc. for anhydrous chitin; c max. = 5.25 mol/kg.

$\not$ kcal/mol.

TABLE 8.

Adsorption of Acids by Unground Chitin.

Acid	Approx. vol. of anion* (A^3)	Amount adsorbed (mmoles/Kg.)	
		pH 3.0	pH 4.5
Hydrochloric	30		450
Formic	55	385	
Acetic	90	255	
Chloroacetic	95	320	
Sulphuric	110		150
Picric	210	235	85
Benzene sulphuric	260	200	100
Aniline-2:5-disulphonic	390	100	55
Naphthalene-2-sulphonic	400	195	
2-Naphthol-6:8-disulphonic (G-acid)	570	105	50

* (Volume of enclosing rectangular box).

TABLE 9.

Apparent Heats of Adsorption ($-\Delta H$ app) of Phenol from Water.

Substrate	Temp. range	C_{Sb}	$-\Delta H_a^{\not}$
Cetyl alcohol	30 - 40	160	3.5
Chitin	50 - 60	500	5.5
Nylon	30 - 50	500	4.5
Wool	30 - 50	500	4.0
$\underline{\gamma}$ -Al_2O_3	40 - 60	100	4
		400	4.5

C_{Sb} = equilibrium concentration in the substrate (m.moles/kg.)

ΔH_a = apparent heat of adsorption (kcal./mole.)

$\not$ = The convention followed here is that a negative value for ΔH_a represents an exothermic adsorption process.

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PART II

COMPARISON OF ADSORPTION MECHANISMS ON CELLULOSE AND CHITIN

INTRODUCTION

Pure cellulose is a carbohydrate and may be hydrolysed almost quantitatively to glucose. Cellulose is now recognised to be built up of β-glucose units joined together by ether linkages in 1:4-positions to form linear macromolecular chains of up to about 2000 units (Howorth, 1940) in the manner shown in Fig.1. The chain length varies in celluloses of different origin. The X-ray evidence of Meyer and Mark, and of Meyer and Misch shows that this fibre, like other fibres, consists of a continuous network of polymer chains which pass through various stages of crystalline and amorphous regions i.e. they may for some part of their length have a regular lateral arrangement forming what are known as crystallites or micelles, while in other regions they may have random or amorphous orientation. One long chain molecule may thus form a part of two or more micelles. The permeability of the amorphous regions is of importance in so far as the dyeing process is concerned because there is no evidence that dye molecules can penetrate into the closely packed structure of the micelles.

Considerable attention has been devoted to the determination of the particle size of dyes and the pore size of cellulose fibres, in solution. On the above view of the

structure of cellulose, the pores must be ill-defined and tortuous. McBain and Kistler found that dry 'Cellophane' (regenerated cellulose film) is practically impermeable to ethyl and amyl alcohols, xylene, and aniline, and that these solvents cause no swelling. If the 'Cellophane' is first soaked in water, however, ethyl alcohol passes through readily, and when the alcohol is replaced by other solvents these also pass through. Boulton et al. (1933) suggested that when water enters cellulose the osmotic forces tend to cause the chains to move apart and such movement can occur only in the disoriented parts of the fibre, so that the swollen fibre consists of compact crystallites linked by open networks of chains through which dye molecules may pass. The diameter of the pores in the latter regions has been found by various workers to vary from 5 Å in the dry state, to about 20 Å in the water-swollen condition.

When the size of a typical direct dye molecule, e.g. Chlorazol Sky Blue FF (length 27 Å, width about 10 Å), is compared with the pore size, it is quite obvious that only single dye molecules or very small aggregates of them can diffuse into the fibre. According to Lenher and Smith dyes having particles of diameter greater than an optimum value of 35-40 Å at 25°C., are not readily adsorbed by cotton, though these authors state that the equilibrium

adsorption of the dye is not affected by its mean particle size, because as the smaller particles are taken up, larger aggregates break down to restore equilibrium conditions. The rate of adsorption does, however, decrease with increase in mean particle size.

Dyeing of a fibre includes a diffusion process and the diffusion of dye inside the fibre is much slower than in the external solution, because of the greater mechanical obstruction to movement presented by the presence of the fibre substance and also because of the restraining forces between fibre and dye. Neale and his associates have shown that the diffusion process in dyeing is governed by Fick's law, which assumes that the rate of diffusion (ds/dt) of a dye across a unit area at a given point in the fibre is proportional to the concentration gradient (dc/dx) of the dye at that point, i.e.

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

where D is the diffusion coefficient. However, it has been shown by Neale and Garvie (1938) that the diffusion constant calculated according to Fick's law varies with the dye concentration. They suggest that the observed experimental data could be better represented by the equation

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

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

Although the kinetics of the process of dyeing cellulose with substantive dyes has received considerable attention (Boulton et al., 1933; Neale, 1936; cf. also Crank's recent work, summarised by Vickerstaff (1954)), there is no general agreement as to the nature of the union of the dyes with the fibre. In the case of proteins, the hypothesis that the basis of substantivity is a normal salt linkage between the basic groups of the protein molecule and the acidic groups of the dye is now regarded as affording an explanation of the main features of the adsorption of acid dyes (Goodall, 1933,1936,1937; Vickerstaff, 1954). Cellulose on the other hand contains no basic groups, so that the chemical or molecular basis of the substantivity of the direct dyes must be other than a salt linkage.

Hydrogen bonding has for some years been considered responsible for the adsorption of water-soluble solutes, particularly dyes on cellulose (Vickerstaff, 1954; Huggins, 1938; Mark, 1940). Lately however, evidence has accumulated which makes it very likely that the affinity is

due to non-polar van der Waals forces and that hydrogen bonds are not formed (Allingham et al., 1954; Derbyshire and Peters, 1955; Giles, 1954; Arshid et al., 1954, 1956b).

In this laboratory, investigations were made of the reactivity of carbohydrates, using the refractive index method. Glucose and cellobiose were chosen as model compounds representing cellulose fibres as a guide to indicate the possible means by which the groups in substrates and solutes might be expected to operate (Arshid et al., 1956 a,b). It has been found that glucose and cellobiose behave monofunctionally towards reactive second solutes and that the reactions are identical with those of aliphatic aldehydes. It is therefore assumed that these carbohydrate molecules react through the aldehyde groups in their open-chain forms, which are thereby stabilised, and not as the pyranose ring structure. The non-reactivity of the hydroxy-groups of the carbohydrates towards most other solutes is consistent with the above interpretation of their behaviour in water, but the non-reactivity of phenols with glucose or cellobiose is unexpected because phenol does normally combine with alcoholic groups in water, even with every group in a straight-chain polyhydric alcohol, e.g. mannitol. This inactivity of the aldehyde group towards phenol in water may be due to the instability of

the open-chain form of glucose under such conditions. It follows that the inactivity of the glucose hydroxy-groups towards phenol in water is a property of the ring form and it seems likely that the water-attracting power of the hydroxy-groups is greater in the ring than in the open-chain form. A study of hydrogen bridging in cellulose using infra-red absorption spectra (Ellis and Bath) revealed that almost all the hydroxy-groups are involved in hydrogen bonds between adjacent cellulose chains. Models also demonstrate that the solvated water molecules on opposite sites of the glucose molecule must be closer together at their nearest distance in presence of the ring form than in the presence of the open-chain form in its most probable crumpled state. The ring structure is stabilised by the affinity of the surrounding water which acts as a protective 'atmosphere' against weak interaction with other solutes. Adsorption on cellulose must take place, if at all, on molecular chains of the non-crystalline regions, and in aqueous solutions these presumably resemble glucose and cellobiose in being surrounded by an atmosphere of water molecules bound so firmly that other solutes cannot normally penetrate it. This explains why phenol, which is readily adsorbed from dilute aqueous solution by fibrous substrates capable of hydrogen bonding, e.g. nylon, wool (Chipalkatti et al., 1954), and cellulose acetate (Marsden and Urquhart, 1942), is entirely unadsorbed under

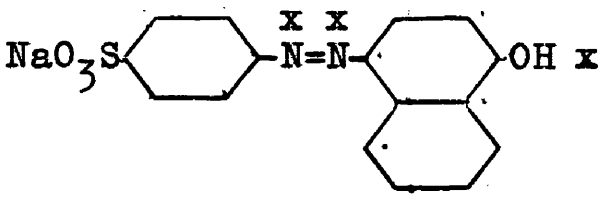
similar conditions (Marsden and Urquhart; also see present work) by regenerated cellulose. Preston and Nimkar, by studying the freezing point curves of adsorbed moisture in cellulose fibres, have shown that the non-crystalline parts of the fibre are in a state resembling solution in water, so they should behave as glucose. It has been found also that glucose is adsorbed on cellulose from aqueous solutions (Chitale), and because the affinity for hydrogen bonding in both substances can be satisfied by water, the only reason for adsorption may be attributed to the operation of non-polar forces.

Allingham et al. have investigated the possible modes of dye-substrate combinations by the use of the unimolecular film balance, with models of dyes and fibres. Their interpretation of the interactions is based on measurements of molecular areas and compressibilities in the films. The results relating to the adsorption of dyes by cellulose from aqueous solutions agree more with a mechanism of van der Waals attraction between the dye and the fibre than with one involving hydrogen bonds. It may be assumed, as suggested previously, that the carbohydrate molecules are too firmly attached to water for hydrogen bonds with dyes in aqueous solution to be formed. Robinson used the new type of accurately-computed Courtauld atomic models to examine the geometry of the cellulose molecule and of typical cotton dye molecules. He found that all these

have rather flat surfaces, so that close approach of dye to cellulose, with an interposed layer of water, seems quite possible.

The benzidine series of direct cotton dyes are highly substantive on cellulose and it has been suggested (Paine and Rose, quoted by Vickerstaff) that planar dyes of this series are highly substantive because the repeat interval (10.8 Å) of potential bonding groups, e.g. $-N_2-$, etc., in their molecules corresponds closely with that (10.3 Å) of the cellobiose unit of cellulose, and thus the best conditions are satisfied for groups taking part in mutual hydrogen bonding to make close contact. However, it has been found that in the case of dyeing cellulose from water solutions with direct cotton dyes, hydrogen bonding cannot be wholly responsible for the adsorption of the dye (Zollinger, 1954). For instance, the substantivity of the dye for cellulose has no relation to their content of potential hydrogen-bonding groups (Giles, 1954), e.g. Orange I (I) has three such groups (x) and Bordeaux extra (II) has two, yet the former is non-substantive while the latter dyes cotton.

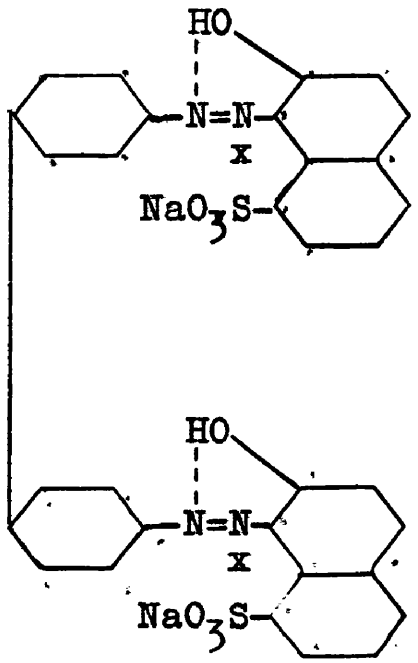
I



Orange I

(Colour Index No.150)

II



Bordeaux extra

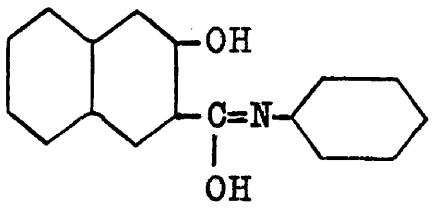
(Colour Index No.385)

Since the van der Waals energy of attraction between a molecule and a surface increases with the size of the molecule and may be inversely proportional to the cube of the distance between the centre of the molecule and the surface, it would be expected that large molecules would have a strong tendency to lie flat on the surface. This was confirmed experimentally by Hendricks for a number of large organic molecules on the layer crystal montmorillonite. Hodgson suggested that in a direct cotton dye, various benzene and naphthalene nuclei should be capable of lying in one plane. 3:3'-Disubstituted benzidine derivatives which have planar molecules are substantive

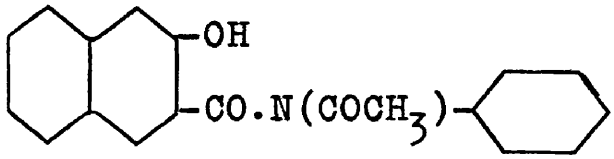
dyes, whereas 2:2′-derivatives give non-substantive dyes, because their molecules are non-planar. In addition to being linear and planar, direct dyes should contain a long conjugated chain of double bonds (Schirm, 1935). It has been also argued that an increasing number of conjugated double bonds is accompanied by increasing substantivity due to the increasing residual valency forces at the ends of the chain (Paine and Rose, 1933).

Peters and Sumner have recently reported an investigation upon the affinity of a series of vat dyes (in the leuco. form) for cellulose and have shown that this affinity probably has its origin in the van der Waals attraction of the large planar dye molecules for the cellulose. They were able to demonstrate a linear relationship between affinity and the logarithm of the extinction coefficient of the dyes, and since the latter is itself a function of the mobility of the π -electrons, it was supposed that it contributes to the physical attraction between dye and fibre. Peters and Sumner found also that all the vat dyes containing -CONH- groups attached to the nucleus have higher affinity than the corresponding ones without this group. They supposed that the large aromatic nuclei of the vat dyes have sufficient physical attraction for the cellulose, in presence of water, to enable the dye molecule to approach close enough for

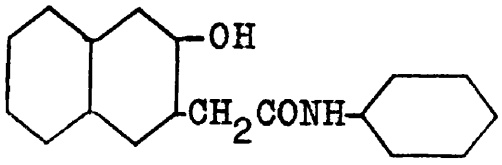
hydrogen bonds to be formed. In view, however, of the negative results obtained in this laboratory (Jain) in attempts to demonstrate hydrogen bond formation in water between glucose or cellobiose and a variety of other second solutes, including dyes, with molecules nearly as large as some of Peters and Sumner's benzoylaminoanthraquinone compounds, their suggestion of hydrogen-bond formation seems unlikely. This is also in agreement with the view held by Krzikalla and Eistert that any change in the constitution which reduces the possibility of conjugation through the enol form of the anilide group in 2-hydroxy-3-naphthoic acid anilides also reduces their substantivity for cellulose. Thus I is more substantive than II or III.



I



II



III

Similarly Hodgson and Holt observed that 3:3'-disazodiphenyl derivatives are of low substantivity, and this

can be explained on the grounds that a conjugated chain is not possible as it is in the 4:4'-derivative.

PRESENT WORK

The present investigation is an attempt to examine and compare the adsorption properties of cellulose and of the closely related natural polymer chitin using both aqueous and non-aqueous solution. Additional work is done on chitin, whenever necessary, parallel to that of cellulose in order to bring about a better understanding of the adsorption mechanism of both substances.

Chitin was chosen for comparison with cellulose because, while the composition of its polymer chain closely resembles that of cellulose (Fig.1), it was expected that the adsorption behaviour of the two substances would differ considerably. This expectation followed from refractive-index measurements made on a variety of aqueous binary solutions, containing N-acetylglucosamine, as a model of chitin, or glucose and cellobiose as models of cellulose, which have shown that the hydroxy groups of all those model compounds are inactive towards any other hydrogen bonding solute in water and that the acetylamino group in N-acetylglucosamine in water is able to form hydrogen bond complexes with many other solutes (Arshid et al., 1956, a,b).

EXPERIMENTAL

Substrates.

Substrates used in this investigation were cellulose in the form of viscose rayon and the closely related natural polymer chitin. Chitin was prepared as in the previous work (Part I) while viscose rayon was purified as follows: loose "Fibro" (Courtaulds viscose rayon), staple (4.5 Den., 6" , bright), was scoured in an anionic detergent (0.3% Lissapol C solution (I.C.I.)) with 0.2% sodium carbonate, for an hour at 80°C. It was then thoroughly rinsed in cold water to which a few drops of dilute acetic acid were added in order to neutralise any traces of alkali. The washed viscose was then dried in an oven at 100°C. and conditioned for 48 hr. at room temperature before use.

Specially dried substrates were required for adsorption studies in dry organic solvents. Samples of chitin and cellulose were dried by extracting with methylene chloride using a Soxhlet apparatus. The samples were then dried in an oven at 100°C., and extracted again with the organic solvent to be used in the respective adsorption experiment, followed by oven drying at 100°C. for 4 hr. They were then immediately weighed and introduced into the adsorption tubes.

Solvents.

Purified solvents were used, benzene was stored over sodium and ethyl alcohol was the commercial absolute quality.

All water used was distilled. The pH buffer solutions were prepared from the Marconi standard buffer tablets.

Solutes.

Most of the compounds employed were obtained in the pure state or as commercial substances, but some were prepared in this laboratory, e.g. the following -

Anthracene-1-sulphonic acid was prepared by the reduction of the corresponding anthraquinone acid by zinc dust and ammonia (Ferrero and Conzeti).

Aniline-2:5-disulphonic acid ⟶ naphthol A.S. was prepared by coupling, in the cold, the diazotised base with Naphtol A.S. dissolved in aqueous alcoholic sodium hydroxide solution.

Naphthalene, anthracene and anthraquinone sulphonic acids were prepared by passing their sodium salt solutions several times through a column of regenerated cationic ion-exchange resin (Latta, 1954).

Flavanthrone leuco-sulphuric ester was supplied as a 14.2% suspension of the sodium salt in 5% sodium carbonate solution by I.C.I. Ltd., Dyestuffs Division.

Most of the dyes employed were purified by salting out from concentrated solution by sodium chloride, and then recrystallised from water. Congo Red was purified by acidifying its aqueous solution. Some other dyes were purified by recrystallisation from ethanol solutions.

