STUDIES IN LIQUID-PHASE SORPTION

AT INORGANIC AND ORGANIC SURFACES

BY

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PREFACE

The present research was undertaken with a view to elucidating the mechanism involved in the sorption of simple organic compounds and dyes from solution, on surfaces of unusual materials. A considerable amount of work has already been done, on such sorption characteristics of all the textile fibres, natural, artificial and synthetic, but scarcely any attention has been paid to materials of a non-conventional type. Therefore it is hoped, in the present work, to examine the sorption properties, from solution, of such substrates and to try to correlate the observed data with those obtained with the various textile fibres, and thus determine the nature of the forces involved herein.

The oxide film of aluminium has been chosen to represent the inorganic substrates since preliminary investigations on the sorption properties of this compound have been carried out in this laboratory before, from which it has been known to display a greater variety of bonding forces than most other similar substrates. Chitin has been chosen as the organic substrate in the present research, since it has a strong similarity to cellulose, in its constitution, as well as to cellulose acetate, in the presence of the acetyl side chains, and also to a certain extent to nylon in its containing the acetylamino groups. Thus it would be expected to demonstrate a wide variety of forces of bonding with different organic

compounds and also with dyes of different classes. Moreover, it forms a major constituent of the cell-walls of bacteria, and hence a knowledge of the nature of its bonding with different types of dyes is invaluable as a means of identifying the presence of such bacteria, in biological tests.

SUMMARY

The present work comprises a study of the sorption of organic compounds by the anodic film on aluminium and also by chitin.

Sorption by the anodic film

The sorption of organic compounds by the anodic film on aluminium from solution in water and a variety of organic solvents has been investigated. Films prepared by anodisation in chromic acid were principally employed. These consist of almost pure amorphous γ-Al_2O_3 in a porous form. The sorptions were carried out under a variety of conditions and thermodynamic data have been determined in some cases.

One or more of the following mechanisms are found to account for the sorption of all the compounds studied: (a) hydrogen bonding between oxygen of the film and a phenolic hydroxyl or an amino-group in the solute; (b) salt formation between aluminium in the film and a sulphonic acid group in the solute; (c) chelation between aluminium in the film and pairs of o-hydroxy etc. groups in the solute; (d) an ion-exchange reaction at the film surface which takes place with certain sulphato-esters; (e) a "bridge-bonding" reaction, whereby a donor group e.g. the azo-group, may be fixed to the oxygen of the film through a "bridge" of a di-hydroxy compound e.g. quinol.

The hydrogen-bonds formed by phenolic hydroxy compounds

appear to be unaffected by the nature of the solvent but those formed by amino-groups have lower affinity and their formation may be prevented and the solute remain unsorbed when benzene or water is the solvent but not when carbon tetrachloride or dioxan is used. Both hydrogen atoms of the amino-group may be capable of simultaneous bonding with the film except in o-aminoazo-compounds, where chelation prevents one from reacting. The sorption of sulphonic acids from water may also be prevented if the aromatic nucleus is so small that the compound has very high solubility; this occurs with benzene sulphonic acid.

The film acquires a positive charge in water and consequently no cationic compounds e.g. basic dyes, are sorbed even when they contain groups capable of forming a hydrogen bond with the film; they may sometimes be sorbed from a non-ionising solvent e.g. dioxan, but even so, they can immediately be washed out by water.

Since the surface has a positive charge, most anionic compounds are readily sorbed. Many sulphonates, particularly acid dyes, are readily sorbed, and appear to take part in salt formation with the metal of the film, there being a measurable heat of sorption. Sulphato-esters, which are also readily sorbed, however, show no measurable heat of sorption. This is believed to be due to a process of ion-exchange at the film surface.

Compounds capable of chelating with aluminium e.g. mordant dyes are readily sorbed by a non-reversible reaction, colouring the film with the characteristic shade of the aluminium lake, as was found by Mehta[34].

No evidence has been obtained that van der Waals attraction plays any significant part in determining sorption on the substrate from solution.

Sorption of simple acids, acid dyes, and hydroxy compounds by chitin.

The sorption of simple mineral acids, acid azo dyes and hydroxy compounds by chitin, obtained from the shells of Nephrops Norvegicus has been investigated. The composition of the chitin sample employed in the present work has not been completely established, but it is well known that chitin is built up of acetylaminoglucose units, through 1:4-glucosidic linkages as in cellulose. The sample employed for the study was of a standard particle size, greater than 200 mesh and in all experiments a constant solid:liquid ratio of 1:2000 was employed throughout.

In the sorption of simple mineral acids, no hydrolysis is observed at 60°C. above pH 2.00, but extensive hydrolysis seems to occur at pH values below this. A maximum sorption of 5.20 equivalents per kilogram of dry chitin is obtained both with hydrochloric acid and with sulphuric acid. This

seems to indicate that the acid is attached to the acetylamino-groups present in the substrate. This also indicates the absence of any specific affinity of the anion for the substrate. An attempt has been made to apply the theories of Gilbert and Rideal and of Donnan, obtained for the acid binding of wool, to the present case. The chitin appears to behave as a membrane, in accordance with the Donnan theory, and hence the results obtained seem to be better explained by the Donnan theory than by that of Gilbert and Rideal. Therefore it may be stated that the combination of simple mineral acids by chitin results in the formation of positively charged sites on the substrate, produced by the sorption of hydrogen ions by the acetylamino-groups present. This leads to the sorption of anions in equivalent amounts in order to maintain electrical neutrality.

Following this work, the sorption of eleven acid azo dyes by chitin was studied. Here the system consisted of sulphuric acid or sodium hydroxide, the sodium salt of the dye and chitin. The saturation values obtained with all these dyes have been found to be different from one another and much below the theoretically expected value of 4.93 equivalents of each dye per kilogram of the substrate, if all the acetylamino groups were saturated. The discrepancy is attributed to a high degree of crystallinity of the chitin structure, whereby the dye anions are unable to reach more than a fraction of the

acetylamino-groups. Some correlation is found between the relative affinity of the dyes and their structural characteristics, e.g., the more sulphonic acid groups there are in the dye molecule, the lower its affinity for chitin.

The dyes must, however, be sorbed by electrostatic attraction between the positively charged sites in the substrate and the negatively charged dye ions, since the amount of each dye taken up at the pH of its maximum sorption decreases with increasing amounts of sodium sulphate present in the system, which indicates the essentially ionic nature of the sorption. The rate of decrease of sorption appears to increase with increasing valency of the dye-anion employed.

Finally, the sorption of hydroxy compounds, viz. phenol and resorcinol, and also of 2:4-dinitrophenol and picric acid, has been investigated. It is suggested that phenol may be taken up through the formation of a hydrogen bond of the type OH.....O. The sorption of 2:4-dinitrophenol and picric acid appears to resemble that of other weak organic acids by wool.

C O N T E N T S

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GENERAL INTRODUCTION

The phenomena involved in the dyeing of textile fibres, both natural and synthetic, have been investigated extensively by many workers, as a result of which certain conclusions have been reached. Both aluminium oxide of the anodic film, and chitin, whose sorption properties have been investigated in the present research, appear to display a variety of forces similar to those observed in the uptake of different classes of dye by the textile fibres. Therefore, a brief review of the existing knowledge in this direction is considered important in order to have a fuller understanding of the mechanism of sorption of dyes and intermediates, by the anodic film and chitin.

In any dyeing system, the important factors to be taken into consideration are the nature of the substrate, that of the dye, and the actual dyebath itself. These may generally be classified under the following groups:- (i) Pore size of substrate; (ii) nature of the fibre potential in neutral solution and its variation by the addition of salt; (iii) particle size of dye in solution; and (iv) the short and long-range electrical forces of attraction between the sorbent and the sorbate.

The dyeing process may be visualised as consisting of two aspects as is the case with any other physicochemical process. These are the kinetic and the thermodynamic aspects.

The kinetic aspect requires the study of the rate at which the system approaches towards the equilibrium condition, and also of the factors which determine the rate of change.

The thermodynamic aspect, on the other hand, requires the study of the conditions governing the equilibrium of a system when sufficient time has passed to allow all change to cease. The equilibrium conditions in a reacting system are governed by the free energy change accompanying the reaction, while the rate of reaction is governed by the activation energy for the process.

The dyeing process consists in the transference of the dye from one phase, the external dyebath, to another, the substrate. This transfer may or may not be accompanied by the transfer of other material. Since most dyes are the salts of a sulphonic acid, the sorption of the acid dye anions by the fibre must be accompanied by an equivalent number of cations, or displace an equivalent number of anions, already present in the substrate; otherwise quite large differences of electrical potential would be set up. Such transfer of inorganic ions which accompanies the dyeing process, varies according to the dye and the fibre. Thus, when a direct dye is taken up by cellulose, it is accompanied by the sodium ions into the fibre. But, when a protein fibre sorbs a dye acid, it brings with it an equivalent number of hydrogen ions into the substrate. The ion of an acid dye, being absorbed by wool in a bath containing sulphuric acid, displaces sulphate ions from the fibre.

A dispersed dye, on the other hand, is electrically neutral and hence its absorption by the fibre does not involve the transfer of inorganic ions.

Now, considering the general nature of any textile fibre, its pore size appears to play an important part in the dyeing process. All fibres are known to comprise both crystalline regions, where the fibre chains or micelles are packed compactly in a highly oriented fashion, and amorphous regions where these are distributed in a random manner. All textile fibres undergo swelling to varying degrees in water, and they sorb the dye in a swollen state. The dyes so sorbed will have to make their way through these swollen pores in order to reach the amorphous region. It has therefore been found by Morton[1] that dyes are unable to pass through these pores in the unswollen state. This evidently emphasises the importance of the particle size in solution.

Although a considerable amount of work has been carried out in this field, the results obtained so far are not definite. It has been stated that levelling acid dyes are less aggregated than direct dyes, although the degree of aggregation varies from dye to dye and decreases with rise in temperature, and with increasing dilution. However, it increases in the presence of electrolytes like common salt. Valkó[2], as a result of some diffusion measurements, has found that some acid dyes (e.g. Orange II) are molecularly dispersed. He also found that their aggregation was not influenced by temperature

to any appreciable extent. Again, Morton[1] has found that direct dyes are not dispersed in uniform particle sizes in solution, but consist of a polydispersed mixture of particles of all sizes from a single molecule to large aggregates in dynamic equilibrium. Therefore, as the particles of the smallest size are broken up by the fibre, the bigger aggregates break down to restore the equilibrium.

Now, with this picture of the importance of the pore size of the substrate, and the particle size of dye in solution, in any dyeing process, we may proceed to consider the nature of the forces of attraction between the dye and fibre. In this connection, it must be stated that all textile fibres acquire a negative potential when they are in contact with a neutral solution. The nature of the potential may be altered by the addition of salt to the dyebath. An electrical theory of dyeing was put forward by Gee and Harrison[3] in which they stated that fibres acquire electrical charge in water and attract or repel dye ions according to the nature of this charge. This theory has been amplified by Neale[4] as follows.

According to him, two types of electrical forces, the short-range electrical force, with a range of less than 5 $\mathring{A}$, and the long-range electrical force, effective over a distance of 100 $\mathring{A}$, take part in the dyeing phenomena. The former is responsible for covalent or hydrogen bonds and the latter may be visualised as being responsible for the attraction or repulsion between the dye ion and the substrate. The colour ions

of acid and direct dyes carry negative charges, while those of basic dyes have a positive charge. Neale[4] has substantiated the view, by dyeing cotton, wool and silk, under neutral conditions, where only the colour ions are stated to be attracted specifically to the fibre, while the oppositely charged ions are only loosely held in the substrate in order to maintain electrical neutrality, without having any specific affinity for the fibre. So, if a colour ion of valency 'n' is present in the system and the fibre has a potential represented by ψ volts, an energy of $n\xi\psi$ electron volts will be required for the colour ions to reach the fibre interface. This energy is supplied by the thermal agitation of the system. Thus, a fraction of the dye ion which reaches the surface is strongly attached to it by the operation of the short-range forces, forming hydrogen bonds or some analogous linkage, if the dye and the fibre have suitable groups or configurations to enable the formation of such bonds. The effect of the long-range electrostatic forces can be varied by varying the surface charges of the fibre or the dye, for example by the addition of a neutral salt to the dyebath, which reduces the negative potential of the fibre, or by using a dye with less highly charged ions such as one containing fewer sulphonic groups in the molecule.

But a dye having a positive charge is actually helped by these forces to become attached to the fibre and the addition of salt decreases the attraction between the dye ion and the

fibre.

Now, after the above review of the general nature of the factors involved in the dyeing of a textile fibre, we may consider the same as applied to each of the following groups in more detail. The groups are (i) cellulosic fibres; (ii) artificial fibres, like cellulose acetate; (iii) protein fibres and (iv) nylon.

Cellulose fibres:-

Cellulose has now been recognised by Meyer and Mark[5] to be built up of ß-glucose units joined together by ether linkages in 1:4-positions to form linear macromolecular chains of up to about 2000 units. As indicated earlier, these units give rise to both crystalline and amorphous regions in the substrate, and the permeability of the latter is of importance in so far as the dyeing process is concerned. The diameter of the pores in this region has been found, by various workers, to vary from 5 Å in the dry state, to about 20 Å in the water-swollen condition. Now, when the size of a typical direct dye molecule, for example Chlorazol Sky Blue FF (length 27 Å, width about 10 Å) is compared with this it is quite obvious that only single dye molecules or very small aggregates of them can diffuse into the fibre. Therefore, considerable attention has been devoted to the determination of the particle size of dyes and the pore-size of cellulose fibres, in solution. It has

been found by Lenher and Smith[6] that dyes having particles of diameter greater than an optimum value of 35-40 Å at 25°C., are not readily sorbed by cotton though according to them the actual dyeing process, or equilibrium sorption of dye, is not affected by the mean particle size of the dye, because as the smaller particles are taken up, larger aggregates break down to restore equilibrium conditions. However, it is stated that the rate of sorption would decrease with increase in mean particle size.

The work of Neale and his associates has shown that dyeing is essentially a diffusion process governed by Fick's law, which states that the rate of diffusion $\frac{ds}{dt}$ of a dye at any point is proportional to the concentration gradient $\frac{dc}{dx}$ at that point or

$$\frac{ds}{dt} = -K. \frac{dc}{dx}$$ where 'K' is the diffusion constant

Neale and Stringfellow[7] have applied McBain's[8] equation for diffusion through plane slabs to the sorption of dyes by cellophane discs and have obtained good agreement between the calculated and observed values. They have also determined the rate of dyeing in different thicknesses of cellophane sheets and have found that the time required to reach a definite degree of saturation is proportional to the square of half the thickness of the sheet, which is in agreement with Fick's law. But it has been shown by Neale and Garvie[9] that the diffusion constant calculated according to Fick's law varies with the

concentration of the dye, and 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 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.

The importance of the rate of diffusion of dye in cellulose, as well as the pore size of cellulose and the minimum particle size of dyes in solution, is realised when the diffusion constant of a dye in water is considered, which has a higher value than in cellulose. The kinetics of sorption are controlled by several factors, such as the chemical and physical variations in cellulose, the concentration of dye and the presence of a foreign electrolyte, etc. The course of the diffusion process in the presence of a foreign electrolyte could be predicted by Donnan's equations, the substrate here being considered as a membrane wherein the diffused dye ions may be regarded as non-permeable through the same. The saturation values obtained with dyes in cellulose seem to indicate that a unimolecular layer of dye is formed in the available surface.

It is now believed that in the dyeing of cellulose with direct dyes, hydrogen bonds are formed between the substrate and the oxygen or nitrogen atom of the dye. This has received support from the investigation on the substantivity of dyes and

its dependence on the spatial arrangement of hydrogen-bond forming groups in the dye molecule. It has been shown by Ellis and Bath[10] that almost all hydroxyl groups in cellulose are involved in hydrogen bonds between adjacent cellulose chains, while the aggregation of direct dyes in solution can also be explained by the assumption of the formation of hydrogen bonds between the polar amino- and hydroxyl groups in the dye molecule. Meyer[11] has assumed that substantive dyes possess linear chain molecules so as to facilitate their being held closely to the cellulose molecule by mutual residual valency forces. This view has been confirmed by Paine[12] who has demonstrated the same, through scale models of dyes. Such models in the case of non-substantive dyes do not fit in closely with the cellulose chain. It was shown by him that in the case of substantive dyes, groups such as azo, ethylene, and amide links appear at regular intervals of e.g. 10.8 Å which corresponds fairly well with the repeat pattern of the cellulose chain (10.3 Å). Another important factor for a dye to be substantive to cellulose has been recognised to be 'coplanarity of structure', i.e. all the benzene rings in the molecule must lie flat in one plane. The non-substantivity of the meta-isomer of the direct dye Benzopurpurine B, where the two methyl groups in the ortho-ortho'-position prevent the structure from becoming coplanar, has been cited in support of this hypothesis. The work of Paine has been extended by F.L.Rose[13] who has put forward a co-ordinated account of substantivity. All groups

which impart substantivity to a dye have been characterised by him either as electron donors or ~~proton~~ acceptors, and he has shown that the spacing of these groups should be suitable for forming hydrogen bonds with the hydroxyl groups of the cellulose molecule. He has indicated that at least two hydrogen bonds between the dye and the substrate should be formed for a dye to be substantive. This view has been confirmed by the work of Willis et al[14] and Marshall and Peters[15].

The dyeing of cellulose may therefore be explained as follows. The fibre, when it comes into contact with the neutral aqueous solution of the dye, develops a negative potential. The dye is already dissociated into oppositely charged ions, in solution, and these exist in dynamic equilibrium of particles of all sizes from a single ion to aggregates made up of several of these ions. At first the single ions or small aggregates are adsorbed on the surface, being helped or opposed by electrostatic forces, and the energy to overcome such opposition is provided by the thermal agitation of the system. Now, as the dyeing proceeds in such a manner, the equilibrium is maintained by the breaking down of the larger aggregates into smaller particles. The dye particles, thus having reached the fibre surface, diffuse slowly through its water-swollen pores in accordance with Fick's law, into the interior of the fibre phase. This rate of diffusion is important, since it determines the rate of dyeing. Thus, having reached the

interior surface of the fibre, the dye ions are assisted by the short range electrical forces to form hydrogen bonds with the hydroxyl groups of the cellulose molecule, and the substantivity or otherwise of the dye will then be determined by the spatial arrangement of polar groups, and the linear coplanar structure of the dye molecule. If these necessary conditions are satisfied, the dye will form hydrogen bonds with the substrate. The mutual attraction between the dye and the fibre could be altered, either by altering the fibre potential, through the addition of an electrolyte, or through the alteration of certain groups in the dye molecule. A completely reversible equilibrium is reached after a certain period of time depending on the concentration of dye and electrolyte present in the system and also on the temperature of the bath. As indicated earlier, the distribution of dye at equilibrium between the fibre and the dyebath as well as the effect of the electrolyte present in the system, could be explained in quantitative terms, by the Donnan theory of membrane equilibrium.

Cellulose acetate rayon:-

This fibre has been found to contain very small pores which do not swell much in water. A hypothesis, that the dyeing of cellulose acetate with dispersed dyes is a process of solid solution, has been put forward by Kartaschoff[16]. This

has been confirmed subsequently by the observation that this fibre is dyed when it comes into contact with dry dye powder. Vickerstaff and Waters[17] have shown the absence of any electrical attraction between the dye and fibre in an aqueous dispersion. They presume that the thermal agitation of the system causes the dye particles to strike against the fibre surface, and since the dispersion contains particles of all sizes, the smaller particles attach themselves to the fibre surface, and are then subsequently dissolved. (Knoevenagel[18] has observed that with increasing concentration a constant partition ratio is observed for the distribution of phenol, and aniline, between the fibre phase and the solution, in exactly the same way as the distribution of a solute between two immiscible solvents). Therefore they considered that cellulose acetate is acting as a solid solvent in such sorption, because according to them, if the process is one of adsorption the amount of solute taken up by the fibre should bear a logarithmic relation to that in solution (Freundlich isotherm). If, however, the Langmuir adsorption isotherm is applicable and if the number of adsorption sites is large, then the isotherm also will be expected to give a constant partition coefficient at low concentration. Therefore the discrimination between adsorption and solution is not possible on the basis of these results alone.

Marsden and Urquhart[19] have investigated the sorption of phenol by cellulose acetate and suggest that it might be through

hydrogen bonding, although the heat of reaction value is lower than is usually associated with a hydrogen bond. The absence of any dichroic effect with dyed cellulose acetate has led to the suggestion that the dyes are not sorbed on the main cellulose chain. A hydrogen bond could be formed between a suitable polar group in the dispersed dye molecule and the carbonyl oxygen of the acetyl side chain in cellulose acetate leading to the sorption of such a dye by the substrate. Therefore this view could be reconciled with the earlier assumption of solid solution of the dye in the fibre, by presuming the hydrogen-bond to act as a 'solvating agent'.

Protein fibres:-

Since wool is a true representative of this group of fibres, a consideration of the dyeing characteristics of this substrate may well apply to the other insoluble protein fibres also.

The extensive investigations of Speakman[20] and Astbury[21] have elucidated the structure of the wool fibre. According to them, wool may be regarded as being built up of micelles lying parallel to the axis of the fibre and consisting of long folded parallel peptide chains linked together by cystine and salt linkages, which keep the molecular chains more or less in one plane. These planes themselves are held together lengthwise by hydrogen bonds or weak forces such as van der Waals forces. The micelles are regarded as lamellar

in shape, about 200 Å thick, and 2000 Å long. The intermicellar space has pores of the order of 6 Å in the dry unswollen state, and about 40 Å when swollen in water and even more in acid solution, through which the dye molecules penetrate the fibre.

Two theories have been put forward to explain the sorption of acid dyes by wool. These are the (i) Donnan theory and (ii) the Gilbert-Rideal theory. The work of Peters and Speakman[22] and Elöd[23] has afforded strong evidence in favour of the Donnan theory.

A chemical theory of wool dyeing has been proposed by Knecht[24] and the same has been developed by Fort[25]. According to this theory, wool, on immersion in the bath, first combines with colourless acid to form a protein salt which is subsequently followed by slower formation of a protein-dye salt. This may be expressed by the following equation:

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

and

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

Here, D represents the dye anion.

This view has been confirmed by Elöd[23] through his investigation on the dyeing of wool with crystal Ponceau R, Thiocarmine B and Sulphorhodamine-T from dyebaths which contained hydrochloric acid. The replacement of chloride ions in the wool fibre by the dye anion has been quantitatively

measured by him. It has been shown by Speakman and Stott[26] that acid combination by wool is a function of the pH of the bath in which the wool is placed, and not of the molar concentration of acid. Speakman has also established that wool has a maximum combining capacity of 0.82 equivalents of monobasic acid per kilogram at pH 1.00, which corresponds closely with the number of amino groups in wool. Therefore, it is obvious that if the chemical theory of wool dyeing is correct then dyed wool would have a lesser combining capacity for acid, as compared to undyed wool. This has been shown to be the case by Elöd[23] in his investigations on the amount of acid taken up by wool, dyed with 2.5%, 5% and 10% respectively of crystal Ponceau. Further evidence in support of this theory has been afforded by Speakman and Stott[26] who have shown that deaminated wool has a considerably reduced acid binding capacity and that whatever absorption takes place in such a case is probably due to imino groups in the peptide chain. Donnan's theory is capable of explaining all these observations if it is assumed that the fibre serves as a membrane, wherein the $R\text{-}\overset{+}{N}H_3$ groups produced by ionisation of the amino groups of the side-chains in acid solution are the non-permeable ions.

It has been suggested by Goodall[27] that colloidal acid dyes are aggregated in solution and correspond to a group of unlevel dyeing dyes. The reason for this involves consideration of the particle size of the dye and the pore size of the swollen fibre.

Gilbert and Rideal's[28] treatment differs from that of Speakman and his associates in that they assume the anions to be adsorbed on specific sites in the substrate, in addition to the cations, whereas, according to the Donnan theory, the anions are taken up only to maintain electrical neutrality and hence they are located in the internal aqueous solution within the substrate. Further, Gilbert and Rideal assume the fibre to contain equal numbers of positive and negative sites possessing the same properties, and that adsorbed ions are free to occupy any site irrespective of whether the adjacent sites are occupied or not. This theory, although it is capable of explaining the observed data, does not impose a limit beyond which the titration curve of wool obtained with hydrochloric acid could not be displaced by additions of increasing amounts of chloride ion concentrations to the system, whereas such a limit is implicit in the Donnan theory and is in accordance with the experimental facts.

Nylon:

This is a purely synthetic fibre produced by condensing stoichiometric proportions of hexamethylene diamine and adipic acid. The polymerisation proceeds until a long chain with a molecular weight of 10,000-12,000 units is built up leaving both free amino and carboxyl groups at the two ends of the chain. The fibre has both crystalline and amorphous regions and has a circular cross-section and does not swell in water.

Nylon can be dyed with dispersed dyes, soluble acetate rayon dyes and acid dyes. The dispersed dyes are the most satisfactory of this group from the point of view of ease of application and uniformity of dyeing. But these are somewhat inferior in fastness to light and washing as compared with the acid dyes.

It has been shown by Peters[29] that the mechanism of dyeing nylon appears to be similar to that of wool in the pH range 3-6, the only difference being that there are fewer basic sites in nylon as compared with wool. Experiments carried out by Lemin[30] have indicated that nylon contains 0.037 equivalent of free amino groups per kilogram while wool has about 0.82 equivalents per kilogram. Therefore it is clear that in the pH range mentioned, dye is taken up by the free amino groups at the end of the chain. Peters has also observed a higher uptake of dye at pH values less than 3.0 and has suggested that the weakly basic amido groups in the chain are responsible for such sorption. This view received strong support from Sookne and Harris[31] who have found by electrophoresis that particles of drawn nylon and dibenzyl diketopiperazine become positively charged at pH 2.70 and 2.90 respectively. In the case of diketopiperazine the amide groups are the only polar groups present, so that it can be assumed that the amide groups in nylon can and do absorb hydrogen ions at pH values below 2.50. Further confirmation of this view has been obtained by Peters[29] by estimating the amount of acid dye, (Naphthalene Orange GS),

taken up by nylon yarn whose free amino groups had been acetylated by a treatment with acetic anhydride in benzene.

Now, regarding the sorption of dispersed dyes by nylon, Carlene et al[32] suggest that these dyes are attached to the nylon fibre by hydrogen bonds between the dye molecule and the carbonyl oxygen of the amide groups. These forces are comparable to those existing between the polyamide chains. Such a view is confirmed by the high degree of dichroism observed with dyed nylon, corresponding to the high degree of orientation of the fibre itself. This suggestion receives much more additional support from the observation (Preston[33]) that the uptake of dispersed dyes of the aminoanthraquinone type is not interfered with even after alteration of the nature of the end amino groups in the nylon chain by suitable chemical treatments.

PART I

SORPTION STUDIES ON ANODISED ALUMINIUM

INTRODUCTION

An extensive research has been carried out in the preparation of anodic oxide films on aluminium as a result of which it is now well established that such films could be obtained in a pure, uniform and consistent quality. The nature of the forces involved in the sorption of different types of compounds and dyes by the film from solution have received very little study, although diverse types of attractive forces are displayed by the same in such sorption from solution. These observations suggested that the sorption of organic compounds from solution, at inorganic surfaces, might be studied, with this anodic film of aluminium as the substrate.

Nature and Constitution of Anodic Film.

The preparation of hard, protective oxide films on aluminium by anodic treatment in acid solution, and their sorption of dyes to give fast and dark shades, was disclosed by Bengough and Stuart[35] in 1924. In such anodisation procedure the aqueous solutions of sulphuric acid[36], oxalic acid[35] or chromium trioxide[37] are normally used as electrolytes. Since these solutions appear to have a partial solvent action on the film, they give the outer layer an open structure and allow the electrolyte to remain in contact with an inner more compact layer, which seems to control the electrical properties. It is possible to build up any desired thickness of the film

even to the point of complete disappearance of the base metal, but owing to the competitive solvent action of the electrolyte the rate of growth reaches a maximum and then decreases.

Many conflicting views have been put forward regarding the nature of such oxide films formed on anodising aluminium. Some investigators are of the view that it is amorphous in character while others hold that it is crystalline in structure. It has been found out by Edwards and Keller[38] that the coatings formed on aluminium by anodic oxidation in dilute solutions of sulphuric, chromic, oxalic and boric acids are amorphous in character, as far as they can be determined by X-ray and electron diffraction methods. They are comprised chiefly of aluminium oxide but also contain substances adsorbed from the electrolyte. Microscopic examination of specially prepared cross-sections of anodically coated aluminium shows evidence that the oxide has a cellular structure. Mahl[39], using the electrostatic electron microscope, found that films produced by electrolytic oxidation showed a fine grain primarily due to fine pores produced during the growth of the layer. The initial layer of aluminium oxide was extremely thin and without any definite structure. The subsequent growth was based on pores formed in the initial layer by electrical breakdown. However the grains are not of crystalline nature, but must be interpreted as variations in thickness (pores) occurring during the growth of the film. Taylor[40], describes a variety of experiments which indicate that an X-ray diffraction pattern

corresponding to that of γ-alumina is obtained, when the formation potential is above 100 v. The formation of a crystalline coating does not seem to be characteristic of the electrolyte, for crystalline coatings were obtained with a variety of electrolytes. A high electrical stress seems to favour the formation of an ordered oxide lattice.

The constitution of the aluminium oxide in the film has not yet been definitely established. Although the anodic films prepared from different electrolytes and under different conditions of electrolysis vary in their physical properties from one another, their chemical composition remains the same. Such a film is mainly an amorphous or very finely crystalline oxide (Al_2O_3) designated as γ-alumina. It is possible that the film contains impurities from the metal or the electrolyte. However, the film obtained in chromic acid has been found to be the purest and it consists almost entirely of γ-alumina of specific gravity ca. 2.70 with only about 0.1% impurity as metallic chromium. An increase in the temperature of electrolysis appears to increase the degree of crystallinity of the film formed. If the film is subjected to dry heating above 100°C. it results in the elimination of any loosely held water, but the absorption capacity of the film does not seem to be in any way affected by this.

Previous Work.

Although considerable attention has been devoted to a study of the nature of anodic films, no serious thought appears to have been given to their sorption properties. However, it may be of interest to note that Gill[41], in a survey of the methods of dyeing the material, has suggested that with those dyes which form aluminium chelate complexes, lake formation takes place, while with those which do not do so, only physical adsorption occurs. It has been suggested by Haller[42] that such sorption is influenced to a certain extent by the degree of dispersion of both the dye and the grains of oxide in the film. Further, comparatively little study has been made of the detailed chemical mechanism of sorption of dyes and simple aromatic compounds by the various other forms of solid or hydrated alumina, though this is such an important factor in chromatography.

Ruggli and Jensen[43] made a variety of chromatographic tests by which they determined the qualitative influence of structural characteristics of dyes, e.g. the position and number of azo, vinyl or sulphonic acid groups upon their ease of adsorption on alumina columns, and several investigators have examined the sorption of acid and basic dyes by various forms of aluminium oxide, whilst Hoyer[44] observed the reduced strength of absorption by alumina of amino or hydroxy compounds when these are involved in intramolecular chelate ring systems.

Present Investigation.

The aim in this research has been to determine the nature of the forces operating in the sorption of organic solutes on anodic films, the actual solutes used being so chosen that the action of each of the possible types of attractive force could be demonstrated. The substances used have been mainly simple aromatic compounds, but a few aliphatic or more complex aromatic compounds have been included where necessary.

Aluminium film, anodised in chromic acid solution, was treated with the selected solutes under a variety of conditions of concentration, temperature, time, and nature of solvent, and the extent of absorption of solute determined by quantitative analysis of the solutions before and after the test.

SECTION I.

EXPERIMENTAL.

(i) Nature of Materials used.

The substrate consisted of a thin sheet of pure aluminium cut to a suitable size (8" x 2") which was employed as the anode in the anodisation cell and the cathode was a lead strip 8" x 2" x 1/16". These two electrodes were suitably positioned in a glass beaker of 2 litres capacity, which served as the anodisation cell. This is shown in Fig.1. The electrolyte employed was a 3% aqueous solution of chromium trioxide (A.R. quality). The electrodes, extending to about 1" above the liquor surface and connected through a variable resistance to a D.C. supply, were maintained at a fixed distance apart, by a skeleton frame of "Perspex". The electrolyte was agitated by a slow-speed stirrer placed between the electrodes, ensuring constancy of film weight over all parts of the anode within $\pm$ 0.5%. Before the treatments, the metal foil is cut to shape, smoothed flat on a hard surface and cleaned of grease by wiping with a pad of cotton wool moistened with carbon tetrachloride. The electrolyte is heated to 45°C. before use and is maintained at 45 $\pm$ 1°C. throughout the treatment. The heat generated by the electrolysis is usually sufficient to maintain the required temperature; if too much heat is generated, cooling water may be circulated through a larger

beaker placed outside the electrolysis vessel. The voltage is adjusted to 45 which ensures a current density of ca 6 amp./ sq.ft. of anode. Electrolysis was continued for one hour with unmodulated D.C. current providing a film 6μ thick, representing about 20% conversion of metal to oxide. The electrolyte may be used repeatedly but should be renewed when a noticeable fall in the rate of formation of oxide occurs.

After removal from the liquor the anode is well rinsed in distilled water, dried at 130°-140°C. for 1 hour, stored in a desiccator and used within 24 hours. Tests with a typical sulphonated azo dye showed that the film began to lose its sorption powers after this period of storage. This is believed to be due to changes in the lattice structure of the alumina affecting the pore size[45]. The material was cut into small strips $\frac{1}{2}$" wide and these were used for the sorption studies in the present investigation, each such strip being weighed before use. The weight of film on each strip was determined by weighing before and after boiling the anodised metal in a stripping solution[46] containing: phosphoric acid (85%), 35 c.c.; chromium trioxide 20 gm.; and made up to 1 litre with distilled water, and then rinsing and drying at 160°C. The process is repeated to constant weight, though usually one treatment for 5 minutes was found to be sufficient. Thus the oxide film is removed while the metal remains intact.

For the sorption tests, small portions of anodised foil about 3" by $\frac{1}{2}$" were placed in 10 c.c. of the required solution

(giving a liquor:film ratio of ca. 300:1) in ground-glass or rubber stoppered test-tubes for aqueous solutions, or sealed glass tubes for solution in organic solvents, these being held by spring clips on a horizontal shaft mechanically rotated at a constant speed of 20 r.p.m. under water in a thermostat tank, which is shown in Fig.2. For compounds exhibiting low sorption, two or more strips of foil were used. Solutions ranging in concentration from 0.1 to 10.0 (usually 0.10 - 0.25) g. per litre were employed at temperatures from 20°C. to 60°C. and for times up to 120 hours. The amount of solute sorbed was determined by quantitative analysis of the solutions before and after treatment, the liquors being filtered to remove traces of abraded alumina after the sorption procedure.

(ii) Methods of Estimation Employed.

Estimation of amino and azo compounds and dyes.

In all cases where the solutions of the compounds sorbed light of wavelength below 4000 Å their concentrations both before and after sorption by anodised aluminium were measured by using either the ultra-violet light obtained from a mercury vapour lamp or the Unicam absorptiometric spectrophotometer which can be employed for light absorption at wavelengths as low as 2000 Å. In the case of coloured solutions the Spekker photoelectric absorptiometer was employed.

Thus for azobenzene, 4-aminoazobenzene, 2:4-dinitrophenol,

2-aminoanthraquinone, 1- and 2-naphthylamine, and 2:4-dinitroaniline, either the Spekker absorptiometer with the mercury vapour lamp or the Unicam spectrophotometer was employed, while for benzeneazo-1-naphthylamine, benzeneazo-2-naphthylamine, benzeneazo-1-naphthol, benzeneazo-2-naphthol, Acid Magenta, Solacet Fast Scarlet, aniline ⟶ R-acid, dodecylaniline ⟶ R-acid and the cyanine dyes, 2-(4'-hydroxylstyryl)quinoline methiodide, 2-(4'-hydroxylstyryl)benzthiazole ethiodide, the Spekker absorptiometer with the ordinary monochromatic light was used. In all the above methods of measurements a calibration curve was first prepared for each compound, from which the unknown concentrations of the solutions under test were determined.

Estimation of phenol

The concentrations of the phenol solution in water both before and after sorption were determined by the bromine method. Approximately decinormal bromine solution was first prepared by dissolving 2.76 gm. of potassium bromate and 15.0 gm. of potassium bromide in distilled water, and diluting to 1 litre. A decinormal solution of sodium thiosulphate was prepared and standardised against standard potassium iodate solution. The bromate-bromide solution was standardised against the standard sodium thiosulphate solution by adding potassium iodide and hydrochloric acid and titrating the liberated iodine in the usual manner. Ten ml. of the phenol solution to be titrated was pipetted out into a 500 ml. glass-stoppered bottle and

50 ml. of distilled water and 5 ml. of hydrochloric acid added to it. The standard bromide solution was added to it from a burette with constant shaking until a permanent yellow colour was obtained. The temperature during the addition was not allowed to exceed 20°C. by surrounding the bottle with cold water to prevent the loss of bromine. The bottle was stoppered and shaken for 1 minute. Ten ml. of ten per cent potassium iodide solution was then added and the liberated iodine was titrated against the decinormal sodium thiosulphate solution using freshly prepared starch solution as indicator. From the amount of bromine solution consumed by the phenol the amount of phenol can be calculated according to the following relationship:

1 ml. of N/10 bromine solution $\equiv$ 0.0015675 gm. of phenol

Estimation of free acids.

The concentrations of all free acids used in the present work were determined by titrating them against suitable strengths of standard sodium hydroxide using phenolphthalein as indicator.

Estimation of surface active anionic and cationic compounds.

The method, as described by Barr et al[47] consists in titrating an anion-active compound against a standard solution of a cation-active compound, using a partition and point based on the solubility in chloroform of a coloured complex formed

between the cation-active agent and bromophenol blue. An M/1000 solution of a cation-active agent (cetyltrimethyl ammonium bromide 100% pure) was first prepared in distilled water and employed as the standard in titrations against the anion-active agents of unknown concentrations.

2 ml. of a solution of the respective anion-active agent of nearly the same order of concentration as the cation-active agent, was taken in a 20 ml. rubber-stoppered test tube. Then 2 ml. of chloroform and about 8 drops of bromophenol blue indicator solution (a 0.04% solution of the indicator by weight in 20% aqueous ethanol brought to a pH between 7.3-7.6) were added to this. Now the solution was purple coloured. Then the standard cation-active agent was added from a microburette, the tube being shaken thoroughly after each addition.

At the beginning of the titration the chloroform emulsifies into the aqueous phase but a quicker separation into two distinct layers occurs as the titration proceeds, especially as the end-point is approached. The end-point is taken as that value of the titrant added at which the first indication of a blue colour appears in the chloroform layer. Any further additions of the cation-active agent beyond the end-point intensifies this blue colour in the chloroform layer. The appearance of this blue colour is due to the presence of the acid dyestuff/cation-active agent complex. Therefore, a slight excess of the cation-active agent over that necessary to neutralise the anion-active agent present is required, and this

excess is determined separately by carrying out a blank titration, omitting only the anion-active agent. When concentrated solutions of an anion-active agent are required to be titrated they are diluted to nearly the same concentration as the cation-active agent being used since this facilitates an easy and quick estimation, as well as resulting in economy of reagents employed.

Determination of sign of charge on film.

Electrolysis was continued until anodisation was complete (ca. 4 hours with D.C. current). At this point the metal disappears and the current falls suddenly almost to zero. The film now becomes a brittle sheet of alumina but isolated specks of free metal may still remain. These make it difficult for the film to be ground down. They were removed by careful treatment with hydrochloric acid after which the oxide was thoroughly rinsed in distilled water until free of acid, and then ground with water in a mortar, to a fine white suspension. The charge was determined by introducing this suspension diluted to 1 g./100 ml. into a standard electrophoresis U-tube, carefully adding more water, and applying a p.d. of 200 v. D.C. The suspension was observed to move towards the negative pole. Addition of sodium chloride in increasing quantities steadily reduced the rate of flow to zero, and then reversed and caused it to increase in the opposite direction, the iso-electric point occurring in solution of about 0.09% NaCl, as was observed

by Johnson[48].

Catalytic action of the alumina film.

Erratic and non-reproducible results obtained by absorptiometric analyses following a number of the sorption tests, are attributed to the anodic film promoting catalytic decomposition of some solutes. Alumina is, of course, well known as a catalyst in organic reactions at high temperatures and some observations have been made upon its ability to decompose substances in the chromatographic column. The following facts were observed in the course of the present work, though no systematic work has been carried out to confirm them. The reaction occurs with some amino, azo and triphenylmethane compounds and appears to take place most readily in hydroxylic solvents. Thus water, aqueous ethanol, dry ethanol, dry dioxan and dry benzene appear to form a descending series in effectiveness and indeed only 1-naphthylamine, a very readily oxidisable substance, was noted as being particularly affected in dry benzene and this at considerable dilution, perhaps partly by air oxidation. This was usually evident in an increased optical density of the solutions though some triphenylmethane dyes, e.g. acid magenta and the two cyanine dyes were irreversibly decolourised. There was also evidence that azobenzene sulphonic acid and some water-soluble azo dyes are also partially decolourised by very prolonged contact with the film (i.e. for periods of up to 4 days). These observations seem consistent

with an oxidation process taking place in the case of the affected azo-compounds, resulting probably in the introduction of hydroxy-groups into the solute molecule. The oxidised product may then itself be sorbed by the film. In one case (anthracene-1-carboxylic acid) a considerable pressure of gas was generated, sufficient in fact, to burst tightly sealed tubes.

(iii) Nature of Compounds employed.[§§]

The compounds which were employed in the present work have been so chosen as to indicate the various types of forces which may be expected to operate in their sorption by anodised aluminium. These compounds may be classified broadly as follows: (i) amino compounds (ii) anionic compounds (iii) hydroxy compounds (iv) cationic compounds (v) proton acceptors (vi) miscellaneous compounds.

(i) Amino compounds:-

4-Aminoazobenzene; benzeneazo-1-naphthylamine; benzeneazo-2-naphthylamine; magenta (C.I.No.677); 2-amino-anthraquinone; 2:4-dinitroaniline; 2-naphthylamine.

(ii) Anionic compounds:-

Azobenzene-4-sulphonic acid; dodecyl toluene sodium sulphonate; naphthalene-1-sulphonic acid; naphthalene-2-

---

[§§] For methods of purification employed see Table 1.

sulphonic acid; sulphonated triphenylmethane dyes e.g. acid magenta (C.I.No.692); tetradecyl sodium sulphate; oleyl sodium sulphate; benzenesulphonic acid; benzene sodium sulphonate; naphthalene-1:5-disulphonic acid; benzeneazo-2-naphthol-3:6-disulphonic acid (Na Salt); dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid (Na Salt).

(iii) Hydroxy compounds:-

Benzeneazo-2-naphthol; 2:4-dinitrophenol; 4-nitrobenzeneazo-NN-ethyl-2-hydroxyethylaniline (Dispersol Fast Scarlet B); phenol; resorcinol.