The determination of the purity and concentration of the compounds used was made as before (see Experimental Section, Part I).

Adsorption tests.

0.1g. of substrate and 10 c.c. of solution, made up in a range of concentrations needed to give the optimum adsorption (the conditions varied with the compounds used), were placed in closed containers. Ground-glass stoppered tubes (Quickfit) were used for aqueous solutions and completely sealed glass tubes for those in organic solvents (on account of the difficulty of preventing loss of solvent through the ground-glass joints). The tubes were then placed in a mechanically agitated thermostat (see Experimental Section, Part I) until equilibrium was reached.

In the case of viscose rayon, the fibre was packed into a separate inner open-ended perforated tube. During agitation the holder falls to-and-fro in the test tube, with a regular motion out of phase with the movement of the liquor, which is thus caused to pulsate into and out of the fibre via the perforations (Arshid et al., 1954). By this method the difficulty of a mass of loose fibre blocking the sorption tube is avoided and adequate contact of fibre with the solution is achieved.

When positive adsorption was noticed, the time required to reach equilibrium was determined at the required temperature before proceeding with the isotherm study.

Solubility determination.

In order that the results might be plotted on a relative solubility basis, the solubilities of the compounds were determined. This was attempted firstly by placing about 1.5g. of the compound in a tube with 10 c.c. water. The tube was then sealed and tumbled in a thermostat at the required temperature for about 24 hr. The contents of the tube were then filtered and the undissolved dye was determined after drying to a constant weight. Results from this method were not reproducible, probably because of changes in temperature (with subsequent

changes in solubility) during the filtration process.

More satisfactory results were obtained from a modified technique incorporating an apparatus similar to that of Thorp, which consists of two conical flasks connected through a Quickfit joint with a fine sintered glass diaphragm (Fig.2). When using 20 c.c. solvent, flasks of 100 c.c. capacity were found to be satisfactory. Using this apparatus the solubility at a definite temperature can be determined as follows - (a) the solvent and excess of the solute are placed in flask A, which is then stoppered, tap T is closed, and then the whole is placed in the thermostat and tumbled at the required temperature until equilibrium is attained; (b) flask A is then removed, the stopper extracted and quickly assembled with the rest of the apparatus as in Fig.2b, then the whole assembly is returned to the thermostat; (c) after tumbling again for some time, the apparatus is overturned so that the solution can flow from flask A to flask B. After this, tap T is opened to permit the air from flask B to rise to flask A through the rubber tubing by-pass. The apparatus is replaced in the thermostat during filtration, after which an aliquot portion of the solution is removed for analysis.

Using the above method for determination of the solubilities of pure and simple compounds, the results

were quite consistent. Unfortunately, however, this was not so in the case of some dyes, presumably due to the effect of impurities or aggregation with formation of colloidal solutions.

RESULTS AND DISCUSSION

Table 1 summarises all the adsorption experiments made on cellulose and chitin respectively, while Table 2 compares the experiments which were duplicated on the two substrates.

Adsorption of Hydroxylic-Compounds.

The isotherms for methanol adsorption from benzene (Fig.3) show that cellulose and chitin adsorb the solute in absence of water in a similar way, and there seems no reason to doubt that the adsorption mechanism in these cases is hydrogen bonding. Assuming that the points A, A_1 represent the completion of a monolayer, the estimates of the surface area covered are 3.8×10^5 $cm^2./g.$ for chitin and 4.8×10^5 $cm^2./g.$ for cellulose; the latter is in close agreement with that given by Harris and Purves, i.e. 4×10^5 $cm^2./g.$ for cellulose. These surface area measurements may be much less than those which might be obtained in the water swollen state.

Phenol and resorcinol were applied to cellulose from aqueous solution, and 2-naphthol from alkaline and 50% alcoholic solution, but they failed to show any adsorption. The results with 2-hydroxyanthraquinone were indecisive

because the optical density was higher after adsorption than before, which may be due to oxidation having occurred.

Phenol is adsorbed from neutral aqueous solution by chitin (also at pH 9 Fig.4) (and by δ -alumina (Giles et al., 1954), nylon and wool (Chipalkatti et al., 1954)).

The behaviour of cellulose and chitin agrees with predictions made from the refractive index investigation (see introduction to the sections on chitin and cellulose). It may also be mentioned that Marsden and Urquhart were unable to detect any adsorption of phenol by regenerated cellulose film in water.

Haematoxylin (Colour Index No.1246) a complex tetrahydric phenol with a fairly large molecule, is adsorbed by cellulose (Arshid et al., 1954) presumably by van der Waals attraction. Its affinity for nylon, however, is undoubtedly due to hydrogen bonding, and is considerably greater than for cellulose.

Simple Sulphonic Acids.

Cellulose and chitin were expected to differ in their behaviour towards simple aromatic sulphonic acids not containing other polar groups. These solutes cannot form hydrogen bonds with the substrate and should be adsorbed, if at all, either by ion exchange or non-polar attraction.

The earlier and present investigation on chitin adsorption has shown that this material exhibits little non-polar attraction for the smaller aromatic anions, which are adsorbed by ion exchange at pH values below 7-9 and not at all from more alkaline solutions (Table 2).

The polyacetylglucosamine molecular chain has a more irregular outline than that of the cellulose molecule, and planar solutes, e.g. aromatic anions, must be unable to approach it so closely as they can approach cellulose, and so they probably have lower non-polar attraction for chitin than for cellulose. Therefore when solutes, especially those with planar molecules, which cannot be adsorbed by hydrogen bonds or by an ion exchange mechanism, i.e. those which can only be adsorbed by non-polar forces, are applied to these two substrates under identical conditions, they would be expected to be adsorbed more readily by cellulose than by chitin.

This is confirmed by the results of the experiments with benzene sulphonic acid, naphthalene-2-sulphonic acid, anthracene-1-sulphonic acid, and anthraquinone-2-sulphonic acid, and their sodium salts. They show increasing affinity for cellulose with increasing molecular size (Fig.5a), the smallest molecule, benzene sulphonic acid, is in fact not adsorbed at all. They are adsorbed by chitin to nearly equal, and considerable, extents (Fig.6 and 7)

as free acids by ion exchange, their sodium salts being less adsorbed; while at pH 9, where the ion exchange reaction is inhibited, no adsorption can be detected.

The normal isotherms of the sulphonic acids of naphthalene, anthracene and anthraquinone and their sodium salts on cellulose differ (Fig.5a). However when plotted with relative solubility (i.e. actual concn./saturation concn.) as abscissa (Fig.5b) they approach each other more closely. By this method of plotting the influence of the solvent upon affinity is cancelled out and any differences which appear between solutes may be attributed solely to real differences in solute-substrate interaction. At the same relative solubility values the amount of anthracene and anthraquinone sulphonates adsorbed are more than those of the corresponding naphthalene compounds, which may be attributed to the larger molecular size of the former with consequently greater possibility of adsorption by van der Waals forces. Considering also the shape of the isotherms, it can be seen that while the naphthalene sulphonated compounds give S-shape isotherms, the anthracene and anthraquinone compounds give ordinary Langmuir-shape curves. This may be explained on the lines of the hypothesis of Giles and MacEwan as showing that the affinity for the substrate, of the anthraquinone and anthracene compounds is greater than that of the naphthalene compounds, and they

are consequently better able to displace adsorbed solvent (water) from the surface.

Sulphonated Compounds with Additional Polar Groups.

These compounds, compared with the former class, would be expected to behave rather differently towards chitin because of possible hydrogen bonding effects, but rather similarly towards cellulose.

Alizarine-3-sulphonate (Na salt), gives results in accordance with prediction when compared with anthracene and anthraquinone sulphonates. On cellulose in pH 9 buffer (Fig.8 and 9) all these compounds behave very similarly and there is no evidence that hydrogen bonding groups increase affinity. They are adsorbed to a lower extent from pH 9 solutions than from acid and neutral solutions presumably due to the increase of the negative charge on cellulose under alkaline conditions, with a consequent increase in repulsion between cellulose and the solute anions. On chitin however at pH 9 the hydroxy-groups in alizarin sulphonate markedly increase the adsorption (Fig.8); the quinone groups appear not to do so, presumably they have weak bonding properties in water.

The affinity of 2-naphthol-6-sulphonic acid is less than that of naphthalene-2-sulphonic acid, for both cellulose and chitin (Fig.10, 5 and 6). This anomaly may be

attributed to dimerisation of the hydroxy-compound by intermolecular hydrogen. The low adsorption on chitin is then accounted for by the dimer having more restricted access to this highly crystalline substrate; and on cellulose by the discontinuity of the conjugated structure between the two molecules of the dimer, due to non-planarity. The solubility of the hydroxy-compound was found to be lower than the sulphonic acid (38g. and 192g. per litre respectively at 50°C.), and was in fact found to be too low for a reliable molecular weight determination to be made.

No adsorption of 2-naphthol dissolved in 50% aqueous ethanol occurs on cellulose, though 2-naphthol-6-sulphonic acid is adsorbed from the same solvent (Fig.10). The sulphonate group may enable the solute to dissolve in the water atmosphere attached to the cellulose chains so that a close enough approach can be made for van der Waals adsorption forces to become significant. Derbyshire and Peters (1955) have offered a similar explanation for the adsorption of ionised dyes by cellulose.

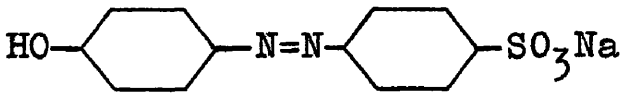
Sulphonated Azo-dyes.

4-Hydroxyazobenzene-4'-sulphonic acid (Na salt) is adsorbed from aqueous solution to a considerable extent on chitin (about 50 times more than on cellulose, Fig.12 and Fig.7 of Part I). The relatively small adsorption

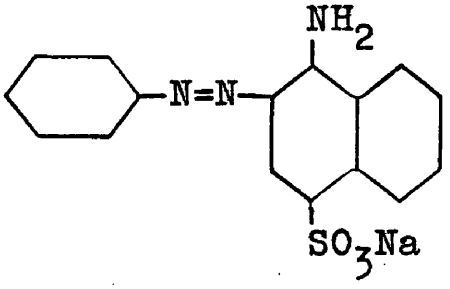
value on cellulose may be due to the comparatively small molecule of the solute and the consequent very small physical force of attraction.

Adsorption of aniline ——→ naphthionic acid (Na salt) was compared with that of the "double" molecule Congo Red (benzidine ——→ $(\text{naphthionic acid})_2$). The two dyes have identical hydrogen bonding groups, but the second dye should have much enhanced van der Waals affinity compared with the first, by virtue of its greater molecular area, linearity and higher conjugation. At pH 9, ion exchange by chitin being suppressed, the second dye is adsorbed a little more than the first by chitin (Fig.11b), but the second is adsorbed very considerably more than the first by cellulose from both neutral and pH 9 solutions (Fig.11a). This is an indication that cellulose can exert increased van der Waals attraction by virtue of the more regular outline of its molecular chain; it is also an indication of the negligible effect of polar forces in adsorption on cellulose. In neutral solution both dyes are considerably adsorbed by chitin, mainly by an ion exchange mechanism.

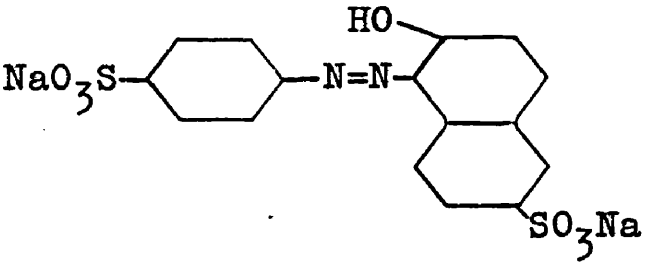
In the series of compounds I - VII it seems that the adsorption results on cellulose from aqueous solution vary according to molecular size and the number of sulphonic groups (Fig.12).



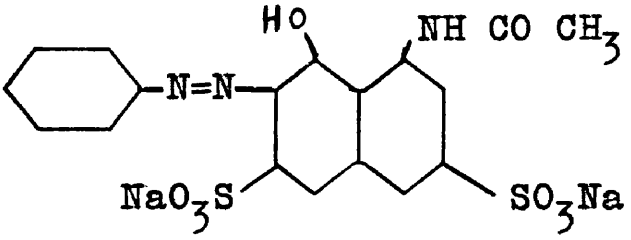
I



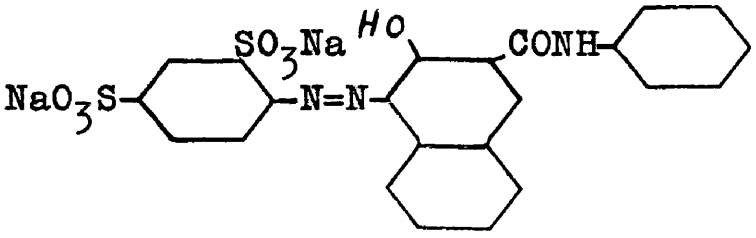
II



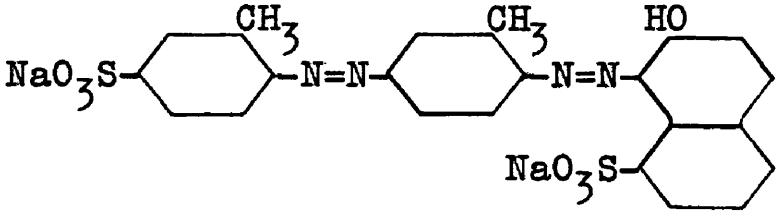
III



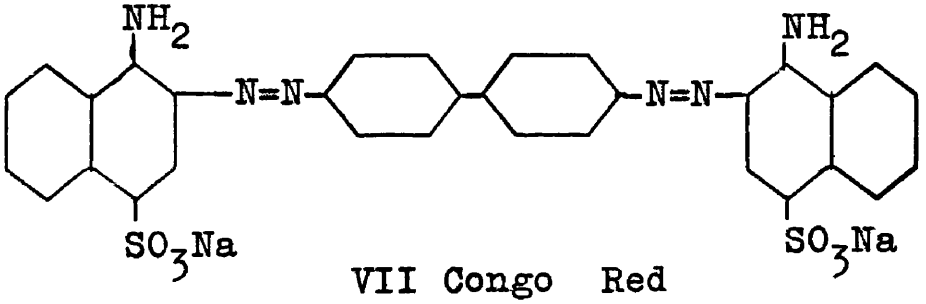
IV Azo Geranine 2G



V



VI Ponceau 6RB



VII Congo Red

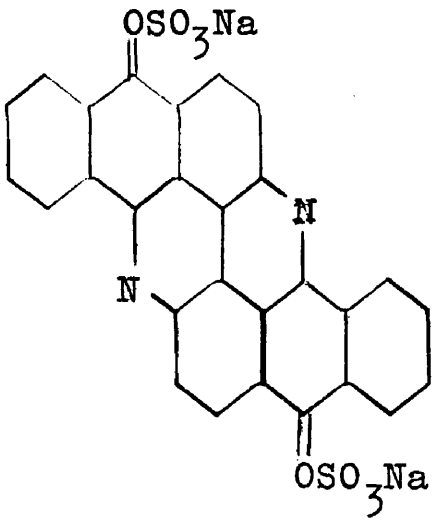
The first two compounds have similar groups, the difference being only in molecular size, but II is adsorbed more than I. Compounds II and III have about the same molecular size, yet the latter is less adsorbed. It may be that the addition of one more sulphonic group increases water solubility so much that there is a corresponding lower adsorption. This statement holds good only for adsorption from water solution and entirely different results might be obtained with organic solvents.

The dyes from III - VII have the same number of sulphonate groups (though their position and the complexity of the molecules affect solubility to a great extent) and are all adsorbed by cellulose. Dye V is adsorbed to a much greater extent than III and IV, which are adsorbed to about the same extent. This illustrates that the -CONH- group is relatively inactive in promoting adsorption and that the degree of conjugation in the solute molecule is much more critical. This view is supported by the work of Krasnovitskii et al., and Krizikalla and Eistert. Dyes V and VI have about the same molecular area, but the latter has more affinity for cellulose. This may be due to the fact that substantivity increases with the length and linearity of the molecular chain of the dye. Congo Red (Dye VII) however, which is a typical direct cotton dye, is

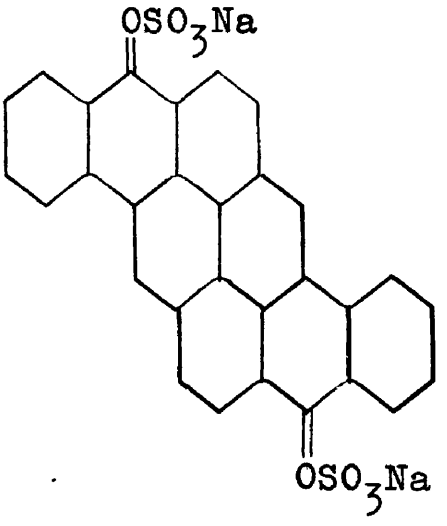
the most adsorbed because it has the longest conjugated structure of those studied during the present work.

Sulphate Esters of Leuco- Vat Dyes.

In order to examine the influence of very large multi-nuclear molecules, samples of the sulphate esters of the leuco-compounds of flavanthrone and pyranthrone were examined.



Flavanthrone leuco sulphate ester.



Pyranthrone leuco sulphate ester.

The pyranthrone compound unfortunately proved to be too insoluble even at pH 9 for any reliable result to be obtained. The other material is adsorbed considerably more on chitin than on cellulose (Fig.13). Since chitin can certainly exert no stronger van der Waals attraction than cellulose can for such a compound, the result is

another indication of the much higher polar affinity of chitin.

Although the flavanthrone molecule is about the same size as that of Congo Red, the latter is more substantive on cellulose under the same conditions. This may be due to the fact that Congo Red possesses a larger chain-like molecule, which can lie close up to the cellulose chain, thus the attractive forces will be more effective in holding the two together than would be the case if the dye was not linear.

Affinity Measurement.

The affinity of some of the compounds used for cellulose in the present work has been calculated from the expression -

$$-\Delta\mu = RT\ (\ln [D]_F + Z \ln [Na]_F - \ln [D]_S - Z \ln [Na]_S - (Z + 1) \ln V)$$

(Vickerstaff), where $[D]_F$ and $[D]_S$ are the concentrations of dye in the fibre and in solution respectively, $[Na]_F$ and $[Na]_S$ are the corresponding sodium ion concentrations, and Z is the valency of the dye anion. V is the "volume" term representing the effective volume of water in the substrate (in litres /kg.), and has been given the value of 0.22 l/kg. fibre (Vickerstaff).

If the affinity of these anionic compounds is entirely due to van der Waals attraction between the cellulose molecular chains and the aromatic nuclei of the anions then there should be a relationship between the affinity and some physical property of the anions connected with their van der Waals attraction. Two such properties have been considered here:

(i) The extinction coefficient. Peters and Sumner found a linear relationship between the affinities for cellulose of a range of vat dyes and the logarithms of their extinction coefficients. They argued that this identified van der Waals attraction as the source of the affinity, since Braude has proved a relationship between the cross-sectional area of the π-electron system in a molecule, on which its van der Waals attraction for a surface should depend, and the logarithm of the extinction coefficient.

(ii) The planar area of the anion. The van der Waals attraction might also be expected to depend upon the area of the dye anion in contact with the cellulose. This area was measured from models as the cross-section of the smallest enclosing rectangle round the anion, which is supposed to be lying flat on the cellulose surface.

Both plots are linear (Fig.14, Table 3). It is

therefore confirmed that the affinity of these dyes for cellulose originates in physical attraction alone. Peters and Sumner found that vat dyes with the benzoylamino-group have consistently higher affinities than those without when plotted on the basis described, and attributed the difference to hydrogen bonding between this group and cellulose, though they also mention that increased conjugation through this group in the enol-form could account for it (substitution of the hydrogen atom in the -CONH- group in the 2:3-hydroxynaphthoic acid anilides "Naphthol AS" compounds is known to reduce their affinity for cellulose considerably (see Vickerstaff). This would also be consistent with the physical attraction hypothesis. In Fig.14 it can be seen that the dyes with -CONH- groups do not have higher affinities than those without, in fact they have lower affinity.

CONCLUSIONS

Chitin can clearly adsorb solutes by hydrogen bonding as well as by ion-exchange and non-polar attraction. Its non-polar van der Waals adsorption properties for aromatic solutes in water are less intense than those of cellulose, presumably because it has a less regular molecular outline, thus preventing so close an approach of aromatic nuclei.

There is no evidence of any significant contribution by hydrogen-bond reaction in adsorption by cellulose. This agrees with conclusions from the refractive-index investigations on water-soluble model carbohydrates already mentioned and with monolayer experiments (Allingham *et al.*), which show that the hydroxy groups in cellulose may be too firmly bound to water for intermolecular bonding with solutes to be possible.

A long planar and conjugated molecule is essential for dyeing cellulose and this may be the result of the need for high van der Waals attraction to hold the dye molecule alongside the cellulose chain, where a layer of water is interposed. Regarding the influence of solute-substrate separation upon van der Waals attraction in such systems no quantitative information is available, but Coulson and Davies have shown theoretically that the interaction energy between pairs of polyene molecules varies by about the

third power of their length for intermolecular separations of about 4 Å. The separation of a planar anion for a cellulose molecule surrounded by a monolayer of water molecules is between 2 and 5 Å, and if the mutual attraction is dependent on conjugate chain length in dye anions as in polyenes, the reason for the substantivity of dyes for cellulose being dependent upon their planarity and high conjugation is clear.

The following general conclusions can be drawn from the present work.

1) Simple hydroxy-compounds, e.g. methanol and phenol, are adsorbed by both substrates in absence of water by hydrogen bonding.

2) Phenol, in aqueous solution, is adsorbed by chitin by hydrogen bonding, but is unadsorbed by cellulose because of preferential attachment of water to the substrate.

3) Simple sulphonic acids are not adsorbed by chitin when salt formation is prevented by an alkaline buffer, but under the same conditions some are adsorbed on cellulose.

4) Free sulphonic acids of different molecular size, and without hydrogen-bonding substituent groups, are adsorbed by chitin to approximately equal extents from

unbuffered solutions; on cellulose some of them are adsorbed, but since neither hydrogen bonding nor salt formation can take place, the adsorption must arise in van der Waals forces, in agreement with the fact that the affinity increases with increasing molecular area of the solute.

5) The effect of hydrogen-bonding groups in different solutes of similar molecular area applied at pH 9, is readily seen in a) anthraquinone-2-sulphonic acid, b) sulphonated alizarin and c) azo dyes containing three benzene nuclei. All these compounds are adsorbed to a similar extent by cellulose, irrespective of the nature of the substituent groups, but on chitin the adsorption differs : the hydroxy- or amino-groups promote stronger adsorption than on cellulose, but the presumably weaker quinone groups are insufficient to cause any adsorption at all.

6) Increase in linearity and conjugation of the solute molecule increases its affinity for cellulose, and it seems that the well-known effect of amido-groups in improving the substantivity of the dyes for cellulose is due to their action in enhancing conjugation.

7) The close approach of the solute molecule necessary to ensure van der Waals adsorption is helped more by the planar structure of the cellulose molecule than by the less planar structure of chitin.

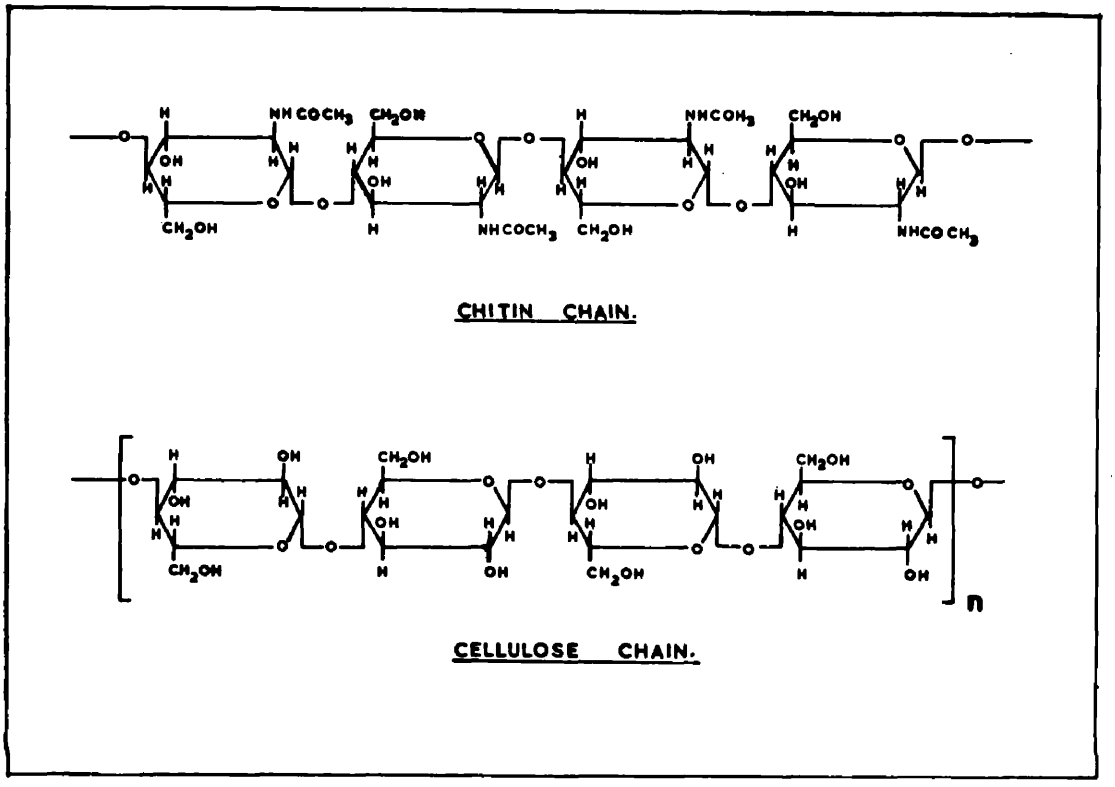


FIG. 1 CHITIN AND CELLULOSE CHAINS.

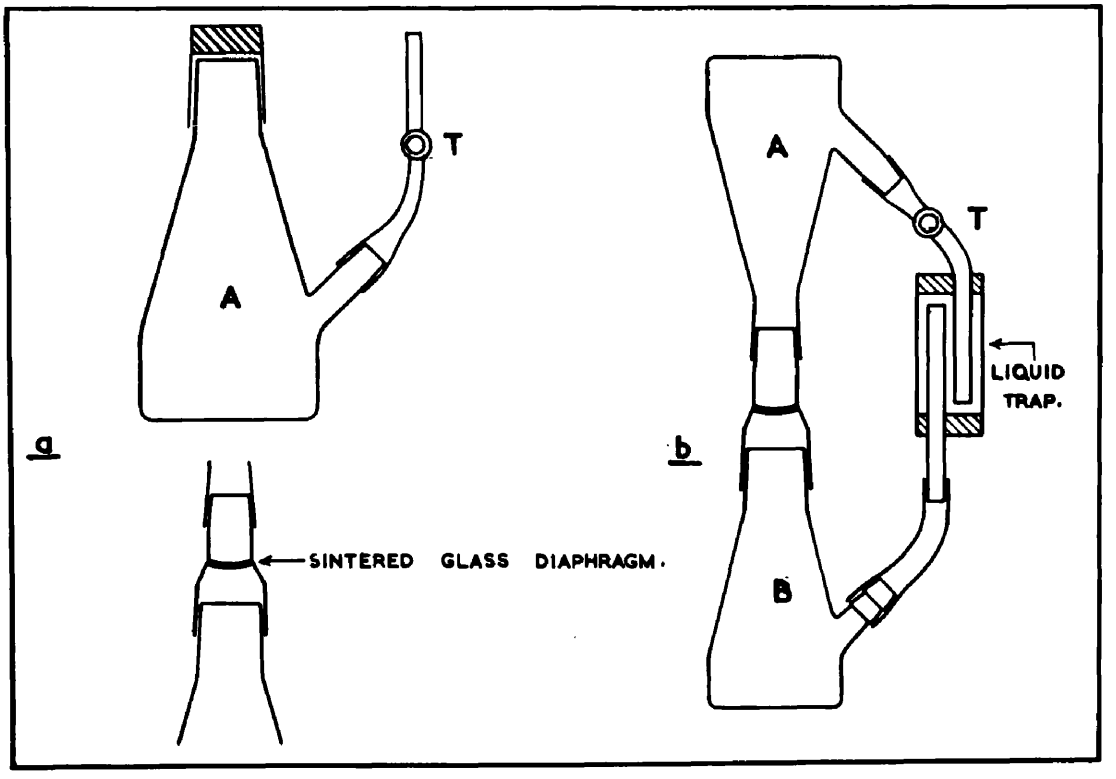


FIG. 2 APPARATUS FOR SOLUBILITY DETERMINATION.

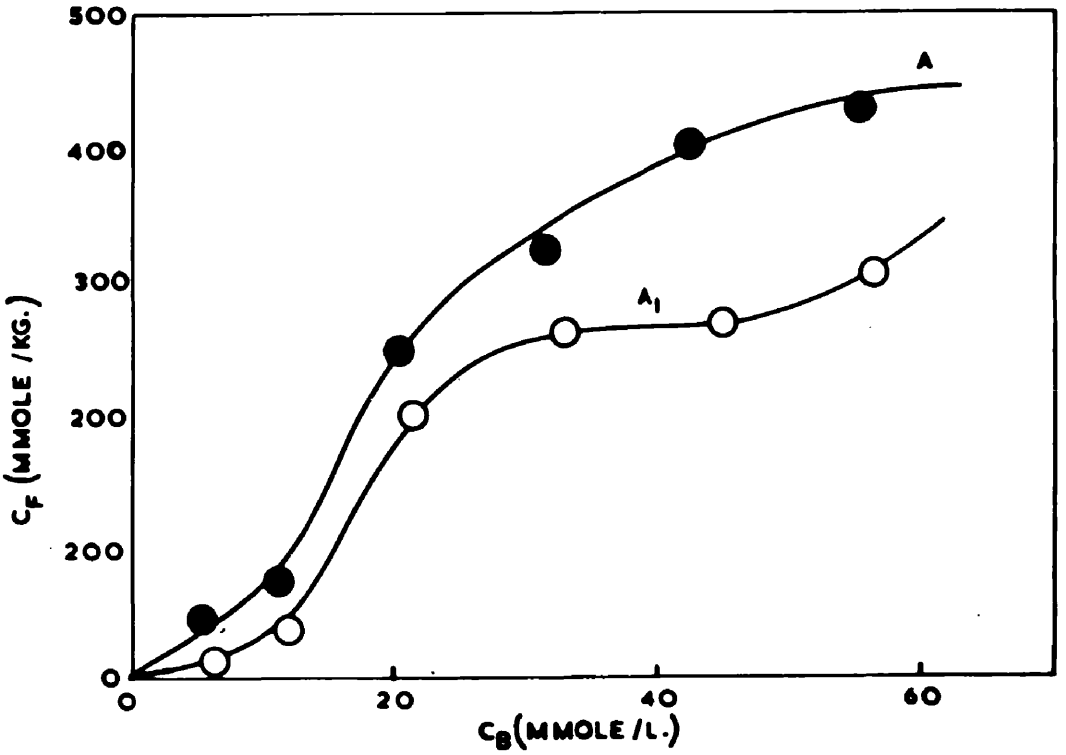


FIG. 3 ADSORPTION OF METHANOL FROM BENZENE AT 50°.

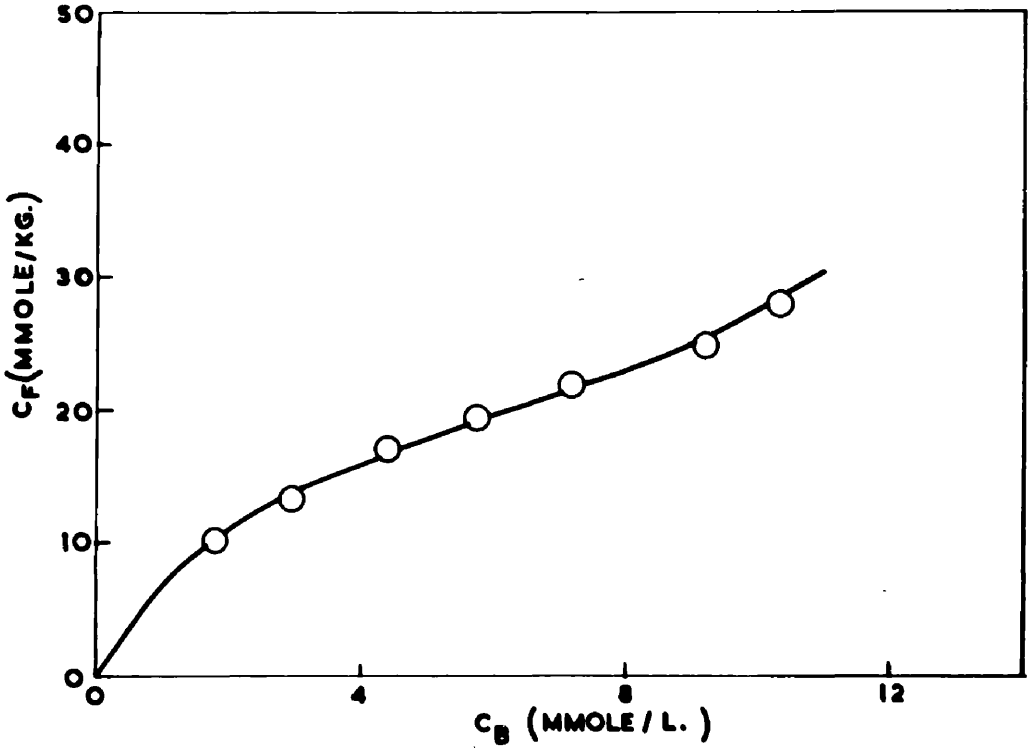


FIG.4 ADSORPTION OF PHENOL ON CHITIN FROM WATER AT pH 9 (50°).