Results uncertain owing to suspected decomposition:-

Anthracene-2-carboxylic acid, sodium salt; anthracene-1-sulphonic acid; 1-naphthylamine;

(iv) Cationic compounds:-

Phenolic compounds:- 2-(4'-Hydroxystyryl)quinoline methiodide; 2-(4'-hydroxylstyryl)benzthiazole ethiodide.

(v) Proton acceptors:- Azobenzene; benzeneazo-2-naphthol; 3-methoxybenzanthrone (Duranol Brilliant Yellow 6G); 4-nitrobenzeneazo-2-naphthol.

(vi)

SECTION II.

RESULTS AND DISCUSSION.

Sorption of Amino Compounds.

At first it was expected that amino compounds would readily form a hydrogen bond with the film and therefore show positive sorption, but actually this is not always so.

The results obtained with 2-naphthylamine, benzeneazo-1-naphthylamine, benzeneazo-2-naphthylamine and 4-aminoazobenzene are given in Tables 2 to 4 and clearly show that the hydrogen atom of the amino group in these compounds is quite incapable of forming any hydrogen bond with the oxygen atom of the anodic film. It has, however, been noticed in other investigations in this laboratory that intermolecular hydrogen bond formation by an amino group may sometimes be prevented by the protective action of a solvent, e.g. water. Carbon tetrachloride or dioxan do not exert such a protective action and it was thought that, used as solvents, they might consequently assist the sorption of amines by the film. This has proved to be so, since water-soluble amino-compounds, e.g. magenta (C.I.No.677) or 4-aminoazobenzene are readily sorbed from dioxan but can be immediately washed away by water.

Both benzeneazo-1-naphthylamine and benzeneazo-2-naphthylamine are readily sorbed from carbon tetrachloride solutions, colouring the film pale yellow and deep bluish-red respectively.

Here the benzeneazo-1-naphthylamine should form twice as many bonds as the benzeneazo-2-naphthylamine, and from a consideration of the structural formulae as shown in Fig.3, these must be with the hydrogen atoms shown, whose availability for intermolecular bonding is confirmed by dielectric constant measurements.

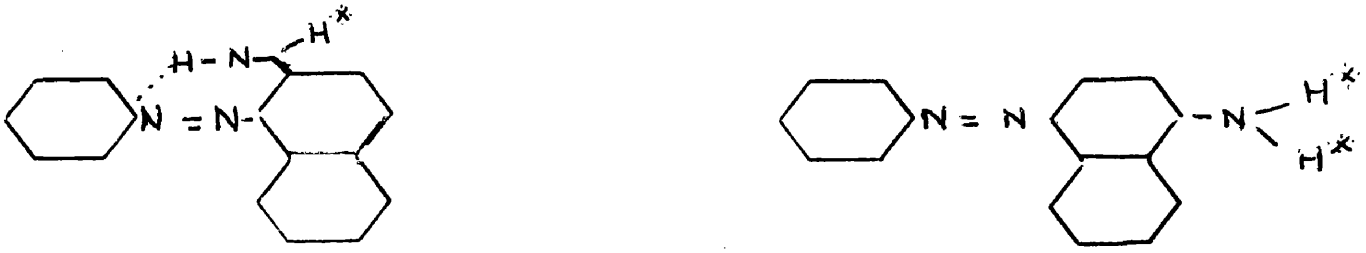


Fig.3. Structural formulae of benzeneazo-2- and 1-naphthylamine showing hydrogen atoms* available for bonding with the film.

Evidently the active oxygen atoms on the surface of the substrate are placed sufficiently close together to ensure that both hydrogen atoms of a single amino group can bond simultaneously. The NH....O bonds formed here are, as expected, weaker than the OH....O bonds formed by the phenols.

Bridge-bonding.

It has been suggested by Mehta[34] that Orange II and Azo-Geranine 2G, the structural formulae of which are shown in Fig.4 are attached to the film by a bridge formed by water molecules thus forming two hydrogen bonds. Jordan-Lloyd and her collaborators[49] in their studies on the absorption of

water by proteins has suggested that the tightly bound water

Fig. 4.

is linked by hydrogen bonds with the oxygen and nitrogen atoms of the carbonyl, hydroxyl, imino and amino groups of the protein structure, and can be represented as shown in Fig.5

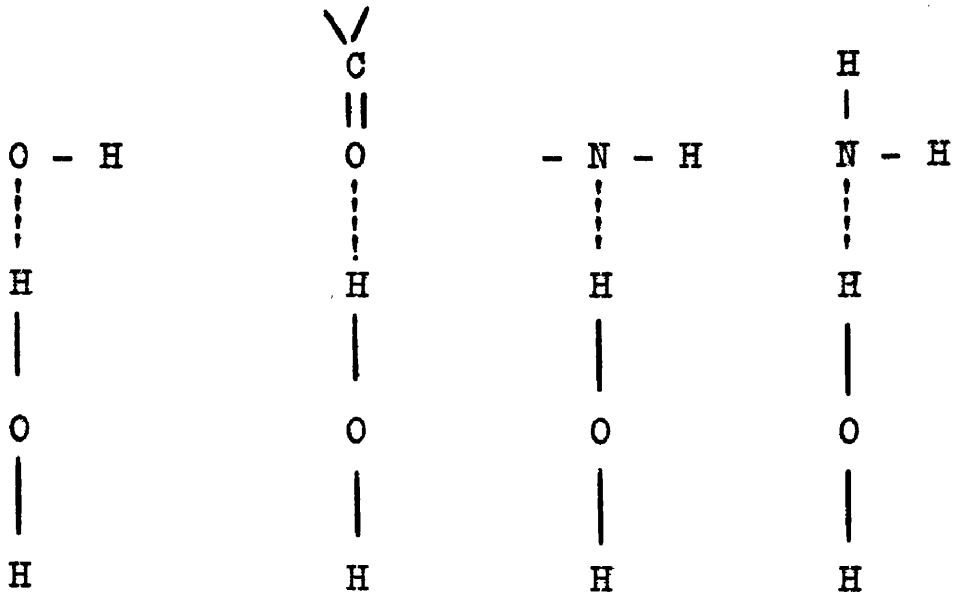


Fig. 5. hydroxyl carbonyl imino amino

This shows that one hydrogen atom of the water molecule forms a bond with a nitrogen atom or oxygen atom. That both the hydrogen atoms can simultaneously form bonds with different

anions is well known (L.K.Pauling[50]) and can best be illustrated by the structure of water itself, as shown in Fig.6.

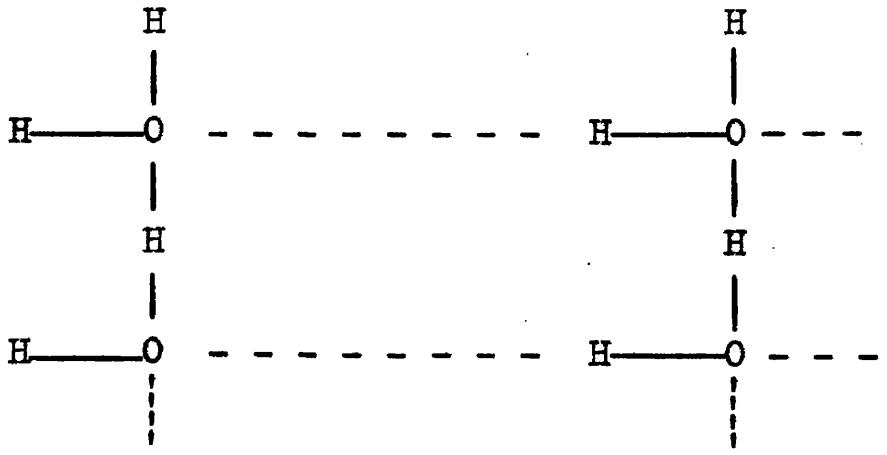
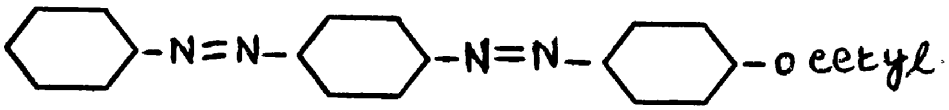
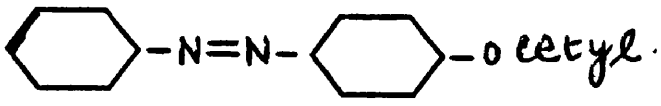


Fig. 6.

The possibility of one or both nitrogen atoms of an azo group taking part in the formation of a hydrogen bond has been shown by Rose[51]. Further, it has been shown by Neustädter[52] that a compound having the structure



forms a monomolecular film on water, whereas the compound



does not form a monomolecular film. This seems to show that the azo group has a slight but definite attraction for water. It has also been shown by him in other experiments that this attraction is much less than that of the phenolic hydroxy group.

In consequence of the detection of numerous such examples of cross-linkage of organic compounds either in solution or in condensed monolayers on water by bifunctional solutes, e.g. water or quinol[53] tests were made to discover whether a somewhat similar type of action can cause the sorption by the film of donor solutes which normally are not sorbed. A number of such compounds, principally azo compounds, were therefore applied to the film from non-aqueous solvents in the presence of a little water or quinol as potential bridging compound.

In view of the possibility of catalytic oxidation vitiating the results, special precautions were taken to exclude air from the sorption tubes. In some cases, films anodised in sulphuric acid were used, in case traces of chromium which might be present in chromic acid treated films should promote catalysis. The solutions were also examined under the Unicam photoelectric spectrophotometer before and after the tests, to detect any change in the nature of the solutes. No evidence was obtained of decomposition except in some solutions of azobenzene in 50% aqueous ethanol (in which the normal peak at 2550 Å was accompanied by a new intense peak at 3200 Å barely visible in the original solutions).

The results are summarised in Tables 5 to 9 and these show some evidence of the expected effect. It will be observed e.g. that, as would be expected on this hypothesis, quinol assists sorption but phenol does not.

The Tables 5 to 9 are self-explanatory and afford strong

evidence in favour of the hypothesis that amino compounds are sorbed by the film from dry solvents only in the presence of a dihydroxy compound like quinol, which seems to act as a bridge between the compound and the substrate. Since such a form of linkage is not possible with phenol, no sorption of these amino compounds from dry solvent should take place in the presence of phenol and this has been found to be the case.

In the case of sorptions from partially aqueous solvents as for example from 50% aqueous ethanol, 25% aqueous dioxan etc., the water molecule present serves to form the same type of linkage as the quinol, and so sorption should take place in such cases, and this has been observed to be the case.

The results obtained with azobenzene are somewhat inconsistent, as could be seen from Tables 10 to 12. A complete light absorption curve for two sets of sorption of these compounds by the films, one from 50% aqueous ethanol and the other from dry benzene in the presence of quinol, has been plotted in Figs.7 and 8. The curve for sorption from 50% aqueous ethanol shows two peaks, one of them at the normal wavelength of 2550 Å and the other intense one at 3200 Å, which is barely visible in the original solution.

The action is not attributable to the free amino-group present in some of the compounds because a typical amino-compound, 2-naphthylamine, is unabsorbed whether quinol is present or not. The bridge bond or cross-link must therefore operate through the azo group.

Considerably more investigation would be needed to demonstrate conclusively the existence of the bridge-bond, but the experimental evidence is at least suggestive of its presence in some systems.

Sorption of hydroxy compounds.

These experiments described in the preceding pages have shown that hydrogen bonding under suitable conditions between these compounds and the anodic film, probably plays an important rôle in their sorption by the film. Evidence has been obtained in confirmation of this hypothesis by Mehta[34], with the dyes Orange I, Orange II and Azo Geranine 2G.

Further confirmation of this hypothesis has been obtained by experiments carried out to study the sorption of phenol and 2:4-dinitrophenol and that carried out by Mehta[34] with benzeneazo-1-naphthol and benzeneazo-2-naphthol and o-nitrophenol.

It has been found that ~~with~~ compounds in which the hydroxy group is firmly chelated in a 6-membered ring, e.g. benzeneazo-2-naphthol and o-nitrophenol (but not 2:4-dinitrophenol in which the hydrogen of the hydroxy group is apparently more labile) are not sorbed.

A solution of phenol was prepared by dissolving 1.0 g. of 'analar' quality compound in a litre of distilled water. This was then diluted to various proportions to give solutions of concentration 0.50 g./l., 0.25 g./l. and 0.10 g./l. respectively.

20 c.c. of phenol solution of the respective concentration was pipetted out into each tube and anodised aluminium strip (2" x 2") was placed in it, and these were kept continuously agitated at 40° and 60°C. for 48 hours, which was found to be sufficient for the attainment of equilibrium. The residual concentration of phenol after sorption was estimated by the bromine method.

The results are shown in Table 13 and the sorption isotherms are drawn in Fig.9. The heats of reaction can be calculated from the equation

$$\Delta H = 4.578 \frac{(T_1 T_2)}{(T_2 - T_1)} \log_{10} \frac{c_1}{c_2}$$

where c_1 and c_2 are concentrations in solution in equilibrium with the same amount of phenol sorbed at temperatures T_1 and T_2 on the absolute scale and ΔH is the heat of reaction.

The average heat of reaction obtained from the above equation for phenol is of the order of +5 kcal.per mol. This indicates that phenol is attached to the film by one hydrogen bond. The fact that phenol is taken up and o-nitrophenol is not, is in itself a definite indication that hydrogen bond formation is involved. Marsden and Urquhart[19] have quoted a figure of approximately 2-3 kcal.per gm.mol. for the heat of sorption of phenol on cellulose acetate, which is lower than the bond energy of a hydrogen bond. However, they have taken that the sorption of phenol and p-nitrophenol, and the non-

sorption of o-nitrophenol is a sufficient indication of hydrogen bond formation in the former.

In the case of 2:4-dinitrophenol, a solution of a pure compound of concentration 0.2000 gm./l. was prepared in distilled water and diluted to various proportions to obtain different concentrations. 20 c.c. of the solution of the respective concentration was taken in a test tube and placed in each was a ($3\frac{1}{2}$" x $\frac{1}{2}$") strip of anodised aluminium. These were kept rotated continuously in the thermostat at 50° and 60°C. respectively for 24 hours, which was found to be sufficient to attain equilibrium conditions. The concentrations of the solutions were measured in the Spekker absorptiometer using the ultraviolet lamp, after diluting each solution in the ratio of 1 c.c. to 20 c.c. with distilled water. The results are shown in Table 14 and the isotherms for the same in Fig.10.

The value for the heat of reaction obtained for the sorption of 2:4-dinitrophenol on anodised aluminium is of the order of +4.0 kcal.per mol. which again indicates that one hydrogen bond is formed between the compound and the substrate in its sorption, as is expected, on the basis of the hypothesis already postulated.

The results obtained by Mehta[34] for the sorption of benzeneazo-1-naphthol from benzene are quoted here in Table 15 and the isotherms for the same are shown in Fig.11 as additional evidence for the necessity of hydrogen bond formation between such compounds and the substrate, for the sorption of the same.

The apparent heat of sorption calculated with the equation mentioned on page 41 is in the order of + 4.5 kcal.per mol. which shows that this compound is sorbed by the film through the formation of a hydrogen bond between the hydrogen of the hydroxyl group of the compound and the oxygen of the film.

Benzeneazo-2-naphthol was not found to be sorbed either from dry benzene or even from 50% aqueous ethanol as shown by Mehta[34]. The non-sorption from dry benzene can be explained as due to the fact that the hydroxy group in the compound, being situated in the ortho-position to the azo group, is involved in a six-membered ring system through an internal hydrogen bond between itself and the azo group. But its non-sorption from 50% aqueous ethanol is quite contrary to what may be expected according to the hypothesis proposed by Mehta[34], whereby any dihydroxy compound present in the system is assumed to act as a bridge between the film and the compound being sorbed, thus leading to the formation of two hydrogen bonds in each such sorption. Chipalkatti[54] also found that the same dye is not sorbed by wool from aqueous alcohol solution even after boiling for a considerable time. These facts seem to suggest that the unbonded nitrogen atom of the azo group is less able to form an external hydrogen bond in the unsulphonated than in the sulphonated dye, Orange II.

The results obtained for the sorption of p-nitrophenol were found to be quite inconsistent, as can be seen from Table 16. As is evident from the results, the p-nitrophenol appears

to be converted into a compound which has a correspondingly stronger or increased light absorptive power as compared with the original solution used. This might have been brought about by a catalytic effect of the oxide film on the compound or it might be due to the fact that this particular compound is decomposed by light.

The surface charge and its effect on sorption.

It has been found that the aluminium anode can be completely oxidised by prolonged electrolysis, resulting in the formation of a layer of brittle alumina containing slight traces of the unoxidised metal. After dissolving the unoxidised material by treating the film carefully with hydrochloric acid the oxide was ground to a fine powder dispersed in water, and examined by electrophoresis. It was found to have a positive electrokinetic potential. Therefore, it may be expected that anions will be attached to the surface of the oxide film in water while cations will be repelled by it. Generally this has been found to be the case as is shown in the following pages. The surface potential of the film has been found to be progressively reduced, and eventually reversed, by addition of increasing concentrations of sodium chloride, an isoelectric point being observed at a concentration of 0.09% sodium chloride.

Sorption of cationic compounds.

Qualitative tests with aqueous solutions of a number of representative basic dyes of the azo, thiazole and triphenylmethane classes have given no significant evidence of sorption except in the presence of sufficient sodium chloride to reverse the surface charge, when some sorption does seem to take place.

Films which have been coloured by e.g. Magenta from dioxan solution are washed clear by thorough rinsing in water, no doubt because of the simultaneous formation of cations of the colouring matter and development of the positive surface charge on the film. This compound contains no hydroxy group free to bond with the film and it was therefore considered that it would be interesting to know if the presence of such a group would be sufficient to cause sorption by hydrogen bonding in spite of the electrostatic repulsive forces. Two cationic compounds with free hydroxyl groups were therefore examined. These were the two cyanine dyes 2(4'-hydroxystyryl)-benzthiazole ethiodide and 2(4'-hydroxystyryl)-quinoline methiodide. It was found, as can be seen from Table 17, that neither of these two compounds is sorbed by the film from water (although the dyes appear to be decolourised).

Even though the Spekker readings do show a decrease in optical density the aluminium strips were not found to be dyed at all. So, it may be stated that the bonding properties of the hydroxy-group are not therefore sufficient to overcome the electrostatic repulsion of the charge in the substrate.

It has been observed that basic dyes can be fixed on to the film if it is pretreated with an anionic mordant, e.g. tannic acid or H-acid (1-amino-8-naphthol-3:6-disulphonic acid). The sorption in such mordanted oxide film is found to be very rapid and is complete in a few minutes.

Anionic compounds:- sulphate esters:

Since the anodic film has a positive electrokinetic potential it would be expected that anions would be readily sorbed by the same from aqueous solution. The sorption of two aliphatic anionic compounds, oleyl and tetradecyl sodium sulphates respectively, was investigated with this end in view.

A commercial sample of oleyl sodium sulphate (Lissapol C. I.C.I.) was purified by repeated extraction with ethanol in a Soxhlet and this purified sample was employed in the present investigation. A solution of the compound of concentration 0.500 g./l. was prepared in distilled water from which solutions of various other concentrations were prepared by suitable dilution. The concentrations of these solutions were measured by titrating them against a standard solution of a cationic agent (cetyltrimethylammonium bromide) by the method described on page 28. The sorptions were carried out both at 40°C. and 50°C. for 48 hours in each case, which was found sufficient to attain equilibrium conditions. The results are given in Tables 18 and 19 and the same is represented graphically in Fig.12.

Both oleyl sodium sulphate and tetradecyl sodium sulphate are readily sorbed but both are found, rather surprisingly, to exhibit no measurable temperature coefficient, as could be seen from Fig.12. This may be evidence of a process of purely physical sorption of ion-exchange, represented by a transfer of solute molecules from association with water in the liquid phase, to association with water molecules held at the solid surface, no chemical valency bonds being formed or broken. It has been found in this laboratory that sorption of cationic dyes from aqueous solution by certain negatively charged surfaces (e.g. graphite, silica) exhibits a similar negligible temperature coefficient. Rothmund and Kornfeld[55] and Paton and Ferguson[56] have pointed out that temperature has little or no effect on base exchange equilibria between ions of the same valency. Negligible or very low temperature coefficients in cation exchange on resins have been observed by Boyd et al, Magistad et al, Paton and Ferguson and Vanselow, quoted by Walton[57].

A physical process of this type could be expected to be a readily reversible type of sorption; so an experiment was devised to study the desorption of tetradecyl sodium sulphate from the film in water. It has been known from previous experiments that Solway Blue B is sorbed by the film, leading to the formation of a coloured lake with the substrate, and hence there will not be any desorption of the compound in water.

Therefore, Solway Blue B was employed as a control in this investigation.

The procedure consisted in placing anodised aluminium strips each of dimensions 3½" x ½" dyed with Solway Blue BNS or which had sorbed tetradecyl sodium sulphate, in a test-tube and placing 20 ml. of water in it. This was kept rotated in a thermostat at 40°C., the temperature at which the sorption of these compounds was carried out. No desorption was observed in the case of Solway Blue BNS dyed films, but measurable desorption occurred with the tetradecyl sodium sulphate sorbed films and such desorption was found to increase with increasing concentration of the tetradecyl sodium sulphate employed for the original sorption study.

A further confirmatory test was carried out qualitatively as follows, with oleyl sodium sulphate and using naphthalene-2-sulphonic acid as the control. Solutions of oleyl sodium sulphate and naphthalene-2-sulphonic acid, of about the same concentration as employed in the sorption experiment, were prepared and 10 ml. of each solution was taken in a test tube which contained a strip of anodised aluminium (3½" x ½"). Each set of solutions consisted of a blank control together with two tubes containing the anodic film. These were kept agitated at 60°C. in a thermostat for 24 hours; they were then taken out, filtered twice, and each solution was tested for the presence of any soluble aluminium salt as follows:-

First a 1% solution of Solochrome Cyanine RS was prepared.

A few drops of this reagent were added to the solution to be tested, then it was warmed and the colour that was developed was observed. If aluminium is present in the solution it would form a deep bluish coloured lake with the reagent. The results obtained are given in Table 20.

The non-development of any blue colour by oleyl sodium sulphate solution containing the anodic film, on the addition of the reagent, shows that there is no soluble aluminium salt present in it. These results seem to prove conclusively that the sorption of surface active anionic compounds by the anodic film is a purely physical process brought about by the electrostatic attraction between the positively charged surface of the substrate and the negatively charged ions of the compound.

It might be argued that such a kind of combination may be due to the surface active nature of the alkyl sulphate. In order to confirm that this is not so and that the sulphate ester group itself is responsible for the observed effect, an azo dye containing the group (kindly supplied by I.C.I.) whose structure is shown in Fig.13, was chosen and its sorption by the film was investigated.

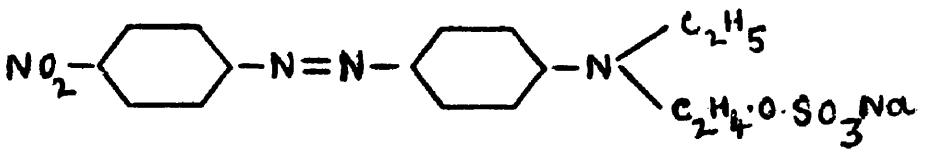


Fig. 13

A commercial sample of this above dye was purified by

salting out a concentrated solution of the dye in water with sodium chloride. The precipitated dye was filtered and freed from any sodium chloride present by boiling it with ethanol for about fifteen minutes, filtered and washed with a little boiling ethanol and then dried at about 100°C.

A solution of this purified sample of the dye of concentration 0.10 g./l. was first prepared in distilled water and diluted to various proportions. Then 20 ml. of this solution were pipetted out into each tube, which contained anodised aluminium of dimensions 3½" x 1" and kept agitated in two thermostats at 37°C. and 50°C. for 48 hours and 24 hours respectively, which were found by preliminary experiments to be quite sufficient for the attainment of equilibrium conditions. The results are tabulated in Table 21 and the isotherm for the same is shown in Fig.14. This dye also shows virtually no temperature coefficient.

It may therefore be stated that sulphate esters in general are sorbed by the anodic film by a physical process of anion exchange. They are not sorbed on to specific sites in the oxide and no chemical reaction appears to be involved.

In the case of oleyl sodium sulphate and tetradecyl sodium sulphate the difference in the amount sorbed might be due to their difference in solubility in water. If this be so, then the results of sorption of these two compounds by the film, plotted with the relative concentration of the equilibrium bath i.e. the ratio of the equilibrium bath concentration to

the saturation value of each compound in this particular temperature range, as abcissa, and the amount sorbed as ordinate, at the two temperatures 40°C. and 50°C., must be the same. This has been found to apply in the sorption of fatty acids on nickel powder (S.G.Daniel[58]). But results shown in Table 22 and the same shown graphically in Fig.15 indicate clearly that the different solubilities of these two compounds have no bearing whatsoever on their sorption by the oxide film.

The saturation value of each compound was determined at 45°C. mid-way between 40°C. and 50°C., the temperatures employed for actual sorption. The actual determination consists in placing an excess amount of the reagent in a test-tube containing about 10 c.c. distilled water and this was kept agitated at 45°C. for about two hours after which the solution was filtered off quickly from the excess solute present and the filtrate was then diluted suitably and its concentration estimated by the titration method already outlined on page 28.

Anionic compounds: sulphonates.

The sorption of sulphonated compounds was next investigated, the simplest aromatic sulphonic acids being examined at first. Benzene sulphonic acid, naphthalene-1-sulphonic acid and naphthalene-1:5-disulphonic acid and their sodium salts all showed no measurable sorption and naphthalene-2-sulphonic acid was sorbed to a negligible extent. Almost all sulphonated dyes, however, colour the film strongly, even if, as in the case

of some sulphonated aminotriphenyl methane and o-hydroxyazo compounds, they contain no other group capable of combining with the substrate in water. The attraction here must clearly be attributed to the sulphonic acid groups and the non-sorption of the simpler acids must be due to their high water solubility which is causing the equilibrium to be shifted too much in favour of retention of the solute in the water phase. (The sulphate esters just described have much lower water solubility). Therefore, attempts were made to promote sorption of the sulphonic acids by reducing their solubility by the use of ethanol-water mixtures as solvents but these were quite unsuccessful and consequently attention was turned to aromatic sulphonic acids in which water solubility is reduced by 'loading' with substituent groups unlikely themselves to take part directly in the sorption process. Four types of compounds were therefore chosen, containing as bonding-groups:

(a) an additional condensed benzene ring

(b) a phenylazo-group

(c) o-hydroxyphenylazo-system in which the hydrogen of the hydroxyl group is involved in a chelate ring and

(d) a long alkyl chain and also one compound containing two of these groups.

Anthracene-1-sulphonic acid was used as an example of type (a) but the results were believed to be complicated by catalytic oxidation to an anthraquinone derivative and its use was therefore not pursued.

Azobenzene-4-sulphonic acid was chosen to represent type (b). This was prepared from azobenzene by heating 1 mol. of azobenzene at 130°C. for 10 minutes with 20% oleum (5 mol.). The mixture was then cooled in ice and carefully drowned in twice its volume of ice and water. The crystalline precipitate obtained was then filtered and washed with minimum amounts of cold water. It was then recrystallised from water, dried between filter papers and dried subsequently in an oven at 100°C. (It was obtained as orange-plates m.p.127°C. as cited in Beilstein Vol.XVI p.270).

The study of the sorption of this compound by the film was made in triplicate for each concentration. 50 c.c. of solution of the respective concentration was taken in each test-tube (6" x $\frac{1}{2}$") so as to leave no air space inside the tube, to prevent the occurrence of any possible oxidation, as was noticed in the case of azobenzene. A pair of aluminium strips anodised in chromic acid, each of dimension (2" x 1") was placed in each test-tube and these were kept continuously agitated for 24 hours at 40°C. and 55°C. respectively. The results are shown in Table 23 and the isotherms in Fig.16.

As is evident from the results, azobenzene-4-sulphonic acid is measurably sorbed and the sorption also shows a significant temperature coefficient but in view of the possibility of oxidation occurring as with azobenzene itself, as shown in Tables 10 to 12, attention was directed more particularly to types (c) and (d). The azo-dye benzeneazo-2-naphthol-3:6-

disulphonic acid (C.I.No.28) was used to represent class (c). This dye was prepared by the usual method of diazotising aniline and coupling it with 2-naphthol-3:6-disulphonic acid. The dye was purified by passing it successively through two ion exchange resin columns (ca. 30 cm. long and 3 cm. diameter). The first one was filled with an anionic ion exchange resin and the second one with a cationic ion exchange resin. The rate of flow through these columns was adjusted to about 3 mls. per minute. The dye solution emerging out of the column was tested with a Congo Red paper which indicated whether the effluent is converted into a free acid or not. After passing the same solution about thrice through the columns it was evaporated to dryness in a water-bath. Then it was converted into the sodium salt by neutralising it with the theoretical amount of sodium bicarbonate and the purity of the resulting sodium salt of the dye was estimated by the method of Arshid et al[59].

A solution of this pure dye of concentration 0.00134 gm. mols./litre in distilled water was first prepared and diluted to various proportions. The sorption was carried out at 30°C. and 57°C. for 65 hours and 24 hours, respectively, the concentrations being measured both before and after sorption with the Spekker absorptiometer. The results are shown in Table 24 and the isotherms in Fig.17.

It is seen that the dye is sorbed by the film to a considerable extent and it also exhibits a measurable

temperature coefficient. The apparent heat of sorption for the compound calculated from the equation is of the order of 10 kcal.per mol. over the temperature range 30°- 60°C.

Next the sorption of a dye, dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid of exactly the same structure as benzeneazo-2-naphthol-3:6-disulphonic acid but containing in addition an alkyl chain composed of twelve carbon atoms was studied. The dye was prepared by diazotising dodecylaniline and coupling it with 2-naphthol-3:6-disulphonic acid and was purified with the aid of the resin column as mentioned in page 54 and ultimately converted into its sodium salt, which was used in the present sorption study.

The object of the study was to find out whether there was any difference in affinity between these two dyes for the anodic film and if so, whether it could be due to the difference in solubilities between these two, owing to the presence of a long alkyl chain in one of them. This could be detected by plotting the sorption isotherms obtained with the two dyes at the same temperature with the relative concentration as the abcissa as explained in the case of oleyl sodium sulphate and tetradecyl sodium sulphate.

A solution of the dye of concentration 2.0 g./l. in distilled water was prepared and diluted to different proportions. The sorption at 50°C. and 60°C. was studied, the results of which are shown in Table 25 and the isotherms in Fig.18.

Evidently this dye also shows quite a considerable sorption and a measurable temperature coefficient. The sorption data plotted on the relative concentration basis for both the dyes is shown in Fig.19 and the data on the basis for the same in Table 26.

The results clearly show that the difference in the sorption of these two dyes by the film is not in any way attributable to their different solubilities in water as was found to be the case with a similar comparison in Fig.15.

Influence of sulphonic acid groups on sorption by the film.

It has been shown that the sulphonic acid group is sorbed by the film through the formation of a salt linkage with the metal of the film. Therefore there should be a larger number of sites available at the surface for attachment of dye molecules containing sulphonic groups. This should therefore result in the formation of a closely packed monolayer. Now Orange II has only one sulphonic group and a hydroxy group in the 2-position, which is prevented from participating in any possible hydrogen bond formation by chelation with the azo nitrogen, and hence is prevented from bonding the dye to the film. It could therefore be assumed that Orange II has only one point of attachment and hence its area when it is sorbed by the film should be that as measured, when the molecule is standing on the sulphonic group. This gives a value of 30 sq. $\overset{o}{A}$. Now, if each molecule of the dye covers the surface

of the film to the same extent at the same temperature, then it should be possible to calculate the area of the other dye molecules by multiplying the area of Orange II (2-naphtholazo-4-sulphanilic acid) by the maximum amount of the dye sorbed and dividing it by the maximum amount of each of the other dyes sorbed. The results obtained by A. Cameron[60] are shown in Table 27. The areas of each dye molecule have been measured in three positions:- (1) standing vertically on one sulphonic group; (2) lying horizontally along an edge bounded by two sulphonic groups if two are present; (3) lying flat with all the sulphonic groups touching the surface.

It is evident from the above data that the areas found by experiment correspond to the calculated area for each dye molecule with the assumption that each one of them is attached to the film through its sulphonic groups. In the case of Orange II it has been shown by Mehta[34] that the dye is sorbed by the film through the cross-linking of its free unchelated azo nitrogen with the oxygen of the film using water molecules as the bridging compound. But the results obtained above do not substantiate this.

The only anomaly appears to occur in the sorption of Orange I. Here the hydroxy group is in the 4-position and as such both the sulphonic as well as the hydroxy group will be expected to partake in its sorption by the film. If this be the case then it should occupy a larger area than Orange II. But actually it has been found to occupy a smaller area, as

shown in Table 27. This may be explained on the assumption that the hydroxy groups of the different molecules are bonded to each other through hydrogen bonds and hence they are not available for attachment to the film, thus leaving only the sulphonic group for sorption as in the case of Orange II.

Thermodynamical data.

The heat of reaction, ΔH, the change in chemical potential on sorption ΔG, and the entropy change can be calculated for these dyes from the above data.

The heat of reaction can be determined from a form of van't Hoff equation. The change in chemical potential or the free energy change on sorption is a measure of the tendency of the equilibrium of the system to move one way or the other. Any increase in the number of sulphonic groups would result in an increased affinity, both for water and the film. The ultimate result could therefore not be predicted. The change in chemical potential can be expressed by the equation

$$\Delta G = RT \ln \frac{\frac{\theta}{1-\theta}}{D_B}$$

if it is assumed that the dye is sorbed in certain specific sites in the film, where θ is the fraction of the total available sites occupied by the dye at temperature T on the absolute scale, and D_B is the equilibrium concentration of the dye in the external solution. Here the activity of the dye

in solution is assumed to be unity and $\frac{\theta}{1-\theta}$ represents the activity of the dye on the film.

After knowing the values of ΔH and ΔG the entropy change ΔS can be calculated by employing the Gibbs-Helmholtz equation as shown below

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

The entropy change on sorption of a dye by the film gives a quantitative measure of the degree of freedom available for such sorbed dye molecules. If for example the dye is attached to the film at three points there will be a considerable restriction on its movement on the film and this will consequently lead to a greater entropy change on sorption.

These parameters calculated by A. Cameron[60] for Orange I, Orange II, benzeneazo-2-naphthol-3:6-disulphonic acid, aniline-4-sulphonic acid-azo-2-naphthol-3:6-disulphonic acid and Chlorazol Sky Blue FF are given in Table 28. As can be seen from this Table, the values of ΔH^{o} and ΔS^{o} increase proportionally as the number of sulphonic groups increase, as predicted before. But the affinity or free energy change ΔG^{o} does not seem to bear any numerical relationship to the number of sulphonic groups present in the dye molecule.

All the available experimental evidence therefore seems to indicate clearly that the mechanism of sorption of a sulphonic acid group by the film must differ fundamentally from that of a sulphate ester group. The heat of reaction ΔH^{o} observed as shown in Table 28 must in fact represent a chemical

reaction probably the formation of a salt between the acid group and aluminium. It has actually been observed, as shown in Table 20 that traces of aluminium are present in solutions of aromatic sulphonic acids but not in those of sulphate esters which had been kept in contact with the film.

Next the sorption of dodecyltoluene sodium sulphonate was studied. A sample of this compound was estimated for its purity by titrating against a pure cation active agent (cetyl trimethyl ammonium bromide) by the method described on page 25. It was found to be 73.5% pure. It has been stated by the suppliers of this compound, that it does not contain any inorganic salts, but that it is likely to contain higher homologues, since it is very difficult to remove them. It is also quite probable that this compound contains a small amount of an unsulphonated fraction, which might emulsify with it and thus not be apparent in solution, but which might account for the low analysis. It appears therefore that the impurities present in this compound are not likely to affect the experimental result. Solutions of different concentrations of this compound in distilled water were prepared and 20 ml. of each was taken in a test-tube which contained about 0.0431 gm. of oxide film in each. These were kept rotated continuously at 37°C. and 50°C. in thermostats for 48 hours and 24 hours respectively. The results obtained are tabulated in Table 29 and the isotherms drawn in Fig. 20.

The results show that there is positive sorption of this

compound by the film. At lower bath concentrations it showed no measurable temperature coefficient as could be seen from Fig.20, but at the higher concentrations a small difference in sorption at the two temperatures investigated is observed. It therefore seems that the surface-active properties of the compound in some manner prevent salt formation by the sulphonic acid group or at the most, allow this to occur only to a small extent at the higher concentrations and in its place an ion-exchange absorption may take place. Anionic micelles are probably involved in the sorption, being surrounded by a layer of solvated water molecules; the affinity between sulphonate groups and aluminium is then insufficient to break through the surrounding water. This behaviour is not characteristic of all long alkyl chain sulphonates because the azo compound 4-dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid which contains weighting groups of both types (c) and (d) does exhibit a fairly high heat of sorption of the order of 10 kcal. per mol. It is probably less able to form micelles in solution and therefore the sulphonic acid groups are not prevented from taking part in salt formation.

It will be observed that the isotherms of the dodecyl-toluene sodium sulphonate compound appear to rise to a maximum and then fall. This apparent anomaly has not been investigated further but it may well be connected with the somewhat complex balance of reactions involved in the simultaneous operation of an ion-exchange process and salt formation.

SECTION 3.

CONCLUSIONS

The anodic film on aluminium prepared by anodisation in chromic acid is used as an inorganic substrate to study the nature of the bonding forces displayed by it in its sorption of organic compounds both from solution in water and in a number of organic solvents. Although the anodic film could be prepared from a number of electrolytes, the one prepared from chromic acid is employed here since it has been found to be very pure and consists of amorphous γ-Al_2O_3 in a porous form. The film has been found to show a variety of bonding forces in its sorption of the different compounds studied, which may be stated as follows:-

The sorption of hydroxy and amino compounds appears to be effected by the anodic film through hydrogen bonding between its oxygen and the phenolic hydroxy or an amino group in the solute. But such bond formation with these two sets of compounds is found to vary with the particular experimental conditions. Thus the hydrogen bonds formed by phenolic hydroxy compounds appear to be unaffected by the nature of the solvent used. But similar bonds formed by the amino groups have lower affinity and their formation appears to be prevented, resulting in their non-sorption by the film when benzene or water is the solvent present in the system. This phenomenon does not occur if carbon tetrachloride or dioxan is used as the solvent.

The sorption studies of phenol, 2:4-dinitrophenol, benzeneazo-1-naphthol and o-nitrophenol from water by the anodic film give ample evidence in favour of the above hypothesis. All these compounds except benzeneazo-2-naphthol and o-nitrophenol are taken up by the substrate. The non-sorption of these two compounds is due to their hydroxyl groups being involved in a stable six-membered ring-structure formed by chelation resulting in the non-availability of hydrogen atoms for bond formation with the film. The values of heats of reaction for phenol, 2:4-dinitrophenol and benzeneazo-1-naphthol, taken up by the film from aqueous solution, have been calculated by using the van't Hoff equation

$$\Delta H^{\circ} = 4.578 \frac{T_1 T_2}{T_2 - T_1} \log_{10} \frac{c_1}{c_2}$$

where ΔH° is the heat of reaction, c_1 and c_2 are the concentrations in solution in equilibrium with the same amount of solute sorbed at temperatures T_1 and T_2 on the absolute scale. The values obtained are of the order of +5.0, +4.0, +4.5 kilo-gram.calories per gram mol. respectively, thus indicating the formation of one hydrogen bond between the substrate and the solute in each case. It may be noted in this connection that the hydrogen of the hydroxy group in 2:4-dinitrophenol appears to be apparently more labile than is the case with o-nitrophenol.

Although amino compounds would be expected to be readily taken up by the film it has actually been found that this is

not so and that it depends on the nature of the solvent used. Thus, 2-naphthylamine, benzeneazo-1-naphthylamine, benzeneazo-2-naphthylamine and 4-aminoazobenzene are not sorbed by the oxide film from either aqueous solution or from dry benzene. But benzeneazo-1-naphthylamine and benzeneazo-2-naphthylamine are readily taken up from solution in carbon tetrachloride, colouring the film pale yellow and deep-bluish red respectively. Therefore, water and benzene appear to have a protective action on the amino groups in such compounds and prevent their partaking in any bond formation, while this is not so with solvents like carbon tetrachloride and dioxan. Therefore, both the hydrogen atoms of the amino group may be capable of simultaneously bonding with the substrate from solvents like carbon tetrachloride and dioxan, except in the case of o-aminoazo compounds where chelation prevents one from reacting.

The sorption of certain compounds which are not sorbed normally from a dry solvent has been investigated. These are mainly azo compounds and their sorption from non-aqueous solvents in the presence of a little water or quinol has been studied. It has been shown by Pauling[50] that both the hydrogen atoms of a bifunctional solute like water are capable of forming bonds simultaneously with different donors. The sorption of 2-aminoanthraquinone, 4-aminoazobenzene, 3-methoxybenzanthrone, benzeneazo-1-naphthylamine, benzeneazo-2-naphthylamine, and azobenzene from dry and also from aqueous benzene, dioxan and ethanol, as well as from these dry solvents

in the presence of quinol has been investigated. The results obtained in all cases except azobenzene indicate clearly that they are taken up by the anodic film from the dry solvents either in the presence of water or quinol but not from the purely dry solvent. Further, these compounds are not taken up in the presence of phenol since it is incapable of forming two hydrogen bonds between the substrate and the solute. This in turn shows that such sorption is due to the formation of two hydrogen bonds between the solute and the substrate, the water or quinol present being responsible for the same and which are accordingly termed "bridging-compounds". Such hydrogen bonds appear to be formed probably with either one or both the azo nitrogen of the solute and the oxygen of the film. Here the free amino groups present in some of the compounds do not seem to be involved in any hydrogen bonding since such a typical amino-compound as 2-naphthylamine has not been found to be sorbed, whether quinol is present in solution or not. These results seem to indicate the definite existence of the bridge-bond in certain systems but a thorough investigation in this direction is necessary before its existence can be demonstrated conclusively. The results obtained with azobenzene are not consistent.

It has been discovered by previous workers in this field that the anodic film has a positive zeta potential in neutral aqueous solution, which could be progressively reduced and ultimately reversed by addition of increasing concentrations

of sodium chloride, an isoelectric point being reached at a concentration of ca. 0.09% sodium chloride. It has also been known before that a positively charged dye ion, like that of a basic dye Magenta, does colour this film from a non-polar solvent like dioxan but that it is removed from the film by rinsing in water, because of the simultaneous formation of the colouring matter and the development of the positive surface charge on the film. Since the dye Magenta contains no free hydroxy groups to bond with the film, the sorption of such compounds containing a positive charge was studied, with a view to determining whether the presence of a hydroxy group is sufficient to overcome the repellent charge in the substrate through hydrogen bond formation with the same. The compounds examined were two cyanine dyes:-

(i) 2(4'-hydroxystyryl)-benzthiazole ethiodide and

(ii) 2(4'-hydroxystyryl)-quinoline methiodide.