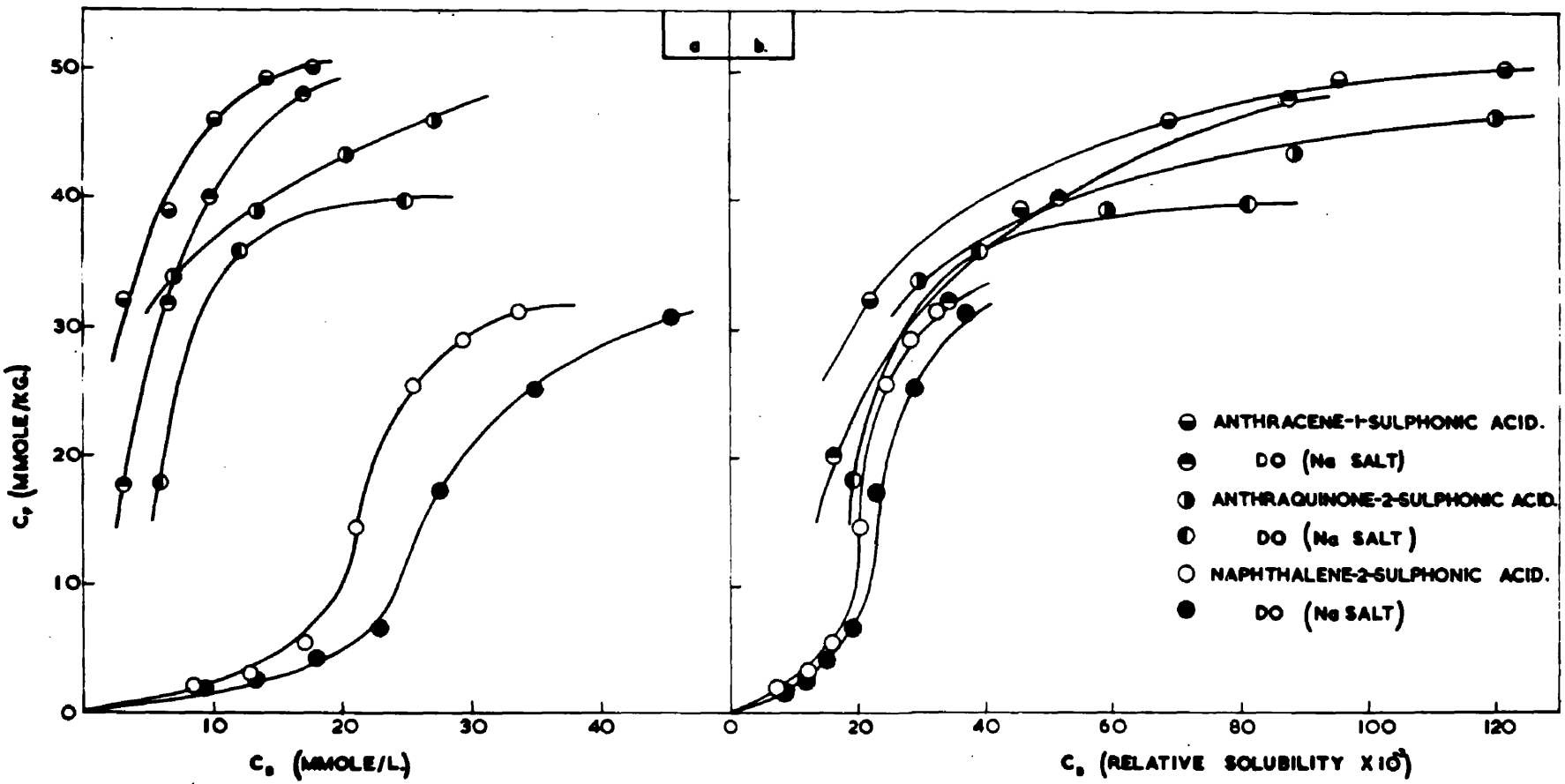


FIG.5 ISOTHERMS FOR ADSORPTION OF SULPHONIC ACIDS AND THEIR SODIUM SALTS BY CELLULOSE AT 50°.

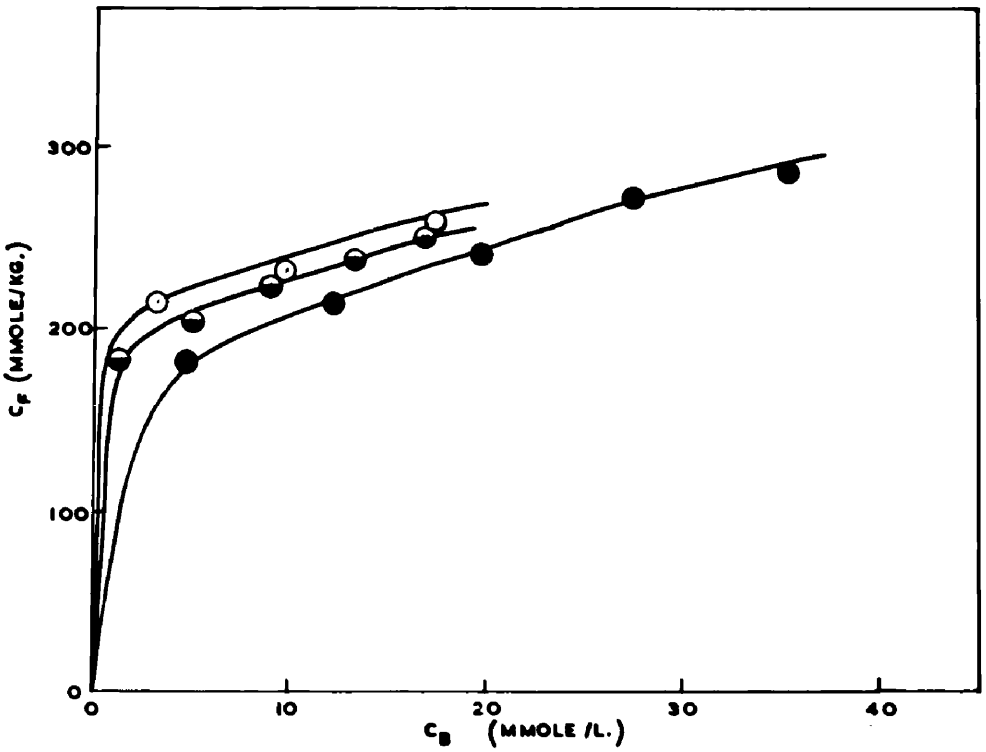


FIG.6 ADSORPTION OF SULPHONIC ACIDS ON CHITIN AT 50°.

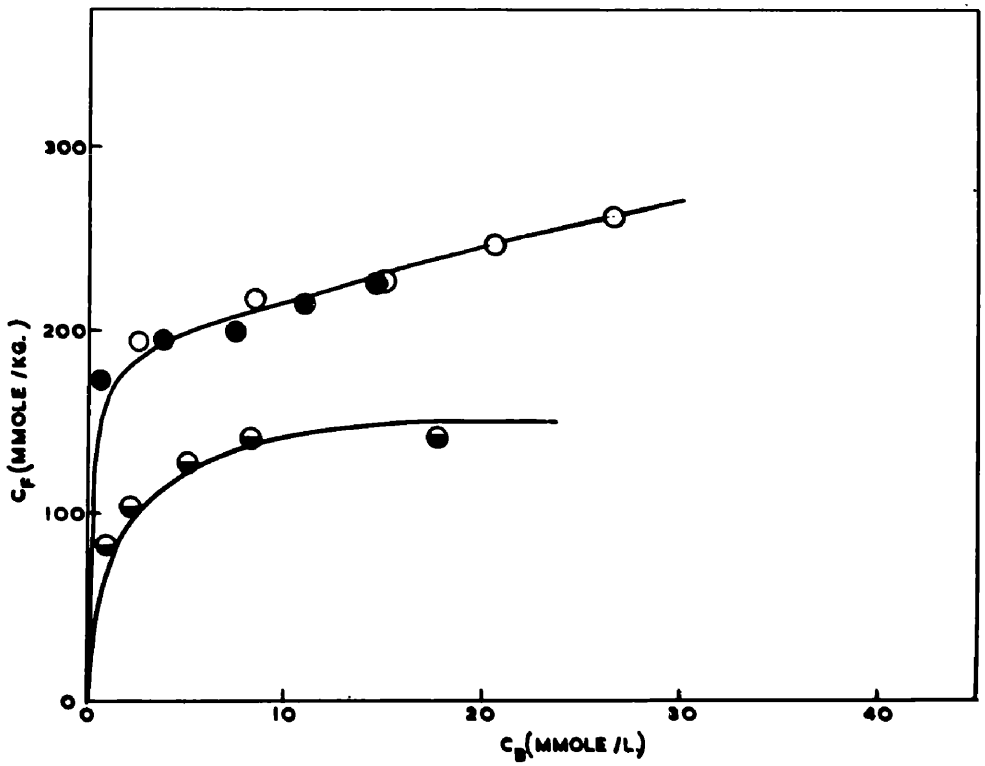


FIG 7. ADSORPTION ISOTHERMS ON CHITIN AT 50°.

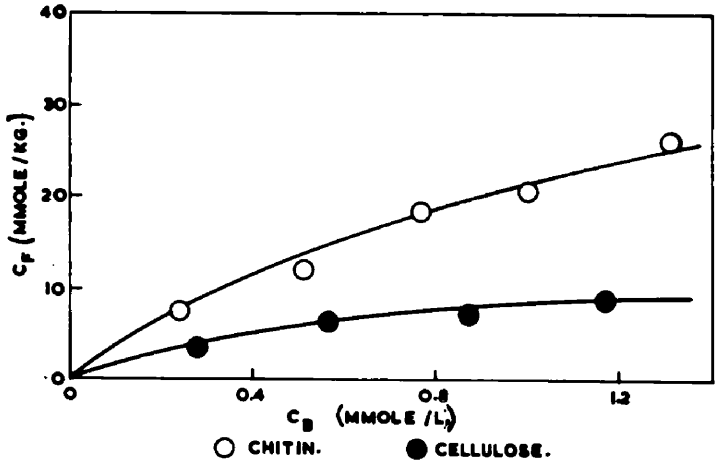


FIG.8 ADSORPTION OF SULPHONATED ALIZARIN FROM WATER AT pH 9.(80°)

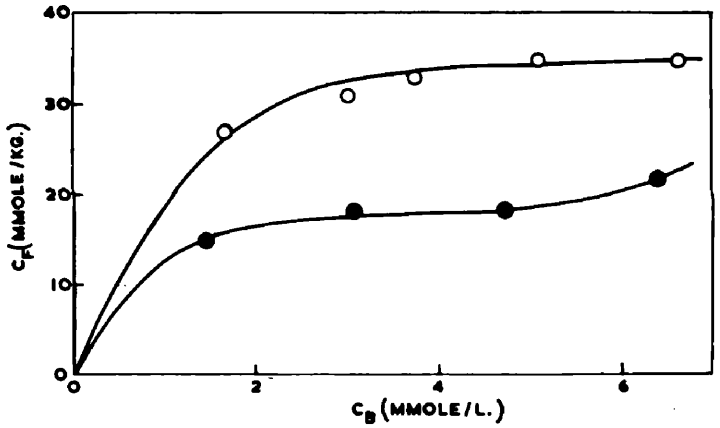


FIG.9 ADSORPTION ISOTHERMS ON CELLULOSE FROM WATER AT pH 9 (80°)

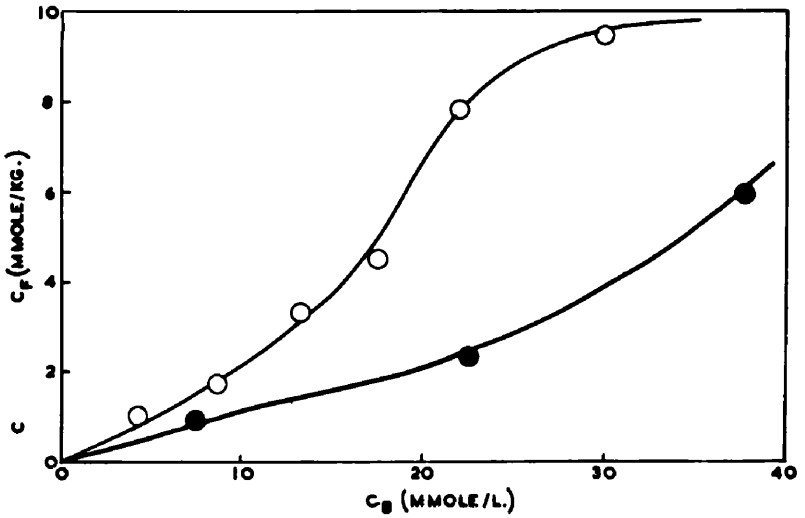
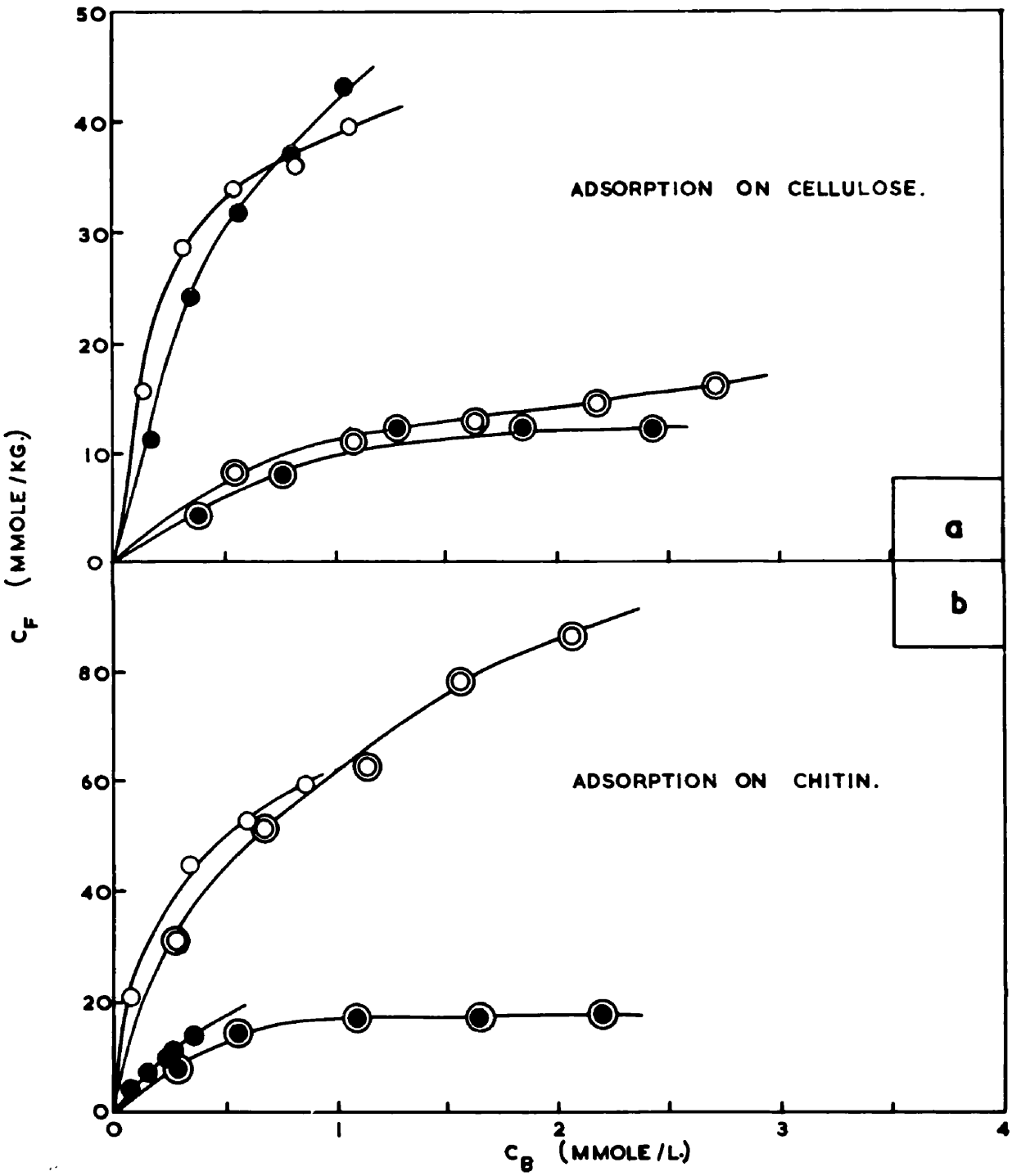


FIG.10 ADSORPTION OF 2-NAPHTHOL-6-SULPHONIC ACID ON CELLULOSE AT 50°.

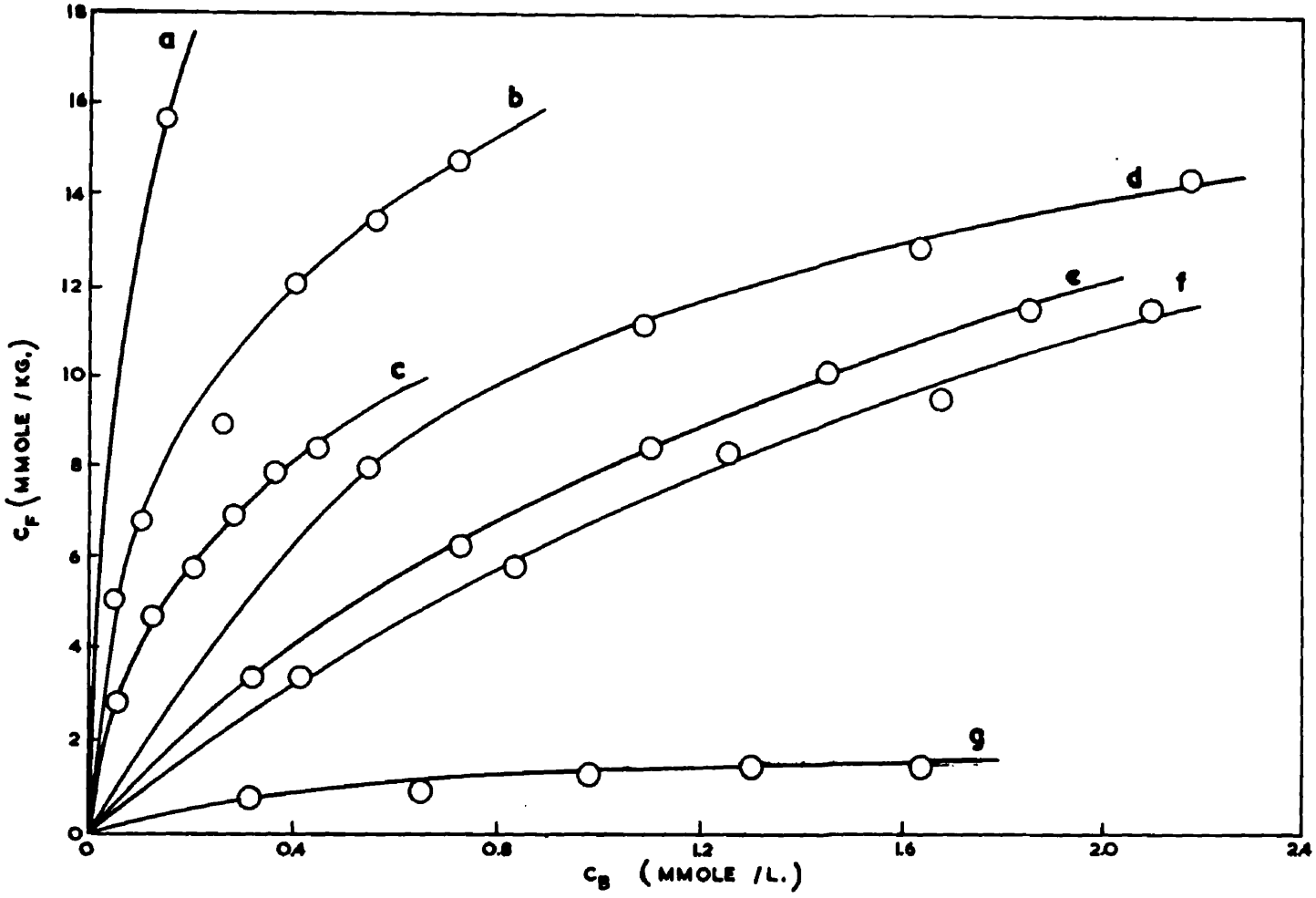


○ ● CONGO RED.(I.C.I). ◎ ◉ ANILINE ⟶ NAPHTHIONIC ACID.

WHITE CIRCLES = WATER SOLUTIONS.

BLACK CIRCLES = BUFFERED WATER SOLUTION (pH 9).

FIG.11 ADSORPTION ISOTHERMS ON CELLULOSE AND CHITIN AT 50°.



a) CONGO RED. (SEE FIG II)

b) PONCEAU 6RB.

c) ANILINE—2:5-DISULPHONIC ACID ⟶ NAPHTOL A.S.

d) ANILINE ⟶ NAPHTHIONIC ACID.

e) AZO GERANINE 2G.

f) SULPHANILIC ACID ⟶ 2-NAPHTHOL-6-SULPHONIC ACID.

g) 4-HYDROXYAZOBENZENE-4'-SULPHONIC ACID.

FIG. 12 ISOTHERMS FOR AZO COMPOUNDS ON CELLULOSE AT 50°.

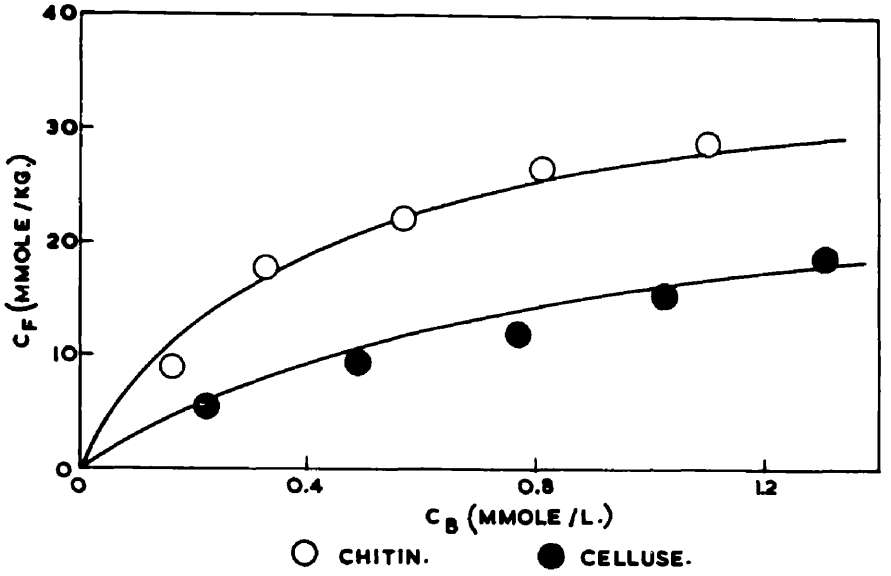


FIG.13 ADSORPTION OF FLAVANTHRENE LEUCO SULPHATE ESTER FROM WATER AT pH 9. (50°)

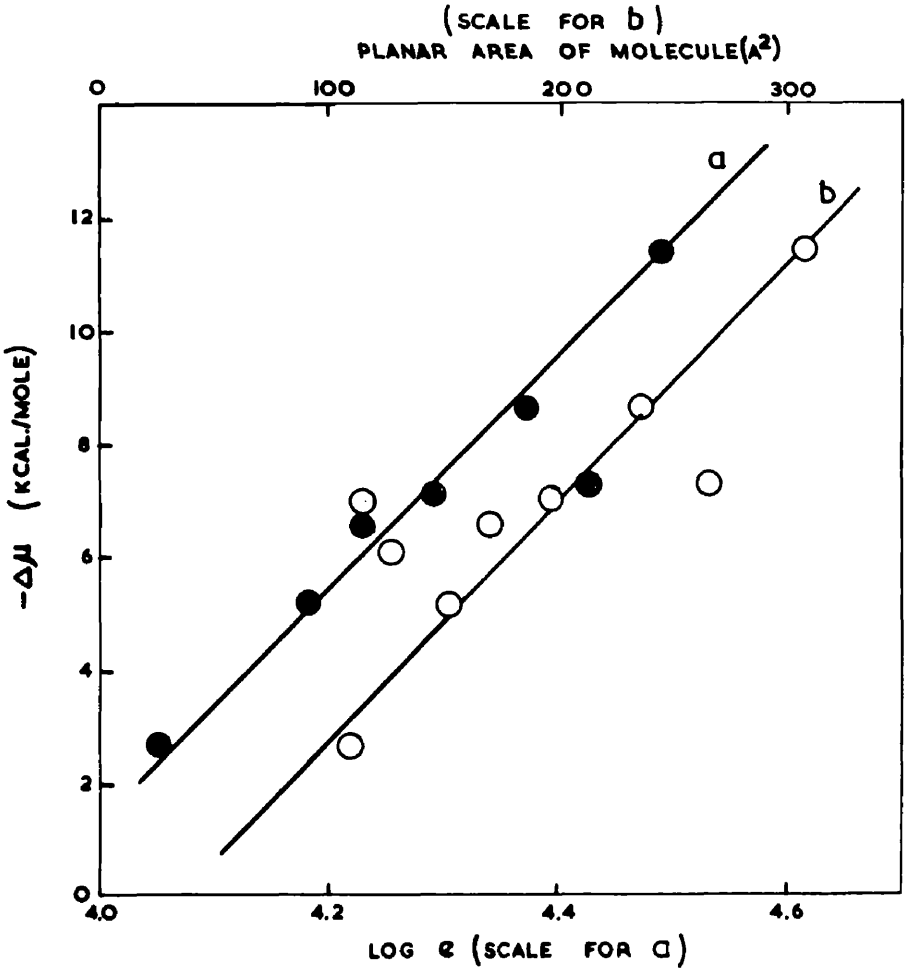


FIG.14 RELATIONSHIP BETWEEN PHYSICAL CHARACTERISTICS AND AFFINITY OF DYES FOR CELLULOSE.

TABLE 1.

1a - Adsorption experiments on cellulose.

Compound	Purity	Solvent	Result	Fig.No.
Methanol	A.R.	B	S	3
Phenol	A.R.	W	NS	
Resorcinol	A.R.	W	NS	
2-Naphthol	A.R.	El,W9	NS	
2-Hydroxyanthraquinone	R	W9	NS*	
Benzene sulphonic acid	A.R.	W	NS	
Naphthalene-2-sulphonic acid	100%	W	S	5
do. (Na salt)	R	W,El	S	5
Anthracene-1-sulphonic acid	97%	W	S	5
do. (Na salt)	R	W,W9	S	5,9
Anthraquinone 2-sulphonic acid	99%	W	S	5
do. (Na salt)	R	W,W9	S	5,9
2-Naphthol-6-sulphonic acid	91%	W,El	S	10
Alizarin-3-sulphonic acid (Na salt)	R	W9	S	8
4-Hydroxyazobenzene-4'-sulphonic acid (Na salt)	94%	W	S	12
Sulphanilic acid ⟶ 2-naphthol-6-sulphonic acid (Na salt)	98%	W	S	12
Azo Geranine 2G (I.C.I.)	91%	W	S	12
Aniline 2:5-disulphonic acid ⟶ naphtol A.S.(Na salt)	90%	W	S	12
Ponceau 6RB	92%	W	S	12
Aniline ⟶ naphthionic acid	92%	W,W9	S	11a,12
Congo Red	94%	W,W9	S	11a,12
leuco-Flavanthrone sulphate ester	C.S.	W9	S	13

TABLE 1 (Cont'd)

1b - Adsorption experiments on chitin.

Compound	Purity	Solvent	Result	Fig.No.
Methanol	A.R.	B	S	3
Phenol	A.R.	W9	S	4
2-Hydroxyanthraquinone	R	W9	NS*	
Benzene sulphonic acid	A.R.	W	S	6
do. (Na salt)	R	W9	NS	
Naphthalene-2-sulphonic acid	100%	W	S	6
do. (Na salt)	R	W9	NS	
Anthracene-1-sulphonic acid	97%	W	S	7
do. (Na salt)	R	W9	NS	
Anthraquinone-2-sulphonic acid	99%	W	S	7
do. (Na salt)	R	W	S	7
do. do.	R	W9	NS	
2-Naphthol-6-sulphonic acid	91%	W	S	6
Alizarin-3-sulphonic acid (Na salt)	R	W9	S	8
Aniline ⟶ naphthionic acid (Na salt)	92%	W,W9	S	11b
Congo Red	94%	W,W9	S	11b
leuco-Flavanthrone sulphate	C.S.	W9	S	13

Abbreviations:-

Solvents: B = Benzene; El = 50% Ethanol; W = Distilled water; W9 = Water buffered to pH 9.

Solutes: A.R.= Analytical reagent; R = Recrystallised; C.S.= Commercial substance.

S = adsorbed; NS = not adsorbed; NS* = doubtful adsorption.

All experiments were made at 50°C. All solutions were kept for about 20 hr. to reach equilibrium.

TABLE 2.

Comparison of results : cellulose and chitin

Compound	Solvent	C_B	C_F		Fig.No.
			Cellulose	Chitin	
Methanol	B	40	385	264	3
Phenol	W9	6	NS	20	4
Benzene sulphonic acid	W	20	NS	270	6
Naphthalene-2-sulphonic acid	W	20	9.5	258	5,6
do. (Na salt)	W9		--	NS	5
Anthracene-1-sulphonic acid	W	20	51	245	5,7
do. (Na salt)	W	20	49	--	5
do. do.	W9	4	34	NS	9
Anthraquinone-2-sulphonic acid	W	20	43	245	5,7
do. (Na salt)	W	20	39	151	5,7
do. do.	W9	4	18	NS	9
2-Naphthol-6-sulphonic acid	W	20	7	247	10,6
Alizarin-3-sulphonic acid (Na salt)	W9	1.2	9	23.5	8
Aniline ⟶ naphthionic acid (Na salt)	W	0.5	7	44	11a,11b
do. do.	W9	0.5	6	12	do.
Congo Red	W	0.5	33	50	do.
do.	W9	0.5	30	18	do.
leuco-Flavanthrone sulphate ester	W9	0.6	6	24	13

N.B. C_B = Equilibrium bath concentration in m.mole/litre.

C_F = Amount adsorbed in m.mole/kg. of substrate.

Solvent abbreviations as in Table 1.

TABLE 3.

Compound	$-\Delta\mu$ (k.cal/ml)	Area (A^2)	log ϵ
Congo Red	11.4	308	4.4886
Ponceau 6RB	8.6	236	4.3729
Aniline-2:5-disulphonic acid naphtol A.S.(Na salt)	7.8	267	4.4265
Aniline ⟶ Naphthionic acid (Na salt)	5.1	154	4.1875
Azo Geranine 2G	7.0	196	4.2923
Sulphanilic acid ⟶ 2-naphthol-6-sulphonic acid (Na salt)	6.5	170	4.2304
4-Hydroxyazobenzene-4'-sulphonic acid (Na salt)	2.8	112	4.0492
Naphthalene-2-sulphonic acid (Na salt)	1.28	88	
Anthracene-1-sulphonic acid (Na salt)	6.56	117	
Anthraquinone-2-sulphonic acid (Na salt)	6.1	126	

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PART III

ADSORPTION STUDIES ON GRAPHITE

INTRODUCTION

The mechanism of adsorption of organic compounds from solutions by inorganic solids has been little studied and what has been reported is not very conclusive. The reaction of acid and basic dyes towards glass was investigated by Lenoir, who concluded that while acid dyes are not adsorbed, basic dyes appeared to be adsorbed by some acid-base reaction. He also suggested that dyes forming true solutions are adsorbed as monolayers, while those forming colloidal solutions are adsorbed in multilayers. Recent work in this laboratory (Jain) seems to show that in the adsorption of basic dyes by silica a monolayer of dye micelles is formed. Harkins and Gaus (1935) adsorbed oleic acid from benzene solution on silica and titania powders and found that if a monolayer was assumed then the adsorbed molecules must have been close-packed and standing on edge perpendicular to the surface.

On the assumption that vapour phase absorption produces layers one molecule in thickness, Langmuir obtained his well-known relation for the adsorption of a gas at the surface of a solid. The surface is supposed to consist of a number of sites each of which can accommodate a molecule of the gas. If N is the number of such sites in unit area of the surface and θ is the fraction occupied by gas

molecules at equilibrium, the rate of adsorption of the gas, being proportional to its pressure and to the number of occupied spaces will be $N(1 - \theta)p$, and the rate at which adsorbed molecules leave the surface, to the number of occupied spaces, viz. $N\theta$. At equilibrium the rates of adsorption and of desorption must be equal, so that $KN(1 - \theta)p = N\theta$, or $\theta/(1 - \theta) = Kp$, where K is a constant which depends on the temperature.

Bartell and Miller (1922), in adsorption studies on silica and charcoal, found that salts of basic dyes become acid in solution due to preferential adsorption of large organic cations, while those of acid dyes become alkaline. It was also found that the amount of the dye adsorbed depends on the charge on the adsorbent surface relative to that of the solution in which it is immersed, and that in the case of adsorption of basic dyes on silica the quantity adsorbed depends on the pH of the solution, decreasing as the pH increases. Freundlich also found that positively charged surfaces will preferentially adsorb anions while negatively charged surfaces will adsorb cations.

Investigation of adsorption on graphite by Macaulay showed that both basic and acid dyes are adsorbed. This interesting fact obviously creates difficulties if adsorption is to be explained only by ionic attraction.

Graphite acquires a negative charge when in contact

with water (Macaulay). According to Helmholtz (1879), at a solid-liquid interface there exists an electrical double layer consisting of two differently charged layers. Latterly, this theory was modified by Stern, who suggested that the diffuse double layer comprises two parts; one of which consists of ions, one molecule deep adhering close to the solid surface and having a sharp fall in potential. The resulting electric field at the solid surface creates a preferential attraction of oppositely charged ions and a gradual fall of potential into the bulk of the liquid. This region of gradual potential fall constitutes the second, diffuse layer.

The negative potential of graphite in water may be due to the firm attachment of hydroxyl ions to the crystal surface, with an equivalent number of positive ions, some held in the fixed layer and the remainder in the diffuse layer. The negative charge could thus be responsible to some extent for the adsorption of dyes on graphite but it is evident that if such is the case only positive ions, i.e. basic dyes, will be adsorbed unless of course there is the complication of mixed adsorption.

The work of Perrin, Haber and Klemensiewicz, Cameron and Oettinger and others has shown that both H^+ and OH^- ions impart to the surface a charge of the sign they carry. They assumed the operation of some force holding these ions on

the surface and considered that an adsorbed layer of water is held at the surface as a result of which the surface may function as a compound and reversible type of hydrogen and hydroxyl electrode. This view was supported by Bartell and Miller (1924) who gave the following explanation for adsorption on charcoal -

1) In water solution H^+ and OH^- ions are held adsorbed in a more or less definite and regular arrangement.

2) The hydroxyl ions thus held can be displaced by almost any anion and are most readily displaced by organic anions.

3) The hydrogen ions thus held can be displaced to any appreciable extent only by cations larger than hydrogen.

4) Radicals containing hydrocarbon groups readily displace either H^+ or OH^- ions. The larger the hydrocarbon chain the greater the adsorption.

By increasing the concentration of solution, the adsorption also increases, but it seems reasonable to assume that the adsorption will reach a limiting value, which can be examined by a modified version of Langmuir's isotherm, assuming a monomolecular film. Paneth suggested that in the adsorption of dyestuffs by diamond a single layer of adsorbed molecules is not exceeded. The basis for this suggestion was experiments in which he adsorbed methylene

blue on crystals and then calculated the surface area of the crystals by two methods, microscopically, and with radioactive isotopes.

This technique suggested itself as a method of measuring surface area, provided that the area and orientation of the adsorbed molecules are known. If the adsorption is due to non-polar forces, it would be expected that large organic molecules would lie flat on the solid surface, because the attraction energy increases with the size of the molecule, and is inversely proportional to the cube of the distance between the centre of the molecule and the surface (Boer). Hendrichs found that large organic molecules appear to lie flat on the surface.

Dyes were adsorbed on activated charcoal by Valasco and he found that monolayers were formed, but at higher concentrations of the solute he got condensation which he suggested was multilayer formation. He also found that adsorption decreases with the rise of temperature.

Wolf and Riehl found that very finely divided graphite has adsorptive powers almost equal to those of active carbon; they supposed that free valence bonds at the crystal surface are responsible and that the edges of the flakes may be more active than the flat sides; thus graphite exposed to radium emanation is more radioactive at the edges than elsewhere.