Both of these compounds were not sorbed, although they were found to be decolourised. This appears to be a catalytic decomposition. Therefore it may be stated that the bonding properties of the hydroxy group are not sufficiently strong enough to overcome the electrostatic repulsion of the charge on the substrate.

But anionic compounds should be readily taken up from aqueous solution by the oxide film since it has a positive

electrokinetic potential. This has been found to be the case with two such surface-active compounds, oleyl sodium sulphate and tetradecyl sodium sulphate. Both show no measurable temperature coefficient as could be seen from Fig.15. This indicates that such sorption should be a purely physical sorption or of an ionic nature represented by a transfer of solute molecules from association with water in the liquid phase to association with water molecules held at the solid surface, no chemical valency bonds being formed or broken. A similar negligible temperature coefficient has been found in this laboratory in the sorption of cationic dyes from aqueous solution by negatively charged surfaces like silica and graphite. Much additional evidence in favour of such an ion-exchange process has been obtained by way of desorption of compounds from the film, which had sorbed the same, and also by the non-formation of any coloured complex of these solutions which had been kept in contact with the films containing these compounds, with a lake-forming dye Solochrome Cyanine RS.

It has also been shown that such an ion-exchange process is not due to the surface-active nature of these compounds but due to the sulphate ester group present in them by studying the sorption of an azo-dye containing this group. The results obtained with this dye also indicate no temperature coefficient as could be seen from Fig.14. These investigations appear to show that sulphate esters in general are taken up by the anodic film by a physical process of anion-exchange. They do not

appear to be sorbed on any specific sites in the substrate and no chemical reaction seems to be involved. It has also been shown that the variation in the total amounts of oleyl sodium sulphate and tetradecyl sodium sulphate taken up by the film are not due to their differences in solubility in water.

Next the sorption of sulphonated compounds was investigated. Simple sulphonated compounds like benzene-sulphonic acid, naphthalene-1-sulphonic acid, naphthalene-1:5-disulphonic acid and their sodium salts were examined at first from aqueous solution. All these compounds showed no measurable sorption, which appears to be due to their high water solubility resulting in the equilibrium being shifted too much in favour of retention of the solute in the water-phase. Attempts made to reduce their solubility by the use of ethanol-water mixtures were quite unsuccessful and consequently aromatic sulphonic acids with reduced solubility in water, obtained by 'loading' them with substituent groups which are in themselves unlikely to take part directly in the sorption process, were used. The compounds so chosen could be classified into the following four categories containing as bonding groups:-

(i) an additional condensed benzene ring

(ii) a phenylazo-group

(iii) o-hydroxyphenylazo systems in which the hydrogen of the hydroxy group is involved in a chelate ring and

(iv) a long alkyl chain and also one compound containing two of these groups.

Anthracene-1-sulphonic acid employed as an example of (i) was found to be catalytically decomposed while azobenzene-4-sulphonic acid chosen to represent class (ii) was found to show a measurable temperature coefficient as shown in Fig.16. Since azobenzene appears to be more easily oxidised, it was thought that the result obtained with azobenzene-4-sulphonic acid might also be not a reliable one. Hence attention was concentrated mostly on compounds of class (iii) and (iv).

The azo-dye, benzeneazo-2-naphthol-3:6-disulphonic acid was chosen to represent class (iii) and dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid to represent class (iv). Benzeneazo-2-naphthol-3:6-disulphonic acid shows a measurable temperature coefficient, the apparent heat of sorption being of the order of 10 kcal. per mol. over the temperature range 30-60°C. in keeping with the formation of two bonds between the two sulphonic groups of the solute and the oxygen of the substrate. The main object in studying the sorption of dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid was to find out whether the difference in amounts of this dye and benzeneazo-2-naphthol-3:6-disulphonic acid taken up by the film was due to their different solubilities in water. But this has not been found to be the case, similar to the result obtained with oleyl sodium sulphate and tetradecyl sodium sulphate. Thus it is quite clear that all these sulphonic compounds mentioned above are adsorbed by the anodic film through salt formation between itself and the sulphonic groups

of these compounds.

Therefore a larger number of sites would be expected to be available at the film surface for attachment of dye molecules containing sulphonic groups resulting in the formation of a closely packed monolayer. This has been shown to be the case with a number of such dyes as Orange I, Orange II, benzeneazo-2-naphthol-3:6-disulphonic acid, benzene-4-sulphonic acidazo-2-naphthol-3:6-disulphonic acid and the direct dye Chlorazol Sky Blue FF. The evidence in favour of this view lies in the good agreement obtained between the observed amount of each dye taken up by the film at saturation and the same calculated with the aid of models, assuming the dye to be standing vertically on its sulphonic acid group, with monovalent dyes, lying horizontally along an edge bounded by two sulphonic groups in the case of a divalent dye, and lying flat with all the sulphonic groups touching the surface of the substrate in the case of trivalent or other polyvalent dyes.

These results are shown in Table 27. Further confirmation of this view has been obtained by calculating the heat of reaction ΔH°, the entropy of dyeing ΔS°, and the affinity or free energy change ΔG°. The heat of reaction is obtained from the van't Hoff equations while the free energy change is calculated from the expression

$$\Delta G = RT \ln \frac{\frac{\theta}{1-\theta}}{D_B}$$

where $\frac{\theta}{1-\theta}$ represents the activity of the dye in the film, its activity in solution being assumed to be equal to unity, and D_B is the equilibrium concentration of the dye in the external solution. This expression is derived on the assumption that the dye is sorbed on certain specific sites in the film, where θ is the fraction of the total available sites occupied by the dye at temperature 'T' on the absolute scale. Thus, having determined ΔH^o and ΔG^o, it is possible to calculate the entropy of dyeing ΔS^o by using the Gibbs-Helmholtz equation

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The values for these parameters obtained for Orange I, Orange II, benzeneazo-2-naphthol-3:6-disulphonic acid, benzene-4-sulphonic acidazo-2-naphthol-3:6-disulphonic acid and Chlorazol Sky Blue FF are given in Table 28. Since the sulphonic groups present in these dyes are assumed to be responsible for the attachment of these dyes to the film, the greater the number of sulphonic groups present in a dye the greater will be its heat of reaction ΔH^o, and entropy of dyeing ΔS^o. This is found to be the case as could be seen from Table 28 but the affinity or free energy change ΔG^o as could be seen from the same Table does not appear to bear any relationship to the sulphonic groups present in the dye molecule.

The available experimental evidence therefore seems to indicate a different type of mechanism for the sorption of a sulphonic acid group by the film from that of a sulphate ester

group. The heat of reaction values ΔH^{o} obtained as shown in Table 28 appear to represent a chemical reaction, probably the formation of a salt between the acid group and the oxide film. This view receives additional support from the results obtained with aromatic sulphonic acids and sulphate esters kept in contact with the film, where traces of aluminium had been detected in the solutions of the former compounds but not in those of the latter.

An anomalous result has been obtained with the sorption of dodecyltoluene sodium sulphonate by the anodic film. It does not appear to show any appreciable temperature coefficient at lower bath concentrations, while at higher concentrations a small difference in sorption at the two temperatures investigated is obtained. Although this compound contains certain impurities, their nature is such that they are not likely to affect the experimental result. Therefore the surface-active properties of the compound seem to prevent any salt formation between the film and the sulphonic acid group, or allows this to occur only to a limited extent at the higher concentrations and in its place an ion-exchange process may be involved. Here the anionic micelles appear to be taking part in the sorption, these being surrounded by a layer of solvated water molecules. Therefore the affinity between the sulphonate groups and the film might then be insufficient to break through this surrounding water barrier. But the characteristic is not observed

with a similar but an azo compound 4-dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid, which exhibits an appreciable heat of sorption of the order of 10 kcal.per mol. Here it is probably less able to form micelles in solution and hence its sulphonic acid groups are not prevented from taking part in salt formation. The nature of the isotherm obtained for the sorption of dodecyltoluene sodium sulphonate is rather ambiguous which may be due to the somewhat complex balance of reactions involved in the simultaneous operation of both an ion-exchange process and salt-formation.

PART II

SORPTION STUDIES ON CHITIN

PART II.

SORPTION STUDIES ON CHITIN

INTRODUCTION

Chitin is a polysaccharide derivative which is fairly well distributed in nature both in the plant and in the animal world. In the animal kingdom it is widely distributed in invertebrates, mainly as protective cuticles, and forms a major constituent of the cuticle of Arthropods. It is present also in the shells of shrimps, crabs, lobsters and other crustacea. In plants it replaces cellulose as the cell-wall material in some fungi and it is present with cellulose in the walls of certain algal cells. Two main characteristics are commonly apparent among the large number of chitin-containing organs of both plants and animals: (i) All specimens of chitin have been shown by recent work to be almost identical both chemically and crystallographically (ii) The chitin always occurs in association with protein.

Sources of chitin.

A number of investigations have been carried out by other workers on chitin obtained from different sources and the following may be mentioned by way of a brief review of the same. Almost all the investigators have chosen crab and

lobster shell as the raw material, since the chitin isolated from these sources appears to be a well defined product of known composition. Odier[61] obtained chitin from the outer casing of articulata, O. Butschli[62] from lobster shells, C.T.W.Krukenberg[63] from the beak of the 'Lolio vulgaris', W.Haliburton[64] from the cartilage of the cepia and limulus and in small proportion, from the cuticle of cockroaches and from the liver of the King Crab.

Recently, chitin has been isolated from the cuticle of the blowflies 'Sarcophaga falculata' and 'Calliphora erythrocephala' by Fraenkel and Rudall[65].

Formulation of chitin.

The formulation of chitin proposed by Ledderhose was $C_{15}H_{26}O_{10}N_2$ and the acetic acid molecule was believed to participate in this structure. This was apparently based on the assumption that chitin is a glucosidic compound formed by the condensation of aminoglucose and acetic acid. This view was opposed by Sundwick[66] and Sundwick and Araki[67] who proposed that the analytical data were best satisfied by the formula $C_{30}H_{50}O_{19}N_4$ or its multiples.

The non-action of periodic acid and its salts prove that hydroxyl groups are separate. Therefore Sundwick's[66] formula $C_{30}H_{50}O_{19}N_4$ appears to be the simplest one, which fully complies with the necessary conditions, although his explanation of the nature of the hydrolysis is grossly incorrect. All the

available data on chitin show clearly that it is relatively stable towards acids, alkalis and oxidising agents and that it does not possess any reducing properties, as shown by the non-reduction of Fehling's solution. Moreover, on hydrolysis, it has been found to yield a definite amount of both glucosamine-hydrochloride and acetic acid. A structural formula for chitin has therefore been proposed by J.C.Irvine[68] which fulfils these characteristics. According to this, one molecule of aminoglucose is condensed with three molecules of acetylaminoglucose through the elimination of four molecules of water. The hydrolysis of such a compound would proceed according to the equation:-

$$C_{30}H_{50}O_{19}N_4 + 7H_2O + 4HCl \longrightarrow 4C_6H_{13}O_5N,HCl + 3CH_3.CO_2H$$

The validity of the above structural formula was confirmed by Irvine[68] by polarimetric investigations on the hydrolysis of his sample of chitin by hydrochloric acid. Several investigators have identified butyric acid as one of the products obtained on hydrolysis of chitin. This has been proved to be completely incorrect by Irvine[68]. Thus, the earlier data lead to the formulation of chitin as $(C_{30}H_{50}O_{19}N_4)_n$, containing acetylaminoglucose and aminoglucose residues.

The chitin prepared by Irvine[68], however, appears to have been partially deacetylated, because recent investigations on this compound (Meyer and Mark[69]; Meyer and Wehrli[70]; Fraenkel and Rudall[65]) seem to show that chitin is built up

of chains of condensed N-acetylglucosamine units and is identical with cellulose, except that the secondary hydroxy group in position 2- is substituted by an acetamide group. This is shown in Fig.21. The main test of purity is the nitrogen content, which should be 6.89%, but this theoretical value appears to be rarely obtained. Darmon and Rudall[71] state that the chitin isolated by them from insect cuticles gives a value for nitrogen content corresponding to about 93% pure chitin. They state that purified lobster tendon chitin has shown a nearer approach to the theoretical nitrogen content.

The structural aspect of chitin has been studied by Meyer and Pankow[72] and also by Fraenkel and Rudall[65,73], and lately by Darmon and Rudall[71]. Meyer and Pankow[72] have given a reasonable interpretation of the structure and find it has a rhombic cell with a = 9.40A, b = 10.46A, c = 19.25A. This interpretation is based on the close similarity of the chitin and cellulose chains composed as they are of chitobiose and cellobiose units respectively. Fraenkel and Rudall[73] state that the highly crystalline condition of the chitin is obtained after removal of the protein and the chitin chains may be brought together either by thermal or mechanical agitation of the natural structure.

The infra-red and X-ray investigations on chitin by Darmon and Rudall[71] suggest that the main feature is hydrogen bonding between CO.NH groups of adjacent amino-acetyl side-chains, to form linked piles of chitin chains within the crystalline

regions.

It has also been suggested that the strengths of these hydrogen bonds in chitin are comparable with those in polyamides and proteins. Thus chitin may be visualised as being built up of parallel chains with structural units similar to those in cellulose but with the formation of lateral hydrogen bridges comparable in strength with those of fibrous proteins, between the CH_3.CO.NH groups of neighbouring chitin chains. But this type of hydrogen bonding between the CO....HN groups of adjacent chains appears to occur only between some of the aminoacetyl groups present (presumably about half of them). The remaining acetylamino groups on the evidence available appear to form hydrogen bonds of the type NH.CO....HO, wherein the hydrogen of the hydroxyl groups present in the molecule, and the carbonyl oxygen of the CO.NH are involved. However it has been stated that such a bond is only a tentative one, purely on spectroscopic grounds, necessitated by an unusual carbonyl frequency and proposed on the evidence of a similar frequency in other hydroxylic peptide structures; all the same, the presence of such a bond has been found to satisfy the X-ray data quite well, regarding both the symmetry of the chains and the inter-chain separations. Therefore, on the basis of these data, the structure of chitin may be illustrated as shown in Fig.22 as given by Darmon and Rudall[71]. According to them there are two main possibilities of bonding involving the carbonyl groups of chain B viz., a cross-linkage between

carbonyl II and hydroxyl I or an intramolecular linking of carbonyl II and hydroxyl II. Further, there is also a possibility of OH.....OH bonding between hydroxyls I and II but if C=O.....HO bonding occurs, the hydroxyl bonding is eliminated. Thus with regard to the apposition and the distance between chains I and II, bonds of the C=O.....HO type are justifiable. Furthermore the infra-red evidence shows the absence of OH.....OH and requires just such a bond as CO.....HO.

Analogy between chitin and cellulose

Chitin as indicated earlier, is obtained from a wide variety of sources. The various investigations so far carried out appear to show that it is a definite compound, which in many ways, plays a part in invertebrate animal structures, similar to that played by cellulose in plants.

We may now proceed to find out whether there is any similarity between chitin and cellulose in so far as their general properties are concerned. Chitin contains the quasi-peptide linkage -NH-CO- arising from the N-acetylation of glucosamine but it also contains hydroxyl groups in common with polysaccharides. Further, chitin is a polymer of acetylamino-glucose residues linked together by 1:4-glucosidic linkages. It might be expected because of its analogous structure to cellulose, that chitin would display properties similar to those of cellulose. But it has been found that in many respects

in general properties, chitin and cellulose are different from each other. Chitin is relatively stable towards acids, alkalis and oxidising agents. Some investigators have employed potassium permanganate and hypochlorites in the isolation of chitin with the object of destroying other substances present in their raw material. It has been found by Knecht and Hibbert[74] that the chitin prepared by them was not attacked by strong (85^{o}TW) nitric acid in the cold. It has also been found to be stable towards potassium permanganate in 10% sulphuric acid. The substance, unlike cellulose, is not soluble in Schweizer's reagent and it also does not reduce Fehling's solution. In dyeing properties, chitin has been found by Knecht and Hibbert[74] to be very different from cellulose, for it is readily dyed with Crystal Scarlet in the presence of a little sulphuric acid. Further, Diamine Sky Blue has been found to dye chitin only a very light shade of blue and Methylene Blue was not found to dye pure chitin.

Preparation of chitin.

Chitin is distributed widely in nature and as may be expected, different methods of extracting it from the raw materials have been adopted by previous workers in this field.

Air-dry crab shell powder has been employed as the raw material for the preparation of chitin by Knecht and Hibbert[74]. Their method consists in extracting the powder first with dilute hydrochloric acid and then with warm dilute sodium

hydroxide and finally subjecting it to another extraction with dilute hydrochloric acid again. The material has been subjected to four such alternate treatments and then extracted with alcohol and ether, and subsequently dried. Then dissolution of the material in concentrated hydrochloric acid was effected and the viscous solution thus obtained was poured into water, when an albumen-like precipitate was obtained which was filtered, washed with water and finally dried.

Kunike[75] has extracted chitin from its incrustations by treating the raw material with dilute alkali. He has also mentioned the use of Diaphanol (dihydroxychloroacetic acid) instead of alkali to remove organic impurities. Du Pont[76] have carried out an extensive investigation into the preparation of chitin and its derivatives. They have employed shrimp meal as the source, from which they have isolated chitin by first digesting the meal with approximately 1% sodium carbonate solution containing a small amount of Cardinol at 100°C. for 12-16 hours and then treating it with dilute hydrochloric acid for 30 minutes. The alternate extraction with acid and alkali has been repeated several times and then the material is finally washed until neutral, and dried.

The following methods have been employed by Fraenkel and Rudall[65] for the isolation of chitin from its incrustations in the cuticle of the blowflies, "Sarcophaga falculata" and "Calliphora erythrocephala".

(i) The cuticles are treated with 5% potassium hydroxide solution at 100°C. for 1-2 days.

(ii) The cuticles are treated with 5% hydrochloric acid at 100°C. for 1-2 days.

(iii) A concentrated solution of chlorine dioxide in 50% acetic acid and known as "Diaphanol" is employed. Here the cuticles are treated at room temperature (18°C.) for about 10 weeks.

They state that the material obtained by any one of these methods is pure or almost pure chitin and this is supported by determinations of its nitrogen content.

An Outline of Previous Work.

A wide variety of investigations have been carried out already with a view to manufacturing fibres and films from chitin, de-acetylated chitin or "Daktose", chitin xanthate and alkali chitin. These researches appear to have been promoted by the striking structural similarity between chitin and cellulose.

Preparation of Daktose.

Du Pont[77] have made pioneering work in this field. Their method consists in treating 25 parts of purified chitin with 1200 parts of 40% sodium hydroxide for 6 hours at 115°C. with substantial exclusion of air. The sodium hydroxide

solution was then drained off and the de-acetylated chitin washed with water until free from alkali and subsequently dried at 65°C. They claim a yield of 20 parts Daktose containing about 0.82 free amino groups per chitosamine residue. Du Pont[77] have also indicated in their patent specification, the effect of concentration of alkali and time, and temperatures of treatment, on the properties of the de-acetylated chitin. An increase in the time of treatment brings about a decrease in the viscosity of de-acetylated chitin as well as in the film strength because of the increased extent of de-acetylation. An increase in the degree of de-acetylation and a consequent diminution in viscosity of the Daktose solutions have also been predicted as inevitable if bigger concentrations of alkali and higher reaction temperatures are employed.

Alkali chitin.

Cellulose is well known to take part in the formation of alkali cellulose as well as in the xanthation reaction. But earlier researches have shown that chitin, although it possesses an analogous structure to cellulose, does not appear to partake in such reactions. However it has been found by Clark and Smith[78] that chitin gives rise to a series of addition compounds with caustic soda when treated with a hot saturated solution of the alkali, but owing to hydrolysis they have found it difficult to isolate the individual compounds. Thor and Henderson[79] have described the preparation of a range of

alkali chitins analogous to the alkali celluloses. An alkali chitin containing 0.75 or more equivalents of combined sodium per acetyl glucosamine unit has been prepared by them, by steeping (150 gm.) chitin flakes obtained from "shrimp bran" in three litres of 43% caustic soda for two hours at 25°C. The alkali chitin is then separated from the residual liquor by centrifuging until the weight of alkali chitin is three times the weight of original chitin and the product obtained is broken up and finely shredded.

It has been observed that no de-acetylation of the alkali chitin occurs when it is prepared by the above method but this degradation process appears to take place a few hours after preparation unless it is stored at 0°C. A rapid dispersion of an alkali chitin of the type described above is obtained when it is mixed steadily with two to four times its weight of chopped ice in an insulated vessel. It has been found that such a dispersion of alkali chitin is stable for several days if maintained near 0°C. However, at room temperatures, separation of chitin commences after several hours.

Chitin xanthate.

A dispersion of alkali chitin prepared by the method described above, when mixed with carbon disulphide at 0-15°C. gives rise to a dispersion of chitin xanthate, as would be expected, by analogy with the manufacture of viscose from cellulose. Chitin xanthate has been prepared by Thor and

Henderson[79] by first converting chitin into alkali chitin and then dispersing it in chopped ice in such a proportion as to give a chitin content of 7% by weight in the final mixture. Then carbon disulphide is added a few minutes after the commencement of mixing, in the course of which the temperature drops to -10°C. and the gelatinisation of the alkali chitin occurs before it disperses again rapidly. The temperature is now allowed to rise to 0°C. and maintained at this level during four hours mixing. The resulting dispersion is stored at 0°C. until it is used.

The viscosities of chitin xanthate dispersions prepared thus are found to be comparable with those of viscose dispersions in common industrial use, although the viscosity value is influenced to a considerable extent by the method employed to purify the chitin. Chitin xanthate bears a close similarity to cellulose xanthate in its reactions and it appears that smooth transparent films of regenerated chitin have been prepared by spreading chitin xanthate on glass and then coagulating it in an acid bath.

Manufacture of artificial fibres from regenerated chitin and Daktose.

Several workers have already devoted a good deal of attention to the possibility of manufacturing artificial fibres from chitin and its derivatives. Their researches may be classified into two distinct groups:-

(1) Production of regenerated chitin fibres from

(i) cold concentrated acid solutions of chitin

(ii) colloidal dispersions of chitin in lithiumthiocyanate solution and

(iii) chitin xanthate

(2) Production of fibres from regenerated de-acetylated chitin ("Daktose").

Kunike[75] isolated chitin by treatment with dilute acid and dilute alkali (about 5%) then dissolved it in 6-10% acid at ordinary temperatures, filtered it and spun it either dry or wet, with or without tension. In the case of wet spinning the coagulating bath comprised any chemical in which the chitin is not soluble, e.g. water, alcohol, dilute acids or alkalis. The fibre was subsequently washed and dried. Thus fibres with a tensile strength of 35 Kg./mm.^{2} (dry) and nearly of heart to round-shaped cross-sections, were obtained. It may be pointed out that their tensile strength is thus comparable with that of silk (35 Kg./mm.^{2}) and normal viscose rayon (25 Kg./mm.^{2}) but Kunike[75] has observed that the wet strength of regenerated chitin is lower than that of viscose rayon.

Von Weimarn[80] has carried out an extensive study on the action of aqueous salt solutions on chitin as a result of which he has indicated the possibility of producing fibres from it. According to him, chitin could be converted into a "ropy-plastic form" and could also be dispersed colloidally by means of salt

solutions like lithiumthiocyanate solution. He has also studied the use of other extremely water-soluble salts in this connection and has given the order of decreasing power of dispersion for the salts as follows:-

$$D_{LiCNS} > D_{Ca(CNS)_2} > D_{CaI_2} > D_{CaBr_2} > D_{CaCl_2}$$

Similar polymeric substances such as cellulose, keratin, casein and fibroin have also been found to be colloidally dispersed by these salt solutions, wherein the same order of dispersion as indicated above has been found to hold good.

Further it was observed that the gelatinous precipitates and jellies obtained by adding ethyl alcohol to colloidal dispersions of chitin in salt solutions were clearly translucent whilst similar preparations of cellulose were opaque although such dispersions of chitin approached those of cellulose in certain respects.

Clark and Smith[78] as a consequence of these observations prepared a syrupy colloidal solution of chitin in lithium thiocyanate at 95°C. and then extruded it through a fine jet into a concentrated solution of acetone in water and thus succeeded in producing artificial fibres. It was also found that a high degree of orientation as shown by sharp parallel extinction between crossed Nicols could be imparted to fibres produced thus by the application of tension to them during their formation.

The preparation of smooth transparent and flexible

regenerated chitin films has been attempted by Thor and Henderson[79]. They filtered chitin xanthate and spread it on glass and followed it up by coagulating in a bath made up of 40% ammonium sulphate and 5% sulphuric acid for several minutes before washing in running water until the disappearance of the initial cloudiness of the film. The film was then immersed in 15% aqueous glycerine for 30 minutes before final drying. The following are comparative data for the tensile strengths, both dry and wet, of chitin and cellulose films as quoted by the above authors.

Film		Tensile strength (Kg./mm.^{2})
Regenerated chitin	Dry	9.49
	Wet	1.75
Regenerated cellulose	Dry	9.10
	Wet	4.77

General correlation of the dyeing behaviour of cellulose and protein fibres with chitin.

In the dyeing of any textile fibre different factors of quite a diverse nature come into operation. Of these the nature of the substrate may be mentioned first.

The substrate varies in its structural configuration depending on whether it is cellulosic or protein in character.

However, in all cases, the fibres have been found to comprise both crystalline and amorphous regions interlaced with each other. Thus certain fibres possess a high degree of crystallinity as indicated by sharply defined spots in their X-ray diffraction pattern, whilst certain others exhibit quite the opposite effect. Further, the pore size of the fibre in the case of each substrate also, appears to play an important part in dyeing phenomena. Thus it has been found by Morton[1] that the pore size of viscose in the form of a sheet is of the order of less than 5 Å in the dry state, whilst in the water-swollen state it increases to an average size of 20-30 Å whilst it has been found by Frey-Wyssling[81] to be of the order of 100 Å for cellulosic fibres. On the other hand, wool fibres have been found by Speakman[20] to have a pore size of 6 Å when dry, which increases to about 40 Å in the water-swollen state, whilst swelling in hot water or acid at temperatures above 40°C. produces similar effects, leading to maximum pore diameters of not less than 41 Å. Secondly, we may consider the chemical nature of the groups in each substrate which appear to play an active part in the binding of dye to the fibre. Extensive investigations have been carried out in this direction as a result of which certain definite conclusions have been reached. In the case of cellulose it has been suggested that direct dyes are bound to fibres through hydrogen bonds. This has led to the suggestion that only those direct dyes which possess suitable hydrogen bonding groups spaced at

appropriate intervals along their length in relation to the fibre chains could dye cellulose. It has also been suggested that van der Waals forces are responsible for cellulose dyeing (Allingham et al[82]).

Cellulose acetate.

The artificial fibre cellulose acetate prepared by acetylation of cellulose has got a similar structure to cellulose, except in that the side dimensions of the chain molecules are altered by the process of acetylation. In spite of this it differs completely from cellulose in its dyeing behaviour. It could be dyed with basic dyes unlike cellulose, whereas the direct dyes which dye cotton do not dye cellulose acetate, and so also is the case with most acid dyes. But cellulose acetate is dyed either by dispersed dyes or water-soluble acetate rayon dyes. A detailed investigation of the dyeing of this fibre with the dispersed dyes shows that the process may be visualised as the entry of the molecularly dispersed dye through narrow pores and adsorption on the side chain ester groupings probably through hydrogen bonding to the carbonyl oxygen atoms.

In the case of dyeing of wool, quite a number of theories have been put forward, notably those of Speakman, Gilbert and Rideal, and of Goodall.

Protein fibres.

Speakman's recognition of the salt linkage in wool reinforced by Elöd's[83] discovery of the existence of Donnan equilibrium phenomena between fibre and acid and between fibre, acid and dye, has made it quite clear that acid dyes in molecular solution combine with wool in a chemical manner. The NH_3^+ groups in wool have been found to participate in such a chemical reaction. But it has also been shown by Goodall[27] that in dyeing wool with colloidal acid dyes, the theory of chemical combination between the dye and fibre does not apply. Therefore the dye aggregate, as it is not able to diffuse through the swollen pores of the wool fibres, is held on to a positively charged NH_3^+ group by electrostatic forces. Nylon is a synthetic polyamide. In the case of fully drawn nylon it has a high degree of orientation. It contains both free amino (NH_2) groups and amide, or quasipeptide (-NHCO-) groups. Peters[29] has studied the sorption of acid dyes by nylon and has shown that the dyeing of nylon with acid dyes is brought about by two reactions. First at high pH values, i.e. above pH 3.00, the end-amino groups present in the fibres take part in combining the dye. Since there is only a limited amount of end-amino groups in nylon, the amount of dye that could be taken up by such groups will naturally be limited. But it has been found that at lower pH values the weakly basic amido-groups in nylon become positively charged and begin to combine with the dye anions and hence the amount of dye that could be taken

up in this way is considerable. So, in comparison with the dyeing of wool with molecularly dispersed dyes, the dyeing of nylon differs only in that it possesses a reduced number of basic sites available for combination with the dye anion.

Chitin.

Now, if we consider the structure of chitin as shown in Fig.21 we may be able to form a theoretical picture of how its dyeing process with various dyes would proceed. It has a strong resemblance to cellulose in that it is a polysaccharide built up of hexose units containing acetylamino groups through 1:4-glucosidic linkages. Therefore it may be expected that direct dyes would dye chitin from aqueous solution perhaps through the formation of hydrogen bonds and van der Waals forces, as evidenced in the case of cellulose. In addition it might also be possible for the -NH- part of the acetylamino group to form a hydrogen bond with the direct dyes. Since chitin has quasi-peptide groups, i.e., its acetylamino groups, it might take up both the molecularly dispersed and colloidally aggregated acid dyes, through electrostatic attraction between the dye ion and its positively charged amido group, under suitable conditions.

Chitin resembles cellulose acetate to a considerable extent since it possesses the acetylamino groups, though these groups are not ester side chains. Hence it might be possible to apply dispersed dyes to chitin wherein the dye could be

expected to be sorbed through the formation of hydrogen bonds between suitable donor groups in itself and the carbonyl oxygen of the acetylamino groups.

Next, if we compare nylon with chitin, it is obvious that a certain relationship could be expected between the two in so far as their dyeing behaviour with acid dyes is concerned. This is because of the presence in chitin of the weakly basic -NHCO- groups as in nylon.

SECTION I.

EXPERIMENTAL DETAILS

Preparation of chitin.

A method of preparing chitin was used in this laboratory by Miss M.Laidlaw (Private communication, 1951). This consisted in removing the proteins present in lobster shells and linings by enzymatic hydrolysis. It was thought that two other methods, those of Clark and Smith[78] and Thor[84], were too drastic. Miss Laidlaw subjected the shell and lobster linings to the treatment described by Burgess[85] for degrading wool by the action of the proteinases, trypsin and pepsin. The proteins present in lobster shells have been found to contain a high proportion of tyrosine (Fraenkel and Rudall[73]), and will therefore be easily hydrolysed by pepsin. The actual treatment consisted in grinding the shells of Nephrops norvegicus to about ¼" size and adding to each gram of shell about 5 c.c. of 5% pepsin solution and 5 c.c. of a buffer solution of pH 1.40. These were incubated at 37° for periods of 6, 7 and 8 days, after which the residual substance was filtered off, washed with hot water in order to remove the hydrolysis products, then treated with 5% hydrochloric acid to dissolve calcium salts and finally washed thoroughly with water. The colouring matter in the shells was removed by extraction

with acetone and the final product obtained was ground to a fine powder in the ball mill, using fused silica balls.

This sample was analysed for nitrogen content and tested for the presence of protein by the biuret test, which gave a less positive test as the time of treatment was increased, though this particular batch of chitin was found to contain about 6.3% of ash. It appears that this ash might be silica, which might have been introduced into the chitin sample, from the silica balls, employed in the ball mill. The enzymatic procedure appears to be worth further investigation, but insufficient time was available for this, so that it was considered better to use an established preparative method. Thus Thor's[84] method has been employed in the present work to isolate chitin from the shells of Nephrops norvegicus.

The shells were broken into small pieces and treated with aqueous hydrochloric acid for about 12 hours at room temperature. Then they were washed with water, and boiled for 8 hours with 1% sodium carbonate solution containing about 0.02% of a detergent (Lissapol N.). They were again washed thoroughly with water, and then allowed to stand for 1-2 hours with 5% hydrochloric acid, again washed with water, and then treated with 1% sodium carbonate solution as before for a further period of 8 hours. Finally, they were washed well with water. The shells were found to be quite white at this stage, so that no extraction of colouring matter was necessary.

The absence of any protein in the treated shells was

ascertained by the biuret test, as follows. A small amount of the treated shells was heated with a strong solution of sodium hydroxide, filtered, and the filtrate was then heated, after adding a dilute solution of copper sulphate. The non-development of any colour in the solution indicated the absence of any protein. In view of the acid treatment given, together with the lack of any effervescence on the addition of a dilute hydrochloric acid solution to the treated shells, it appears that no insoluble carbonate may be present in this treated material. Now, the cleaned treated shells were dehydrated by washing with ethanol and then with ether, and subsequently dried at about 50°C. These shells were ground in a rubber-lined ball mill provided with fused silica balls for about four hours, after which they were taken out, washed well with water, and then dehydrated again by washing with ethanol, and then with ether, and finally dried at 50°C. for about two days.

This powdered chitin was then sieved in an automatic sieving machine for 30 minutes, using sieves ranging from 120 mesh to 200 mesh. It was found that the major amount of the chitin had been sieved through the 200 mesh. This sample of chitin was conditioned for about 7 days at room temperature and relative humidity, and was subsequently used in the present investigation. The conditioned sample was found to have a moisture content of 8.7% determined by drying and weighing to constant weight at 100°C.

Characterisation of chitin.

A sample of chitin from the batch prepared by the above method was dried at 110°C. in a drying pistol under vacuum, over phosphorus pentoxide for about thirty-six hours and then analysed for the elements. The results were as follows:-

Found C, 42.1; H, 6.3; N, 6.6%.

The above sample was found to possess an ash content of 7.5%. Therefore the above values calculated on an ash free basis give:-

C, 45.3; H, 6.7; N, 7.1%.

The ash cannot be organic in nature, and probably does not contain any water-insoluble carbonate, in view of the acid treatment given together with the absence of any effervescence on the addition of hydrochloric acid to the ash, but it may contain silica, which may have been introduced from the silica balls employed for grinding the shells in the ball mill. The mill and balls were very thoroughly cleaned by washing with water and blowing with compressed air before introduction of the shells. The presence of silica in the product must arise from the abrasive action of the hard shell material on the balls. It may be pointed out here, that the ash present in the chitin sample prepared by Miss Laidlaw also might have been introduced in the same way, since she ground the shells in the same mill.

The present ash was tested for silica, by two methods.

(1) It was treated with concentrated hydrochloric acid, and was found to be insoluble, both in the cold as well as in the boiling acid. Next, the ash was fused with sodium-potassium carbonate in a platinum crucible, and the melt so obtained was treated with a hot nitric acid solution of ammonium molybdate in the platinum crucible itself, when a very pale yellow solution was obtained. This indicated the presence of silica, which was confirmed as follows:- A drop of the yellow solution was spotted on a filter paper, and was gently warmed over a wire gauze. Then a drop of a solution of benzidine in acetic acid was added to the spot; and the filter paper was held over ammonia, when a blue colour slowly developed, thus indicating the presence of silicic acid. This test is given by Feigl[85a].

(2) The ash was fused with sodium borate in a platinum crucible, and the melt so obtained was dissolved in about 10 c.c. of water, and the solution transferred to a Lusteroid tube. Then 2 c.c. of an acidified 5% solution of ammonium molybdate were added to the test solution, when a yellow colour developed slowly, after about five minutes. Then 5 c.c. of a reducing solution comprising sodium sulphite and hydroquinone were added to the test solution. A blue colour developed slowly, thus again indicating the presence of silica. Here, the yellow colour developed at first is due to the formation of silico-molybdic acid, and this on reduction gives rise to a blue complex. This test is given by J.Brown[85b].

It may be stated here that the chitin isolated from both Sarcophaga larval cuticle and puparia by extracting with 5% sodium hydroxide for 2 days at 100°C. or by prolonged treatment with diaphanol as used by Fraenkel and Rudall[65], is stated by Trim[86] to contain about 0.8% of material, which is not removed by more prolonged treatment with any of the reagents concerned. The presence of free amino groups in the present sample was tested for by the van Slyke method. Negative results were obtained, but it is possible that the method is not sensitive enough to detect the small proportion which might be present.

Irvine[68] has proposed a formula for chitin on the basis that it is a polymer of N-acetylglucosamine and glucosamine units, these being in the proportion of 3:1. The theoretical analysis is then: C, 46.8; H, 6.5; N, 7.3%, but it appears that his sample was probably partially de-acetylated.

On hydrolysis with acids, glucosamine and acetic acid are produced from chitin in equivalent proportions, and under certain conditions the compound acetylglucosamine is obtained. Therefore Meyer and Mark[69] have proposed the constitution shown in Fig.21. This is a polymer built up of N-acetylaminoglucose units, through 1:4-glucosidic linkages, as in cellulose. This formula has been confirmed by later workers (Meyer and Wehrli[70] Fraenkel and Rudall[65]; and Darmon and Rudall[71].). The theoretical analysis calculated on the basis of this formula is:-

C, 47.3; H, 6.4; N, 6.89%.

The analysis of the sample prepared in the present work is not quite consistent with either the formula proposed by Irvine or that proposed by Meyer and Mark, but since the ash present appears to be silica it will not interfere with the combination of either simple mineral acids or acid dyes[§§]. It has been found by Cullen[(87)] that silica acquires a negative potential in aqueous solution, and does not take up acid dyes.

Iso-electric point of chitin.

Next it was thought best to examine the possibility of the existence of an iso-electric point in the sample of chitin as has been found to be the case by C.M.Yonge[(88)] who has found a value of pH 5.10 for the iso-electric point of the cuticle in lobsters and a pH 3.5 for that of the chitin in lobster shells. Moreover Pantin and Rogers[(89)] have examined the radula of Buccinum which according to them, comprises two zones, a young newly formed part denoted as chitin (A) and the other, an older part, designated as chitin (B). They have shown that, whereas chitin (A) has no iso-electric point, chitin (B) has an iso-electric point at about pH 2.60.

In order to confirm the presence or absence of any iso-electric point in the sample of chitin prepared, the following experiment was carried out. Two sets of buffer solutions ranging in pH from 2.0 to 3.90 were prepared. Then a constant volume of each was added to a constant weighed quantity of

[§§] About 7.5% ash was noted in each analysis (three) of the present material. All sorption data are calculated for ash-free chitin.

chitin. A few drops of a solution containing Ag^+ were added to one set of buffer solutions containing the chitin, whilst a few drops of a solution containing CNS^- were added to the other set of buffer solutions and these were kept at room temperature with occasional shaking for about 48 hours. Afterwards, these were filtered and the chitin present in each solution was washed thoroughly with water, so that only the ions combined with the chitin might be still present in the sample. Now a known volume of a solution of hydroquinone was added to each chitin sample which was formerly in contact with the Ag^+ and similarly a constant volume of $FeCl_3$ solution was added to each chitin sample of the other set, which had contained the CNS^-. These were kept at room temperature for about 24 hours after which they were filtered, washed well with water, dried and finally examined for the development of any colour.

It was found that all the chitin samples which were treated with Ag^+ had developed a light-grey colour, whilst all the others which had been in contact with CNS^- had developed a light-reddish brown colour, thus indicating that they have sorbed both the positive and negative ions over the range of pH 2.0-3.90. This shows that the sample of chitin does not possess an iso-electric point in this range and so it appears to be similar to the young, newly formed chitin, denoted as Chitin (A) by Pantin and Rogers (loc.cit.). Further, the nature of the charge on the solid in aqueous solutions has been

examined by electrophoresis. A small amount of the sample was kept in aqueous suspension in a U-tube of the electrophoresis apparatus, and then a potential was applied across the ends of the tube. It was observed that the boundary layer of the suspension near the cathode slowly moved farther away from it, whilst that near the anode became thicker in its concentration, thus showing that the sample develops a negative charge, like all other textile fibres, both vegetable and animal, when it comes into contact with an aqueous solution.

Preparation, purification and estimation of dyes.

The dyes employed for sorption studies are all acid-azo dyes which were prepared by the conventional methods. The purification procedure consisted in salting out the dye from its concentrated solution by using either sodium chloride or sodium acetate. The precipitated dye was then recrystallised at least thrice from water. Then it was extracted with boiling ethanol for a few minutes in order to remove any trace of residual salt, which might still be present, filtered, and the residue washed with a little hot ethanol and finally dried at 100°C.

The purity of some of the dye samples was estimated by the titanous chloride method of Knecht[90], whilst that of the other samples was determined by the method developed in this laboratory by Arshid et al[59]. This method consists in oxidising the dye with a dilute solution of potassium dichromate

and sulphuric acid and measuring the volume of nitrogen produced in a micronitrometer.

Experimental Technique and Method of Estimations Employed.

Standardisation of experimental procedure.

In all the sorption studies in the present work an approximate goods to liquor ratio of 1:2000 has been employed. Further, in the case of dyes, a constant concentration, viz., 0.0001106 gm.moles./litre of pure dye has been used throughout. All the solutions were prepared in distilled water. The sorption studies have been investigated at two temperatures, 50°C. and 60°C.

The experimental procedure consists in weighing a known required weight of chitin in a quick-fit tube of 25 c.c. capacity and then pipetting 20 c.c. or 25 c.c. of the appropriate solution into it, which was then mounted on a horizontal revolving shaft contained in a thermostat by means of spring clips and kept continuously rotated for the necessary period in each case. A Sunvic thermostatic control unit maintained the temperature in the thermostat to an accuracy of ± 0.5°C. of the desired temperature.

The thermostat, together with its other details, is shown in Fig.2.

The solutions, after the establishment of equilibrium conditions, were filtered through a filter paper and the

filtrate obtained was estimated by suitable methods. Here, it may be pointed out, that at first filtration through a plug of glass wool was attempted since the filter paper is slightly coloured in the case of dye solutions and even otherwise would absorb a certain amount of the solutions being filtered through them and thus would give rise to inaccuracies in the procedure. But it was not found to be feasible, owing to the escape of the chitin particles through the glass wool, on account of their small size. Later on, filtration through sintered glass filter funnels was attempted and this was successful. But it was found to be quite a laborious procedure since the funnel had to be cleaned and dried for filtering each solution. Hence it was decided to effect the filtration through ordinary filter papers as before, and it was found by preliminary experiments that the errors likely to occur, consequent upon such use, are negligible.

Nature of Compounds Studied.

The compounds employed in the present sorption studies may be classified into the following groups:- (1) acids; (2) acid azo dyes and (3) hydroxy compounds.

(1) Acids

(i) HCl alone; HCl + NaCl

(ii) H_2SO_4 alone

(2) Acid azo dyes (sodium salts)

(i) Benzene-4-sulphonic acid azo-2-naphthol

(ii) Naphthalene-4-sulphonic acid azo-2-naphthol

(iii) Benzeneazo-2-naphthol-3:6-disulphonic acid

(iv) Benzene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid

(v) Naphthaleneazo-2-naphthol-3:6-disulphonic acid

(vi) Naphthalene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid

(vii) Benzene-2:5-disulphonic acid azo-2-naphthol-6-sulphonic acid

(viii) Benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid

(ix) Naphthalene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid

(x) Benzene-2:5-disulphonic acid azo-2-naphthol-3:6-disulphonic acid

(xi) Naphthalene-3:6-disulphonic acid azo-2-naphthol-3:6-disulphonic acid.