PRESENT WORK

This work describes a study of the mechanism of adsorption of certain organic compounds by graphite. The adsorptive power of charcoal is well known, but the mechanism by which it adsorbs solutes from solution has not received so much attention as has its vapour phase adsorption properties. Graphite was chosen here because it is a fairly simple solid material having a known crystal structure which is unlikely to complicate the results by chemical reaction with the solutes and thus the mechanism of adsorption should be more readily detected than by using, e.g. fibres. Graphite can be obtained in a high state of purity and is physically homogeneous and non-porous, so that problems of diffusion of solutes into pores do not arise. It is also less liable than charcoal is to be contaminated with potential hydrogen bonding groups (Studebaker et al.). It was also hoped that the results of this work would supplement and help in interpreting that done on cellulose.

A number of isotherms and rate curves for basic and acid dyes on graphite were determined in this laboratory by N. Macaulay (B.Sc. thesis, 1951), N. W. Macmillan (1952), D. C. McAllister (B.Sc. thesis, 1955), and A. G. Halliday (B.Sc. thesis, 1955). Some of their work has been repeated

by the present writer. All the data in this section of the present thesis are from experiments by the author.

EXPERIMENTAL

The substrate used in this investigation was graphite, which was supplied in a pure state (0.43% ash) by the General Electric Co. Ltd.

Purified solvents were used, the benzene and iso-octane were stored over sodium and all the water used was distilled.

The solutes used were purified and estimated as mentioned above (Part I and II). The following are the compounds used

Non-ionic dyes.

I - Aniline ——→ 2-naphthol.

Aromatic sulphonic acid.

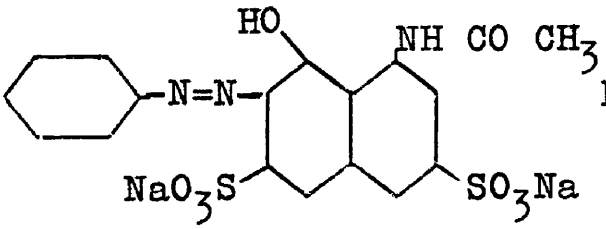
II - Benzene sulphonic acid.

III - Naphthalene-2-sulphonic acid

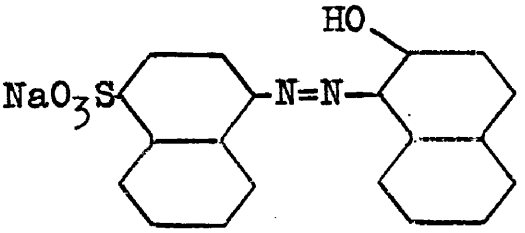
Sulphonated azo-dyes

(shown overleaf)

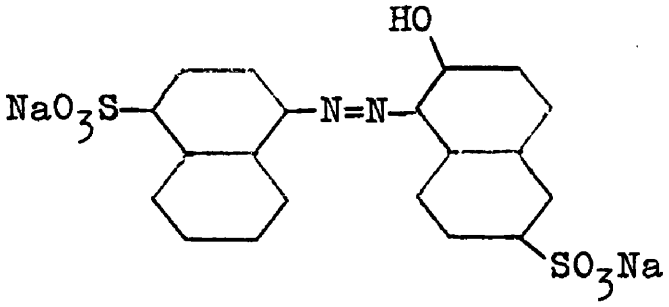
Sulphonated azo-dyes.



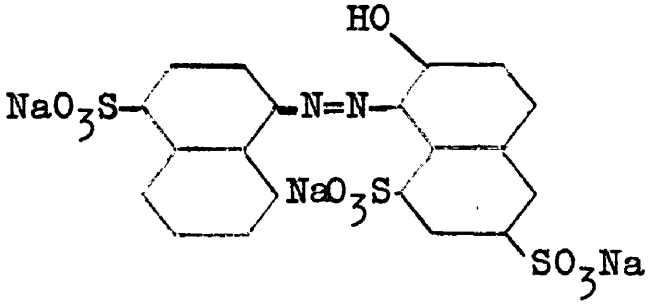
IV - Azo Geranine 2G.



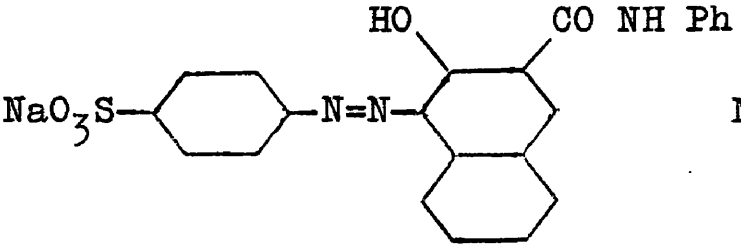
V - Naphthalene Red J.



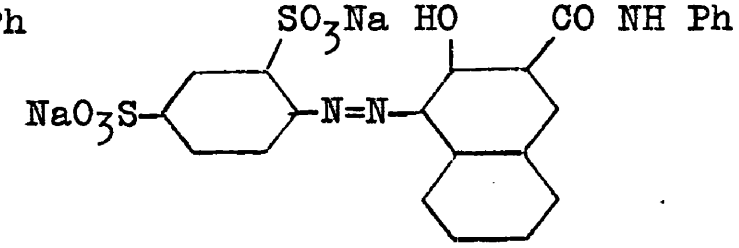
VI - Naphthalene Red EAS



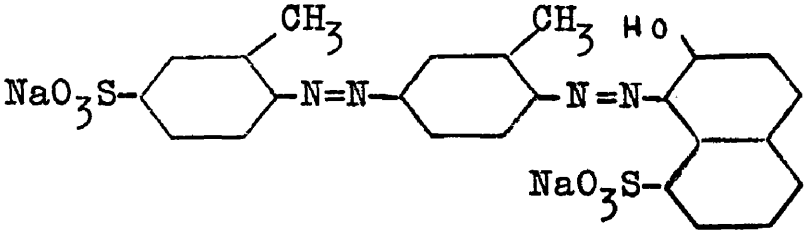
VII - Naphthalene Scarlet 4R



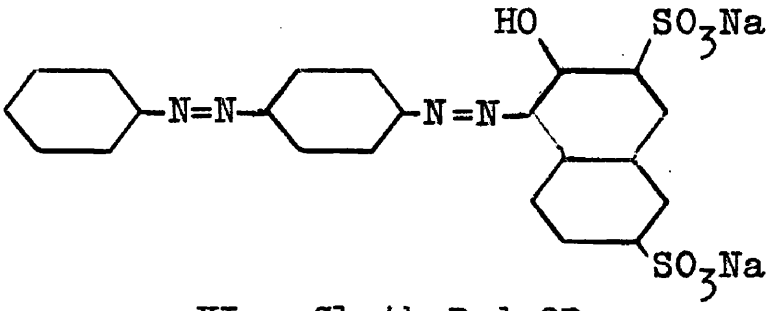
VIII



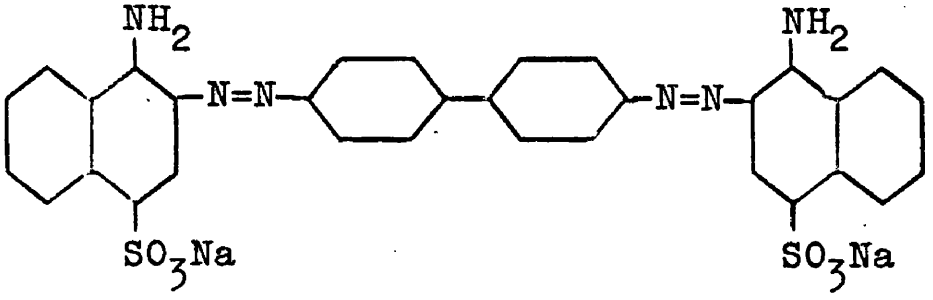
IX



X - Ponceau 6RB

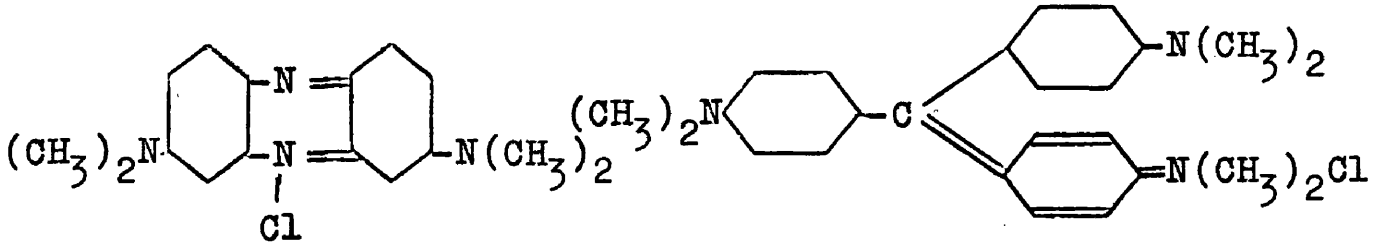


XI - Cloth Red 2R



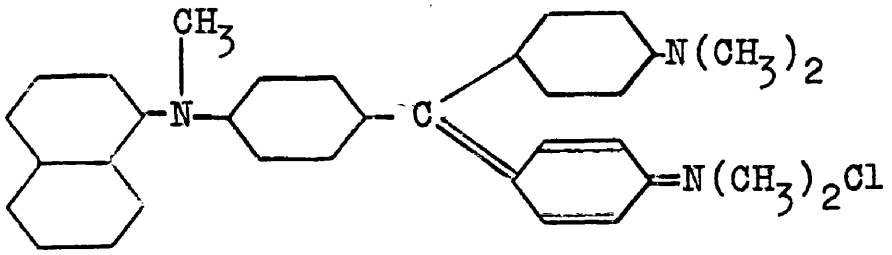
XII - Congo Red.

Basic dyes.



XIII - Methylene Blue B.

XIV - Methyl Violet 10B.



XV - Victoria Pure Blue BO.

Sugars. D-Glucose

Sucrose

Measurement of Particle Size of Graphite.

In order to calculate the apparent number of layers adsorbed on graphite, its surface area must be known. The average particle size was measured using a Fairs graticule (cf. Pidgeon and Dodd) and from the data the surface area per kg. was calculated. It was assumed first that the particles are spherical in shape, but using the electron microscope to determine the particle thickness it was found that the particles are thin flakes with irregular edges. The average height of the graphite particles was estimated as follows : a sample of the particles was dispersed in distilled ethyl alcohol and sprayed on a supporting nitrocellulose film mounted on a grid for electron microscopic investigation. The sample was shadow cast with gold and the average height of the particles was measured as a function of the length of the shadow (Fig.1). The electron micrographs were taken in a Metropolitan Vickers E.M.3 Electron Microscope. Readings and calculation are given later.

Measurement of the surface area by the air permeability method (Lee and Nurse) was attempted but owing to the lack of consistent results the attempt was abandoned.

Molecular Area of Compounds Used.

Another figure necessary for the calculation of the

number of layers adsorbed is the area of the molecules corresponding to various positions of orientation. This was measured using molecular models for measuring the volume of the smallest enclosing rectangular box.

The apparent number of layers of molecules was calculated for each compound from a knowledge of the molecular area, the amount of solute adsorbed and the total surface area of graphite (Table 2).

Sample Calculations.

a) Surface area calculation.

Density of graphite (measured) $= 2.2$ g./cm^3.

Average particle radius (r) (Pidgeon and Dodd method) $= 0.442 \times 10^{-3}$ cm.

$$\pi r^2 = 3.14 \times (0.442)^2 \times 10^{-6} \text{ cm}^2.$$
$$= 0.613443 \times 10^{-6} \text{ cm}^2.$$

Average height of particles (from electron microscope measurements)
$$= 0.414 \times 10^{-4} \text{ cm.}$$

Vol. of average particle $= 0.613443 \times 0.414 \times 10^{-4} \times 10^{-6}$ cm^3.
$$= 0.2539 \times 10^{-10} \text{ cm}^3.$$

Mass of average particle $= 2.2 \times 0.2539 \times 10^{-10}$ g.
$$= 0.5586 \times 10^{-10} \text{ g.}$$

Number of particles per g. $= {}^1/_{0.5586 \times 10^{-10}}$ particles
$$= 1.79 \times 10^{10} \text{ particles}$$

Surface area per g. $= 1.79 \times 10^{10} \times 1.34 \times 10^{-6}$ cm^2.
$$= \underline{2.4 \times 10^4 \text{ cm}^2}.$$

Surface area per kg. $= \underline{2.4 \times 10^7 \text{ cm}^2}.$

b) Specimen calculation of number of layers adsorbed (aniline ⟶ 2-naphthol)

Area of graphite per kg. = 2.4×10^7 cm^2.

= 2.4×10^{23} $\mathring{A}^2$

Planar area of the dye = 121.5 $\mathring{A}^2$

Area of 1 mmole = $\frac{121.5 \times 6.02 \times 10^{23}}{1000}$ $\mathring{A}^2$

= 0.73×10^{23} $\mathring{A}^2$

Number of mmoles adsorbed per kg. (at first isotherm inflection)

= 5.2 mmole/kg.

Total area of dye adsorbed = $5.2 \times 0.73 \times 10^{23}$ $\mathring{A}^2$

Number of layers = $\frac{3.79 \times 10^{23}}{2.4 \times 10^{23}}$

= 1.6

RESULTS AND DISCUSSION

Rates of adsorption and their significance.

Rate measurements demonstrate a rapid adsorption of all the compounds studied. Adsorption from solutions down to 10^{-4} M. is complete in $<$ 20 min. (Fig.2). The short period required to attain equilibrium suggests that adsorption is entirely superficial, i.e. that the adsorbed molecules do not penetrate any pores or fissures in the solid. This was further confirmed by Macaulay as follows: a sample of graphite was separated by elutriation into three portions of different average particle size. The maximum amount of a basic dye adsorbed by each sample was then plotted against l, l^2 and l^3 respectively, where l is the average linear dimension of the particles of the sample. The plot of l^2 is linear while those of l and l^3 are not. Hence the adsorption is proportional to the superficial area alone and not to the volume; proportionality to l^3 would of course imply adsorption in internal pores.

Closer study of the rate curves shown in Fig.2 reveals that they can be divided into two classes (Table 1), in one of which 75% of maximum adsorption is complete in $<$1 min. at room temperature, whereas in the other it requires up to about 5 mins. Further, the rapidly adsorbed dyes are all either acid dyes with small molecules or with ionic groups

'symmetrically' placed, i.e. placed at either end, or are basic dyes; whereas the slowly adsorbed dyes are 'unsymmetrical', i.e. their ionic groups are placed at one end only. The unsymmetrical compounds are clearly more likely to aggregate into ionic micelles by association of the hydrophobic portions of their molecules. This type of association is less likely in the symmetrical compounds because of the repulsive effect of the ionic groups at either end of their molecules. This can readily be demonstrated qualitatively by the fact that the symmetrical dye Ponceau 6RB spreads much more rapidly on filter paper than the unsymmetrical one, Cloth Red 2R, which has a similar aromatic structure.

In all normal dyeing systems diffusion of the dye molecules in the internal pores of the substrate is the rate controlling factor in attaining equilibrium. In the present case there is no internal diffusion and the rate controlling factor is the speed at which the adsorbed species can be supplied to the graphite surface, and in the case of anionic dyes, the species must be individual dye anions and not micelles. With the non-colloidal acid dyes, which exist as single ions or small aggregates only, there is an ample supply of single anions for adsorption and the rate is high. With the colloidal dyes there is a much smaller concentration of single anions, and clearly their supply to the graphite

surface must depend upon the rate at which they are detached from the micelles.

Unlike anionic dyes, the cations of basic dyes will be readily attracted to the negatively charged surface of graphite and consequently the basic dyes all have high rates of adsorption.

Sugars are also adsorbed at a high rate presumably due to the lack of charge and hence facilitation of attraction to graphite by physical forces.

Apparent heat of adsorption.

The adsorption of cationic dyes has no measurable temperature coefficient (Fig.8), thus it resembles ion-exchange adsorptions (Giles et al., 1954). The mechanism may be suggested to be the replacement of a hydrogen ion in the electrical double layer at the graphite surface by a dye cation (Bartell and Miller, 1924). Both ions in their adsorbed and unadsorbed state will be surrounded by an atmosphere of oriented water molecules. The adsorption in this case would not be accompanied by any formation or breakage of bonds on any disturbance of the electronic structure of the solute molecule.

The adsorption of the anionic compounds however is exothermic (Fig.3 and 4). It seems very unlikely that any solute-substrate bonds are formed. The hydrogen bonding

theory is unlikely here unless traces of atmospheric oxygen present on the surface are responsible for bond formation. In this connection it has been noted in the case of charcoal (Adam), which has been sufficiently oxidised, that molecules of higher molecular weight can be adsorbed than could be adsorbed before oxidation, but this may be due to the widening of the pores by removal of material from smaller pores. On non-porous graphite such a reason does not seem sufficient to explain the adsorptive capacity. Lowry and Morgan found that there is no relation between the degree of oxidation and the amount of gas adsorbed on graphite. Their data obtained were in general agreement with the hypothesis that any treatment which increases the ratio of surface to mass of a solid adsorbent, will increase its adsorptive capacity.

The adsorption of anionic dyes by cellulose, which is thought to be non-polar (Vickerstaff) is also exothermic and so is the partly non-polar adsorption of direct dyes by chitin.

Orientation of adsorbed molecules.

The specific surface area calculated from the electron micrographs can be considered a minimum, because it does not take account of any irregularities, e.g., edges of stepwise portions of the graphite flakes. A study of the isotherm

data (Table 2) does in fact suggest that the actual surface area available for adsorption is about 50 percent higher than the value obtained physically.