(3) Hydroxy compounds.

(i) Phenol

(ii) Resorcinol

(iii) 2:4-dinitrophenol

(iv) 2:4:6-trinitrophenol (picric acid).

Methods of Estimation Employed.

Estimation of hydrogen ion concentration.

When the initial or final pH of the acid solutions was less than 3.0 then hydrogen ion concentrations were estimated by potentiometric titration, whilst in the case of solutions of lower hydrogen ion concentration the concentration was determined by finding out their respective pH values with the help of a glass-electrode system.

Estimation of dyes.

The concentrations of all the dye solutions, both before and after sorption, were estimated by means of the Spekker absorptiometer.

Estimation of hydroxy compounds.

Phenol: The concentrations of this compound in aqueous solutions were estimated by the bromide-bromate method as described on page 27. Its concentrations in dry isooctane were determined by means of the Unicam photoelectric spectrophotometer. Here a calibration curve is plotted first, from which the other unknown concentrations are interpolated.

Resorcinol: The concentrations of resorcinol in aqueous solution were determined by the method of Pence[91]. This method consists in oxidising resorcinol by potassium

permanganate, first under alkaline conditions and then under acid conditions. It is quite well known that under acid conditions oxalic acid is oxidised to carbon dioxide and water by potassium permanganate, but under alkaline conditions potassium permanganate has been found to oxidise some aromatic compounds into oxalic acid only. Therefore if such an oxidation under alkaline conditions is followed up by oxidation under acid conditions, leading to the ultimate decomposition of such compounds into carbon dioxide and water, the same can be estimated by this method.

The actual estimation is carried out by placing 25 ml. of N/10 potassium permanganate in a 250 ml. quick-fit stoppered conical flask and adding 2-3 gm. of pure sodium bicarbonate to it; then 10 ml. of the solution of resorcinol to be estimated is pipetted into this flask with gentle shaking. The mixture is boiled for about five minutes and then cooled to about 60°C. It is then acidified with dilute (2N) sulphuric acid (25 ml.), allowed to stand for about two minutes and cooled to room temperature. It is afterwards diluted with the addition of 25 ml. of distilled water, after which 5 ml. of ten per cent potassium iodide solution is added to it, and the flask quickly stoppered. The iodine liberated is titrated against standard N/10 sodium thiosulphate solution as usual, using starch as indicator.

The reaction may be equated as follows:-

$$C_6H_4(OH)_2 + 13\,O \longrightarrow 6CO_2 + 3H_2O$$

Now, both under acid as well as under alkaline conditions, potassium permanganate liberates 2.5 atoms of oxygen for each molecule as shown in the following equation:-

$$2KMnO_4 \longrightarrow K_2O + 2MnO + 5(O)$$

Therefore every molecule of resorcinol would require 5.2 molecules of potassium permanganate for complete oxidation into carbon dioxide and water. Therefore the factor for N/10 permanganate in terms of phenol becomes:-

1 ml. of N/10 $KMnO_4$ $\equiv$ 0.0004232 gms. of resorcinol.

Estimation of nitrophenols.

Since the aqueous solutions of both 2:4-dinitrophenol and 2:4:6-trinitrophenol are coloured yellow, their concentrations were measured on the Unicam photoelectric spectrophotometer, using the tungsten lamp with the T.L. filter at wavelength 3550 Å. The concentrations of the free acids of these two compounds both before and after sorption were determined by the pH meter (Cambridge type) using the glass electrode.

SECTION II.

RESULTS AND DISCUSSION

Sorption of Hydrochloric Acid.

The sorption of hydrochloric acid by chitin was investigated with a view to determining at first the nature of the mechanism involved. An elucidation of this reaction between chitin and simple acids is a prerequisite in any investigation in which the sorption of acid dyes in the presence of simple mineral acids is studied.

In the present work the sorptions were carried out at 60°C., the experimental procedure being that described in page 103, the concentrations of the acid solution in distilled water being measured both before and after sorption by the methods described in page 106. Although chitin has been found by previous workers to be relatively stable to acids, alkalis and oxidising agents, some hydrolysis might take place under strongly acid conditions, at the temperature of sorption, viz., 60°C., especially below pH 2.50 or so. This might be expected to lead to the formation of ammonia and acetic acid in the case of chitin. If the hydrolysis occurs to a considerable extent, as has been found to be the case when chitin is boiled with concentrated hydrochloric acid, butyric and formic acids might also be expected in the degraded product.

In order to confirm the absence of any degree of hydrolysis, at least up to a final pH value of 2.50 where the maximum sorption of the acid by chitin seems to occur, though not at lower pH values where extensive hydrolysis definitely seems to be taking place as indicated by a considerable increase in acid sorption at these pH values, the acid solutions employed in the sorption study, after being filtered of the chitin, were tested for the presence of ammonia by the addition of Nessler's reagent to each. A negative result was obtained in the case of all solutions whose final pH values were above pH 2.50.

If a limited amount of hydrolysis did take place under the conditions of sorption employed here, leading to the formation of acetic acid, then it would not be possible to estimate it accurately by quantitative methods of titration on account of the large solid:liquor ratio employed, and obviously, the errors of such estimation may be expected to be considerable. Hence it was decided to ascertain the possibility of such hydrolysis by carrying out the sorption of hydrochloric acid at 60°C., under identical conditions as before, but with acid of strength 2N, and of two suitable initial pH values, which after sorption, would give approximately, pH values 2.0 and 2.50 respectively. These three solutions were filtered after sorption and the three samples of chitin washed thoroughly with distilled water until free of any acid, and then dried at 100°C. for 7 days, after which they were analysed, the results of which are given in Table 30.

The analytical results clearly show that at pH 2.50 no hydrolysis occurs, whereas at pH 2.00 a good amount of hydrolysis seems to occur, probably tending to the formation of ammonia, as indicated by a lower nitrogen content, whilst with acid of 2N strength, considerable hydrolysis seems to occur, as expected. Thus, the absence of any hydrolysis or degradative decomposition under the experimental conditions of sorption of hydrochloric acid investigated above pH 2.00 has been established.

The sorption of hydrochloric acid by chitin both alone and in the presence of 0.1M and 1.0M constant chloride concentration, obtained by the addition of appropriate amounts of sodium chloride to the solutions of different pH's at 60°C. has also been studied. The results are summarised in Table 31 and the isotherms for the same are shown in Fig.23. Since these sorptions appear to follow the Donnan theory of membrane equilibrium as seen from Fig.23, it is thought pertinent to consider in brief the theories put forward by Steinhardt and Harris[92], Peters and Speakman[22] and Gilbert and Rideal[28] for the combination of wool with acids.

Theory of Steinhardt and Harris.

Steinhardt and Harris[92], as a result of their investigation on the sorption of acids by wool have put forward a series of expressions to explain the observed data. But their theory has been criticised by Speakman[22], on the grounds

that the law of mass action is not applicable to the ionisation of salts.

General theoretical considerations of acid sorption by wool.

Now, considering the Donnan and Gilbert-Rideal theories put forward to account for the combination of hydrochloric acid with wool, the main difference between them lies in the fact that while both of them assume the hydrogen ions to be mainly combined with the proteins, the Donnan theory assumes that some of the chloride ions are combined with the protein, while the Gilbert-Rideal theory assumes that all the chloride ions are combined on specific sites provided by the fibre.

A protein fibre may be visualised as comprising protein chains packed in a manner in certain regions more ordered and compact than in others, thus giving rise to the crystalline and amorphous parts. The crystalline lattice may be impermeable to large ions such as dye ions, although it appears from previous investigations that the whole structure is permeable to the small hydrogen ions. The water-swollen protein fibre may be regarded as consisting of a mass of interlocking protein chains containing imbibed water and forming an equipotential volume. The potential difference between the fibre and dye-bath is assumed to be located at, or very near, the surface of the fibre. When such a fibre adsorbs an electrolyte, it must sorb the cations and anions in equivalent quantities in order to maintain electrical neutrality, although their exact location

inside the fibre may differ. Some ions probably become closely associated with the protein, being either combined with it or adsorbed upon it, while other ions remain unattached and are in effect dissolved in the imbibed water within the substrate. As indicated earlier, the properties of this internal solution have aroused a good deal of discussion, the proponents of the Donnan theory regarding it as having the properties of a normal aqueous solution, whereas others regard it as a highly concentrated solution of protein, having quite different properties, the activity of dissolved ions, for example, being greatly affected by the presence of the large number of charged groups in the protein.

The ions which combine with the protein may be regarded as being adsorbed on specific sites, the sites for anions and cations being quite distinct and independent of one another. It will also be assumed that no interaction between the sites occurs, each such site being in effect, situated in a separate unit, so that the adsorption of an ion on any particular site is not influenced by whether the neighbouring sites are occupied or not.

Now, with the above picture of the nature of combination of acids with protein fibres in mind, we may consider the adsorption of a monobasic acid like HCl, by a protein fibre. The hydrogen ions within the fibre will be partly combined with, or adsorbed upon the protein on sites provided by negatively charged carboxyl groups, and partly dissolved in the water

contained inside the fibre. If θ_H is the fraction of the total available sites which are occupied by hydrogen ions, then the activity of the adsorbed ions may be represented by the expression $\frac{\theta_H}{1 - \theta_H}$. Now, in order to distinguish clearly the nature of the sites on which the ions are sorbed, the following suffixes will be used to denote the different sites on the fibre, hereafter.

The suffix α will be used to denote the specifically adsorbed ion while i will be used to indicate those ions remaining in solution inside the fibre phase. The suffix σ will be used to denote concentrations in the external solution, this being expressed normally in moles per litre.

Now, using the above notations, the chemical potential of the adsorbed hydrogen ions may be written as

$$\mu_\alpha = \mu_\alpha^\circ + RT \ln \frac{\theta_H}{1 - \theta_H} \qquad (1)$$

where μ_α° is the standard chemical potential of the adsorbed hydrogen ions, when half the available sites are occupied. If the fibre has an internal volume represented by V litres/Kg. fibre, then the chemical potential of the hydrogen ions remaining in the internal solution in the fibre could be shown to be equal to

$$\mu_i = \mu_i^\circ + RT \ln \frac{[H]_i}{V} \qquad (2)$$

where $[H]_i$ is the concentration of dissolved hydrogen ions in

equivalents per kilogram of fibre and μ_i^o is the standard chemical potential in solution.

In both the equations, the activity coefficients have been neglected. When the system is in equilibrium the two chemical potentials should be the same. Hence

$$-(\mu_\alpha^o - \mu_i^o) = -\Delta\mu H^o = RT \ln \frac{\theta_H}{1-\theta_H} - RT \ln \frac{[H]_i}{V} \qquad (3)$$

The electrical potential of the fibre does not enter into the above equations since it has been assumed that the whole volume of the fibre is an equipotential volume and hence this equation reduces in effect to assuming a Langmuir adsorption of hydrogen ions with dissolved protein. But, the electrical potential difference between the solution inside the fibre and the external solution must be taken into account when the equilibrium between the two phases is considered. If the potential difference is γ then the electrochemical potential of hydrogen ions inside the fibre may be stated as

$$\bar{\mu}_i = \mu_i^o + RT \ln \frac{[H]_i}{V} + \gamma F \qquad (4)$$

where F is the Faraday. In the external solution

$$\bar{\mu}_\sigma = \mu_\sigma^o + RT \ln [H]_\sigma \qquad (5)$$

where $[H]_\sigma$ is the hydrogen ion concentration in equivalents per litre. If it is assumed that the internal solution has

the properties of a normal aqueous solution, then $\mu_i^o = \mu_\sigma^o$ so that, at equilibrium, when these two electrochemical potentials are equal

$$RT \ln \frac{[H]_i}{V} = RT \ln [H]_\sigma - \psi F \qquad (6)$$

Now, substitution in equation (3) leads to the expression

$$-\Delta\mu_H = RT \ln \frac{\theta_H}{1-\theta_H} - RT \ln [H]_\sigma + \psi F \qquad (7)$$

Equation (7) gives the relationship between the fractional saturation of the protein fibre with hydrogen ions and the external pH. A certain amount of work must be done against the electrical repulsion in order to bring the hydrogen ions into the fibre. Since the fibre potential ψ cannot be calculated, it should be eliminated from the above equation in order to make it intelligible. This could be done by considering the distributions of the anions wherein an exactly analogous treatment leads to the expression

$$-\Delta\mu_{Cl}^o = RT \ln \frac{\theta_{Cl}}{1-\theta_{Cl}} - RT \ln [Cl]_\sigma - \psi F \qquad (8)$$

Now, if equations (7) and (8) are added, it leads to the expression

$$-(\Delta\mu_H^o + \Delta\mu_{Cl}^o) = RT \ln \frac{\theta_H}{1-\theta_H} \cdot \frac{\theta_{Cl}}{1-\theta_{Cl}} - RT \ln [H]_\sigma \cdot [Cl]_\sigma \qquad (9)$$

If this equation is a true representation of the nature of acid adsorption by protein fibres in general, then it should give constant affinity values when applied to the sorption of any acid over the whole range of hydrogen and anion concentrations. The singular difficulty in applying the above equation to any experimental data lies in the determination of the distributions of the adsorbed ions between the internal solution and the substrate itself. This could be done only if the affinity of the individual ions is known and it has been pointed out by Guggenheim that it is impossible to determine the affinity of a single charged ion. It is possible to calculate only the total affinity of an electrically neutral molecule. Hence the above equation can be evaluated only by making certain simple assumptions and as indicated earlier, the various theories on acid adsorption differ from one another in the nature of these assumptions.

The carboxyl groups in the protein fibre are definitely known to be the sites responsible for the sorption of hydrogen ions. The number of such groups present in the substrate is known and probably their dissociation constants are of the same order as those of the soluble proteins, with a pK value of about 4.0. In the case of wool the fibre , when half-saturated with acid, would absorb about 0.4 equivalent of hydrogen ions per kilogram while the internal solution will have a pH of 4.0 and will thus contain 0.0001 equivalent of hydrogen ions per litre, or 0.00003 equivalent per kilogram of

fibre, assuming that it has an internal volume of 0.3 l./kg. Therefore, on comparison with the hydrogen ions specifically sorbed by the substrate, the amount of hydrogen ions in the internal solution is negligible and could be omitted in calculating acid adsorption. However, as will be discussed later on, the pH of the internal solution is of considerable significance in applying the Donnan treatment to such a system.

Now, most divergent views are held regarding the nature of the sites on which the anions are adsorbed. If the particular case of the adsorption of hydrochloric acid is considered, then, according to the proponents of the Donnan theory, no definite combination between the chloride ions and the protein occurs, all the chloride ions being dissolved in the internal aqueous solution without restraint. The work of Procter and Wilson[93] on the swelling of gelatin gels in hydrochloric acid solutions in relation to the amount of acid combined with the fibre supports this view. But Harris et al[94] have shown that the titration curves of wool with different acids differ according to the nature of the anion. If anions do not combine with the proteins in any way, all monobasic acids should yield nearly the same titration curve, whereas the pH range over which the adsorption takes place has in fact been found to differ greatly. But such differences could be explained if it is assumed that an appreciable fraction of the anions contained within the fibre are restrained and therefore not free to move in the internal aqueous solution.

The affinity of the anion will determine the extent to which such combination could occur and consequently this will vary from acid to acid.

Gilbert-Rideal Theory.

Gilbert and Rideal[28] have developed a theory of combination of acids with protein fibres and their view is opposed to that held by the Donnan treatment of the same problem. They hold that the internal solution cannot be regarded as a normal aqueous solution; further they state that the anions within the fibre must inevitably be repelled from one another and from negative groups in the fibre and will therefore tend to associate with the positively charged basic groups in the protein. Therefore, according to them, nearly all the anions in the fibre may be regarded as being associated in this way and hence may be taken as being adsorbed on a limited number of positively charged sites so that the activity of the anions in the fibre could be represented by the term $\frac{\theta_X}{1-\theta_X}$ where $\theta_X = \frac{[X]_\alpha}{[S_X]}$, $[X]_\alpha$ being the total concentration of anions within the fibre, the amount of uncombined anions being regarded as negligible, and (S_X) the saturation concentration of the anion sites within the fibre. Thus Gilbert and Rideal deny the presence of a separate internal aqueous phase and regard the fibre as a homogeneous phase containing only adsorbed ions.

Gilbert-Rideal vs. Donnan Theory.

The above discussion indicates clearly the main differences between the Donnan and Gilbert-Rideal theories on acid adsorption by protein fibres. However, it is difficult to discriminate between the two since both seem to explain the experimental data quite well. This could be illustrated by the following examples. According to the Gilbert-Rideal theory, the sites for cations and anions are the carboxyl and basic groups in the fibre, and since in wool these are present in almost equal numbers, and since the concentration of adsorbed hydrogen and chloride ions must be the same (neglecting the uncombined ions in the fibre), it follows that $\theta_H = \theta_X$

Hence

$$-(\Delta\mu_H^o + \Delta\mu_X^o) = 2.0\ RT\ ln \frac{\theta_H}{1-\theta_H} - RT\ ln [H]_\sigma . [X]_\sigma \quad (10)$$

If the adsorption of hydrochloric acid from solution, in the absence of any other electrolyte is considered, the concentrations of ions in the external solution must be equal also, i.e. $[H]_\sigma = [X]_\sigma$ so that

$$-(\Delta\mu_H^o + \Delta\mu_{Cl}^o) = 2\ RT\ ln \frac{\theta_H}{1-\theta_H} - 2\ RT\ ln [H]_\sigma \quad (11)$$

or

$$-\frac{(\Delta\mu_H^o + \Delta\mu_{Cl}^o)}{2.3\ RT} = 2 \log_{10} \frac{\theta_H}{1-\theta_H} + 2\ pH \quad (12)$$

Here 'X' is replaced by 'Cl' for the sorption of hydrochloric acid. Therefore, on the basis of this theory, a plot of

$$\log \frac{\theta_H}{1-\theta_H} \quad \text{or} \quad \log \frac{[H]_\alpha}{[S_H] - [H]_\alpha}$$

against the external pH should give a straight line of unit slope.

But on the basis of the Donnan theory, no specific combination between the anions and the protein takes place, and hence the activity of the chloride ions within the fibre cannot be represented by $\frac{\theta_{Cl}}{1-\theta_{Cl}}$ but the term $\frac{[Cl]_i}{V}$ must be used to represent it, to a first approximation.

In the absence of any other electrolyte in the system, this could be put equal to $[H]_\alpha + [H]_i = a$, the total acid contained within the fibre. Since $[H]_i$ is negligible when compared to $[H]_\alpha$, it can be neglected and thus equation (9) may be written as

$$-\Delta\mu_H^o = RT \ln \frac{\theta_H}{1-\theta_H} \cdot \frac{[H]_\alpha}{V} - RT \ln [H]_\sigma \cdot [Cl]_\sigma \qquad (13)$$

Since no combination of the chloride ions with the protein fibre occurs, on the basis of this theory, the affinity of these anions is equated to zero in the above equation. Now, subtracting $RT \ln [S_H]$ from both sides of the equation

$$-\Delta\mu_H^o - RT \ln [S_H] + RT \ln V = RT \ln \frac{\theta_H}{1-\theta_H} \cdot \frac{[H]_\alpha}{[S_H]} - RT \ln [H]_\sigma \cdot [Cl]_\sigma \qquad (14)$$

or

$$-\frac{\Delta\mu_H^o}{2.3\,RT} - \log_{10}\frac{[S_H]}{V} = \log_{10}\frac{\theta_H^2}{1-\theta_H} + 2\,pH \qquad (15)$$

Therefore, according to the Donnan theory, if $\log_{10}\frac{\theta_H^2}{1-\theta_H}$ is plotted against the external pH, a straight line with a slope of 2.0 should be obtained.

The experimental data of Steinhardt and Harris[92] for the sorption of pure hydrochloric acid alone by wool, when plotted on the basis of the two methods indicated above, give straight lines, the slope of the lines obtained in the Gilbert-Rideal treatment being equal to 0.87 as against the theoretically required value of 1.0, whilst in the case of the straight line obtained by the Donnan treatment the slope is 1.40 as against the expected value of 2.00. Thus both the methods of approach to this problem seem to explain the experimental data adequately.

The sorption of hydrochloric acid by wool from solutions of constant chloride concentrations, obtained by the addition of sufficient quantities of potassium chloride, has been studied by Steinhardt and Harris[92]. It has been observed that the effect of increasing the chloride ion concentrations is to increase the pH value at which any particular degree of saturation occurs, as compared with the titration carried out with hydrochloric acid alone. These are also explained quite satisfactorily by both the Donnan as well as the Gilbert-Rideal treatment.

Titrations in the presence of constant chloride concentrations.

Gilbert-Rideal treatment.

Now, taking the Gilbert-Rideal treatment at first, equation (12) which explains the sorption of hydrochloric acid alone by wool, becomes in the presence of another electrolyte, say, potassium chloride, as follows:-

$$-\frac{\Delta\mu H^{o} + \Delta\mu Cl^{o}}{2.3\ RT} = 2 \log \frac{\theta_H}{1-\theta_H} + pH_{\sigma} - \log [Cl]_{\sigma} \qquad (16)$$

Hence, when the chloride ion concentration is kept constant a plot of $\log \frac{\theta_H}{1-\theta_H}$ against pH of external solution should give a straight line of slope 0.50, as compared with the value of 1.0 obtained for the same plot with acid alone. Now, as the chloride ion concentration is increased, it is obvious that such a plot should yield a series of parallel straight lines, displaced by an amount corresponding to the increase in $\log [Cl]_{\sigma}$. This has been found to be the case with the data of Steinhardt and Harris[92]. It follows from equation (16) that when $\log \frac{\theta_H}{1-\theta_H}$ is 0, which occurs when the fibre is half-saturated, the pH of the external solution, at this point, should bear a linear relationship to $\log [Cl]_{\sigma}$ and this has been found to apply also to the experimental details of Steinhardt and Harris[92]. The validity of this treatment has been further tested by calculating the value of the total

affinity $-(\Delta\mu_{H}^{o} + \Delta\mu_{Cl}^{o})$ of the acid for wool, for each experimental point. This has been possible as a result of the determination of the saturation value $[S_H]$ of wool for hydrochloric acid by extrapolation of the Langmuir plot for the same. The affinity values thus calculated both for the acid alone, as well as in the presence of constant chloride ion concentrations have been found to be constant.

The Donnan treatment.

Now, taking the Donnan approach, it has been stated by Peters[95] that here the main emphasis is placed on the pH of the internal solution. The equilibrium between the internal and external solutions may be defined by the equation

$$\frac{[H]_i \cdot [Cl]_i}{V^2} = [H]_{\alpha} \cdot [Cl]_{\alpha} \qquad (17)$$

Since there must be equality between the amounts of sorbed cations and anions in the fibre

$$[H]_{\alpha} + [H]_i = Cl_i = a \qquad (18)$$

where a is the total hydrogen ions taken up by the fibre. Now taking logarithms,

$$\log_{10} \frac{[H]_i}{V} + \log_{10} \frac{[Cl]_i}{V} = \log_{10}[H]_{\alpha} + \log_{10}[Cl]_{\alpha} \qquad (19)$$

or

$$pH_i - \log \frac{a}{V} = pH_{\alpha} - \log [Cl]_{\alpha} \qquad (20)$$

Further $[H]_o = [Cl]_o$ in the presence of hydrochloric acid alone, so that

$$pH_i = 2\,pH_o + \log \frac{a}{V} \qquad (21)$$

Now, when the fibre is half-saturated with acid $a \simeq 0.4$, $V \simeq 0.3$ and $pH_o = 2.1$ which give a value of $pH_i = pK' = 4.2 + 0.1 = 4.3$ which in turn is in good agreement with the dissociation of free amino acids.

In the presence of salt, equation (21) becomes

$$pH_i = pH_o - \log [Cl]_o + \log \frac{a}{V} \qquad (22)$$

According to this equation for a given external pH value the internal pH will decrease with increasing ionic concentration and hence more acid will be taken up by the fibre. Therefore when the fibre is half-saturated with hydrogen ions which would occur at a constant internal pH, namely pK, the external pH would be a linear function of $\log [Cl]_o$. This has been found to be the case with the results of Steinhardt and Harris (loc. cit.) wherein for all the external ionic concentrations and pH values recorded, Peters has calculated the internal pH values and thus has proved the validity of the Donnan treatment in this particular case. When the amount of acid bound by the fibre is plotted against the internal pH, instead of the external pH, all the curves obtained for the sorption of acid by wool, both in the absence and in the presence of constant chloride ion concentration, are found to be superimposed on one another. Thus both the theories of Donnan and Gilbert and

Rideal appear to explain quite satisfactorily the combination of acids with protein fibres.

The relative merits of the Gilbert-Rideal and Donnan theories.

But there has been quite an amount of controversial discussion regarding the relative merits of these two theories recently and therefore it would be worthwhile to consider these in brief. The Gilbert-Rideal theory has been criticised by Peters and Speakman[22] on the following grounds.

First of all, Gilbert and Rideal have, as shown in equation (4), introduced the term γF into the Fowler and Guggenheim[96] equation for the adsorption of molecules and thus have extended it to the adsorption of ions, which is not justified. Secondly, according to their treatment with titrations at different constant ionic strengths, there should be no limit to the displacement of the pH of the mid-point of the titration curve, as the concentration of salt is increased, whereas the plot of the pH of the external solution against $\log [Cl]_{\sim}$ is linear only over a range of low chloride concentrations and decreases rapidly in the neighbourhood of 1.0M. According to Peters and Speakman[22] the limitations of the Gilbert-Rideal theory are fundamentally related to the assumption that the anions of the combined acid occupy positively charged sites in the fibre. Further, Gilbert and Rideal assume that the law of mass action is applicable to the combination of anions with proteins. If the combination of

acids with protein fibres is dealt with on the basis of the Donnan theory of membrane equilibria, then all these assumptions are quite unnecessary as stated by Peters and Speakman[22]. Further, the Donnan treatment predicts that the graph obtained by plotting the external pH value when the fibre is half-saturated with acid, against log $[Cl]_o$ should asymptotically approach a limiting value, viz., the internal pH value at half-saturation ($pK_{int.}$) which is about 4.50. This has been found to be the case by Steinhardt and Harris[92] but the Gilbert-Rideal theory does not predict such a departure from the linear relationship. In this respect the Donnan treatment appears to be superior to that of Gilbert and Rideal.

But it has been stated by Kitchener and Alexander[97] that although the Donnan theory is necessarily valid, it does not throw any new light on the acid binding equilibrium and is in fact much less powerful than the Gilbert-Rideal theory[28]. These authors are of the view that the law of mass action is applicable to the acid-binding of wool and eventually leads to the same superimposition of the titration curves observed both in the absence and in the presence of salt, without having recourse to ill-defined quantities, such as the internal pH values, which are incapable of direct measurement. Such superimposition of the curves is obtained by plotting the amount of acid combined as a function of the product of the activities of the hydrogen and chloride ions in external solution instead of the external pH value alone.

But it has been shown by Peters and Speakman[98] that the Donnan approach still gives much more precise agreement than that of Gilbert and Rideal. Now, equation (20) may be put as follows:-

$$pH_i = -\log a_H \cdot a_{Cl} + \log \frac{a}{v} \qquad (23)$$

Hence in plotting the quantity of combined acid against $-\log a_H \cdot a_{Cl}$ instead of against the internal pH, Kitchener and Alexander[97] have neglected the term $\log \frac{a}{v}$ which leads to a much less precise agreement between the curves. Further, Kitchener and Alexander[97] have suggested the possibility of calculating the pK values of the carboxyl groups of wool from the Gilbert-Rideal theory. But it has been shown by Peters and Speakman[98] that the basic assumption on which they derive the above conclusion is in itself tantamount to rejecting the Gilbert-Rideal theory and accepting the Donnan theory.

Thus, Peters and Speakman have clearly shown the existence of a common internal titration curve for hydrochloric acid, sulphuric acid and hydrochloric acid in the presence of various concentrations of potassium chloride. Further they have pointed out that the external titration curves of hydrochloric acid cannot be displaced beyond the internal titration curve by addition of potassium chloride and sodium sulphate, respectively, which is not capable of any explanation by the Gilbert-Rideal theory, whereas it is a requirement of the Donnan theory when the anion affinity is low. The "internal pH concept" according

to Peters and Speakman also offers a satisfactory explanation of the increasing rate of hydrolysis of proteins with acids of increasing anion affinity or with single acids in the presence of increasing concentrations of neutral salts in solutions having the same external pH value.

Sorption of hydrochloric acid by chitin.

Now, with the review given above on acid combination with insoluble fibrous proteins as a background, we may consider the sorption of hydrochloric acid by chitin, both in the absence and in the presence of different constant concentrations of chloride ions brought about by the addition of sufficient amounts of sodium chloride to the system. The nature of the substrate has been indicated earlier and therefore it would suffice to point out here that the groups in it, which may be expected to play an active part in acid combination are the acetylamino groups.

The combination of acid with chitin differs from that with fibrous proteins because, since there are no carboxyl groups present, there is no back titration. The combination may be visualised as equivalent to a single acid-base reaction, except that here the weakly basic groups are situated in the solid substrate. In such an acid-base combination, it is assumed that the hydrogen ions are attached specifically to the weakly basic amido groups, and with the lowering of the pH of the acid solution, these become fully saturated.

Now, as regards the sorption of the anions, they might either be sorbed on specific sites as is supposed to be the case with wool, by the proponents of the Gilbert-Rideal theory, or they might be randomly dispersed in the internal aqueous phase, without any specific affinity for the positively charged sites in the substrate but just remaining there in amounts equivalent to the cations sorbed, in order to maintain electrical neutrality.

In order to find out clearly the nature of the mechanism involved in the sorption of anions by chitin, the combination of both hydrochloric and sulphuric acids with the substrate was investigated at 60°C. These experiments were conducted under identical conditions; the results are summarised in Tables 31 and 32 and the titration curves plotted in Fig.23. The absence of any appreciable difference in the amounts of HCl and H_2SO_4 adsorbed indicates clearly that the anion has no specific affinity for the positively charged sites in the substrate. Therefore it seems that titration of chitin with acids could be explained by the Donnan theory, rather than by that of Gilbert and Rideal.

Since both cations and anions are sorbed by chitin in equal amounts it may be assumed that there are equal numbers of positively and negatively charged sites in the substrate, although it must be made quite clear that it is only the ionic attraction of the positively charged sites for the anions which gives rise to the assumption, since there are no carboxyl groups

present in the system. Hence an attempt has been made to apply both the theories to the experimental data obtained for the sorption of hydrochloric acid by chitin both alone and in the presence of two different constant chloride ion concentrations viz. 0.1M and 1.0M/litre.

Now, if the first assumption is correct, that this acid combination with chitin amounts to its sorption by the acetylamino groups, until they are fully saturated, it should reach a maximum value equivalent to the total acetylamino group content of chitin. According to the formula of chitin already established by recent investigations, there are 4.93 equivalents of acetylamino groups per kilogram of dry chitin. Therefore according to our assumption a maximum of 4.93 equivalents of a monobasic acid should be bound by one kilogram of chitin. The experimental data obtained at 60°C. for the sorption of hydrochloric acid alone were plotted on the Langmuir basis as shown in Fig.24 when a saturation value of 5.20 equivalents of acid per kilogram of dry chitin was obtained. This appears to provide good evidence in favour of our assumption, even though the composition of the chitin has not been established completely. It may be repeated here that the ash present in the sample will not affect this result. This maximum sorption capacity is reached at an external pH of about 2.30, after which there is a considerable increase in the amount of acid sorbed. This has been shown, earlier on, to be due to strong hydrolysis of the substrate by the acid under the experimental

conditions employed.

Application of Gilbert-Rideal theory.

The validity of this theory in the present case can be verified by making use of equation (12). Accordingly a plot of $\log \frac{\theta_H}{S_H - \theta_H}$ against the external pH for the sorption of both hydrochloric acid alone as well as in the presence of both 0.1M and 1.0M constant chloride ion concentration by chitin at 60°C. has been shown in Fig.25 and the same tabulated in Table 33. Here the notations have the same significance, as explained earlier, and (S_H) - the saturation value for the cations - is taken as equal to 5.20 equivalents per kilogram of dry chitin. The straight line obtained with HCl alone has a slope of -1.00 as against a theoretical slope of -1.000. Similarly the slopes of the straight lines obtained for the sorption in the presence of 0.1M and 1.0M constant chloride ion concentrations are -0.50 and -0.50 respectively as against the theoretical value of -0.50 as required by equation (16). These results indicate that the Gilbert-Rideal theory may be applied to the sorption of hydrochloric acid by chitin and the assumptions made are essentially on the right lines. However if the affinity values of this acid for chitin are calculated using equation (12) for acid alone and equation (16) for sorption at 0.1M and 1.0M constant chloride ion concentrations then these values should be constant throughout in all cases which would

justify the application of this theory to this particular problem. However, as can be seen from Table 34 although the affinity values are constant over the whole range of pH values in each case, those obtained with acid alone are not the same as those obtained at constant chloride ion concentrations which themselves differ from each other to a certain extent. Thus the results obtained so far are inconclusive to justify any application of the Gilbert-Rideal theory to the sorption of simple acids by chitin.

Application of the Donnan treatment.

It is thought better to consider the essential aspects of the Donnan theory at first, before applying the equations obtained through this treatment, to the sorption of acids by chitin. This theory concerns itself with systems of ions including a membrane permeable by all the ions present except one which is usually regarded as being held inside the membrane. According to this theory the ratio λ between the concentration of any univalent cation outside the membrane to the concentration of the same cation inside the membrane is the same as the ratio between the corresponding values for any other univalent cation present and is the reciprocal of the corresponding values for all univalent anions present i.e.

$$\lambda = \frac{[H_o^+]}{[H_\alpha^+]} = \frac{[Na_o^+]}{[Na_\alpha^+]} = \frac{[Cl_\alpha^-]}{[Cl_o^-]} \qquad (24)$$

If we consider the case of wool the fibre itself forms the membrane and the $R\text{-}NH_3^+$ ions derived from acid sorption by the side-chain $R\text{-}NH_2$ groups serve as the non-diffusible ions. Elöd[23] has shown that wool behaves in accordance with the characteristic Donnan equation.

$$\lambda = \frac{[H_\alpha^+]}{[H_\beta^+]} = 1 + \frac{C_1}{C_2 + C_3} \qquad (25)$$

where C_1 is the concentration of the non-diffusing protein ion in the fibre, C_2 is the acid concentration in the external solution and C_3 is the concentration of any other electrolyte outside the fibre.

Now in the case of titration of wool with acid alone $C_3 = 0$ and $\lambda = 1 + \frac{C_1}{C_2}$ and since wool is an amphoteric protein the value of C_1 is dependent on C_2. Therefore if $C_2 = 0$ since no ionisable protein would be formed in the absence of acid, the wool will be at its iso-electric point. Therefore the first additions of acid to the system would be rapidly and largely absorbed by the wool and hence C_1 would be large in comparison to C_2 but as there is a limit to the increase of C_1 on account of the nature of the proteins, the value of λ must, with increasing addition of acid, rise to a maximum and then fall.

The dependence of acid sorption on this external pH as well as the existence of a maximum acid-combining capacity is thus explained by the Donnan theory. This clearly demonstrates

the importance of the pH of the external solution in determining the distribution ratio between the inside and outside of the fibre phase. Another important point which should be noted is that Donnan equilibria deal with only ionic concentrations and not with molar reactions, and accordingly the amount of acid taken up by a given amount of wool is unaffected by changes in total quantity of acid available provided the acid concentration remains the same.

According to the Donnan treatment as outlined earlier it is only the cations which are specifically attached to the carboxyl groups in wool when it combines with acids, whilst the anions are simply randomly distributed in an internal aqueous solution, these accompanying the cations into the substrate in order to maintain electrical neutrality. Therefore in the sorption of simple acids by chitin the acetylamino groups which become positively charged may be considered as the non-permeating ions, the chitin itself being regarded as a diffusion membrane through which all other ions could pass freely. If this be the case then the sorption of the acid should reach a maximum and then begin to decrease with continuous lowering of the external pH value. But although a maximum sorption with hydrochloric acid is indicated as shown by the Langmuir plot, there is still considerable increase in acid sorption, with further increase in acidity of the external solution. However, this has been established to be brought about by extensive hydrolysis of the substrate itself under such conditions as

indicated on page 111. Further, its validity in the present instance could be tested by applying the equation (15) to the experimental data obtained with hydrochloric acid both alone and in the presence of 0.1M and 1.0M constant chloride ion concentration. Thus a plot of log $\frac{\theta_H^2}{S_H - \theta_H}$ against the external pH of the solution is represented in Fig.26 and the same summarised in Table 35. It is seen that the slope of the straight line obtained for hydrochloric acid alone is equal to -1.74 as against the theoretically required value of -2.00. In the presence of 0.1M and 1.0M constant chloride ion concentrations, straight lines with slopes of -0.75 and -0.700 are obtained as against the theoretical value of -1.00. So far, there seems to be a fairly good agreement between the observed data and the theoretically predicted values. However, the affinity values calculated using equation (15) for hydrochloric acid alone and the following equation (26) derived from (15) for the sorption of the acid at 0.1M and 1.0M constant chloride ion concentrations are found to be different from one another, although in each individual case the values obtained over the whole range of external pH values are found to be fairly constant. These are summarised in Table 36.

$$-\frac{\Delta\mu_{H^+}}{2.3RT} = \log\frac{\theta_H^2}{S_H - \theta_H} + pH_o - \log[Cl]_o \qquad (26)$$

It is thus clear that the Donnan theory also does not justify its application to the sorption of simple acids by chitin. However the very fact that the Donnan theory recognises that there is a limit, viz., the internal titration curve beyond which the external titration curve of hydrochloric acid cannot be displaced by increasing addition of another electrolyte (say) sodium chloride, combined with the observed agreement between the theoretical and experimental data, go to show that of the two theories proposed, that of Gilbert and Rideal and of Donnan, the latter appears to represent the true state of affairs in the binding of simple mineral acids by chitin, rather than the former.

Sorption of acid dyes.

Thus, having established the nature of the mechanism involved in the sorption of acids by chitin we may proceed to study the combination of acid dyes by the same substrate. The system consisted of sulphuric acid or sodium hydroxide, sodium salt of the dye and chitin. The sorptions of the eleven dyes shown on page 105 were investigated at temperatures of 50°C. and 60°C. respectively under identical conditions of goods:liquor ratio, concentrations of each dye solution employed, etc.

At first the time necessary to attain equilibrium conditions was investigated at both the temperatures with three typical dyes employed in the present work, under exactly the

same conditions as employed in the actual experiments. These preliminary investigations showed clearly that the adsorption takes place very rapidly as shown in Figs.27 to 29, attaining equilibrium conditions in about 15 minutes to 45 minutes.

The results for the same are given in Tables 37 to 39. This rapid attainment of equilibrium indicates that the reaction involved might be of an ionic nature and further, it also shows that the active groups in the substrate which are responsible for the sorption of the dye anions are readily accessible as has been found to be the case by McLean and Wooten[99] in their studies on the exchange reactions of cellulose with acids.

Thus although a period of 45 minutes was found to be quite sufficient to attain equilibrium conditions at the temperatures 50° and 60°C. in the case of these acid dyes, still, they were all left in the bath for 24 hours. The main object in doing so was to find out whether in addition to forces of ionic attraction between the dye anion and the active groups in chitin some other effects such as diffusion, van der Waals attraction, etc., were involved.

It may be anticipated on the basis of the theory postulated earlier for the combination of acids with chitin that the dye anions also would be entering into the substrate in amounts equivalent to the cations sorbed, and they replace the sulphate anions present in the system. Therefore the amount of different acid dyes sorbed by 1 kilogram of dry chitin should be

equal to 4.93 equivalents which in turn is the total acetyl-amino group content of chitin. It may be repeated, that the ash being mainly silica, cannot interfere with the combination of any acid dyes. The sorptions with the dyes mentioned in page 105 were investigated at two temperatures 50°C. and 60°C. over the pH range stretching from 1.0 to 10.0, the system comprising sulphuric acid or sodium hydroxide, sodium salt of the dye and chitin. In the case of each dye the maximum sorption is obtained at a different pH value and the general tendency is towards the displacement of these values to higher acid concentrations, the higher the sulphonic group content of the dye. Further, in each case the amount of dye sorbed after reaching a maximum value at a particular pH begins to decrease as the pH of the external solution is lowered still further. The same phenomenon has been observed by Pelet Jolivet and Hans-Siegrist[100] in their investigations on the effect of sulphuric acid and other inorganic electrolytes on the sorption of crystal ponceau by wool. Therefore it appears that this particular phenomenon could be attributed to a competition of the sulphate ions with the dye anions when the concentration of the former is sufficiently high as is to be expected at low pH values in such systems. These results are given in Tables 40 to 50 and the isotherms for the same are shown in Figs.30 to 40. It is evident from these data that there is not an appreciable temperature coefficient for the sorption of these acid dyes by chitin. This again seems to support the

view that the combination of such acid dyes with chitin may be regarded as essentially of an ionic character.

Determination of saturation values for acid dyes.

It was now decided to establish the saturation value for chitin with these acid dyes at a particular temperature. The temperature chosen was 60°C. since it has already been established that there is no temperature coefficient for such sorption and hence any temperature chosen should not affect the essential sorption process, although it might affect the rate of dyeing. Hence one of the temperatures employed (60°C.) for the actual sorption studies was used here. The experimental procedure consisted in the case of each dye, in choosing the initial pH value which under equilibrium conditions at the temperature of sorption studied (60°C.) gave a maximum sorption and a series of solutions of this dye of different concentrations but of the same chosen pH value were prepared. Again the system comprised sulphuric acid, sodium salt of the dye and chitin and with the same goods:liquor ratio as used in the actual sorption studies. These were kept continuously rotated at 60°C. in the thermostat for 24 hours and estimated colorimetrically as before. The results obtained are given in Table 51. It is evident from these results that the saturation values obtained under these conditions fall far short of the theoretically expected value of 4.93 equivalents of dye per kilogram of dry chitin.

Suggested explanation for variation in saturation values of acid dyes.

The variation in saturation values obtained with the eleven acid dyes (Table 52) used here is difficult to explain, but a number of factors must be operating. Therefore attempts have been made to correlate these variations on the basis of the following factors:- (i) Affinity of the dye for chitin as determined by the pH at half-saturation and its relation to the sulphonic group content of the dye. (ii) The influence of the presence of an unsulphonated benzene or naphthalene nucleus in the dye molecule. (iii) The nature of the orientation of the dye ion in chitin, depending on the position of its sulphonic group or groups. (iv) The possibility of hydrolytic decomposition of the substrate, under the experimental conditions employed, affecting the saturation values obtained with some dyes.