Some of the isotherms show inflections, and in cases where the solubility of the dye permits high concentrations of solution to be used, they rise ultimately to very high values, far higher than can be accounted for by a normal monolayer. In drawing the conclusions described below it is assumed that (with one exception (dye IV), where the low position of the first inflection makes an analytical error more likely) the first inflection (measured by the 'point B' method of Brunauer) represents the completion of the monolayer. This, as will be seen, enables a logical explanation of all the data to be given. Subsequent inflections may be due to a rearrangement of adsorbed molecules with some interlocking occurring, or to the presence of a proportion of micelles. The very high adsorptions ultimately reached are attributed to the formation of monolayers of ionic micelles or aggregates. Spectroscopic tests and measurement from isotherms show that basic dyes are adsorbed on silica entirely in this form from concentrated solutions, no initial inflections in the isotherms being noticed (Jain). The following are the detailed conclusions reached regarding the orientation of adsorbed solutes -

a) Sugars.

Glucose and sucrose were used at first to avoid the complication of anionic charge in measuring monolayer areas. Adsorption at the concentrations used was however found to be far too high for monolayer formation (Fig.5). It may be that in the solutions used the molecules are associating together with water in some form of large aggregated system and a monolayer of these aggregates is being formed, but it is admittedly difficult to understand such an adsorbed system. Clearly the facts open up an interesting new field for research (cf., also the unaccountably high adsorption of hydrochloric acid by chitin (above)).

b) Non-ionic azo-dye. (I)

This is adsorbed flat with all its aromatic nuclei in contact with the surface. Adsorption is complete from the aliphatic solvent but from benzene a complete monolayer is not formed, on account of the competitive effect of the solvent itself, which because of the shape of its molecules, should be firmly attached to graphite (Fig.6).

c) Mono-sulphonates. (II, III, V)

These form condensed monolayers in which the molecules probably stand perpendicular to the surface, the sulphonate groups being in the water and the unsulphonated end of the molecules nearest the graphite surface.

The large molecule with the -CONHPh group (VIII) is not adsorbed as single molecules, but apparently as multilayers or a monolayer of micelles. The isotherm is of 'HA' type (Fig.7 (IIIa)) indicating very high affinity, and the dye was observed to form colloidal solutions at high concentration.

d) Disulphonates. (IV, VI, X, IX, XI, XII)

When the two ionic groups are situated along one side or at opposite ends of the dye molecule (IV, VI, X, XII) the latter is oriented edge-on, but if they are both at one end (IX, XI), it is end-on, as with the mono-sulphonates.

e) Trisulphonates. (VII)

In this case where the sulphonate groups are widely separated, a flat orientation seems likely, and the data are in agreement with this.

f) Basic dyes. (XIII, XIV, XV)

Similar principles govern the orientation of basic dyes to those described for anionic dyes. It is assumed that resonance makes the substituted amino-groups equivalent, and therefore, as expected from a study of their molecule shapes, Methylene Blue (XIII) is oriented edge-on and Victoria Pure Blue (XV) end-on, the ionic groups presumably

being towards the water. The triphenylmethane derivatives do not have planar molecules, and a model shows that the Methyl Violet molecule (XIV) cannot lie flat with each amino-group in contact with or equidistant from the surface. It appears to orient edge-on.

Isotherm shapes.

The initial portions of the isotherms represent three of the four types in Giles and MacEwan's classification of solution-adsorption isotherms, viz. 'S', 'L' (a normal 'Langmuir') and 'HA' (high affinity) (cf., Fig.7 (IIc, Ia and IIIa). These three shapes of curve were stated to represent a progressive increase in the ability of the solute to displace solvent molecules at the substrate surface and thus to be adsorbed thereto.

The data in Table 3 show that as the number of sulphonate or other ionic groups is decreased, the curves change in type from S to L to HA. In fact with two exceptions the L curve is not obtained unless only a single sulphonate group is present; the two exceptions are Cloth Red 2R, in which the very large unsulphonated aromatic system will clearly give the dye added stability in a condensed monolayer, and Congo Red, which has an exceptionally large conjugate system. Unlike the other dyes used here Congo Red has in fact high affinity for cellulose, probably for the same reason, viz.

high physical attraction for the surface of the substrate, in this case the cellulose chain molecules.

Affinity measurement.

On the assumption that the anionic dyes are adsorbed as monolayers covering the whole surface and that there is no adsorption at specific sites, the following expression may be used to calculate the affinity (Vickerstaff)

$$-\Delta\mu = RT \ln \frac{\theta_D}{1-\theta_D} + z\,RT \ln \frac{\theta_{Na}}{1-\theta_{Na}} - RT \ln [D]_S - z\,RT \ln [Na]_S$$

where z is the number of negative charges on the anion, θ_D and θ_{Na} are respectively the fraction of the total available surface covered at equilibrium by dye anions and sodium ions respectively, and $[D]_S$ and $[Na]_S$ are the activities (assumed equal to the concentrations) of the dye anions and the sodium ions in the external solution at equilibrium.

Table 4 shows values of the affinities thus calculated on the assumption that the first inflection in the isotherm represents the completion of a monolayer and for $\theta = 0.75$ of this value. Calculations would be simpler if a value for θ of 0.5 could be used, but on account of the shape of some isotherms this is not possible.

As in the case of adsorption on cellulose, discussed

above, and for the same reason, viz. that there should be a direct relationship between the affinity, which is thought to originate entirely in the van der Waals attraction between the flat surface of graphite crystal and the aromatic nuclei in the dye anion, the affinity values have been plotted against both log e (extinction coefficient) and the area of the dye anion (Fig.9). The area of the anion is measured from models as the smallest rectangle enclosing the cross-section of the anion projected on to the graphite surface in the orientation assumed for the first inflection of the isotherm in the case of dyes forming monolayers (Table 2). It will be observed that both these methods of plotting demonstrate a linear relationship (although there is a considerable scatter of points). This may confirm the validity of the hypothesis that the origin of affinity is mainly van der Waals attraction forces.

CONCLUSIONS

1) Adsorption on graphite seems to be entirely superficial. This is shown by the short period required to reach equilibrium.

2) The rate-controlling factor in adsorption is the speed at which the adsorbed species can be supplied to the graphite surface.

3) Adsorption of basic dyes is due to electrostatic attraction, while that of anionic dyes and non-ionic compounds is due to physical forces of attraction.

4) Basic dyes are adsorbed quickly due to their attraction for the negatively charged surface of graphite. Acid dyes are adsorbed quickly when they form true solutions, but when they are in the form of micelles the rate is slower, and it seems that equilibrium in the latter case depends upon the rate at which the dye anions can be detached from the micelles.

5) In general sulphonated compounds at low concentrations appear to form condensed monolayers oriented so that the sulphonate groups are as far away as possible from the graphite surface. Thus dyes with sulphonate groups at only one end appear to be oriented end-on, those with one group at each end, edge-on, and those with sulphonate groups all round, flat.

Similar principles apply to the orientation of basic dyes. At high concentrations basic dyes can be adsorbed as micelles.

Non-ionic azo-dyes appear to be adsorbed flat with all the aromatic nuclei in contact with the surface.

6) In the case of graphite physical attraction seems to be much stronger than in the case of cellulose. While cellulose can only adsorb large planar aromatic solutes graphite is able to attract and adsorb molecules of much smaller size.

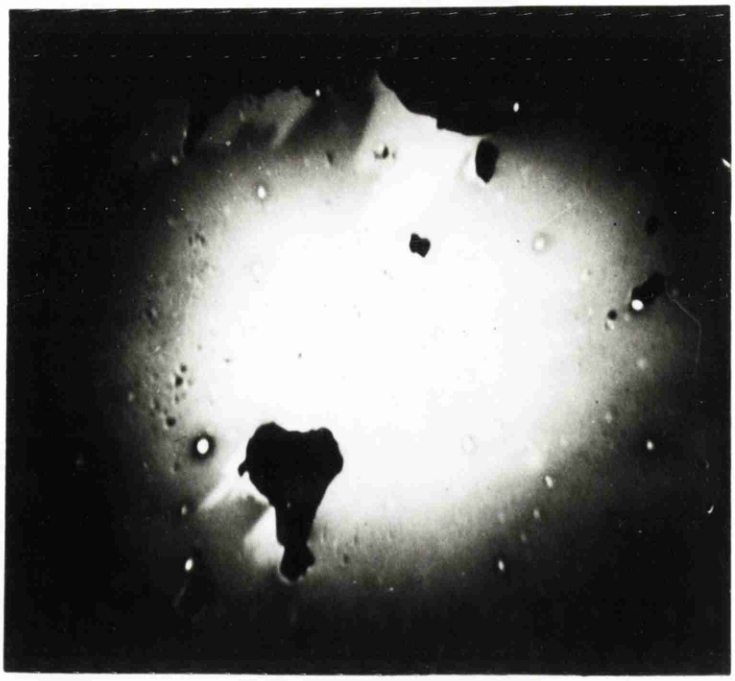


FIG.1 MICROGRAPHS OF GRAPHITE PARTICLES

(2000 x , Angle of shadow-casting 1:5)

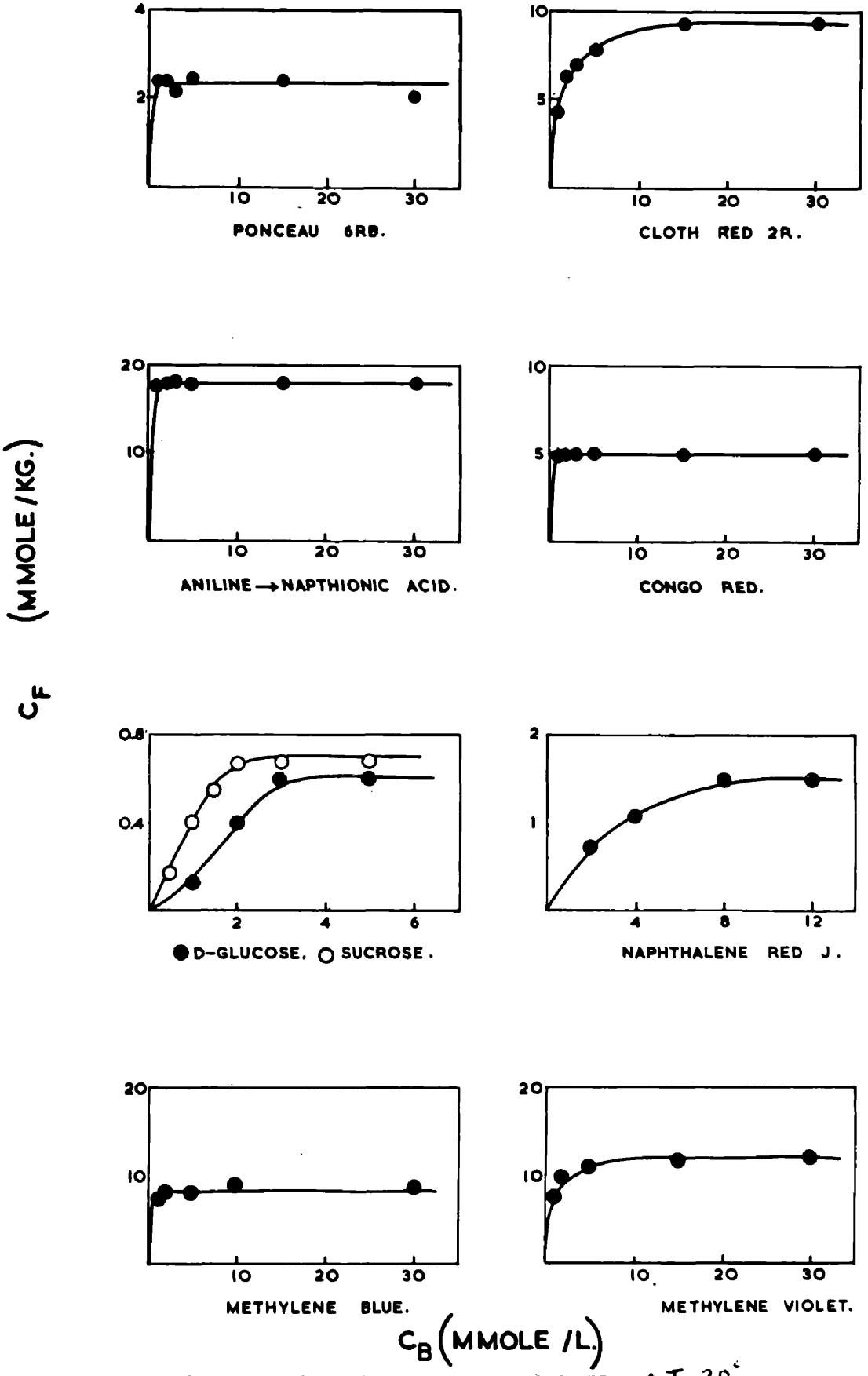


FIG. 2 RATES OF ADSORPTION ON GRAPHITE. AT 20°.

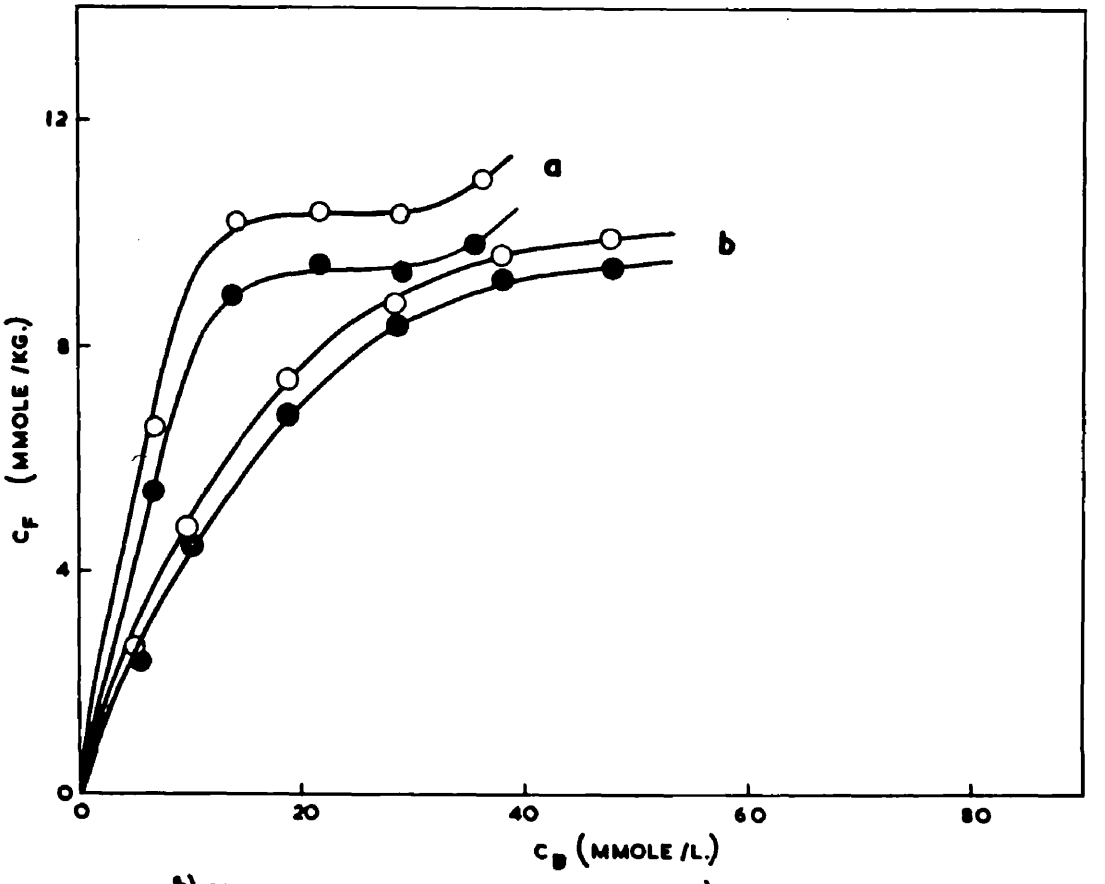


FIG.3 ADSORPTION OF SULPHONIC ACIDS ON GRAPHITE.

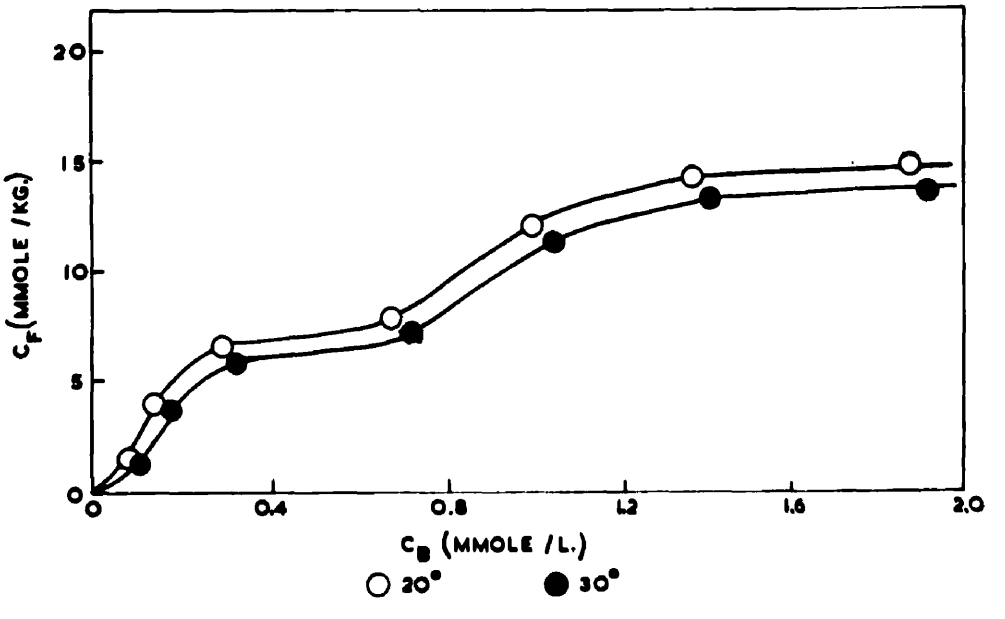


FIG 4. ADSORPTION OF NAPHTHALENE. RED EAS ON GPAPHITE.