The reference numbers of the dyes are those given in Table 52. There seems to be a general correlation between the average affinity of the dye ion and its sulphonic group content, the affinity being higher the fewer the number of sulphonic groups. This relationship is shown in Table 53. Next, it appears that the greater the number of unsulphonated benzene or naphthalene nuclei present in dyes containing the same number of sulphonic groups, the greater is the saturation value. This is shown in Table 54. This may be because the

absence of ionic groups may promote intermolecular association and monolayer stability at an adsorbing surface, but the present evidence is insufficient to establish this point.

Thirdly, the saturation values may be placed generally in two broad classes. (i) Those given by dyes containing only one sulphonic group or two, if in the same component of the dye molecule, in which case the dye molecule is probably oriented perpendicularly to the surface, and (ii) those given by dyes containing either two or more sulphonic groups situated in both the components of the dye molecule, in which case the dye is probably oriented horizontally. The saturation values obtained with these two classes of dye appear to show a fairly good degree of correlation on the basis of this particular type of orientation. A detailed comparison of these dyes is given in Table 52. There are of course certain anomalous results, which could be accounted for by one of two other factors:- (i) The presence or absence of unsulphonated rings in the dye molecule; and (ii) the possibility of some hydrolysis of the chitin under the severe acid conditions employed in some cases. There is no definite correlation between the molecular weight of the dye ion and its affinity for chitin as can be seen from Table 52.

In order to confirm the effect of the possible modes of orientation, the total area covered by each dye ion at saturation at 60°C. was calculated from a model. The result should be constant for all the dyes, if the total surface in

chitin accessible to each dye is the same. The values are however not constant (Table 55), and therefore it appears that the total surface area available for each dye may not be constant, or some other unknown factor is affecting the result. Further investigations are in progress to elucidate the different factors likely to be involved.

Sorption of acid dyes in the presence of sodium sulphate.

In order to confirm the ionic nature of the dyeing of chitin with acid dyes, a series of dyeings of chitin with these dyes in the presence of various concentrations of sodium sulphate were carried out. Since according to the theory already postulated the dye ions are sorbed by chitin only to maintain electrical neutrality, without their having any specific affinity for the substrate, there should be competition between these dye ions and the sulphate anions, in the presence of sodium sulphate, leading eventually to a decrease in the dye sorption as compared to that obtained in the absence of sulphate ions, because the sulphate ions are much smaller in size than the dye ions and as such will be able to penetrate into the crystallites of the substrate, unlike the dye ions. A similar phenomenon is observed in the sorption of acid dyes by nylon in the presence of sodium sulphate.

The system consisted of chitin, sodium salt of the dye, sulphuric acid and sodium sulphate. A series of solutions of

the same concentration of dye as used for sorption in the case of all dyes, viz., 0.0001106 gm.moles/litre, but with different concentrations of sodium sulphate (Dry AR) ranging from 1.0 gm./l. to 10.0 gm./l. were prepared in distilled water and their pH in each case brought to the initial value at which the maximum sorption was obtained at 60°C. by the addition of sulphuric acid. Now, the sorption was carried out under identical experimental conditions as those employed before and the results obtained are tabulated in Tables 56 to 66.

Gilbert and Rideal[101] on the basis of their theory for the sorption of acids and acid dyes by wool, have derived the following expression to predict the course of combination of acid dyes of different valencies with wool, in the presence of sodium sulphate.

$$\ln \frac{n_i}{c_i} = -\tfrac{1}{2} Z.\ln \frac{SO_4}{n_{SO_4}} - \left(\frac{\Delta\mu_i - \tfrac{1}{2} Z.\Delta\mu_{SO_4}}{RT}\right) \qquad (27)$$

where n_i = number of dye ions sorbed per gm. of keratin
and c_i = equilibrium bath concentration in moles/litre.

It has been found by them that as the valency of the dye ion is increased, the value of the slope of straight lines obtained by plotting log n_i/c_i against log 'SO_4' also increases and further that these slopes are of nearly the same value as predicted by the equation. Here, the amount of sodium sulphate added per litre of solution is taken as a measure of the sulphate ion concentration.

The results obtained in the present investigation in the presence of sodium sulphate have been plotted on similar lines as shown in Figs.41 to 47. In all cases the plot gives quite good straight lines and their slopes are, with a few exceptions, found to increase as the valency of the dye anion is increased. But values of these slopes are not in accordance with those predicted by equation (27). This could naturally be expected because it has already been shown in connection with the sorption of simple acids by chitin that the Gilbert-Rideal theory does not seem to apply, whilst the same phenomenon seems to be governed by the Donnan theory.

However, these straight lines, thus obtained, are not superimposed on one another, which should be the case if the dye anion had no specific affinity for chitin. Therefore it may be stated that each dye does seem to possess a certain intrinsic affinity for chitin different from the other one. This might be due to the operation of hydrogen bonding, van der Waals forces, etc., in such sorption in addition to the main electrostatic attraction involved.

Moreover, the solubility of the dye in water also may be partly responsible for this effect, because the higher the sulphonic group content of the dye, the greater will its solubility in water be, and hence, the more difficult to remove it from water and sorb it on the substrate. The very fact that the higher the concentration of sodium sulphate present in the system, the greater is the decrease in the amount of

acid dye sorbed by chitin, shows that the process of combination of acid dyes with chitin is ionic in nature.

Sorption of hydroxy compounds.

A number of investigators have studied the sorption of different types of hydroxy compounds by both cellulosic and protein fibres. In this laboratory a good deal of work has been carried out on the hydrogen bonding properties of these compounds under various conditions, as obtaining in the actual sorption of such compounds by various substrates. Hence, the sorption of phenol, resorcinol, 2:4-dinitrophenol, and 2:4:6-trinitrophenol by chitin has been studied.

It might be stated that in the sorption of these compounds by chitin either the formation of a bond having a partially covalent nature or a hydrogen bond, or various types of polar forces which might be either electrostatic (coulombic) in nature or otherwise, and including van der Waals forces, may be expected to operate. Therefore the following sorption studies were carried out, with a view to elucidating the exact nature of such forces involved therein.

Phenol.

A pure AR sample of phenol was used for the sorption studies here. The concentrations of solutions varied from ca. 0.10 gm./l. to 1.0 gm./l., which were estimated by the

bromide-bromate method mentioned under experimental procedure, in the case of aqueous solutions, and by the Unicam photoelectric spectrophotometer for solutions in dry iso-octane. In all cases it was found by preliminary rate of absorption experiments, that equilibrium was reached both at 50°C. and 60°C., in less than 24 hours. So, these sorptions were carried out for 24 hrs. at each of the two temperatures. The results for the sorption of phenol from aqueous solution are given in Table 67 and the isotherms in Fig.48. It may be pointed out here that the chitin used in this particular experiment was a sample conditioned at room temperature and relative humidity and had a moisture content of about 8.7%. Now, the heat of reaction values have been calculated for the sorption of phenol by chitin under such conditions, using van't Hoff's equation. These are of the order of +4.8 kcal. per mole. It was anticipated, as a result of previous studies (Arshid[102]) that the nitrogen of the acetylamino group in chitin would be involved in hydrogen bond formation with the hydrogen of the phenolic hydroxyl group and hence a value of the order of +3.0 kcal. per mole should have been obtained for the heat of reaction. But the value of +4.8 kcal. per mole obtained is perhaps an indication of a hydrogen bond formation between a hydrogen and oxygen.

Next, the sorption of phenol by conditioned chitin, having a moisture content of about 8.7% from dry iso-octane was studied. Here, iso-octane was chosen as the solvent since it absorbs

very little at frequencies of the order of 2780 Å and therefore, quite appreciable readings could be obtained with phenol in iso-octane, at this wavelength. The sorption results are summarised in Table 68 and the isotherms are shown in Fig.49. It would be observed that there is something unusual regarding the shape of these isotherms, but without further evidence it is not possible to suggest an explanation. A maximum sorption of about 2.0 moles of phenol per kilogram of dry chitin is obtained from iso-octane, as compared to 0.90 moles per kilogram of dry chitin from water.

This seems to indicate that in addition to hydrogen bonding, van der Waals forces of attraction might also be operative under such conditions, for when water is used as the solvent, phenol might be expected to have a higher affinity for it than for chitin, whilst when a dry solvent is used, and the substrate contains water of hydration, the affinity of phenol for the substrate might be higher and hence more of it would naturally be taken up from a dry solvent than from water. In order to substantiate this conclusion, the sorption of phenol by thoroughly dried chitin, from dry iso-octane, under similar experimental conditions as before, was studied. It was found that there was no sorption of phenol by chitin under such circumstances, which seems to justify our earlier conclusion. In addition it seems to indicate that the hydrogen bond formed in the sorption of phenol by chitin, both from water and from iso-octane, should be one between water present as water of

hydration in the substrate and the hydroxy group of phenol. This will naturally be a bond between a hydrogen and an oxygen atom instead of between a hydrogen and a nitrogen atom as was anticipated at first, which is again confirmed by the value of approximately +4.80 kcal. per mole obtained for the heat of reaction between phenol and chitin.

Next the sorption of resorcinol from aqueous solution by chitin both at 50°C. and 60°C. was investigated under identical experimental conditions. The concentration of resorcinol used ranged from 0.20 g. to 2.0 g. per litre and these were estimated by the method of Pence, mentioned under experimental procedure.

The results are shown in Table 69 and the isotherms for the same in Fig.50. The heat of reaction calculated as before using van't Hoff's equation is of the order of +1.75 kcal. per mole. This low value appears to show that the sorption of this compound by chitin may be akin to a process of selective solvation. In other words, it amounts to the replacement of water of hydration held by the substrate, by resorcinol, a compound showing a slightly higher affinity and as such, the heat changes involved in such a reaction would naturally be quite small.

A similar result has been obtained by Steinhardt et al[103] for the sorption of monochloroacetic acid on wool. According to them, this acid is sorbed in an undissociated state, and a value of 300 or 400 calories per mole of acid is obtained for the heat of reaction. But it has been found by Speakman and

Stott[104] that the heat of combination of wool with monochloroacetic acid is of much higher value.

But, again, this heat of reaction is the sum of the averages of heats of both the ionic and the non-ionic reactions and could therefore be expected to be higher. So, according to Steinhardt et al[103] when one solvated molecule is replaced by another which is held very slightly more strongly, the heat changes involved would probably be very small. This seems to apply in the sorption of resorcinol by chitin.

Sorption of nitrophenols.

The object of these experiments was to study the nature of the mechanism involved in the sorption of weak acids by chitin. So, the sorption of such compounds as 2:4-dinitrophenol and its higher analogue 2:4:6-trinitrophenol (picric acid) has been investigated here.

2:4-Dinitrophenol.

A pure dry AR sample of this compound of m.p. 114°C. was employed. The concentrations of the solutions varied from 0.05 g. to 0.40 g. per litre, which was estimated after suitable dilution, on the Unicam photoelectric spectrophotometer at 3550 Å. Preliminary rate-studies showed that equilibrium is attained in the sorption of this compound by chitin in 48 hours at 50°C. and in about 24 hours at 60°C. respectively. Tables 70 and 71 give the results obtained and the isotherm for the

sorption of this compound is shown in Fig.51, while the titration curve of this compound is shown in Fig.52. It is seen from both Figures that there is scarcely any appreciable temperature coefficient. This seems to indicate that the sorption might be construed as of an ionic nature, but since this is only a weak acid, it will only be partially dissociated and hence, most probably, both sorption of the ions, as well as the undissociated molecules, might take place.

2:4:6-Trinitrophenol.

A pure dry AR sample of m.p. 122°C. was employed for this investigation. A range of concentrations varying from 0.1 g. to 1.0 g. per litre in distilled water were used and their strengths were determined after suitable dilution, by means of the Unicam photoelectric spectrophotometer at 3550 Å. The sorption was carried out at 50°C. for 48 hours and at 60°C. for 24 hours. No measurable difference in the concentrations of the solutions after sorption could be obtained, although the substrate was distinctly coloured yellow. This might be due to a large liquor:goods ratio of the order of 2000:1 employed, so that the relative concentration change after sorption would in any case be very small. A titration curve (Fig.53, Table 72) was obtained, however, by pH measurements, but its exact interpretation is difficult.

SECTION III

CONCLUSIONS

In the present work the sorption properties of chitin with diverse types of compounds have been investigated. Chitin is fairly widely distributed in nature, both in the animal and plant worlds. The best source of this compound is stated to be shrimp shells. A number of investigators have extracted this material through different methods, depending on the nature of the source from which it is obtained.

Chitin employed in the present investigation was prepared from the shells of '<u>Nephrops norvegicus</u>' and ground to a uniform size, of dimension greater than 200 mesh.

Chitin has been found to comprise both crystalline and amorphous regions as is the case with any textile fibre. Here the chains of polyacetylaminoglucose units, linked together by 1:4-glucosidic linkages as in cellulose, are found to be held laterally by hydrogen bonds formed between the acetylamino group side-chains of adjacent units, and also between the acetylamino groups and hydroxyl groups present in the system. Thus, the whole substrate may be visualised as being built up of compact bundles of chains, constituting the crystalline regions interspersed with a certain random distribution of the same, giving rise to amorphous parts.

The proportion of degree of crystallinity to amorphous part in the sample of chitin used in the present series of investigations is being examined by means of X-ray photographs of the sample obtained through copper radiation. So far, although a considerable volume of work has been carried out on the nature of the sources containing chitin and its extraction from the same, practically no work seems to have been done to determine the pore size, the swelling property in aqueous as well as acid and alkaline solution, and also the sorption of simple acids, alkalis and different types of dyes by this substance.

The amount of work that has already been expended in attempts to manufacture alkali chitin, chitin xanthate, and regenerated transparent chitin film has shown that artificial fibres and film could be prepared from this and thus has clearly indicated its immense scope and importance in the textile world. Therefore it was thought worthwhile as a first step to investigate the sorption of simple mineral acids, acid dyes and a few selected hydroxy compounds, in order to elucidate the mechanism of binding of same by chitin. As indicated in the earlier part of this investigation, the very composition of this substance leads one to think that it might display properties similar to those of cotton, wool, nylon and acetate rayon, in its combination with different compounds, such as simple mineral acids, alkalis, simple organic acids, hydroxy compounds, direct dyes, dispersed dyes, and soluble

acetate rayon dyes. This view seems to have been justified by the results obtained in the present research on the sorption of some simple mineral acids and certain acid dyes as well as a few hydroxy compounds, wherein it seems to behave like protein fibres. Therefore it is hoped that the present work will serve as a preliminary survey in the particular field chosen and thereby inspire others to investigate in detail the other avenues still unexplored, so far as this substance is concerned, and put them on a sound quantitative basis.

Chitin, according to the established formula, is a polysaccharide containing N-acetylaminoglucose units, these being built up through 1:4-glucosidic linkages, but the constitution of the sample used here has not been completely established. It contains about 7.5% ash, which appears to be mainly silica, and therefore cannot interfere with acid or acid dye adsorption. It contains no carboxyl groups and hence its combination with acids like hydrochloric acid may be expected to be equivalent to a simple acid-base combination. The amount of a monobasic acid sorbed by this compound may therefore be expected to be of the order of 4.93 equivalents per kilogram of chitin, which is the total acetylamino group content of the substrate. It was not known till now whether this maximum could be reached, since there is the risk of the chitin being hydrolysed at high acid concentrations and temperatures at which the sorption is carried out. But it has been established in the present work that no hydrolysis by hydrochloric acid occurs at 60°C. at pH

values above 2.0 whereas below this value extensive hydrolysis is found to occur. Fortunately the maximum sorption is found to occur both with hydrochloric and sulphuric acids at a pH value of about 2.30 in the presence of the acid alone.

Thus, after having established the absence of any hydrolysis under the experimental conditions employed, it was decided to investigate the exact nature of the forces involved in such sorption. Since this substrate appears to behave in a manner similar to the insoluble fibrous proteins, in its combination with mineral acids, two theories put forward to explain the phenomena involved in such acid combination by wool, have been examined.

The first one is that of Gilbert and Rideal[28]. These authors, on the assumption that there are equal numbers of acidic and basic sites in wool keratin, have derived expressions to account for the sorption of simple mineral acids by the same. Their main postulate is that both cations and anions of the compound being sorbed are specifically attached to the negatively and positively charged sites in the fibre. The Donnan theory, which is the second one, on the other hand, proposes that only the cations of the sorbate are specifically attached to the substrate, while its anions are randomly distributed in an internal aqueous solution within the substrate, and thus, having no affinity whatsoever for the substrate, are sorbed in amounts equivalent to the cations taken up by the fibre, in order to maintain electrical neutrality.

In the present case, although there are no carboxyl groups in chitin, an attempt has been made to apply the Gilbert-Rideal theory, after making an assumption that the anions of an acid sorbed, are attached to the positively charged sites in the chitin. Thus it is assumed that there are equal numbers of cations and anions of the sorbate inside the substrate at any time. The results obtained in the sorption of hydrochloric acid alone and in the presence of 0.1M. and 1.0M, constant chloride concentrations have been found to yield straight lines of the required slopes of -1.0, and -0.5 respectively, when plotted on the basis of $\log_{10} \frac{\theta_H}{S_H - \theta_H}$ against the external pH of the solution. But the affinity values calculated from these data, according to the expression

$$-(\Delta\mu_{H^o} + \Delta\mu_{Cl^o}) = 2.3\ RT\ (2 \log_{10} \frac{\theta_H}{1 - \theta_H} + 2\ pH_o)$$

for the sorption of HCl alone and with the expression

$$-(\Delta\mu_{H^o} + \Delta\mu_{Cl^o}) = 2.3\ RT\ (2 \log_{10} \frac{\theta_H}{1 - \theta_H} + pH_o - \log [Cl]_o)$$

for the sorption of HCl in the presence of 0.1M. and 1.0M. constant chloride concentrations have been found to be of the order of | -10.8, -7.8, -7.0 | kg.cal. respectively, although in each individual case, fairly constant values for all points on the straight lines are obtained. Further, it is observed that the affinity of the acid for chitin becomes higher the greater the

chloride ion concentration present in the system. This is predicted by the Gilbert-Rideal theory, but according to it, there is no limit to the displacement of the actual titration curve obtained with hydrochloric acid, by increasing the chloride ion concentration employed, whereas this is not true in practice. Moreover the sorption of sulphuric acid by chitin, investigated in the present research is found to be the same as hydrochloric acid, thus indicating that the anions of the acid have no specific affinity for chitin as was assumed earlier on. Therefore all these data go to show that the Gilbert-Rideal theory is not applicable to the sorption of simple mineral acids by chitin.

Hence the applicability of the Donnan theory to this problem has been considered in detail. The Donnan theory derives an expression

$$\lambda = \frac{[H^+_\sigma]}{[H^+_\alpha]} = \frac{[Cl^-_\alpha]}{[Cl^-_\sigma]}$$

for the particular case of sorption of hydrochloric acid by wool, on the assumption that the fibre acts as a membrane, through which all ions in the system are diffusible, except the protein ion formed by the ionisation of the basic side chains in acid solutions. Again, it assumes that only the cations of any sorbate are sorbed specifically by the substrate, whilst the anions have no specific attraction but are sorbed by the fibre in order to maintain electrical neutrality, within it, and that

the anions thus sorbed are therefore assumed to be randomly distributed in an internal aqueous solution. This solution is again assumed to have the same properties of a normal external aqueous solution.

The results obtained with the sorption of hydrochloric acid both alone and in the presence of 0.1M and 1.0M constant chloride ion concentrations have been plotted on the Donnan basis, when straight lines with slopes of the value of -2.0, -0.750 and -0.700 respectively are obtained, as against the theoretically required values of -2.0, -1.00 and -1.00. But the affinity values calculated for hydrochloric acid alone using the expression

$$-\Delta\mu_{H^o} = 2.3\ RT \left[\log_{10} \frac{\theta^2_H}{S_H - \theta_H} + 2\ pH_\sigma \right]$$

and for hydrochloric acid at 0.1M and 1.0M constant chloride ion concentration, using the equation

$$-\Delta\mu_{H^o} = 2.3\ RT \left[\log_{10} \frac{\theta^2_H}{S_H - \theta_H} + pH_\sigma - \log [Cl]_\sigma \right]$$

are of the order of 10.90, 6.70 and 5.50 kg.cals. respectively, although the affinity values obtained for each individual case for all the points in the straight line, have been found to be fairly constant. Thus there seems to be the same discrepancy here also, as observed with the results obtained by applying the Gilbert-Rideal theory. However, this theory predicts the

existence of a limit to the displacement of the titration curve obtained with hydrochloric acid by increasing the chloride ion concentration, unlike the Gilbert-Rideal theory. Further, the absence of any difference in affinity between hydrochloric and sulphuric acids for chitin, as found in the present investigation, goes to confirm the postulates proposed by the Donnan theory. Therefore, as between the two theories it appears that the Donnan theory is better able to explain the observed phenomena, in the binding of simple mineral acids by chitin than the Gilbert-Rideal theory. Therefore the sorption of such acids by chitin may be visualised as follows.

First, under acid conditions, the hydrogen ions are attached specifically to the weakly basic amido groups in chitin; this process comtinues with the lowering of the pH of the acid solution until all such groups present are saturated with acid. The positively charged sites thus obtained serve as the ions non-permeable through the chitin which in turn acts as a membrane obeying the Donnan theory. Therefore, with the sorption of the hydrogen ions by chitin there is a simultaneous equivalent sorption of chloride ions, which are situated in the aqueous solution within the substrate, in order to maintain electrical neutrality, without them having any specific affinity for the substrate. Again, when the concentration of the chloride ion present in the system is increased, the distribution of the ions both within and without is governed by the Donnan equations leading to a greater

affinity of the hydrogen ions for the substrate, as compared to that in the presence of HCl alone. Therefore the titration curve obtained for hydrochloric acid with chitin will be displaced towards higher pH values, with increase in chloride ion concentration, in accordance with the theory. This has been found to be the case in the present work.

After thus having established the nature of the forces involved in the combination of simple mineral acids with chitin, the sorption of certain monoazo acid dyes by this substance has been studied. These acid dyes differ from one another as regards their sulphonic group content and the position of the sulphonic groups. Since there is assumed to be no specific affinity of the anions for chitin, it would be anticipated that all the dyes would be sorbed in amounts equivalent to the total acetylamino group content of chitin. This is not so, the sorption values being very low, which may be an indication that the substrate is highly crystalline (cf. Fraenkel and Rudall[73]) and that much of it is inaccessible to the large dye anions. As far as the limited amount of experimental data will allow, some correlation has been obtained between the affinities of the dyes and their structures, thus, the more sulphonic groups there are present, the lower the affinity, because the water-solubility is higher; and on the other hand the presence of unsulphonated nuclei in the dye molecule increases the affinity. Thus there is no direct correlation between molecular weight and affinity.

Experiments carried out to study the amount of dye sorbed by chitin in the presence of varying concentrations of sodium sulphate clearly indicate that the binding of acid dyes by chitin is essentially of an ionic character. The sorption isotherms for all the dyes in this instance when plotted on the basis of the logarithm of partition of dye between substrate and external solution, against the logarithm of the sulphate ion concentration in the bath, give straight lines. The slopes of these straight lines increase with increasing valency of the dye ion used, with a few exceptions.

A similar phenomenon has been obtained by Gilbert and Rideal in their investigation on the sorption of acid dyes by wool keratin and the slopes obtained by them are in good agreement with the theoretical values predicted by their expression. It has already been shown that this theory is not applicable to the sorption of acid dyes by chitin and as such their expression cannot be expected to indicate the nature of the dependence of the slopes of straight lines obtained by plotting the logarithm of the partition of dyes between substrate and external solution against the logarithm of the external sulphate ion concentration in the present instance. But the increased amount of desorption observed with dyes of increasing valency, for the same concentrations of sodium sulphate used, shows that the sulphate ions compete with the dye ions to reach the substrate, in order to maintain electrical neutrality. In such a competition the sulphate ions are most

likely to succeed on account of their smaller size as compared with the dye ions. Further, the greater the number of sulphonic groups present in the dye, the greater will be its solubility in water, and hence, in the presence of sufficient amounts of sodium sulphate, the sulphate ions would naturally be expected to be taken up much more easily than the dye ions. All this evidence goes to show that the sorption of these acid dyes by chitin is mainly brought about by electrostatic attraction between the positively charged sites on the substrate and the dye ions. It has also been found that dyes of the same valency give straight lines of nearly the same slopes.

The results obtained with the sorption of phenol and other hydroxy compounds appear to illustrate a variety of forces active in their sorption by chitin. When phenol is sorbed from water by chitin containing about 8.7% moisture it may be bound by a hydrogen bond of the type OH.....O instead of one between the nitrogen of the acetylamino group and the phenolic hydrogen, because the heat of reaction, about +4.75 kcal.per mole is considered to be more consistent therewith. The sorption of phenol by the same conditioned sample of chitin from dry iso-octane has been studied; but the irregular shape of the isotherms obtained is difficult to interpret. It seems that the hydrogen bond formed under such circumstances should be between the phenolic hydroxyl group and the water present in the substrate. This view has been confirmed by

the absence of any sorption of phenol by fully dry chitin from dry iso-octane.

The sorption of resorcinol from aqueous solution was then investigated with a view to obtaining some additional evidence to confirm the conclusion arrived at for the sorption of phenol by chitin. A heat of reaction of the order of only +1.8 kcal. per mole has been obtained for this quantity, in the temperature range of 50°C.-60°C. This low value may show that the mechanism involved is one of competitive solvation of resorcinol by chitin in preference to the water present. (cf. the similar result obtained by Steinhardt et al[103] with the sorption of monochloroacetic acid by wool).

The combination of weak acids 2:4-dinitrophenol, and 2:4:6-trinitrophenol, has been studied, but some experimental difficulties described above have made the interpretation of results difficult, thought it appears that in these cases also, the adsorptions have low temperature coefficients, and thus resemble adsorption of other weak acids by wool.

Note regarding sign convention for heats of adsorption.

All the adsorption reactions studied are exothermic and the convention adopted is to give the ΔH values a positive sign.

TABLE 1.

Nature of Compound	Method of Purification
Dyes	
Benzeneazo-1-naphthylamine Benzeneazo-2-naphthylamine Benzeneazo-2-naphthol 4-Nitrobenzeneazo-2-naphthol 4-Nitrobenzeneazo-NN-ethyl-2-hydroxyethylaniline	Recrystallised about three to four times from benzene or petroleum ether.
Magenta	Recrystallised three times from water.
Amino and nitro compounds	
4-Aminoazobenzene 2-Aminoanthraquinone 2:4-Dinitroaniline 2-Naphthylamine 2:4-Dinitrophenol 1-Naphthylamine	Recrystallised from benzene about three times
Alkyl sulphates	
Oleyl sodium sulphate	Soxhlet extracted four times with ethanol and then dried at 100°C.
Sulphonic acids and their sodium salts	
Azobenzene-4-sulphonic acid Naphthalene-1-sulphonic acid Naphthalene-2-sulphonic acid Benzene sulphonic acid Benzene sodium sulphonate Naphthalene-1:5-disulphonic acid Anthracene-1-sulphonic acid	Recrystallised about four times from water, then washed with warm ethanol, and dried.

TABLE 1. (Contd.)

Nature of Compound	Method of Purification
Sulphonic acids and their sodium salts (contd.)	
Benzeneazo-2-naphthol-3:6-disulphonic acid Dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid	Passed successively through ion exchange resin columns containing anion and cation exchange resins respectively
Methoxybenzanthrone	Duranol Brilliant Yellow 6G (I.C.I.) was extracted three times in a Soxhlet apparatus with benzene and the benzene evaporated off. The residue was recrystallised twice from benzene.
The following compounds were obtained from the sources given and were not further purified.	
Acid Magenta Tetradecyl sodium sulphate Dodecyl toluene sodium sulphonate	I.C.I. Ltd.
Phenol Resorcinol (AR) Azobenzene	B.D.H. Ltd.
2-(4'-hydroxystyryl)quinoline methiodide 2-(4'-hydroxylstyryl)benztriazole ethiodide	Ilford Ltd.
Anthracene-2-carboxylic acid	Dr.E.Klar.

TABLE 2.

Time 24 Hours				Temperature 48°C.		
Compound	Solvent	Initial concn. (gm./l.)	Nature of bath	Initial Spekker Reading	Final Spekker Reading	Amount sorbed per k.gm. Film
		0.10	Blank control	0.080	0.080	-
2-naphthyl amine	Dry benzene	"	With oxide Film	0.080	0.080	-
4-aminoazo benzene	"	0.20	Blank control	0.760	0.760	-
		"	With oxide Film	0.760	0.760	-

TABLE 3.

Time 44 Hours				Temperature 40°C.		
Compound	Solvent	Initial concn. (gm./l.)	Nature of bath	Initial Spekker Reading	Final Spekker Reading	Amount sorbed per k.gm. Film
1-benzene azo-4-naphthyl-amine	Dry benzene	0.10	Blank control	0.35	0.35	-
		"	With oxide Film	0.35	0.35	-

TABLE 4

Time 92 Hours					Temperature 18°C.	
Compound	Solvent	Initial concn. (gm./l.)	Nature of bath	Initial Spekker Reading	Final Spekker Reading	Amount sorbed per k.gm. Film
1-benzene azo-2-naphthyl-amine	Dry Benzene	0.20	Blank control	1.062	1.062	-
			With oxide Film	1.062	1.062	-

TABLE 5

Benzeneazo-1-naphthylamine

Time 24 - 48 Hours			
Nature of bath	Temperature	Initial concn. (gm./l.)	Amount sorbed per k.gm.Film (millimoles)
Alone in dry benzene	20°C.	0.10	-
	40°C	"	-
With 25% aqueous dioxan	18°C	0.15	-

TABLE 6.

Benzeneazo-2-naphthylamine

Time 24 - 48 Hours

Nature of bath	Temperature	Initial concn. (gm./l.)	Amount sorbed per k.gm.Film (millimoles)
Alone in dry benzene	20°C.	0.20	-
With 0.20 gm./l.quinol in dry benzene	"	"	5.00
With 25% aqueous ethanol	40°C.	"	80.00

TABLE 7.

2-Naphthylamine

Time 24 - 48 Hours

Nature of bath	Temperature	Initial concn. (gm./l.)	Amount sorbed per k.gm.Film (millimoles)
Alone in dry dioxan	20°C.	0.10	-
With 0.20 gm./l. quinol in dry dioxan	"	"	-

TABLE 8.

3-Methoxybenzanthrone

Time 24 - 48 Hours			
Nature of bath	Temperature	Initial concn. (gm./l.)	Amount sorbed per k.gm.Film (millimoles)
Alone in dry benzene	40°C.	0.10	-
With 0.10 gm./l. phenol in dry benzene	"	"	-
With 0.10 gm./l. quinol in dry benzene	"	"	40.0

TABLE 9

1:2-Naphthaquinone

Time 24 - 48 Hours			
Nature of bath	Temperature	Initial concn. (gm./l.)	Amount sorbed per k.gm.Film (millimoles)
Alone in dry benzene	40°C.	0.10	-
With 0.10 gm./l. phenol in dry benzene	"	"	-
With 0.10 gm./l. quinol in dry benzene	"	"	40.00

TABLE 10.

Azobenzene

Time 24 - 48 Hours			
Nature of bath	Temperature	Initial concn. (gm./l.)	Amount sorbed per k.gm.Film (millimoles)
Alone in dry benzene	24°C.	0.20	-
"	48°C.	"	-
With 0.50 gm./l. quinol in dry benzene	24°C.	"	112.00
	48°C.	"	83.00
	55°C.	"	65.00
Alone in dry dioxan	40°C.	"	-
In 25% aqueous dioxan	"	"	8.00

TABLE 11.

Azobenzene in 25% aqueous ethanol

Time 24 Hours		Temperature 38°C.
Initial concentration (gm./l.)		Spekker reading
0,02	a)	0.025
	b)	0.125
	c)	0.072
	d)	0.038
0.05	a)	0.070
	b)	0.210
	c)	0.230
	d)	0.200
0.10	a)	0.168
	b)	0.230
	c)	0.280
	d)	0.380
0.15	a)	0.250
	b)	0.380
	c)	0.380
	d)	0.342
0.20	a)	0.310
	b)	0.415
	c)	0.465
	d)	0.440

a - Original blank solution
b - Blank control in bath
c - With oxide film
d - With oxide film

TABLE 12.

Azobenzene in 50% aqueous ethanol

Time 24 Hours		Temperature 38°C.
Initial concentration (gms./l.)	Spekker Reading	Amount sorbed per k.gm. Film (millimoles)
0.10	a) 0.110	-
	b) 0.115	-
	c) 0.170	-
0.20	a) 0.260	-
	b) 0.270	-
	c) 0.270	-
0.40	a) 0.450	-
	b) 0.420	40.0
	c) 0.410	52.0
0.80	a) 0.685	-
	b) 0.830	-
	c) 0.820	-

a - Original blank solution; b - With oxide film
c - With oxide film

TABLE 13.

Sorption of Phenol

Time - 48 Hours Temperature 40°C		60°C.	
Equilibrium bath concentration (moles/litre)	Amount sorbed per k.gm.Film (moles)	Equilibrium bath concentration (moles/litre)	Amount sorbed per k.gm.Film (moles)
0.0008316	0.0537	0.0009977	0.01576
0.001663	0.1108	0.001830	0.07112
0.004160	0.2787	0.004459	0.1976
0.008316	0.5537	0.008978	0.3955

TABLE 14.

Sorption of 2:4-dinitrophenol by anodised aluminium

Time - 24 Hours Temperature - 50°C		60°C.		
Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.Film (moles)	Equilibrium bath concentration (millimoles/l.)	Amount sorbed per kgm Film (moles)	Mean (kcal/ mole)
0.1700	0.028	0.2120	0.010	
0.2540	0.154	0.2680	0.110	
0.2950	0.310	0.3200	0.260	+4.00
0.3900	0.460	0.3700	0.364	
0.5000	0.536	0.4620	0.474	
0.6200	0.554	0.6400	0.514	

TABLE 15.

Sorption of benzeneazo-1-naphthol from benzene

Time Temperature	48 Hours 40°C	60°C	
Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.Film (moles)	Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.film (moles)
0.745	0.072	0.766	0.048
1.570	0.101	1.550	0.077
2.310	0.130	2.330	0.106
3.080	0.154	3.120	0.120
3.780	0.173	3.910	0.144
7.850	0.225	7.890	0.178

TABLE 16.

p-Nitrophenol from aqueous solution

Initial concentration (moles/l.)	Spekker reading 50°C.	Spekker reading 60°C.
0.002	a) 0.160 b) 0.175	a) 0.160 b) 0.176
0.005	a) 0.310 b) 0.350	a) 0.310 b) 0.350
0.008	a) 0.365 b) 0.540	a) 0.365 b) 0.600
0.010	a) 0.600 b) 0.650	a) 0.600 b) 0.510

a) - Blank control solution

b) - With oxide film

TABLE 17

I - 2:(4'-hydroxystyryl)-benzthiazole ethiodide

II - 2:(4'-hydroxystyryl)-quinoline methiodide

Concentration of sodium chloride solution = 0.10%

	Nature of bath	Spekker reading
I	Without sodium chloride	a) 0.440 b) 0.105
	With sodium chloride	a) 0.460 b) 0.125
II	Without sodium chloride	a) 0.680 b) 0.380
	With sodium chloride	a) 0.640 b) 0.490

a) - Blank control solution

b) - With oxide film.

TABLE 18.

Sorption of Oleyl Sodium Sulphate (Lissapol C)

Time: 48 Hours	Temperature: 40°C. and 50°C.
Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm. of Film (moles)
0.038	0.176
0.216	0.260
0.346	0.304
0.927	0.352

TABLE 19.

Sorption of Tetradecyl Sodium Sulphate

Time: 48 Hours	Temperature: 40°C. and 50°C.
Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm. of Film (moles)
0.065	0.088
0.130	0.172
0.150	0.224
0.260	0.248
0.510	0.304

TABLE 20.

Compound	Colour developed with Solochrome Cyanine RS
Naphthalene-2-sulphonic acid	a) Orange b) Bluish red c) Bluish red
Oleyl Sodium Sulphate	a) Yellow b) Yellow c) Brownish-yellow

a) - Blank control solution
b) and c) - With oxide film

TABLE 21.

Time	48 Hours	24 Hours	
Temperature	37°C.	50°C.	
Equilibrium bath concentration (moles x 10^{-5})/l.	Amount sorbed per k.gm.Film (moles x 10^{-2})	Equilibrium bath concentration (moles x 10^{-5})/l.	Amount sorbed per k.gm.Film (moles x 10^{-2})
3.00	0.70	3.00	0.70
6.00	1.40	6.00	1.40
8.70	2.74	8.70	2.74
10.60	4.00	10.60	4.00
12.80	5.32	12.80	5.32

TABLE 22.

Influence of alkyl chains upon sorption

I - Tetradecyl sodium sulphate

II - oleyl sodium sulphate

Time: 48 Hours		Temperature: 40°C. and 50°C.	
I		II	
$C/C_S \times 10^{-2}$	C_F	$C/C_S \times 10^{-2}$	C_F
0.045	0.088	0.060	0.176
0.090	0.172	0.120	0.260
0.120	0.224	0.150	0.304
0.225	0.304	0.300	0.352
0.300	0.316		

C - Equilibrium bath concentration in millimoles/l.

C_S - Concentration of saturated aqueous solution in millimoles/l.

C_F - Amount sorbed in moles/k.gm. film.

TABLE 23.

Azobenzene-4-sulphonic acid

Time: 24 Hours			
Temperature	40°C.	55°C.	
Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.Film (moles)	Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.Film (moles)
0.384	0.284	0.768	0.079
0.768	0.459	1.524	0.167
1.524	0.550	1.908	0.196
1.908	0.550		

TABLE 24.

Benzeneazo-2-naphthol-3:6-disulphonic acid (Na salt)

Time	65 Hours		24 Hours
Temperature	30°C.		57°C.
Equilibrium bath concentration (millimoles/l)	Amount sorbed per k.gm.Film (moles)	Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.Film (moles)
0.2667	0.113	0.2667	0.104
0.5333	0.165	0.5333	0.146
0.8067	0.198	0.8067	0.167
1.0740	0.215	1.0740	0.181
1.3400	0.213	1.3400	0.178

TABLE 25.

Dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid (Na salt)

Time	96 Hours		24 Hours
Temperature	50°C.		60°C.
Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.Film (moles)	Equilibrium bath concentration (millimoles/l.)	Amount sorbed per k.gm.film (moles)
0.40	0.360	0.590	0.065
0.90	0.560	1.235	0.085
1.47	0.673	1.890	0.113
2.10	0.847	2.570	0.119

TABLE 26

I - Benzeneazo-2-naphthol-3:6-disulphonic acid (Na salt)

II - Dodecylbenzeneazo-2-naphthol-3:6-disulphonic acid (Na salt)

Time: 24 Hours			
Temperature: 57°C.		60°C.	
I		II	
$(C/C_S) \times 10^{-2}$	C_F	$(C/C_S) \times 10^{-2}$	C_F
0.77	0.104	3.63	0.065
2.92	0.146	7.60	0.085
5.59	0.167	11.63	0.113
8.36	0.181	15.81	0.119
11.49	0.178		

C - Equilibrium bath concentration in millimoles/l.

C_s - Concentration of saturated solution in millimoles/l.

C_F - Amount sorbed per k.gm. film in moles.

TABLE 27

I = Orange II; II = Orange I;

III = Benzeneazo-2-naphthol-3:6-disulphonic acid

IV = Benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid.

V = Chlorazol Sky Blue FF.

Dye	Temp. °C.	Saturation value from Langmuir Isotherm	Molecular Area in Sq.Å in monolayer			
			Calculated value			Observed value
			(a)	(b)	(c)	
I	57	12.40	30	43	120	30§§
	30	14.00				30§§
II	57	14.15	30	43	120	26.0
	30	15.90				26.5
III	57	5.43	30	50	136	68.0
	30	6.25				67.0
IV	57	2.16	30	46	140	172
	30	2.78				151
V	57	1.28	45	90	284	290
	30	1.53				275

a) - Standing vertically on one sulphonic group

b) - Lying horizontally along an edge bounded by two sulphonic groups.

c) - Lying flat with all the sulphonic groups touching the surface.

§§ - Control value.

TABLE 28

I = Orange I; II = Orange II;
III = Benzeneazo-2-naphthol-3:6-disulphonic acid
IV = Benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid
V = Chloraxol Sky Blue FF

Dye	Temperature Range °C.	ΔH° (k.cal./mole)	ΔG° (kcal./mole)	ΔS° cals/mol/°
I	27	-4.58	-4.70	+0.37
II	27	-4.07	-5.15	+3.22
III	27	-9.85	-5.50	-13.20
IV	27	-13.16	-5.51	-24.60
V	27	-17.60	-5.70	-35.10

TABLE 29

Dodecyl toluene sodium sulphonate in aqueous solution

Time	48 Hours	24 Hours	
Temperature	37°C.	50°C.	
Equilibrium bath concentration (millimoles/l.)	Amount sorbed (moles)	Equilibrium bath concentration (millimoles/l.)	Amount sorbed (moles)
0.061	0.028	0.061	0.028
0.101	0.057	0.101	0.057
0.167	0.127	0.177	0.122
0.389	0.106	0.439	0.082

TABLE 30.

Samples treated with hydrochloric acid at 60°C. for 24 hours.

Nature of Sample	Analysis		
	C	H	N
In equilibrium with acid at pH 2.50	45.50%	6.60%	6.80%
In equilibrium with acid at pH 2.00	45.60%	6.60%	4.90%
In equilibrium with acid of 2N (Initial Strength)	41.00%	6.30%	3.70%

TABLE 31.

Sorption of hydrochloric acid by chitin

I - Hydrochloric acid alone
II - At 0.1 Molar constant chloride concentration
III - At 1.0 Molar constant chloride concentration

Time: 24 Hours Temperature: 60°C.

Final pH of bath			Acid sorbed in equivalents/kgm. of chitin		
I	II	III	I	II	III
5.60	5.50	5.80	0.3000	0.9694	1.0230
5.10	5.18	5.20	0.3000	1.2490	1.6820
4.50	4.68	4.60	0.4500	1.7360	2.4210
4.17	4.30	4.10	0.6410	2.5100	3.3290
4.13	3.60	3.50	0.6896	3.4100	3.9510
4.06	3.10	2.90	0.7905	3.9510	4.5560
3.92	2.56	2.57	1.0300	5.3000	6.0500
3.87	2.25	2.26	1.1360	6.4500	9.0000
3.76	2.10	2.05	1.3700	10.2000	18.0000
3.56	1.87		1.9040	18.3000	
3.18			3.0000		
2.79			4.0820		
2.60			4.3500		
2.40			4.8770		
2.30			5.2000		
2.04			7.2800		
1.80			15.0000		
1.70			19.2000		

TABLE 32.

Sorption of sulphuric acid alone by chitin at 60°C. - 24 Hours.

Final pH of bath	Acid sorbed in equivalents/k.gm. chitin
5.32	0.3000
4.93	0.3000
4.35	0.6000
3.82	1.1000
3.43	2.5000
2.96	3.5600
2.52	4.6500
2.20	6.0000
1.90	12.0000
1.77	17.7500

TABLE 33.