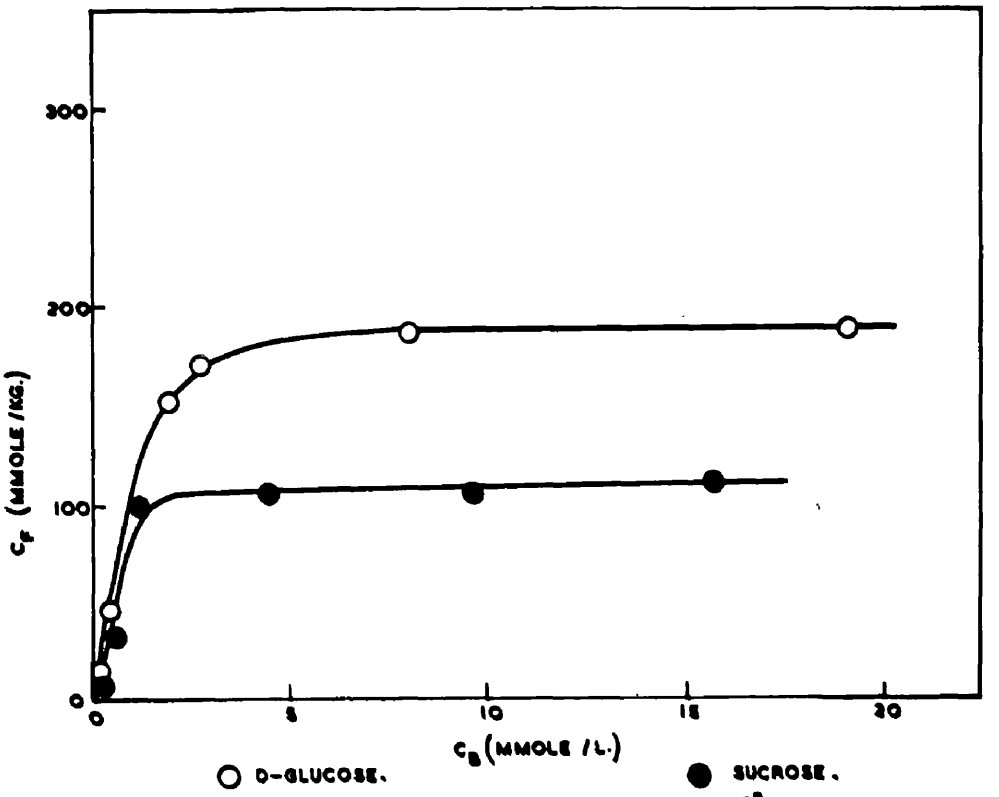


FIG. 3 ADSORPTION OF SUGERS ON GRAPHITE AT 20°.

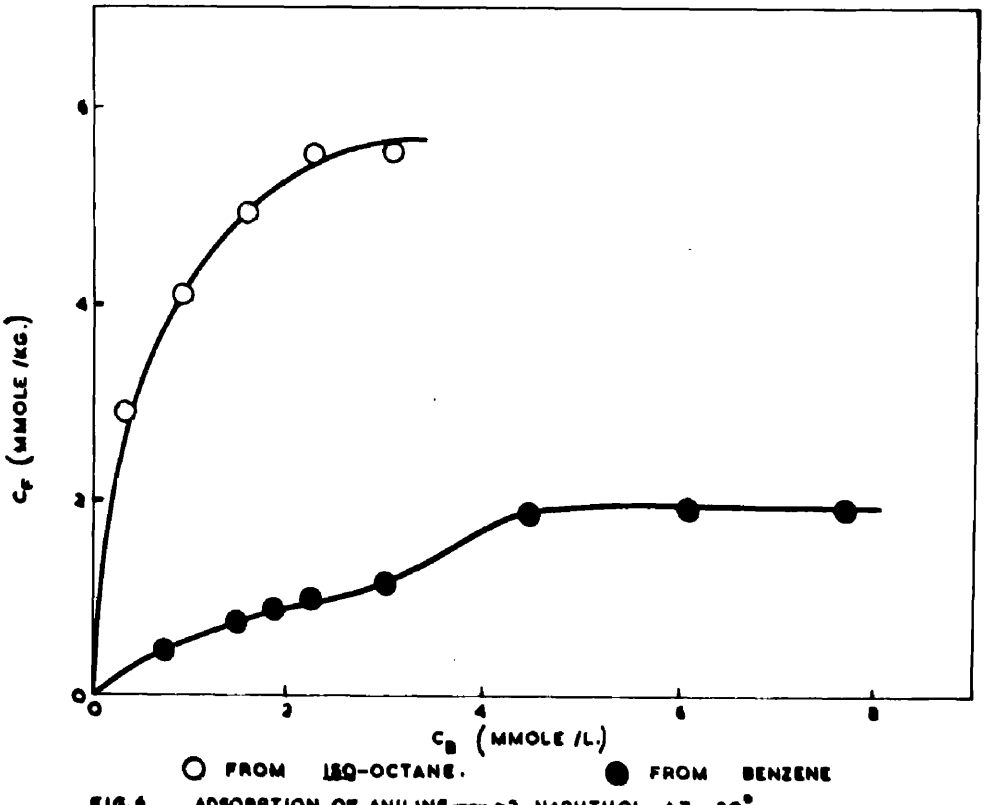
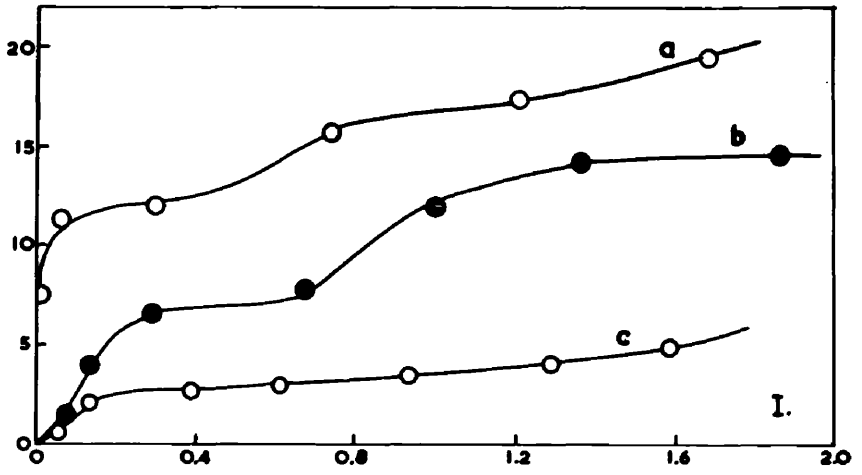
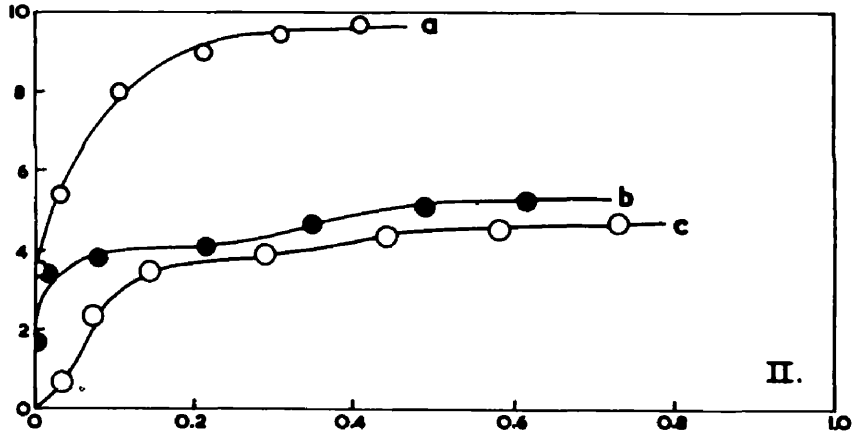


FIG. 4 ADSORPTION OF ANILINE ——→ 2-NAPHTHOL AT 20°.

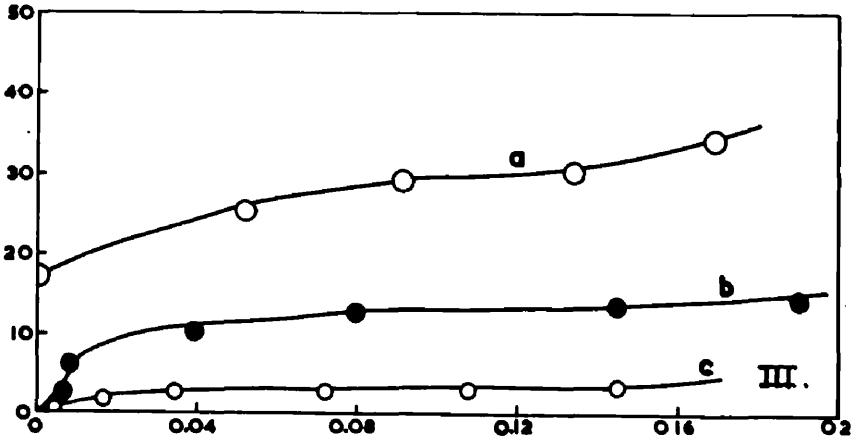


a) NAPHTHALENE RED J. b) NAPHTHALENE RED EAS.
c) NAPHTHALENE SCARLET 4R



C_F (MMOLE /KG.)

a) CLOTH RED 2R. b) CONGO RED.
c) PONCEAU 6RB.



a) SULPHANILIC ACID → NAPHTOL AS. b) ANILINE-2:5-DISULPHONIC
c) AZO GERANINE 2G. ACID → NAPHTOL AS.

C_B (MMOLE /L.)

FIG.7 ADSORPTION OF AZO DYES ON GRAPHITE AT 20°.

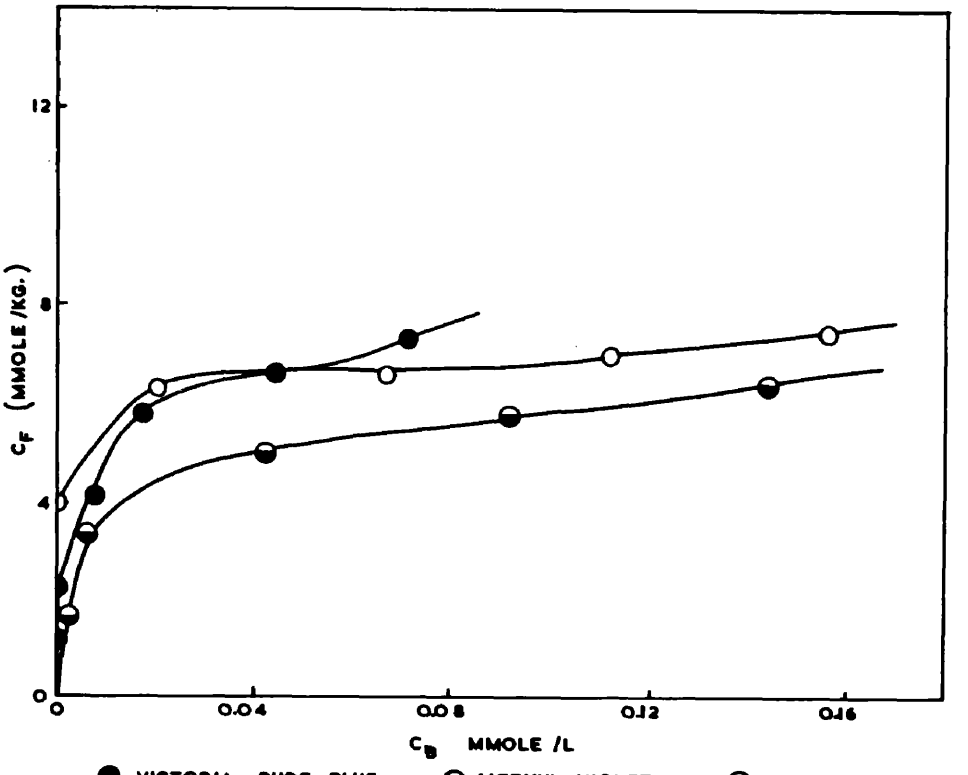


FIG. 8 ADSORPTION OF BASIC DYES ON GRAPHITE AT 20° AND 30°.

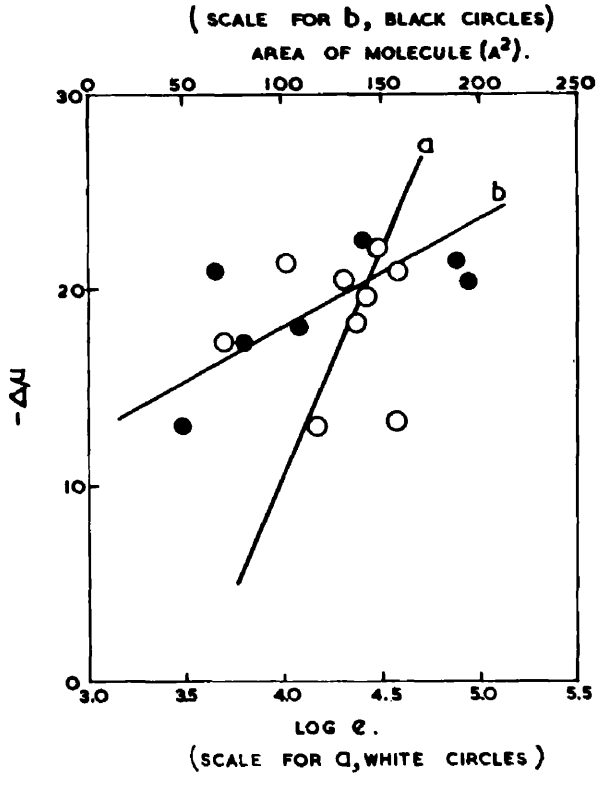


FIG. 9 RELATIONSHIP BETWEEN PHYSICAL CHRACTERISTICS AND AFFINITY OF DYES FOR GRAPHITE.

TABLE 1.

Relative Adsorption Rates on Graphite

Compound	Time (min.)*	g./litre**
Acid dyes		
"Symmetrically" sulphonated.		
Aniline ⟶ naphthionic acid	< 1	0.5
Ponceau 6RB	< 1	0.5
Congo Red	< 1	0.5
"Unsymmetrically" sulphonated.		
Cloth Red 2R	5	0.5
Naphthalene Red J	4.5	0.05
Basic dyes		
Methyl Violet 10B	< 2	0.25
Methylene Blue B	< 2	0.25
Sugars		
D-Glucose	2	5.0
Sucrose	1.5	5.0

* Time required to reach 75% of equilibrium value from the most concentrated solutions.

** Initial concentration used.

TABLE 2.

Orientation of Adsorbed Solutes

Solute	Approx. molecular dimensions (A)	Adsorption*	Coverage factor** Flat	Edge-on	End-on
I	13.5 x 9 x 3 (from iso-octane)	5.2	1.6	0.5	0.4
	(from benzene)	1.2	0.4	0.1	0.08
		2.0	0.6	0.2	0.15
II	8.5 x 8 x 5	10.0	1.7	1.1	-
III	11 x 8 x 5	11.0	2.4	1.1	1.0
IV	17 x 11.5 x 5	2.5	1.2	0.5	0.4
		(52) from high concn. solns.	25.3	11.0	7.5
V	15 x 10 x 5	12	4.5	2.3	1.5
		16.5	6.2	3.1	2.1
		20	7.5	3.8	2.5
VI	16 x 12 x 5	7.0	3.4	1.4	1.1
		15	7.2	3.0	2.3
VII	18 x 10.5 x 5	2.5	1.2	0.6	0.3
VIII	20.5 x 12.5 x 5	30	19.2	7.7	4.7
IX	20.5 x 13 x 5	13.5	9.0	3.5	2.2
X	21.5 x 11 x 5	5	3.0	1.4	0.7
XI	20 x 13 x 5	10	6.5	2.5	1.6
XII	28 x 11 x 5	3.8	2.9	1.3	0.5
XIII	16 x 8 x 4	6.0	2.2	1.0	0.5
XIV	14 x 14 x 5	6.4	4.0	1.5	-
XV	18 x 16 x 5	6.2	4.8	1.5	1.2

* mmole/kg. of graphite; where more than one figure is quoted the last figure refers to the isotherm maximum and the others to intermediate points of inflection.

** i.e., total area of adsorbed solute oriented as shown/ specific surface area of graphite.

TABLE 3.

Classification of Isotherm Shapes

Compound	Number of Benzene nuclei	Number of Sulphonate groups
S-Curves		
Azo Geranine 2G	3	2
Naphthalene Red EAS	4	2
Naphthalene Scarlet 4R	4	3
Ponceau 6RB	4	2
Aniline-2:5-disulphonic acid ⟶ Naphtol AS	4	2
L-Curves		
Benzene sulphonic acid	1	1
Naphthalene 2-sulphonic acid	2	1
Naphthalene Red J	4	1
Cloth Red 2R	4	2
Congo Red	6	2
Methylene Blue B	3*	1
HA-Curves		
Sulphanilic acid ⟶ Naphtol AS	4	1
Methyl Violet 10B	3	1
Victoria Pure Blue BO	5	1

* Including one heterocyclic ring. This curve approaches the HA type very closely.

TABLE 4.

Thermodynamic Data for Dyes Adsorbed on Graphite

Compound	$-\Delta\mu$ (kcal/ml)	Log c	Area* (A^2)
Naphthalene Red J	13.6	4.1761	50
Naphthalene Red EAS	17.4	3.716	80
Naphthalene Scarlet 4R	21.5	4.02	189
Cloth Red	21	4.69	65
Ponceau 6RB	18.3	4.37	108
Congo Red	22.5	4.4886	140
Sulphanilic acid Naphtol AS (sodium salt)	13.1	4.59	-
Aniline-2:5-disulphonic acid Naphtol AS (sodium salt)	19.8	4.426	-
Azo Geranine 2G	20.5	4.2923	196

* Area of the anion in the orientation assumed for the first inflection of the isotherm for dyes forming monolayers.

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