"Gilbert-Rideal" plot for sorption of hydrochloric acid alone and at 0.10 Molar and 1.0 Molar chloride concentration.

HCl alone		At 0.1 Molar chloride concentration		At 1.0 Molar chloride concentration	
Final pH	$\log \frac{\theta_H}{S_H - \theta_H}$	Final pH	$\log \frac{\theta_H}{S_H - \theta_H}$	Final pH	$\log \frac{\theta_H}{S_H - \theta_H}$
4.17	$\bar{1}.1480$	5.50	$\bar{1}.3600$	5.80	$\bar{1}.3900$
4.13	$\bar{1}.1844$	5.18	$\bar{1}.5000$	5.20	$\bar{1}.6800$
4.06	$\bar{1}.2535$	4.68	$\bar{1}.7000$	4.60	$\bar{1}.9400$
3.92	$\bar{1}.3927$	4.30	$\bar{1}.9700$	4.10	$\bar{0}.2500$
3.87	$\bar{1}.4465$	3.60	0.2800	3.50	0.5000
3.76	$\bar{1}.5535$	3.10	0.5000	2.90	0.8500
3.56	$\bar{1}.7617$	2.60	0.7600	2.26	1.1000
2.79	0.5626				
2.40	1.1789				

θ_H - Equivalents of acid sorbed per k.gm. of chitin

S_H - Saturation value of acid for chitin viz. 5.20 equivalents per k.gm. of chitin

TABLE 34

Affinity values calculated on "Gilbert-Rideal" basis for sorption of hydrochloric acid alone and at 0.10 Molar and 1.0 Molar chloride concentration.

HCl alone		At 0.10 Molar chloride concentration		At 1.0 Molar chloride concentration	
Final pH	$-\Delta\mu^\circ$ (Kg.cal.)	Final pH	$-\Delta\mu^\circ$ (Kg.cal.)	Final pH	$-\Delta\mu^\circ$ (Kg.cal.)
4.50	13.8	5.50	7.2	5.80	7.1
4.17	10.2	5.18	7.9	5.20	7.0
4.06	10.2	4.68	7.8	4.60	6.9
3.87	10.2	4.30	8.1	4.10	7.2
3.56	10.2	3.60	7.9	3.50	6.9
2.79	10.3	3.10	7.8		
	Mean = 10.8		Mean = 7.8		Mean = 7.0

TABLE 35.

"Donnan" plot for sorption of hydrochloric acid alone and at 0.10 Molar and 1.0 Molar chloride concentration.

HCl alone		At 0.10 Molar chloride concentration		At 1.0 Molar chloride concentration	
Final pH	$\log \frac{\theta_H^2}{S_H - \theta_H}$	Final pH	$\log \frac{\theta_H^2}{S_H - \theta_H}$	Final pH	$\log \frac{\theta_H^2}{S_H - \theta_H}$
4.17	$\bar{2}.9549$	5.50	$\bar{1}.3470$	5.80	$\bar{1}.3988$
4.13	$\bar{1}.0230$	5.18	$\bar{1}.5963$	5.20	$\bar{1}.9053$
4.06	$\bar{1}.1314$	4.68	$\bar{1}.9394$	4.60	0.3241
3.92	$\bar{1}.4055$	4.30	0.3696	4.10	0.7624
3.87	$\bar{1}.5019$	3.60	0.8127	3.50	1.0969
3.76	$\bar{1}.6902$	3.10	1.0969	2.90	1.5083
3.56	0.0414	2.60	1.4063	2.26	1.7822
2.79	1.1735				
2.40	1.8670				

TABLE 36

Affinity values calculated on "Donnan" basis for sorption of hydrochloric acid alone and at 0.10 Molar and 1.0 Molar chloride concentration.

HCl alone		At 0.10 Molar chloride concentration		At 1.0 Molar chloride concentration	
Final pH	$-\Delta\mu_H^o$ (Kg.cal.)	Final pH	$-\Delta\mu_H^o$ (Kg.cal.)	Final pH	$-\Delta\mu_H^o$ (Kg.cal.)
4.17	11.126	5.50	7.522	5.80	6.365
4.13	11.039	5.18	7.090	5.20	4.927
4.06	10.993	4.68	6.852	4.60	5.950
3.92	10.988	4.30	6.853	4.10	5.857
3.87	10.975	3.60	6.539	3.50	5.454
3.76	10.931	3.10	6.205	2.90	5.167
3.56	10.853	2.60	5.922	2.26	4.612
2.79	10.241				
2.40	10.109				
	Mean = 10.900		Mean = 6.712		Mean = 5.476

TABLE 37.

Rate of dyeing of chitin by benzene-4-sulphonic acid azo-2-naphthol (Na salt)

Temperature: 60°C.	pH 4.70
Time	Amount sorbed per gm. of chitin (gm.moles x 10^{-5})
15 minutes	5.00
30 minutes	9.500
45 minutes	10.00
1 hour	10.00
2 hours	10.25
4 hours 15 minutes	10.75
6 hours	10.25
8 hours	10.25
10 hours	10.00
12 hours	10.90
16 hours	10.25
24 hours	10.40

TABLE 38.

Rate of dyeing of chitin by naphthalene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid (Na salt)

Temperature: 60°C.	pH 1.40
Time	Amount sorbed per gm. of chitin (gm.moles x 10^{-5})
15 minutes	7.25
30 minutes	8.50
45 minutes	8.75
1 hour 15 minutes	9.00
2 hours	9.00
4 hours	8.50
6 hours	8.75
8 hours	9.00
12 hours	9.50
16 hours	9.00
24 hours	9.00

TABLE 39.

Rate of dyeing of chitin by naphthaleneazo-2-naphthol-3:6-disulphonic acid (Na salt)

Temperature: 60°C.	pH 2.60
Time	Amount sorbed per gm. of chitin (gm.moles x 10^{-5})
15 minutes	12.50
45 minutes	13.20
75 minutes	13.30
2 hours	13.40
4 hours	13.30
6 hours	14.00
8 hours	14.00
10 hours	13.00
12 hours	13.20
16 hours	13.00
24 hours	13.00

TABLE 40.

Benzene-4-sulphonic acid azo-2-naphthol (Na salt)

Time	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.40	8.10	1.70	8.40
2.40	10.10	1.90	9.40
2.90	10.00	2.50	10.50
4.00	10.10	3.65	10.20
4.70	10.40	4.45	10.58
5.30	8.40	5.20	9.20
5.70	6.40	5.50	7.40
6.60	5.20	6.20	6.20
7.20	4.50	7.00	5.00
8.00	3.55	7.90	3.80
9.00	2.50	8.80	2.90
11.00	0.00	9.80	1.20

TABLE 41.

Naphthalene-4-sulphonic acid azo-2-naphthol (Na salt)

Time	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.65	14.60	2.05	15.00
2.15	15.20	2.80	15.50
2.88	15.30	3.60	16.10
3.60	15.75	4.20	15.80
4.20	15.80	4.88	12.60
4.80	13.20	5.70	10.50
5.40	10.70	6.22	8.70
5.90	10.10	6.60	6.45
6.35	7.80	7.50	4.70
6.82	5.25	10.00	0.00
8.10	4.10		
10.00	0.00		

TABLE 42.

Benzeneazo-2-naphthol-3:6-disulphonic acid (Na salt)

Time	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.65	11.25	1.80	12.00
1.90	15.00	1.70	14.50
2.60	17.20	3.00	18.50
3.65	20.00	3.60	19.20
4.20	15.00	4.30	17.00
4.50	11.50	4.40	13.50
5.90	8.60	5.20	10.00
7.10	5.40	6.40	6.50
8.40	4.60	7.80	5.00
9.60	2.25	9.40	3.00
10.60	0.00	10.20	00.00

TABLE 43.

Benzene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid (Na salt)

Time:	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.75	10.50	1.92	11.80
2.43	13.30	2.55	14.60
2.80	15.50	3.25	17.50
3.28	18.25	3.60	15.50
3.98	13.40	4.10	11.50
4.30	10.00	5.10	7.50
4.80	8.10	6.10	5.50
5.38	6.70	6.90	2.00
6.40	4.70	7.80	0.00
7.15	1.40		
8.30	0.00		

TABLE 44.

Naphthalene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid (Na salt)

Time:	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.55	33.00	1.90	35.00
2.60	37.50	2.60	37.00
3.00	35.25	3.10	34.25
3.60	31.50	4.10	27.50
4.35	25.00	4.70	22.50
4.85	19.70	5.25	15.00
5.10	16.25	5.65	6.25
5.30	12.50	6.00	0.00
5.40	9.50		
5.90	2.50		
6.15	0.00		

TABLE 45.

Naphthaleneazo-2-naphthol-3:6-disulphonic acid (Na salt)

Time:	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.50	21.90	1.50	23.00
2.65	25.50	2.40	26.00
3.65	21.80	3.00	24.40
3.90	20.30	3.70	23.30
4.70	15.90	4.20	19.00
5.30	12.00	4.45	16.30
5.90	7.75	5.30	13.00
6.70	6.30	5.80	9.10
7.20	6.70	6.40	7.50
8.60	3.25	7.40	7.00
10.00	0.00	8.10	4.00
		9.60	0.00

TABLE 46.

Naphthalene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid (Na salt)

Time:	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.40	18.20	1.40	18.50
2.20	17.75	2.20	17.75
2.60	17.40	3.00	16.50
3.30	16.25	3.70	14.50
3.84	13.00	4.00	11.50
4.10	10.50	4.50	7.50
4.30	8.70	5.30	3.70
4.74	6.10	5.98	1.50
5.66	2.80	7.40	0.00
6.30	0.90		
7.20	0.00		

TABLE 47.

Benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid (Na salt)

Time: 24 Hours			
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.75	12.30	1.72	14.00
1.95	15.50	2.25	20.00
2.15	17.80	2.60	24.50
2.40	21.00	2.95	20.00
2.68	23.70	3.60	16.00
3.00	17.50	4.00	13.50
4.00	14.40	4.80	11.00
4.60	11.50	5.50	8.80
5.10	8.80	6.50	8.00
6.00	8.75	7.40	5.00
6.62	8.80	8.63	1.50
7.60	3.70		
8.10	2.30		
9.18	0.00		

TABLE 48.

Benzene-2:5-disulphonic acid azo-2-naphthol-6-sulphonic acid (Na salt)

Time: 24 Hours			
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.80	16.75	2.00	17.50
2.30	17.40	2.80	20.00
2.70	18.70	3.40	16.50
3.00	19.70	3.60	12.10
3.36	15.00	3.72	12.00
3.76	9.00	4.20	7.90
4.85	6.50	5.30	5.50
5.66	3.80	5.90	2.90
6.34	2.50	7.10	2.75
6.80	2.40	7.80	0.50
7.70	1.35		
8.55	0.00		

TABLE 49.

Benzene-2:5-disulphonic acid azo-2-naphthol-3:6-disulphonic acid (Na salt)

Time:	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
1.12	7.90	1.50	14.50
1.33	12.50	1.92	22.00
1.74	19.00	2.45	25.00
2.45	25.80	2.90	20.60
3.00	18.40	3.40	15.70
3.65	12.90	4.20	10.20
4.65	8.40	5.08	6.50
5.25	4.80	5.85	4.00
6.30	2.40	7.00	2.00
8.00	2.50	8.50	1.50
8.85	2.20	10.00	0.00
10.35	0.00		

TABLE 50.

Naphthalene-3:6-disulphonic acid azo-2-naphthol-3:6-disulphonic acid (Na salt)

Time:	24 Hours		
Temperature	60°C.		50°C.
Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})	Final pH	Amount sorbed per gm. of chitin (gm.eq. x 10^{-5})
0.65	21.80	0.80	22.40
1.35	23.40	1.50	24.00
2.00	23.00	2.40	22.80
2.60	21.90	3.10	20.80
3.25	20.20	3.78	18.00
4.00	16.60	4.50	14.00
4.88	12.80	5.43	10.80
5.75	9.30	6.48	8.80
7.00	8.30	7.20	7.20
8.60	6.30	9.10	4.00
9.90	0.00		

TABLE 51.

Saturation values of acid dyes for chitin, obtained by Langmuir plot

	Dye (Na salt)	Saturation value per K.gm. chitin (gm.moles dye ion)
1)	Naphthaleneazo-2-naphthol-3:6-disulphonic acid	0.2343
2)	Naphthalene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid	0.1703
3)	Benzeneazo-2-naphthol-3:6-disulphonic acid	0.1615
4)	Benzene-4-sulphonic acid azo-2-naphthol	0.1544
5)	Naphthalene-4-sulphonic acid azo-2-naphthol	0.1515
6)	Naphthalene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid	0.1149
7)	Benzene-2:5-disulphonic acid azo-2-naphthol-6-sulphonic acid	0.0960
8)	Naphthalene-3:6-disulphonic acid azo-2-naphthol-3:6-disulphonic acid	0.0836
9)	Benzene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid	0.0826
10)	Benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid	0.0737
11)	Benzene-2:5-disulphonic acid azo-2-naphthol-3:6-disulphonic acid	0.0499

TABBE 52

Dye (used as Na salt)	Molecular weight of dye ion	Number of sulphonic groups	Saturation value (mol./kg.)	pH of maximum sorption	pK value
1. Benzene-4-sulphonic acid azo-2-naphthol	327	1	0.154	4.70	6.60
2. Naphthalene-4-sulphonic acid azo-2-naphthol	377	1	0.152	4.20	6.25
3. Benzene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid	406	2	0.083	3.27	4.50
4. Benzeneazo-2-naphthol-3:6-disulphonic acid	406	2	0.162	3.60	5.24
5. Naphthaleneazo-2-naphthol-3:6-disulphonic acid	456	2	0.234	2.56	5.40
6. Naphthalene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid	456	2	0.170	1.40	4.24
7. Naphthalene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid	535	3	0.115	2.60	4.94
8. Benzene-2:5-disulphonic acid azo-2-naphthol-6-sulphonic acid	485	3	0.096	3.00	3.92
9. Benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid	485	3	0.074	2.68	4.84
10 Benzene-2:5-disulphonic acid azo-2-naphthol-3:6-disulphonic acid	564	4	0.050	2.46	3.70
11 Naphthalene-3:6-disulphonic acid azo-2-naphthol-3:6-disulphonic acid	614	4	0.084	1.29	5.40

TABLE 53.

Relationship between affinity and sulphonic group content of dye

Number of sulphonic groups	pK (Average)
1	6.43
2	4.85
3	4.57
4	4.55

TABLE 54

Relationship between number of unsulphonated rings present in the dye and its saturation value on chitin at 60°C.

Dye number	Number of unsulphonated ring	Saturation value (mol./kg.)
4	1	0.162
5	2	0.234
3	nil	0.083
6	1	0.170
9	nil	0.074
7	1	0.115

TABLE 55.

Total area covered by each dye at saturation at 60°C. on the assumptions given.

Dye	Area per dye molecule ($Å^2$)	Saturation (mol./kg.)	Total surface area covered ($cm.^2$ per g.)
1	45	0.154	4.2×10^5
2	45	0.152	4.3×10^5
3	85	0.083	4.3×10^5
4	70	0.162	7.0×10^5
5	70	0.234	10.0×10^5
6	90	0.170	9.3×10^5
7	224	0.115	15.6×10^5
8	176	0.096	10.0×10^5
9	216	0.074	9.7×10^5
10	208	0.050	6.3×10^5
11	247	0.084	12.5×10^5

TABLE 56.

Sorption of naphthalene-4-sulphonic acid azo-2-naphthol in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C. pH 4.20	
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	1.1476	
0.3010	1.2691	
0.6021	1.1147	-0.063
0.7782	1.0960	
0.9031	1.2324	
1.0000	1.0103	

TABLE 57.

Sorption of benzene-4-sulphonic acid azo-2-naphthol in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C. pH 4.70	
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	$\bar{1}$.9298	
0.3010	$\bar{1}$.8223	
0.7782	$\bar{1}$.8591	-0.117
0.9031	$\bar{1}$.8871	
1.0000	$\bar{1}$.8275	

C_F - Dye sorbed per gm. of chitin in gm. moles

C_S - Equilibrium dyebath concentration in gm. moles/l.

TABLE 58.

Sorption of naphthalene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C.	pH 1.40
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	0.2818	
0.3010	0.0966	
0.6021	$\bar{1}$.9916	
0.7782	0.0569	
0.9031	$\bar{1}$.9364	-0.614
1.0000	$\bar{1}$.7911	

TABLE 59.

Sorption of naphthalene azo-2-naphthol-3:6-disulphonic acid in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C.	pH 2.56
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	0.5643	
0.3010	0.3886	
0.6021	0.2181	
0.7782	0.1900	-0.574
0.9031	0.1500	
1.0000	0.0206	

C_F - Dye sorbed per gm. of chitin in gm. moles

C_S - Equilibrium dyebath concentration in gm.moles/l.

TABLE 60.

Sorption of benzeneazo-2-naphthol-3:6-disulphonic acid in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C.	pH 3.60
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	0.1988	
0.3010	0.0524	
0.6021	$\bar{1}$.9236	-0.474
0.9031	$\bar{1}$.8755	
1.0000	$\bar{1}$.8896	

TABLE 61.

Sorption of benzene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C.	pH 3.27
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	$\bar{1}$.8353	
0.3010	$\bar{1}$.5809	
0.6021	$\bar{1}$.2731	-0.979
0.7782	$\bar{1}$.2348	
0.9031	$\bar{2}$.8840	
1.0000	$\bar{2}$.6901	

C_F - Dye sorbed per gm. of chitin in gm.moles

C_S - Equilibrium dyebath concentration in gm.moles/l.

TABLE 62.

Sorption of benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C.	pH 2.68
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	0.0110	
0.3010	0.0064	
0.6021	$\bar{1}$.8450	-0.647
0.9031	$\bar{1}$.7670	
1.0000	$\bar{1}$.5676	

TABLE 63.

Sorption of benzene-2:5-disulphonic acid azo-2-naphthol-6-sulphonic acid in the presence of sodium sulphate.

Time: 24 Hours	Temperature: 60°C.	pH 3.00
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	$\bar{1}$.7027	
0.3010	$\bar{1}$.5339	
0.7782	$\bar{1}$.4651	-0.655
0.9031	$\bar{1}$.1138	
1.0000	$\bar{1}$.0425	

C_F - Dye sorbed per gm. of chitin in gm.moles

C_S - Equilibrium dyebath concentration in gm.moles/l.

TABLE 64.

Sorption of naphthalene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C.	pH 2.60
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	$\bar{1}$.6716	
0.3010	$\bar{1}$.5632	
0.6021	$\bar{1}$.4534	-0.556
0.7782	$\bar{1}$.2615	
0.9031	$\bar{1}$.0149	
1.0000	$\bar{1}$.1282	

TABLE 65.

Sorption of naphthalene-3:6-disulphonic acid azo-2-naphthol-3:6-disulphonic acid in the presence of sodium sulphate

Time: 24 Hours	Temperature: 60°C.	pH 1.29
log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	$\bar{1}$.9665	
0.3010	$\bar{1}$.9665	
0.6021	$\bar{1}$.9153	-0.250
0.7782	$\bar{1}$.8489	
0.9031	$\bar{1}$.8768	
1.0000	$\bar{1}$.8211	

C_F - Dye sorbed per gm. of chitin in gm.moles

C_S - Equilibrium dyebath concentration in gm.moles/l.

TABLE 66

Sorption of benzene-2:5-disulphonic acid azo-2-naphthol-3:6-disulphonic acid in the presence of sodium sulphate

Time: 24 Hours Temperature: 60°C. pH 2.46

log "SO_4"	log $\frac{C_F}{C_S}$	Value of slope
0.0000	$\bar{1}$.8623	
0.3010	$\bar{1}$.9645	
0.6021	$\bar{1}$.6438	
0.7782	$\bar{1}$.6775	-0.833
0.9031	$\bar{1}$.4093	
1.0000	$\bar{1}$.4589	

C_F - Dye sorbed per gm. of chitin in gm.moles

C_S - Equilibrium dyebath concentration in gm.moles/l.

TABLE 67.

Sorption of Phenol from aqueous solution

Time: 24 Hours

Temperature	50°C		60°C		
C_E	C_F	C_E	C_F	$-\Delta H^o$ (kcals/mol.)
2.10	1.28	2.08	0.38	
2.20	1.70	2.26	0.40	
2.88	3.86	3.05	2.08	
3.60	4.48	3.70	3.26	+4.80
4.92	6.00	5.68	5.60	
7.40	7.87	7.04	6.50	
9.60	8.50	9.50	7.60	

C_E Equilibrium bath concentration in (moles x 10^{-3})/litre

C_F Amount sorbed per gm. of chitin in (moles x 10^{-4})

TABLE 68.

Sorption of Phenol from dry iso-octane

Time: 24 Hours			
Temperature 50°C.		60°C.	
C_E	C_F	C_E	C_F
0.80	0.150	0.37	0.333
1.80	0.378	1.22	0.721
2.87	1.757	2.87	1.064
3.38	2.300	3.29	1.407
4.36	3.032	4.20	2.110
		5.04	2.109

TABLE 69.

Sorption of Resorcinol from aqueous solution

Time: 36 Hours		24 Hours		
Temperature 50°C.		60°C.		
C_E	C_F	C_E	C_F	$-\Delta H^o$ (kcals/mol.)
0.1254	0.0321	0.1292	0.0301	
0.1370	0.0408	0.1177	0.0307	
0.3408	0.0957	0.3408	0.0774	
0.6931	0.1820	0.3453	0.0837	+1.75
0.7008	0.2036	1.1530	0.2739	
0.8684	0.2409	1.1770	0.2958	
1.4000	0.3880	1.5030	0.3913	

C_E - Equilibrium bath concentration in millimoles/l.

C_F - Amount sorbed per gm. of chitin in millimoles.

TABLE 70.

Sorption of 2:4-Dinitrophenol from aqueous solution

Time:	48 Hours		24 Hours	
Temperature	50°C.		60°C.	
	C_E	C_F	C_E	C_F
	0.1848	0.0999	0.1739	0.0988
	0.4338	0.1294	0.4130	0.1358
	1.0060	0.1194	0.9674	0.1533
	1.5380	0.1620	1.4890	0.1811

C_E - Equilibrium bath concentration in millimoles/l.
C_F - Amount sorbed per gm. of chitin in millimoles.

TABLE 71.

Sorption of 2:4-Dinitrophenol (Free acid)

Time:	48 Hours		24 Hours		
Temperature	50°C.		60°C.		
Initial pH	Final pH	Acid bound per gm. of chitin (Milliequivalents)	Initial pH	Final pH	Acid bound per gm. of chitin (Milliequivalents)
4.05	5.00	0.0909	4.05	5.00	0.0799
4.05	4.96	0.0849	3.86	4.84	0.1287
3.86	4.67	0.1493	3.70	4.55	0.1842
3.70	4.56	0.2291	3.59	4.33	0.2695
3.70	4.44	0.1793			
3.59	4.40	0.2441			

TABLE 72.

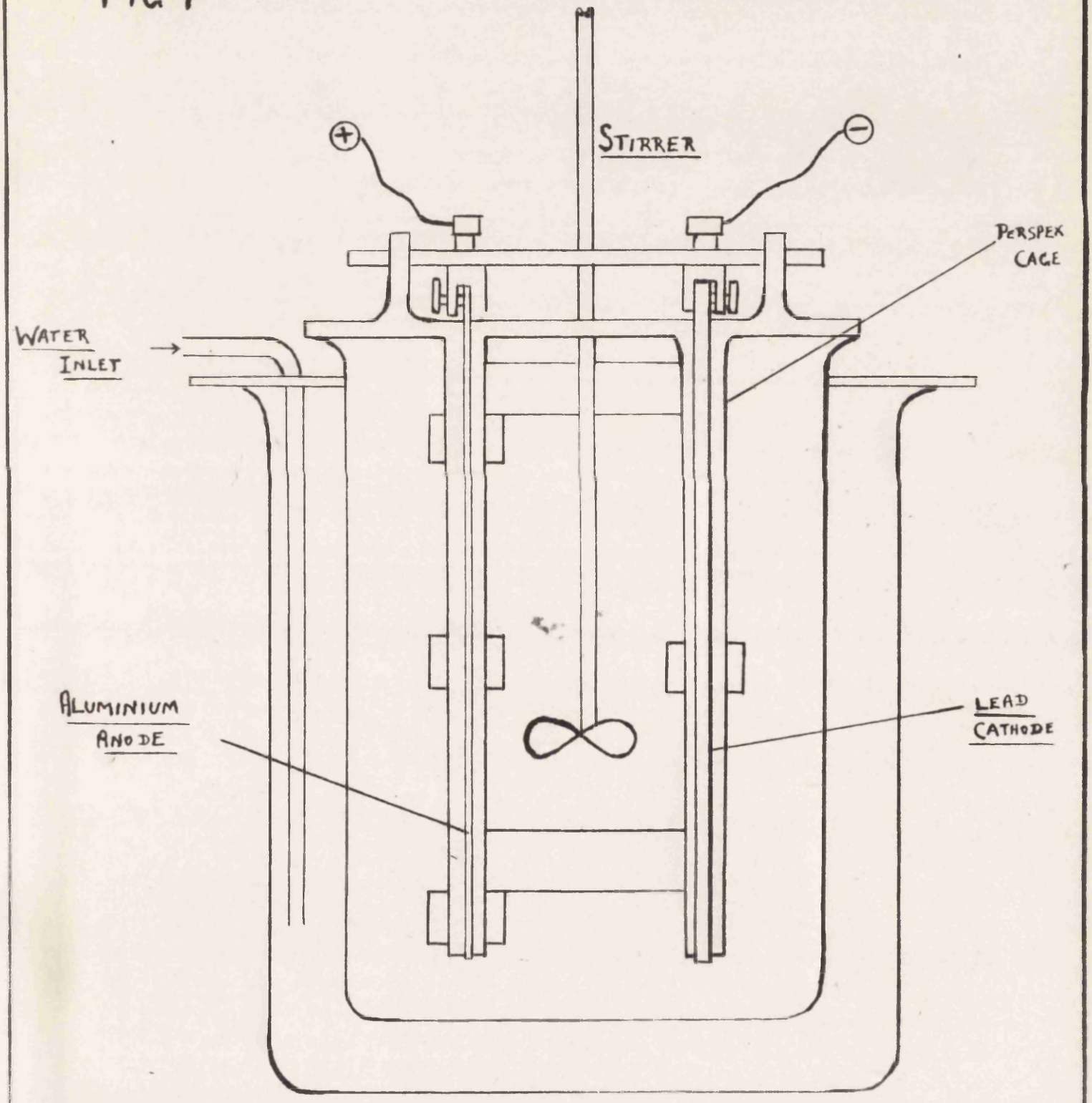
Sorption of 2:4:6-Trinitrophenol (Free acid)

Time:	48 Hours			24 Hours	
Temperature	50°C.			60°C.	
Initial pH	Final pH	Acid bound per gm. of chitin (Milliequivalents)	Initial pH	Final pH	Acid bound per gm. of chitin (Milliequivalents)
3.90	4.76	0.1409	3.90	4.66	0.1424
3.45	3.99	0.3608	3.45	4.00	0.3489
3.18	3.61	0.6486	3.18	3.80	0.6974
3.10	3.50	0.8387	3.10	3.94	0.9149
2.78	3.66	0.9228	2.78	3.62	0.9059
2.84	3.67	0.9228	2.84	3.64	0.8002

FIGS. 3, 4, 5, 6, 13, are given in the body of this thesis.

++++++++++++++++++++++++++

Fig 1.



ANODISATION CELL

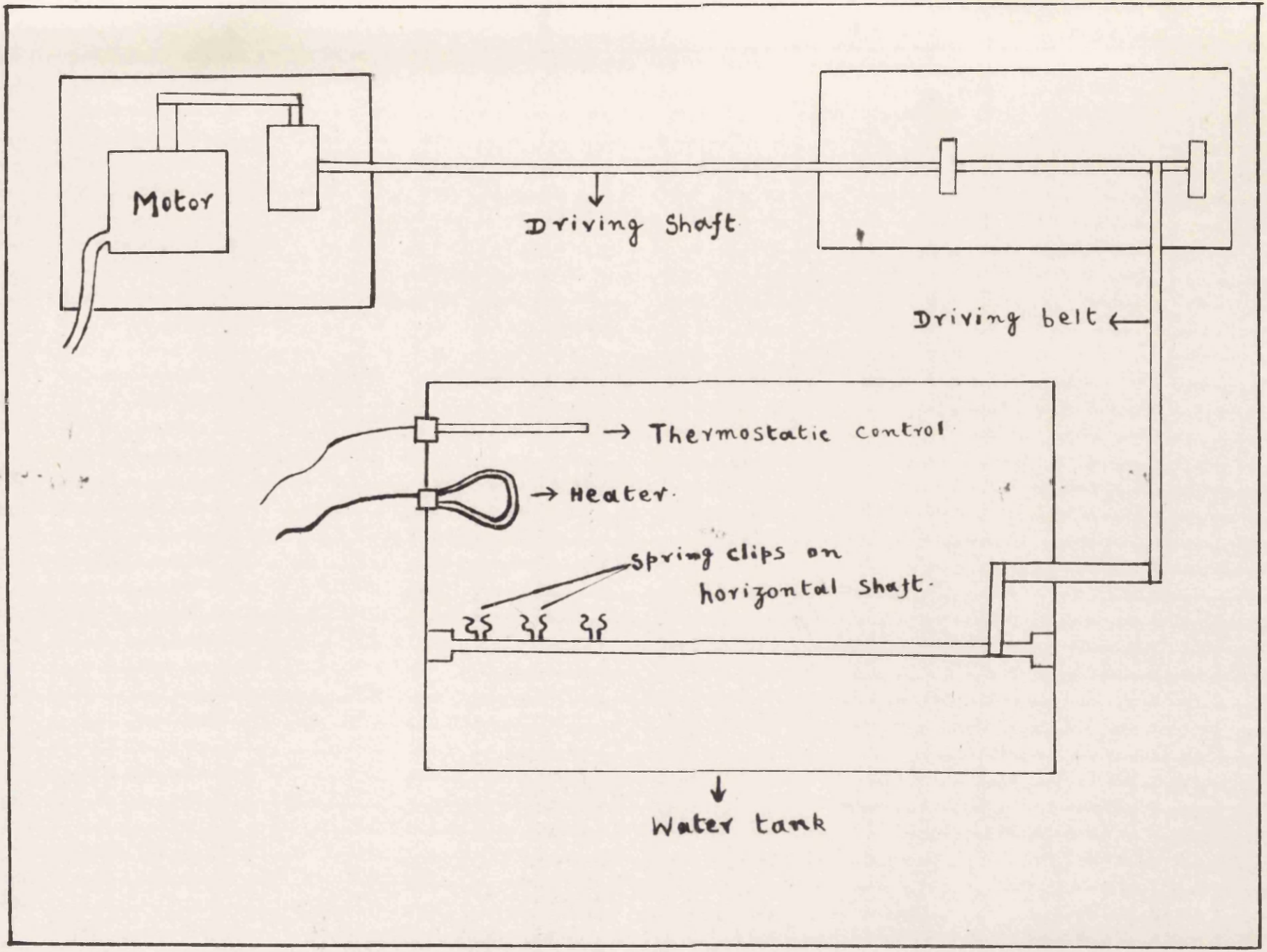

Motor
Driving Shaft
Driving belt
Thermostatic control
Heater
Spring clips on horizontal shaft
Water tank

FIG. 2.

Light absorption curve for azobenzene in 50% Aqueous Ethanol

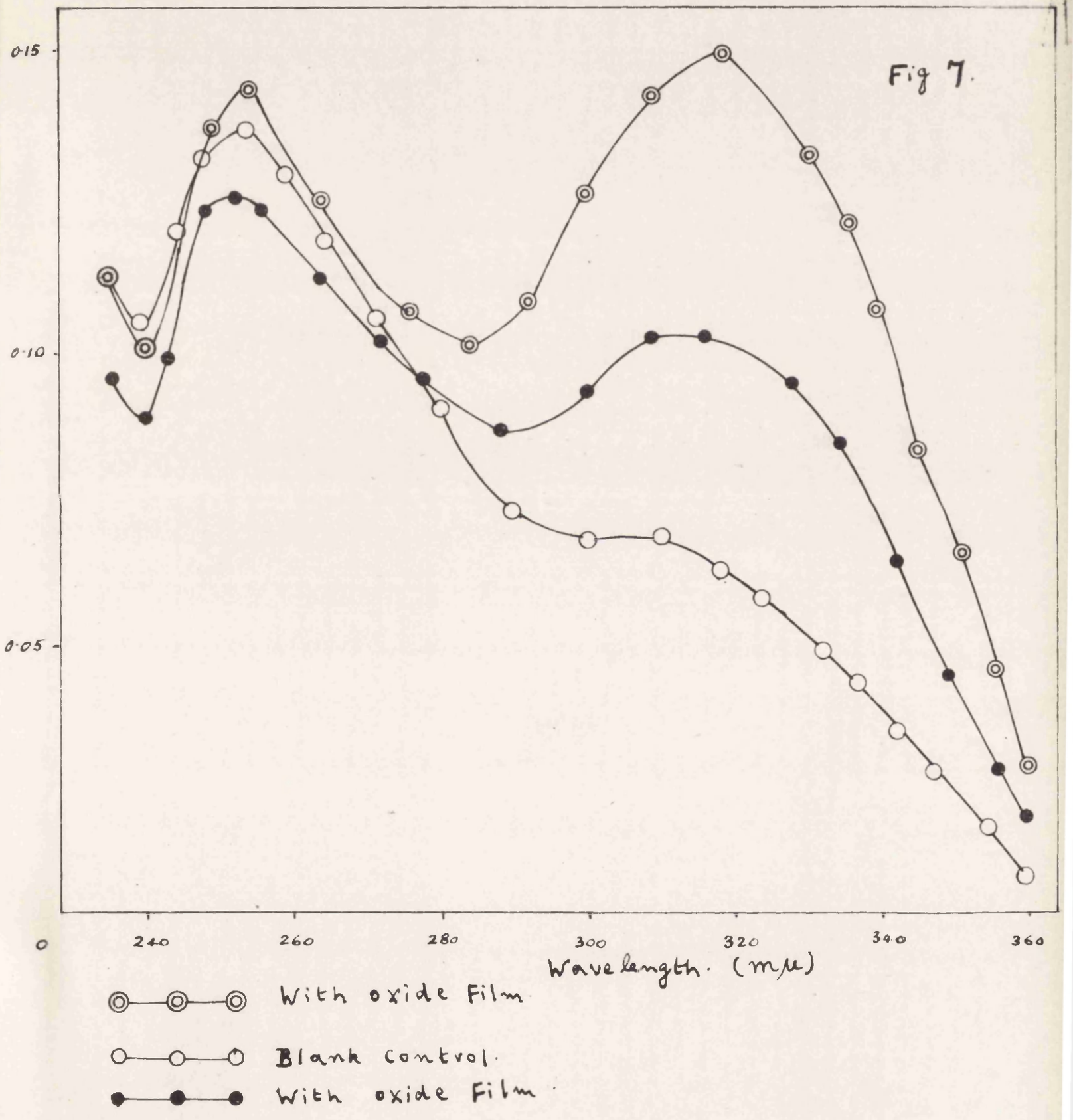
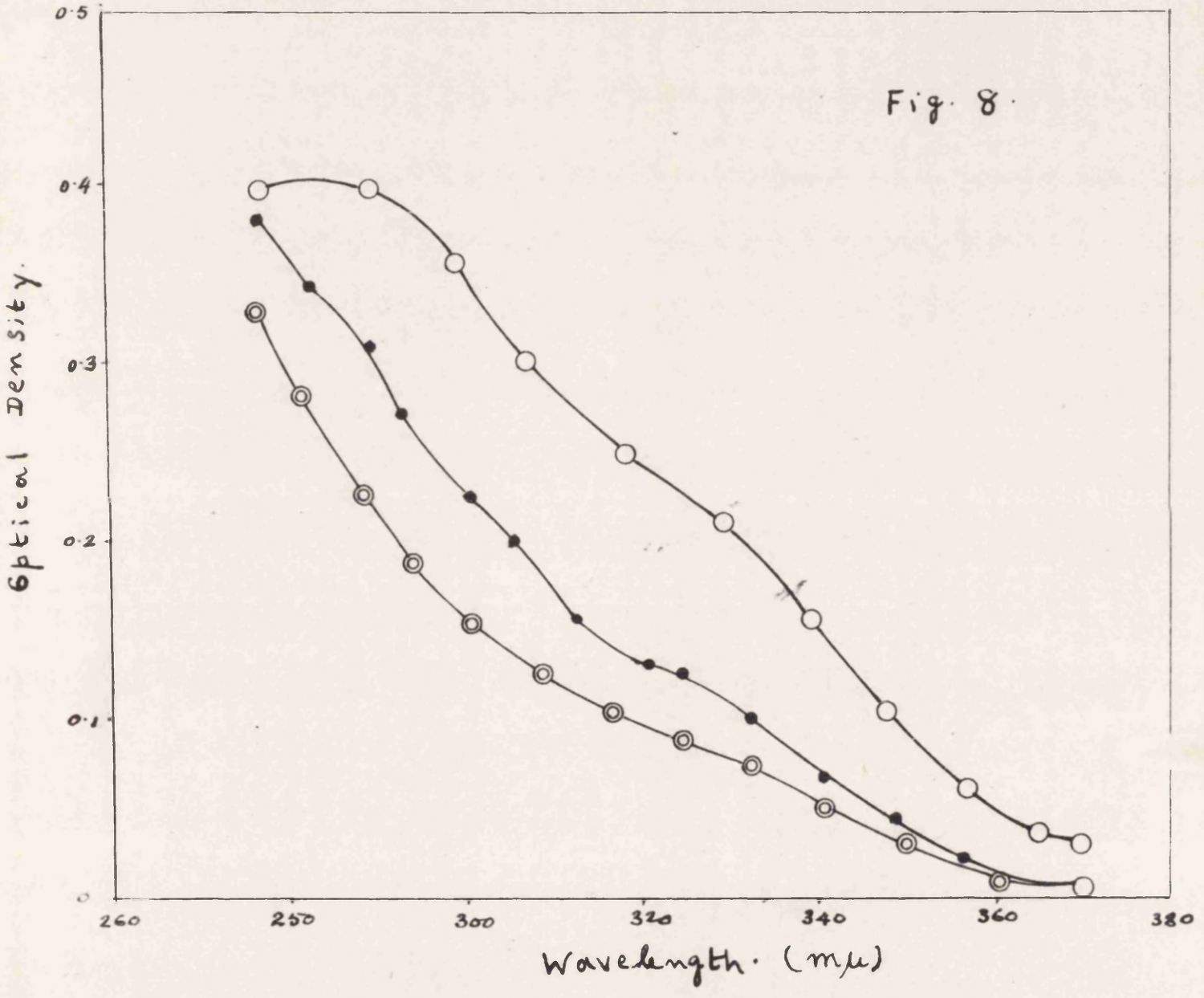


Fig 7.

Light absorption curve for azobenzene in dry benzene.

Fig. 8.

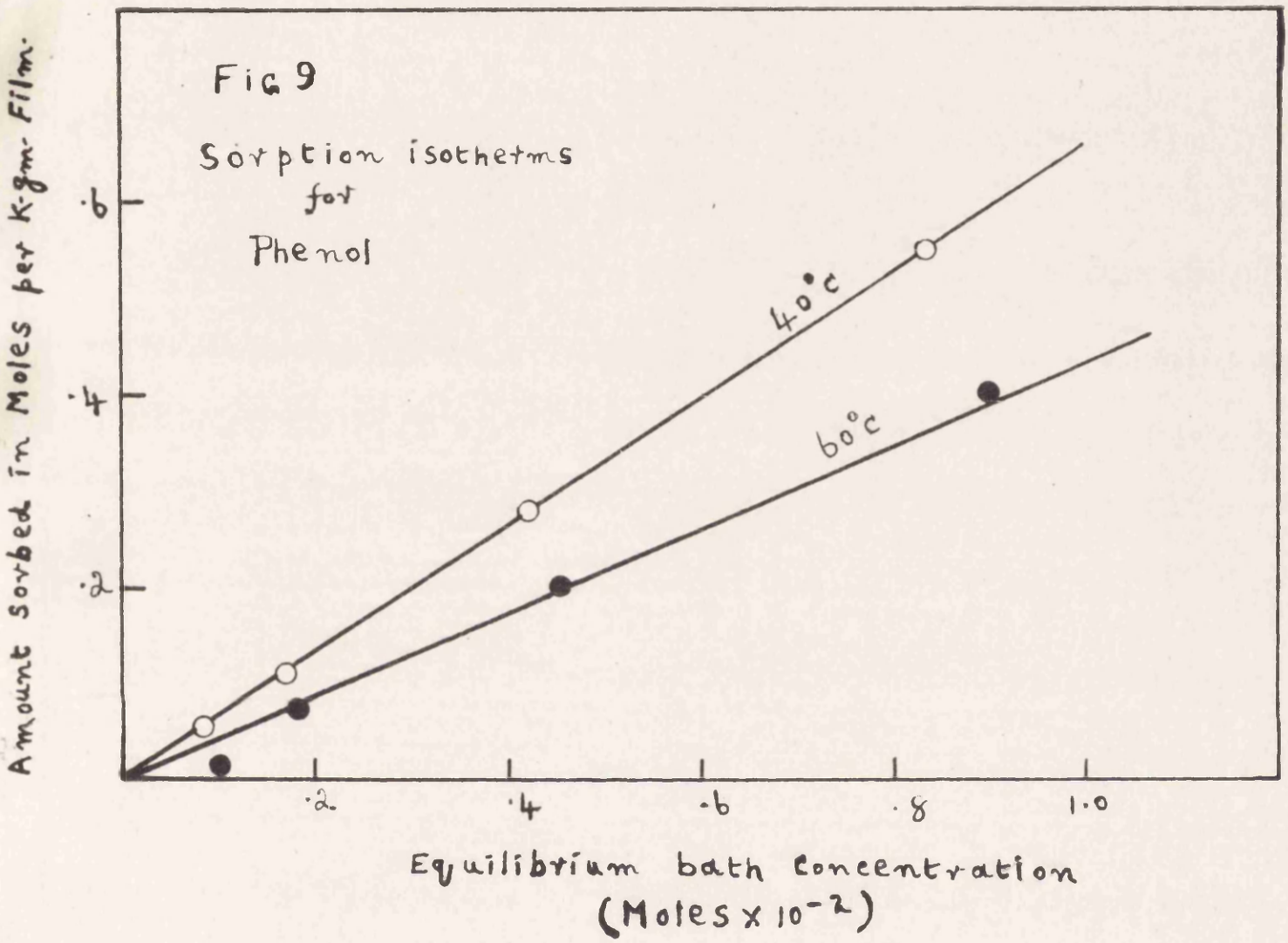


Blank bath.

With oxide Film

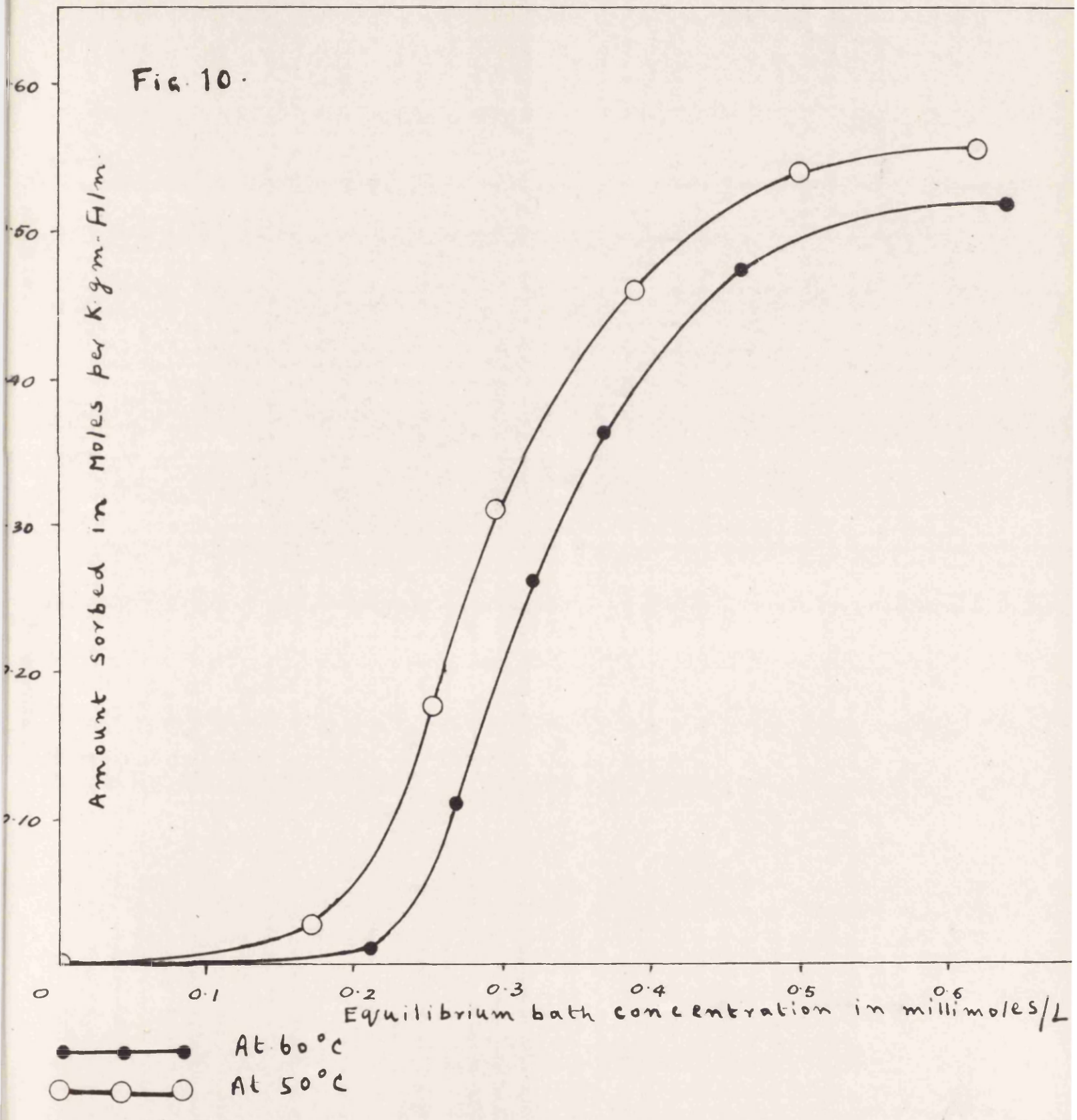
With oxide Film.

Fig 9


Sorption isothetms
for
Phenol
40°c
60°c
·6
·4
·2
·2
·4
·6
·8
1·0
Amount sorbed in Moles per K-gm-Film.
Equilibrium bath concentration
(Moles x 10^{-2})

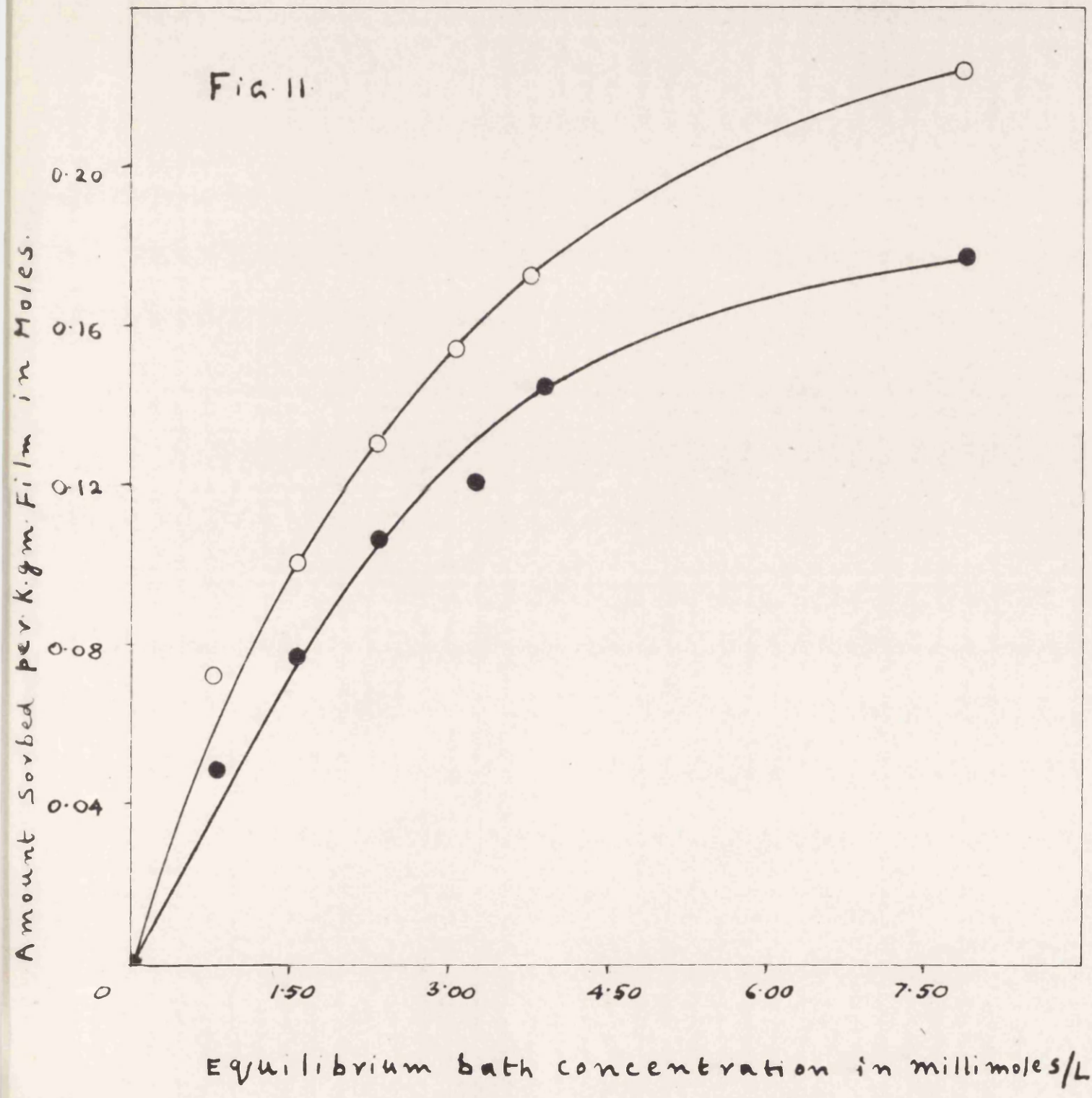
Sorption of 2:4-dinitrophenol

Fig 10.



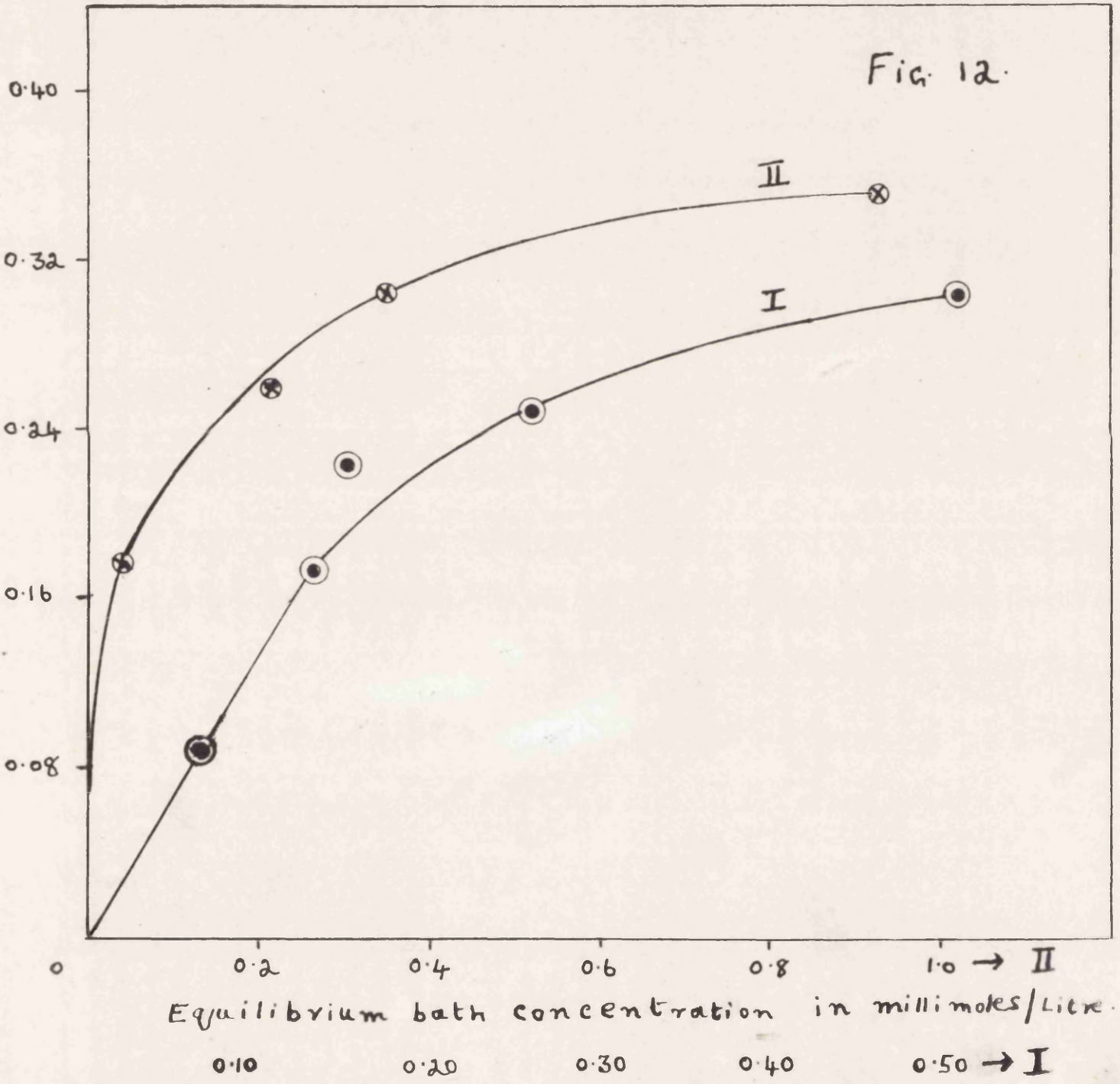
Sorption of benzene azo-1-naphthol

Fig. 11



Sorption of Oleyl Sodium Sulphate and Tetradecyl Sodium sulphate } At 40°C and 50°C

Fig. 12.



I ○—○—○ At 40°C
● ● ● At 50°C } Tetradecyl Sodium Sulphate

II ○—○—○ At 40°C
× × × At 50°C } Oleyl Sodium Sulphate.

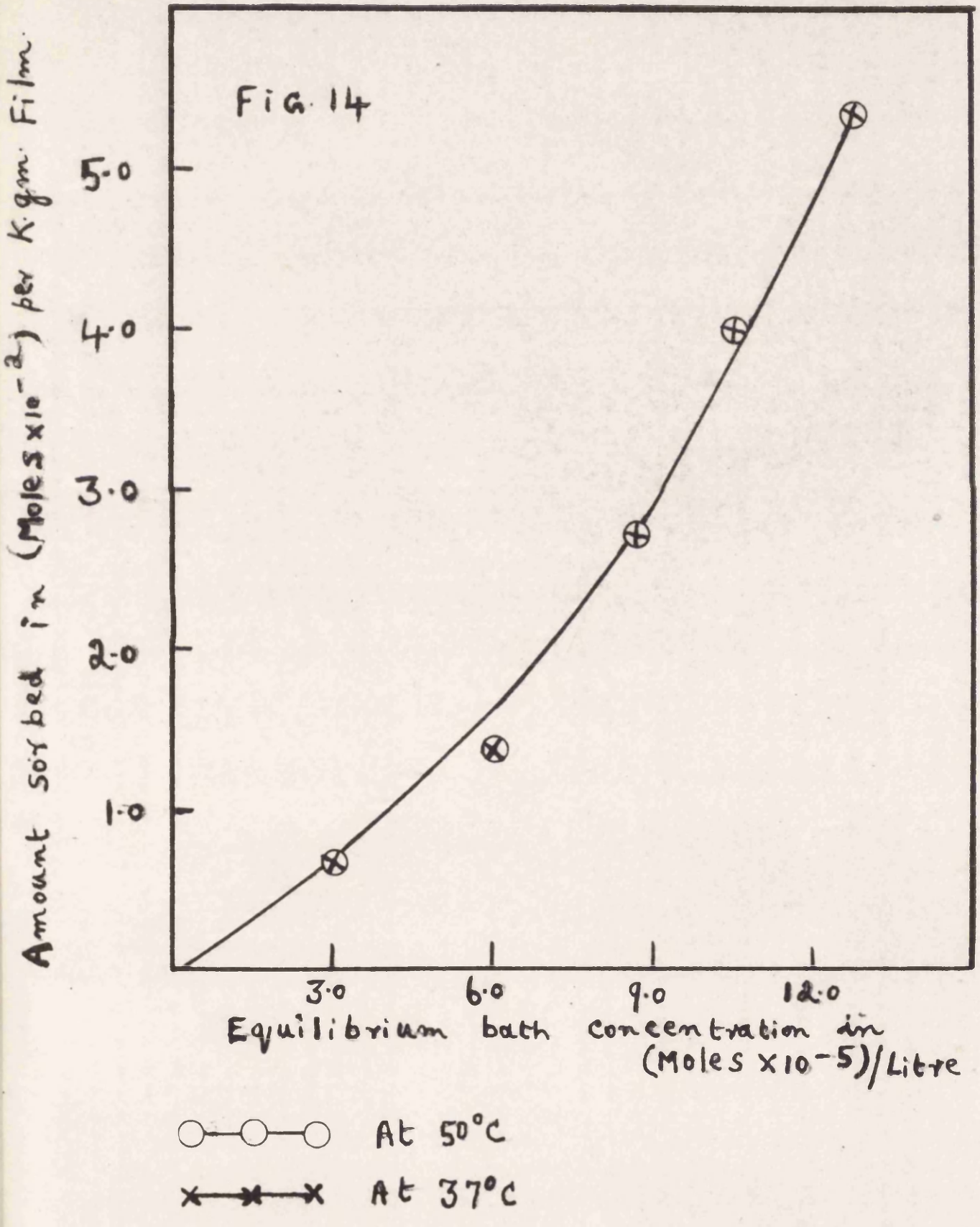
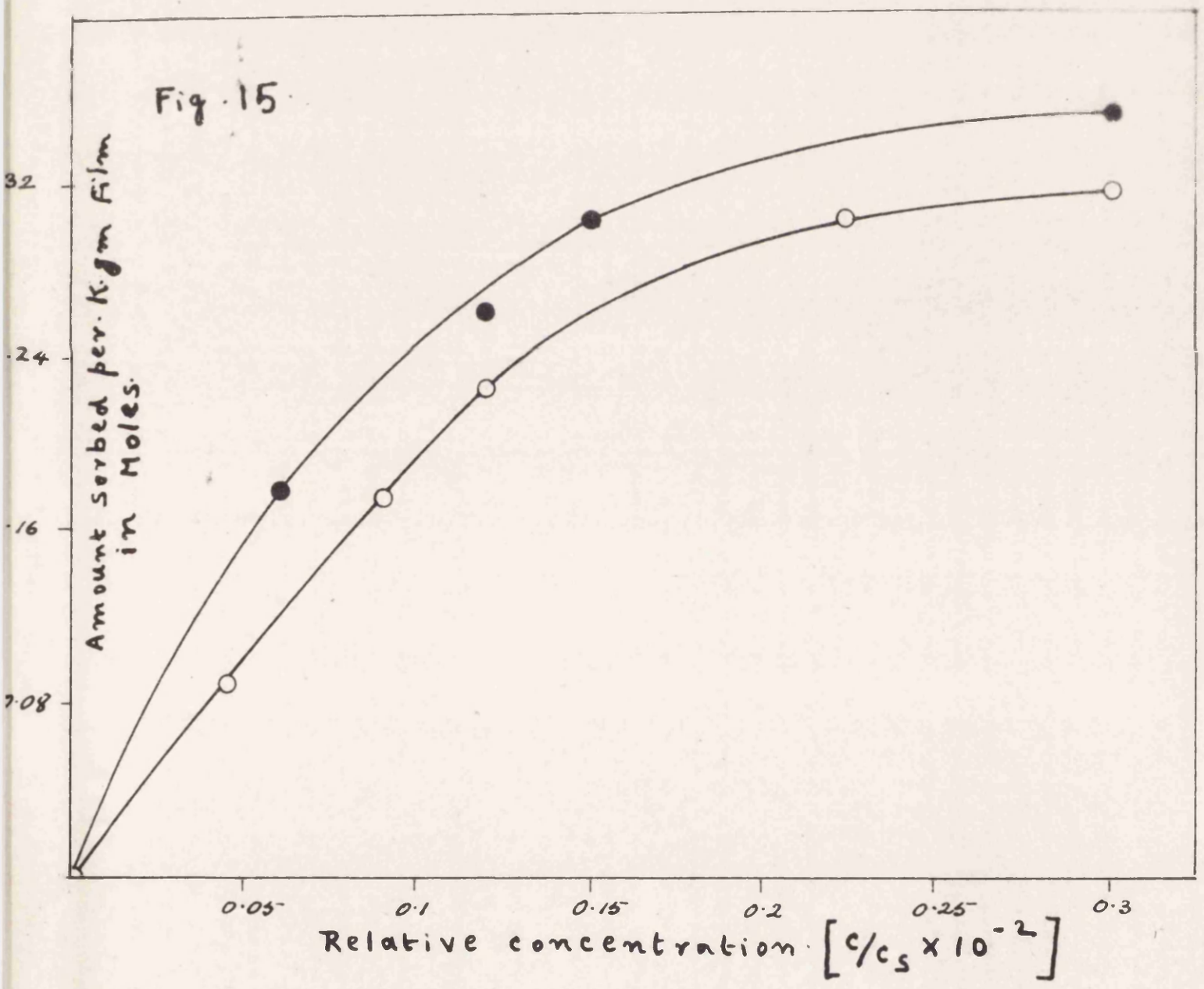


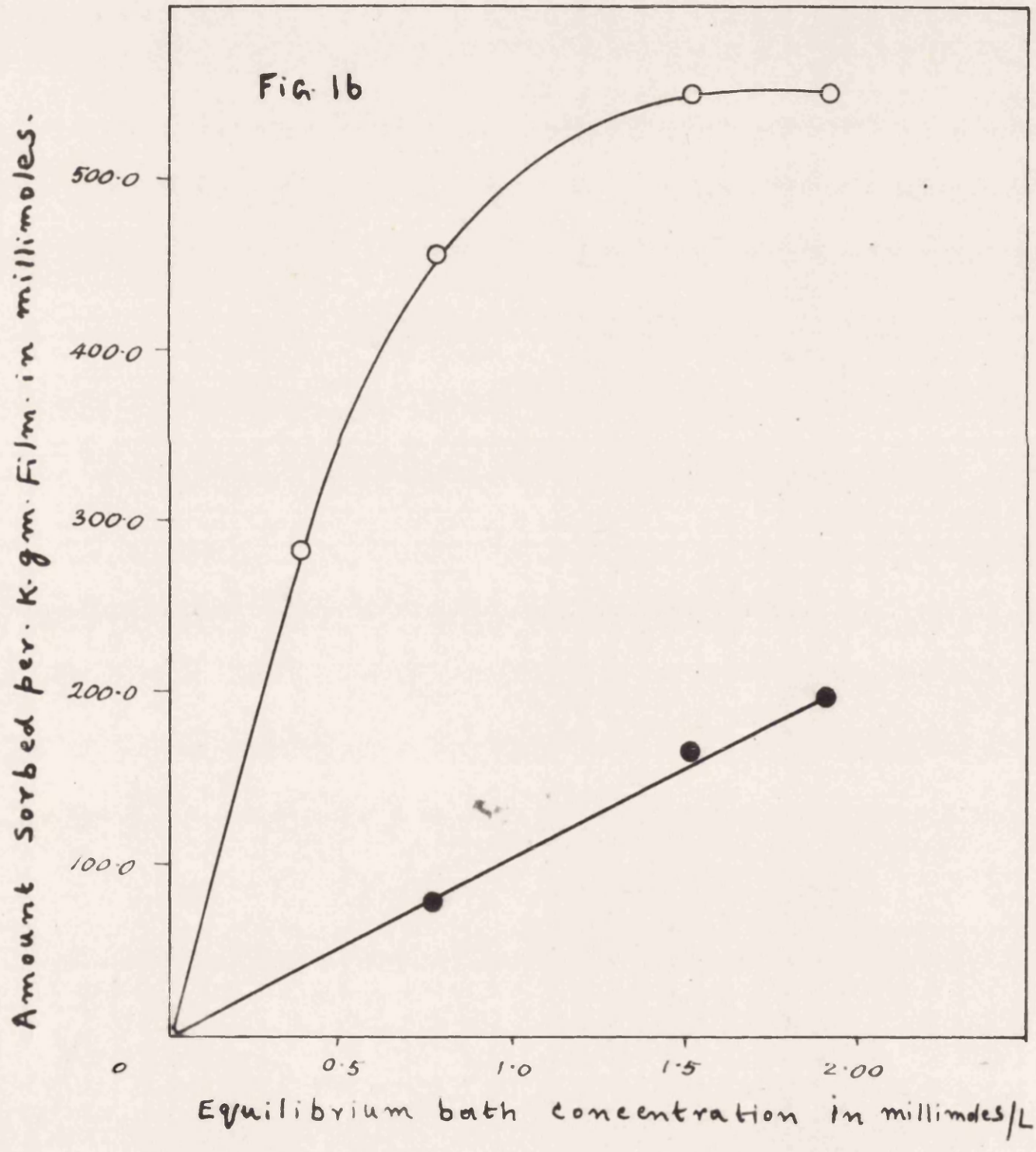
Fig. 14
Amount sorbed in (Moles x10⁻²) per K.gm. Film.
5·0
4·0
3·0
2·0
1·0
3·0
6·0
9·0
12·0
Equilibrium bath concentration in (Moles x10⁻⁵)/Litre
At 50°C
At 37°C

Sorption of Oleyl Sodium sulphate and Tetradecyl Sodium sulphate. } At 40°C and 50°C

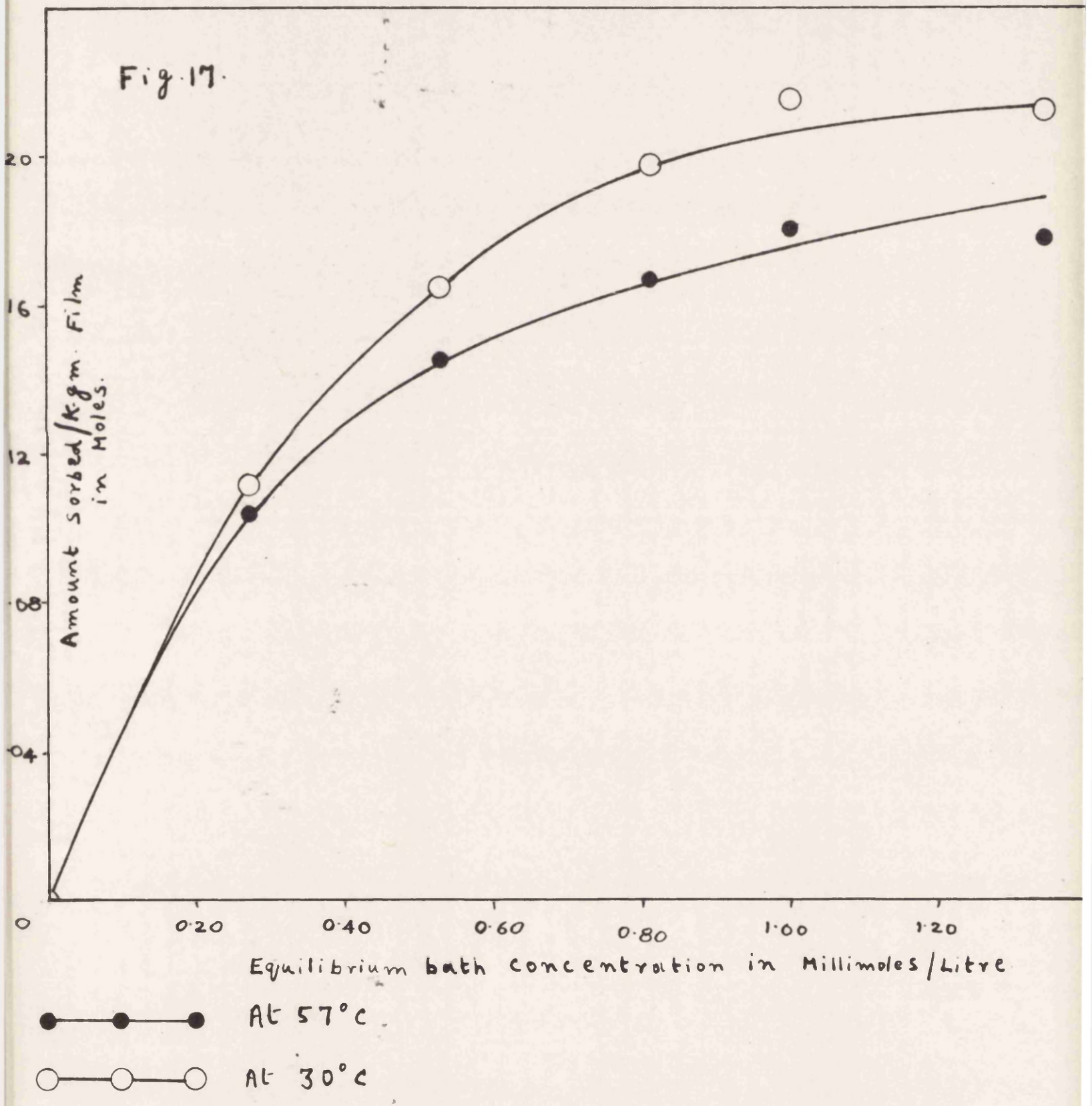
Plot on "Relative concentration basis".



Sorption of Azobenzene-4-Sulphonic acid.

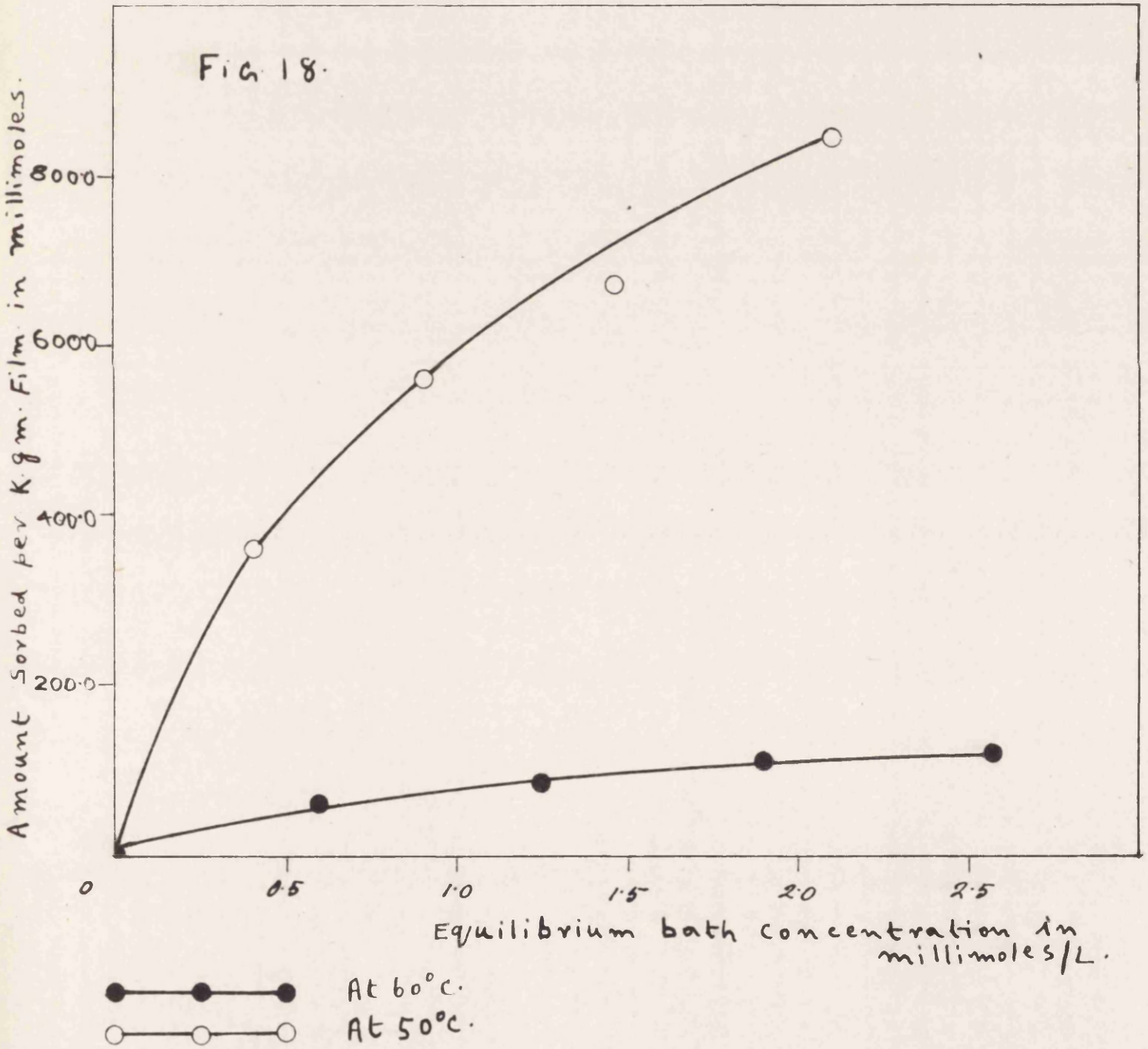


Sorption of benzene azo-2-naphthol-3:6-disulphonic acid.



Sorption of dodecylbenzeneazo-2-naphthol-3:6-disulph-onic acid.

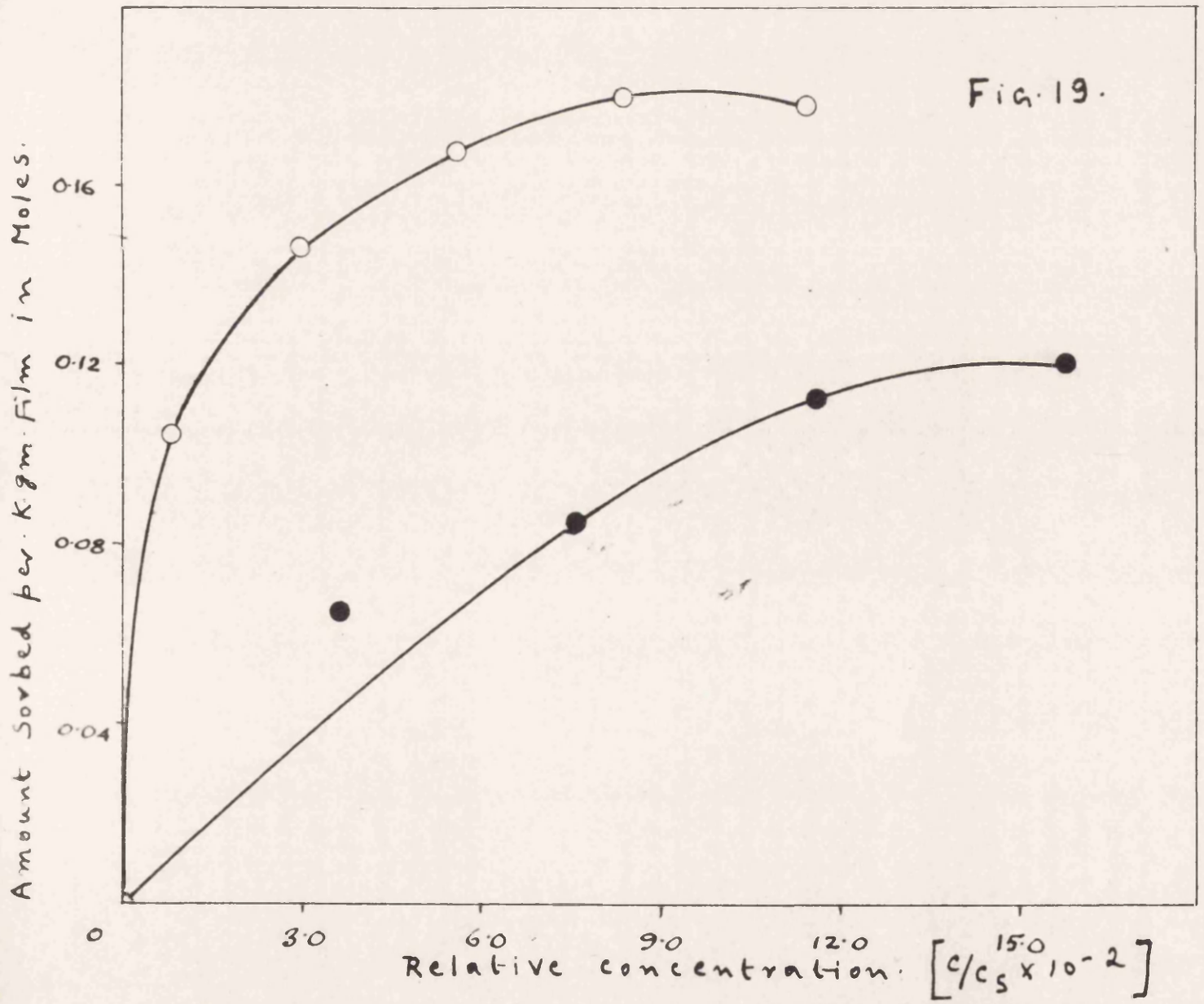
Fig. 18.



Sorption of benzeneazo-2-naphthol-3:6-disulphonic acid and dodecyl benzeneazo-2-naphthol-3:6-disulphonic acid.

Plot on "Relative concentration basis"

Fig. 19.



●——●——● Dodecyl benzene azo-2-naphthol-3:6-disulphonic acid.

○——○——○ Benzene azo-2-naphthol-3:6-disulphonic acid

Sorption of dodecyl toluene sodium sulphonate

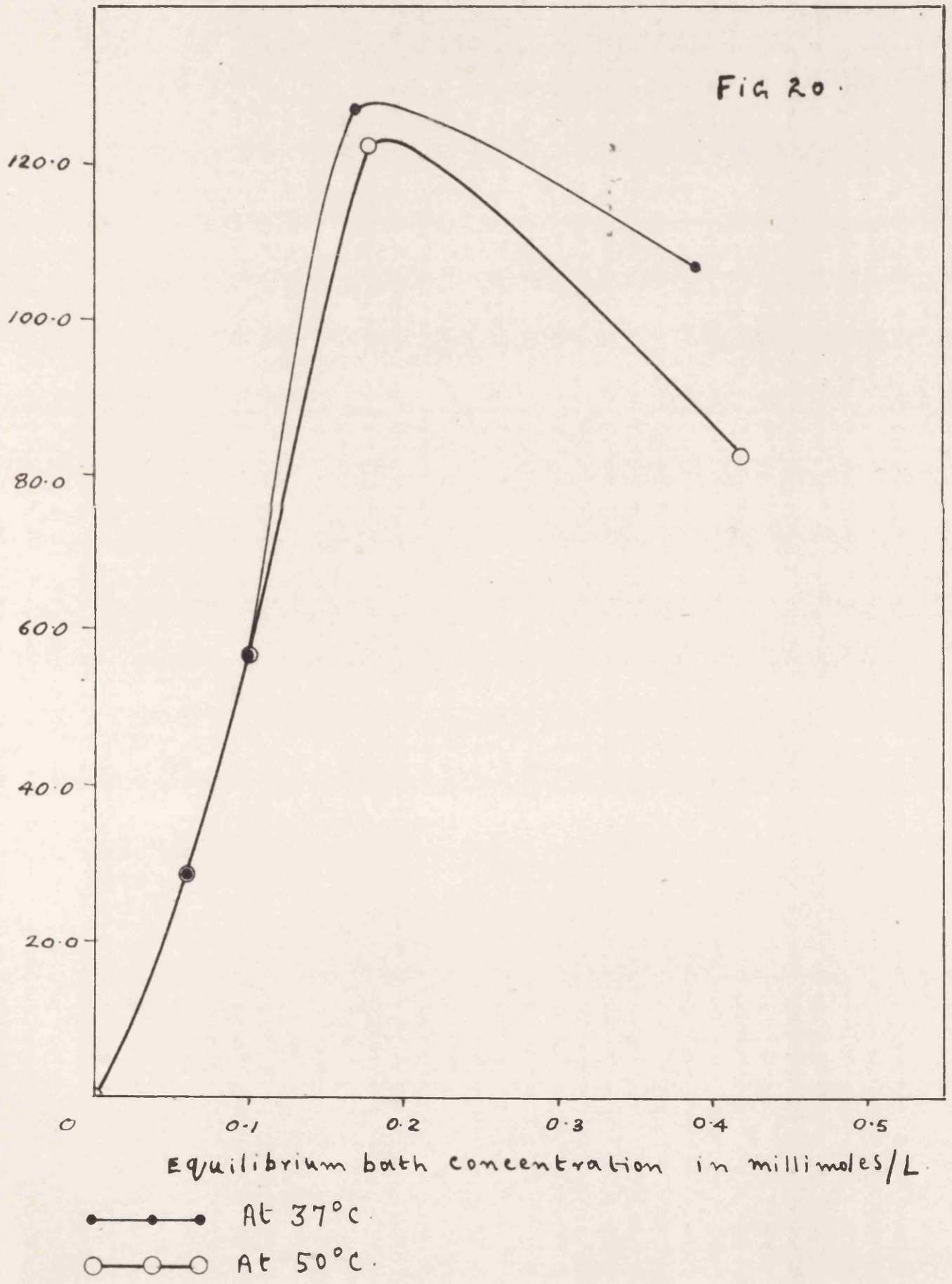
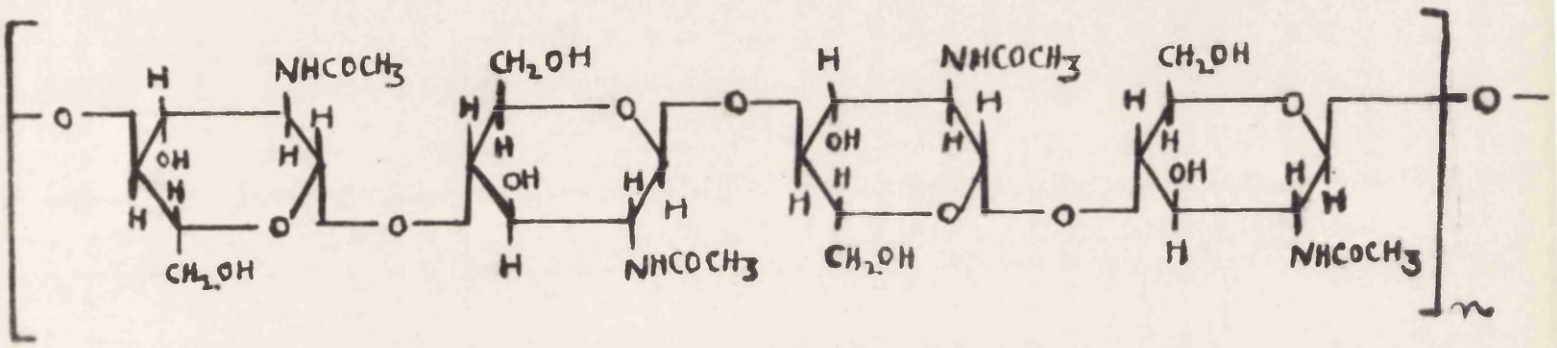
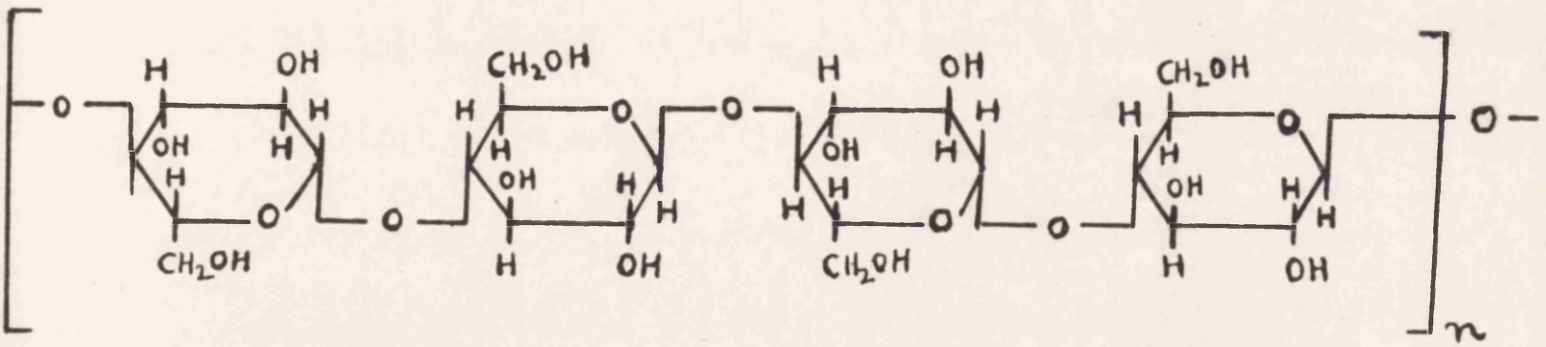


Fig 21



CHITIN.



CELLULOSE.

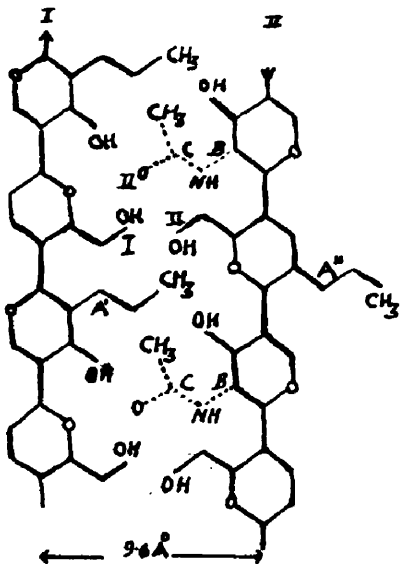
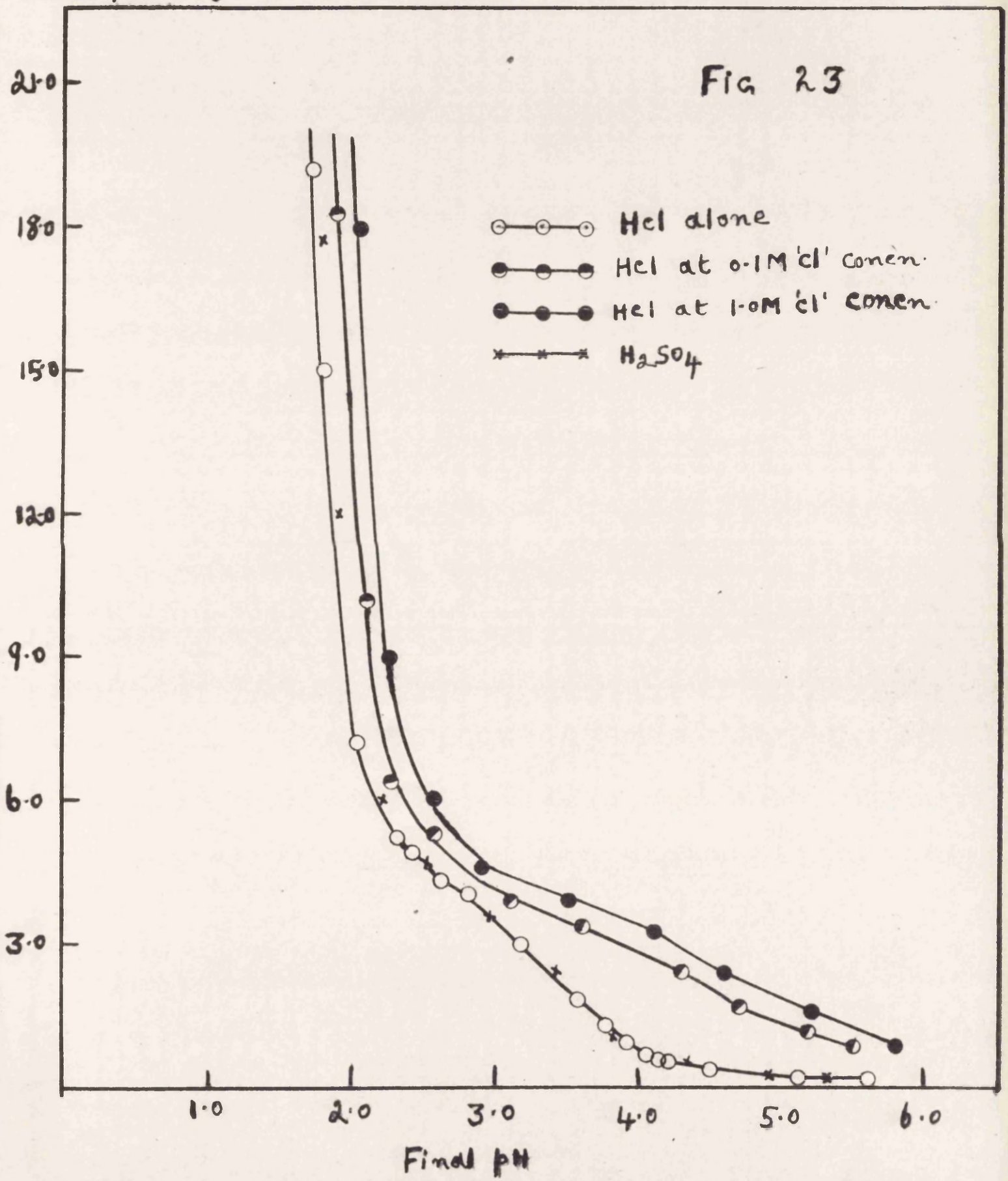


Fig 22.

(1) Sorption of hydrochloric acid alone, and at 0·1M and 1·0M Constant Chloride Concentration.
(2) Sorption of Sulphuric acid.

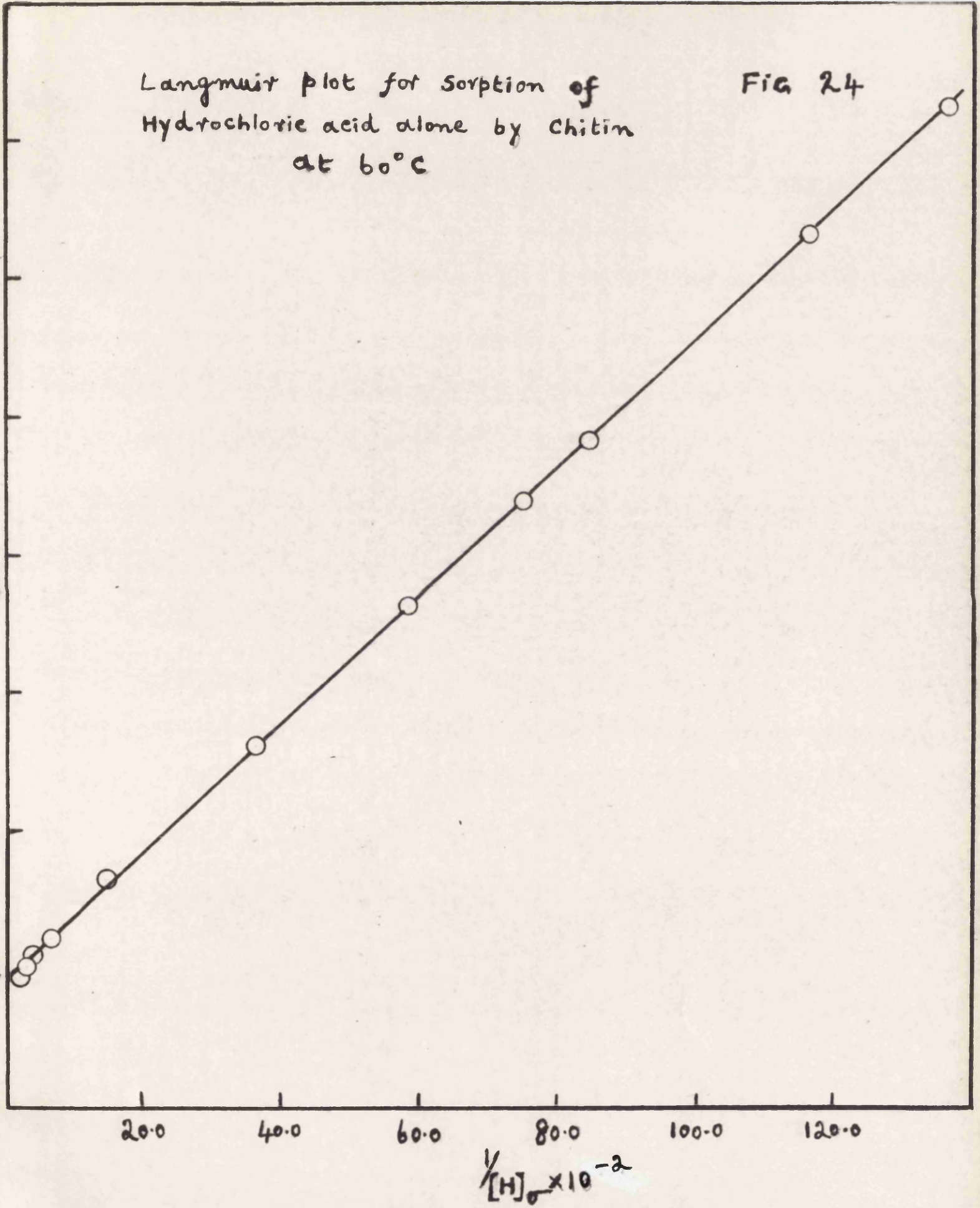
} At 60°C

Fig 23



Langmuir plot for Sorption of Hydrochloric acid alone by Chitin at 60°C

Fig 24



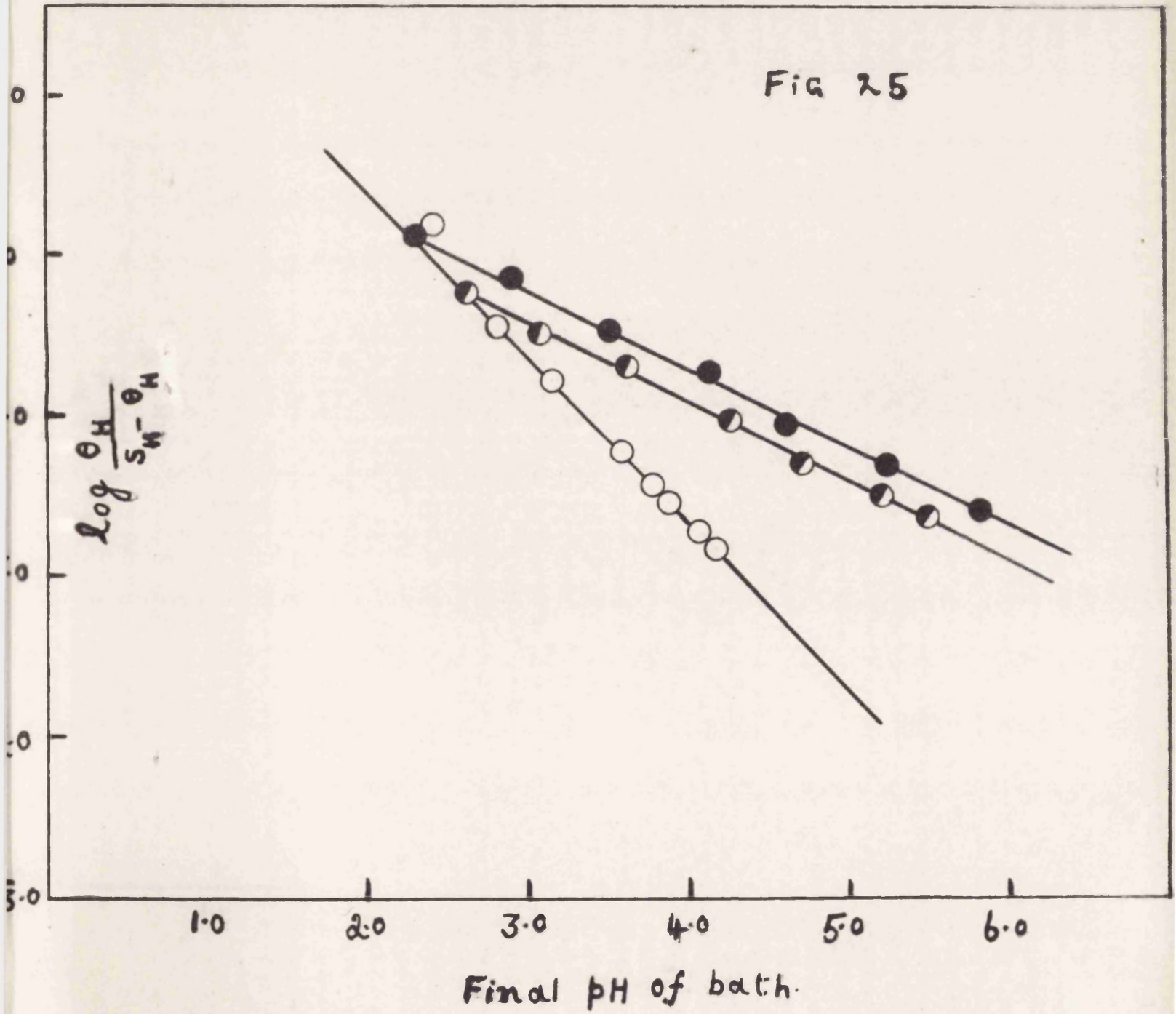
$[H]_0$ - Equilibrium bath concentration of hydrogen ions in gm·ion per Litre

$[H]_d$ - Amount sorbed per K·gm· of Chitin in equivalents of acid·

Sorption of hydrochloric acid by chitin, alone and at 0·1M and 1·0M constant chloride concentration, at 60°C

"Gilbert-Rideal plot"

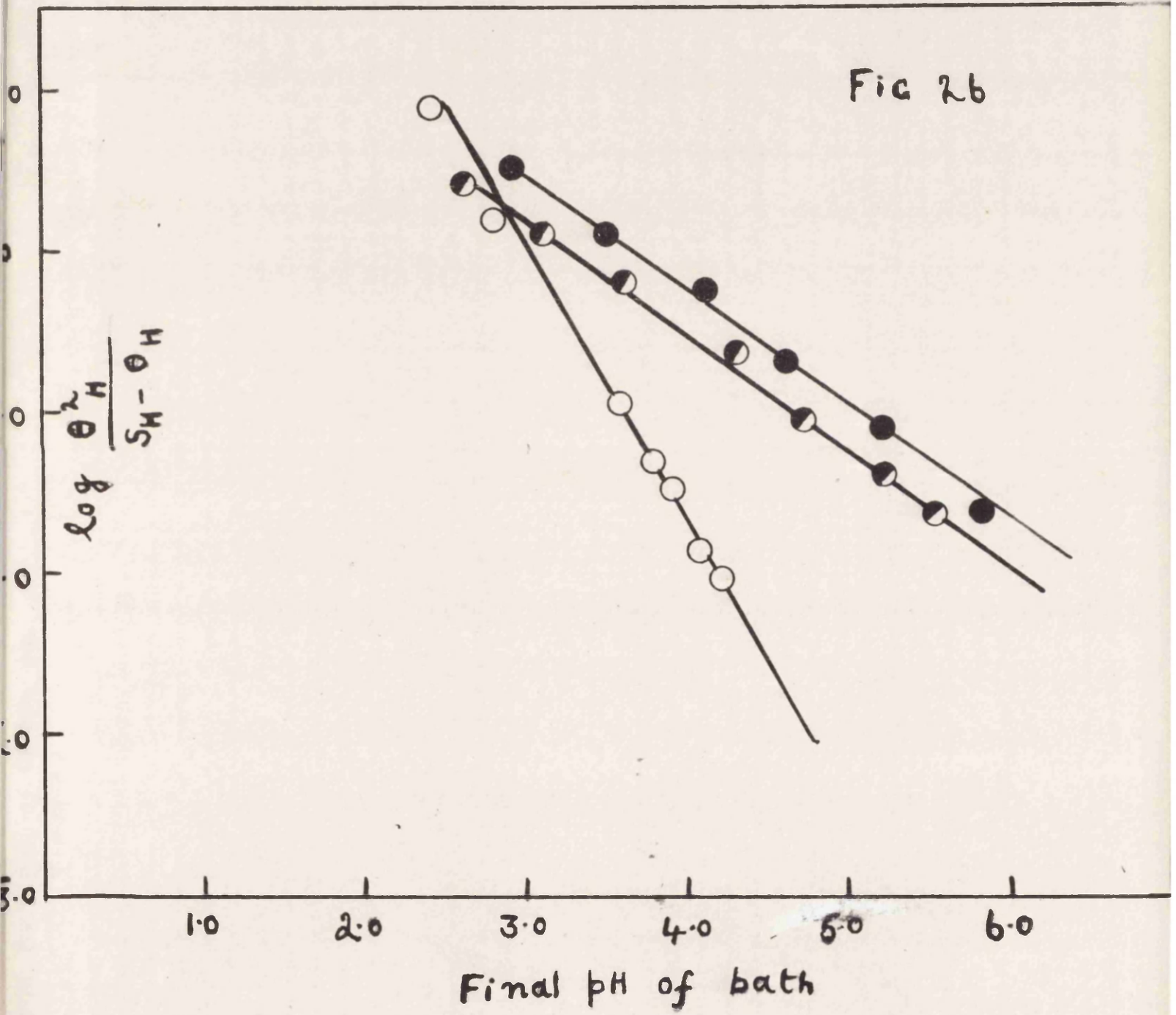
Fig 25



Sorption of hydrochloric acid by Chitin alone and at 0·1M and 1·0M Constant Chloride Concentration at 60°C

"Donnan plot"

Fig 2b

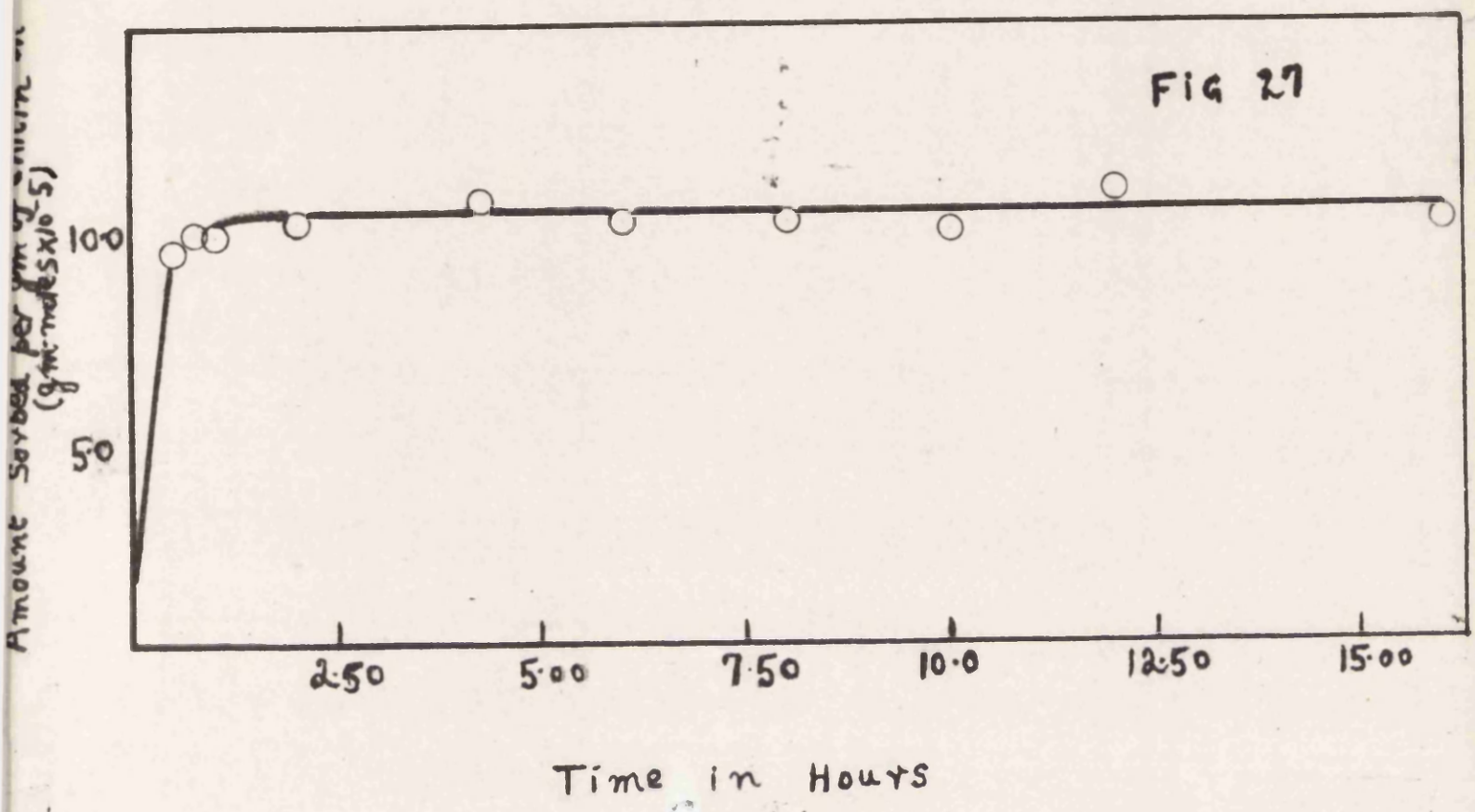


HCl alone

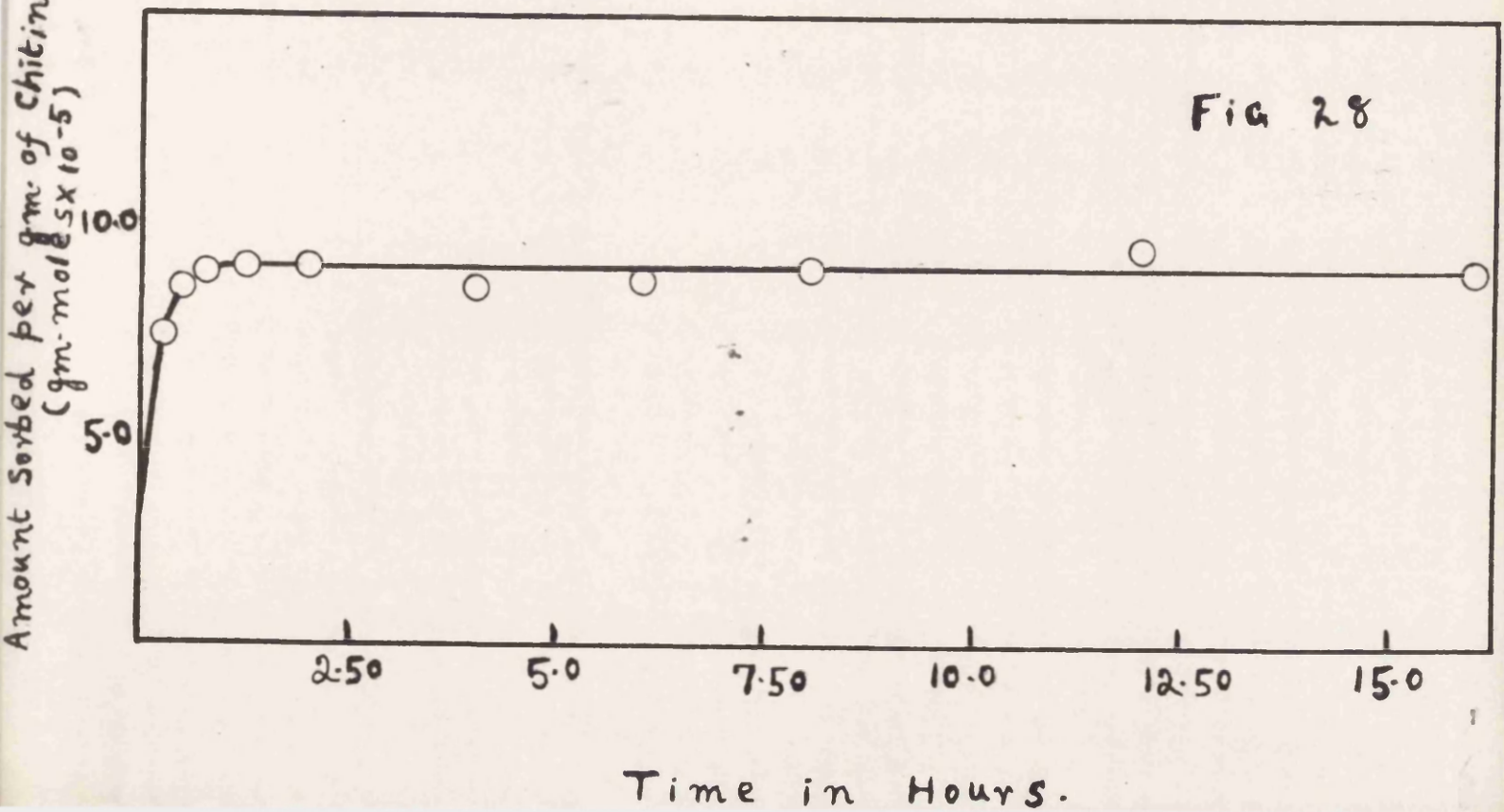
HCl at 0·1M 'Cl' Concentration

HCl at 1·0M 'Cl' Concentration

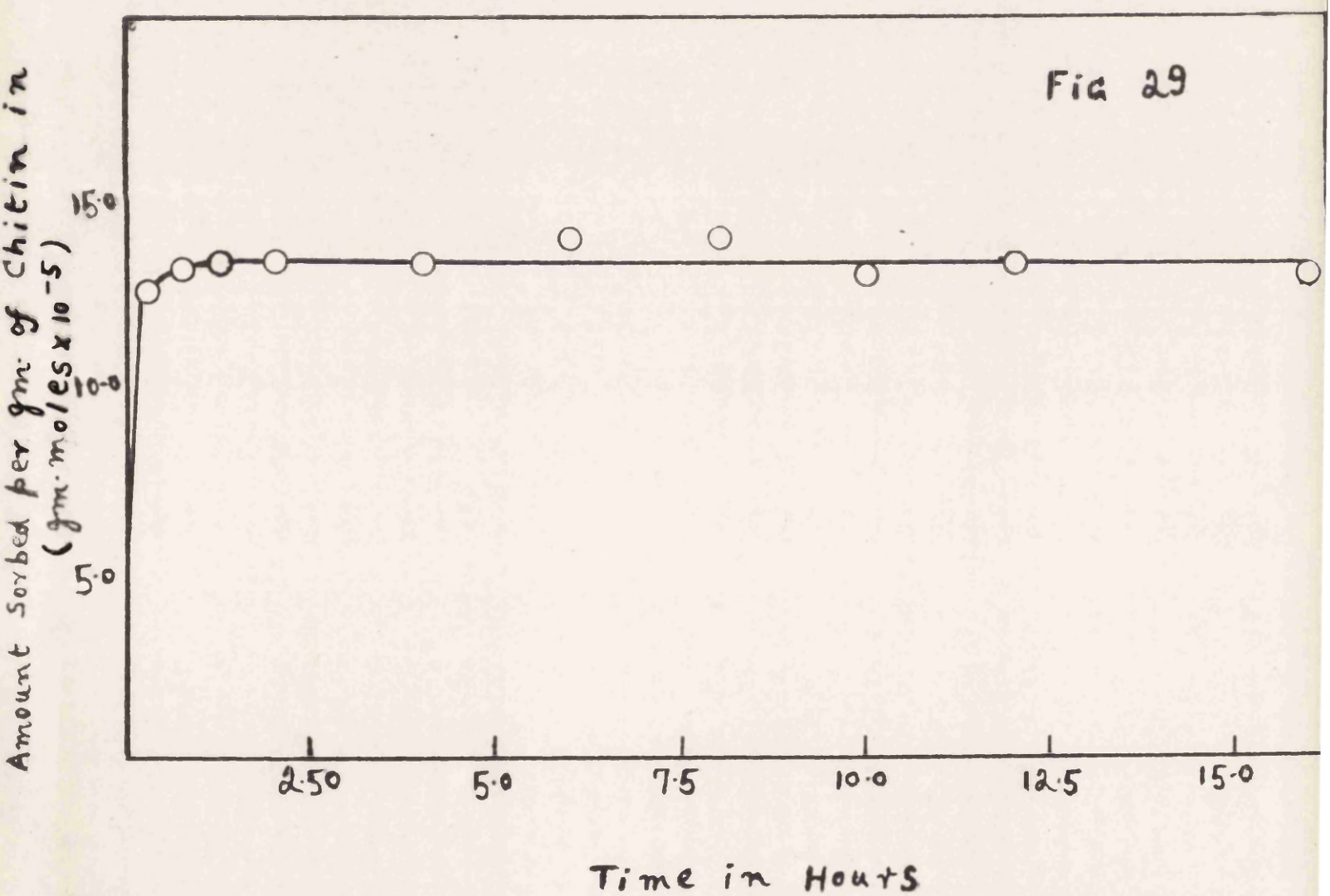
Rate of dyeing of Chitin by benzene-4-Sulphonic acid azo-2-naphthol at 60°C



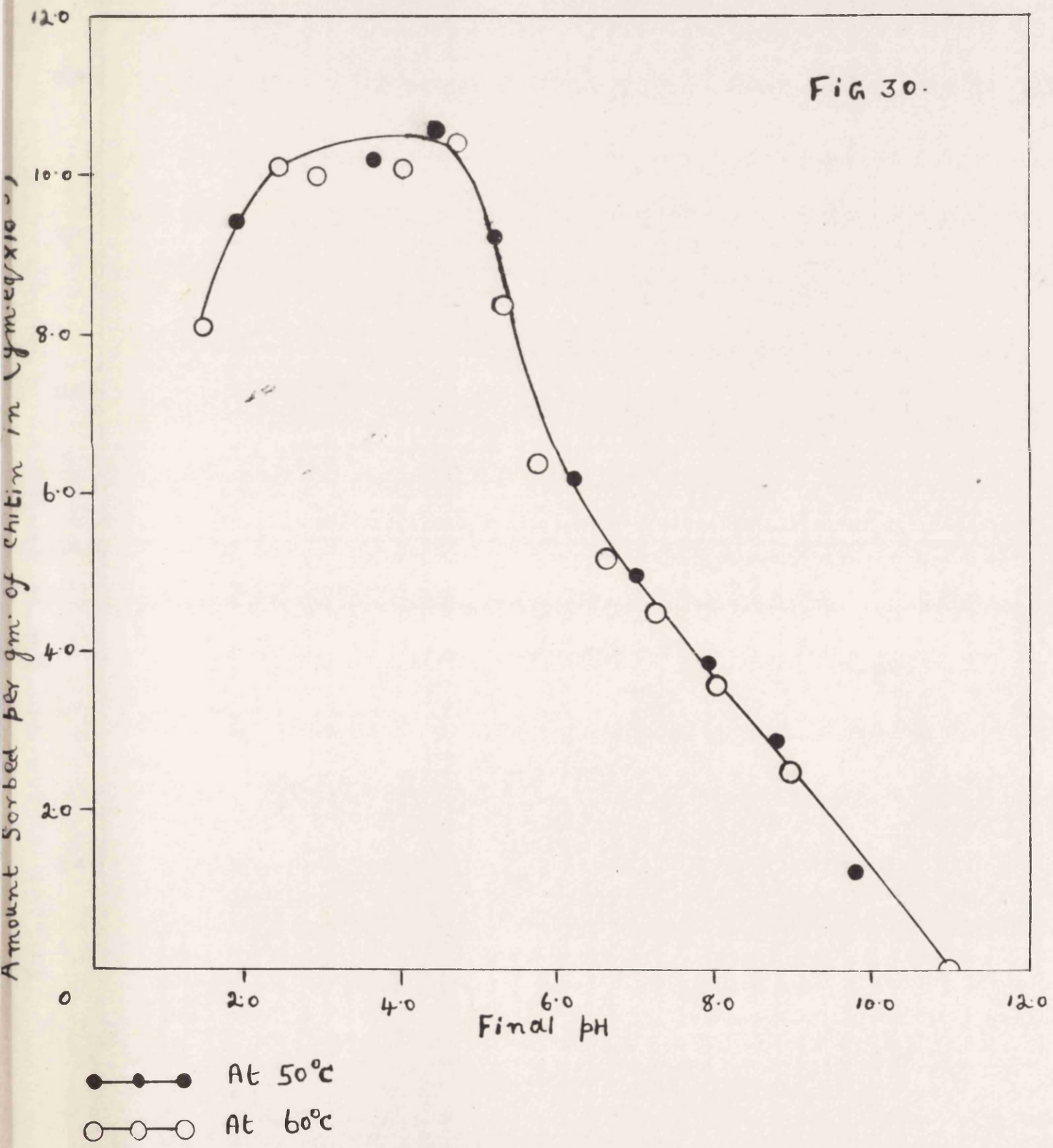
Rate of dyeing of Chitin by naphthalene-4-Sulphonic acid azo -2-naphthol-6-Sulphonic acid at 60°C



Rate of dyeing of chitin by naphthaleneazo-2-naphtho
-3:6-disulphonic acid at 60°c

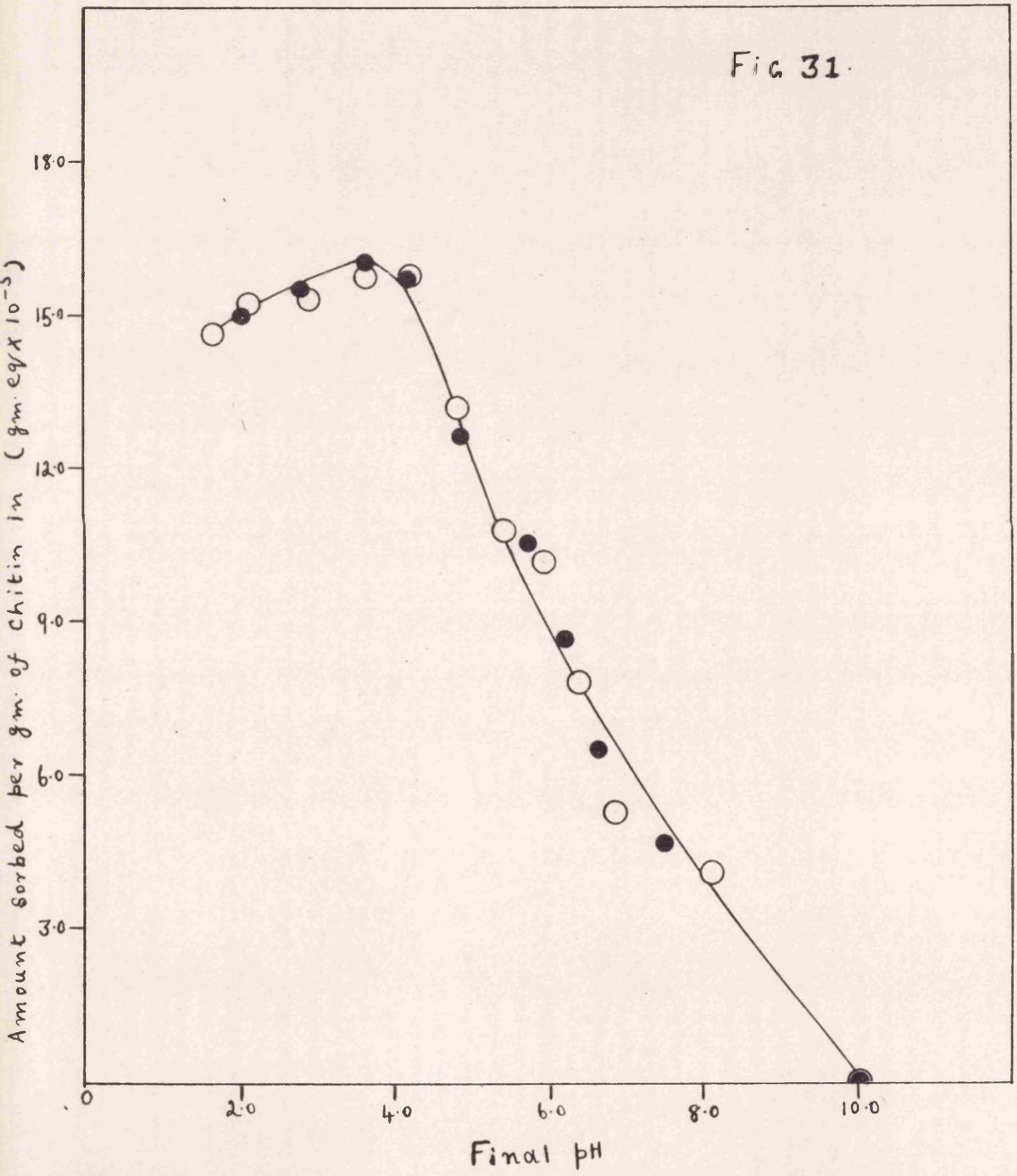


Sorption of benzene-4-sulphonic acid azo-2-naphthol.

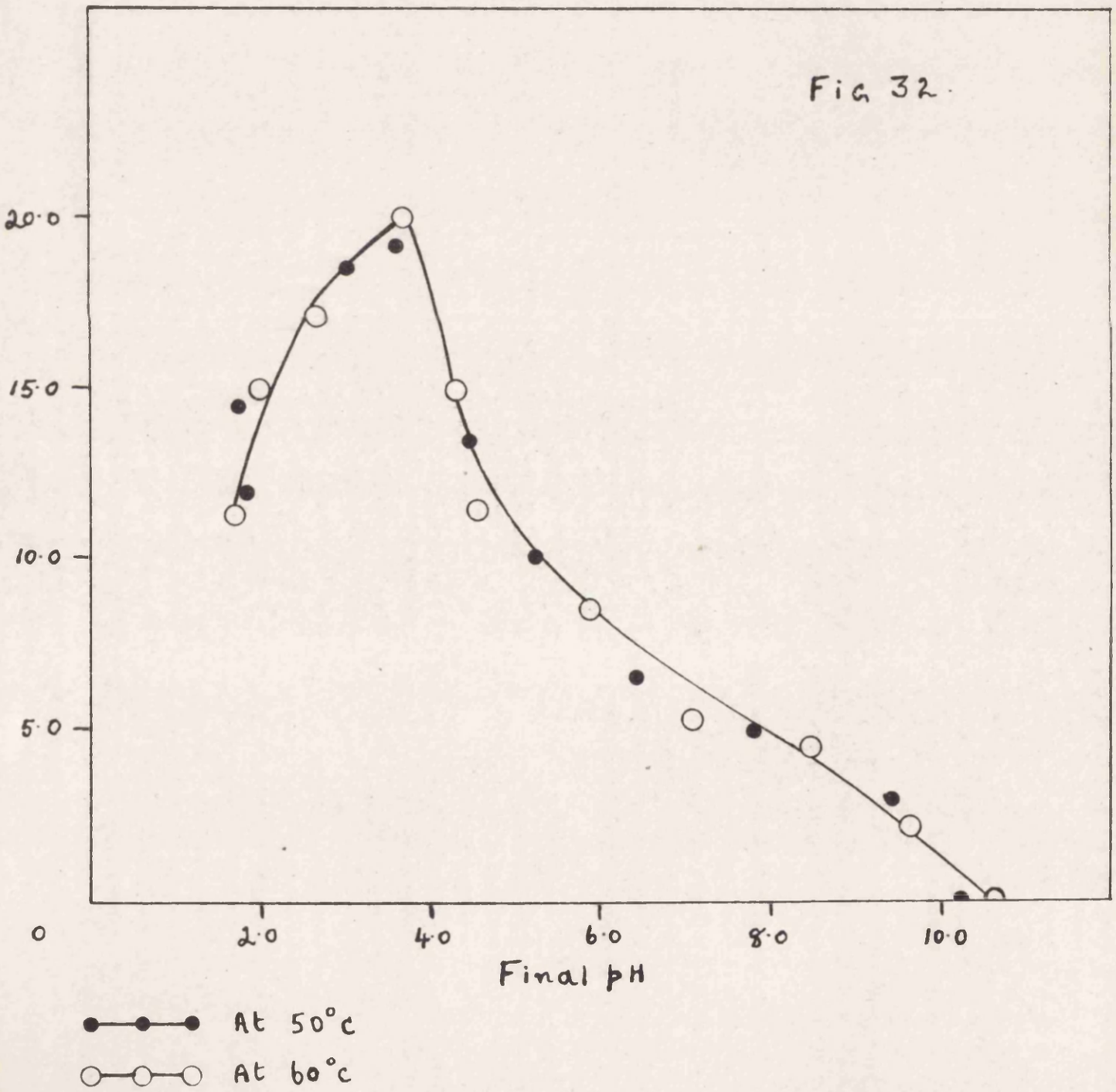


Sorption of naphthalene-4-Sulphonic acid azo-2-naphthol

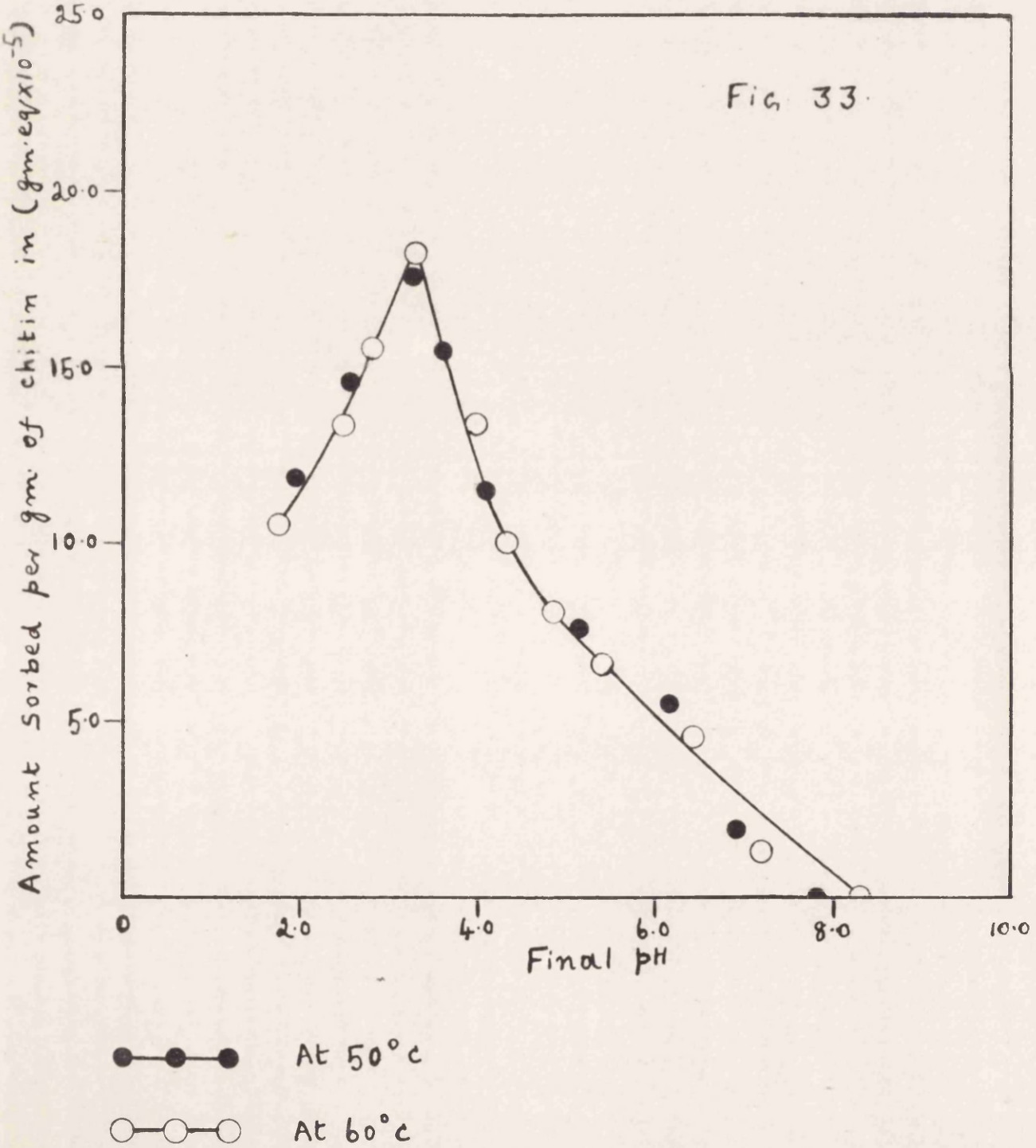
Fig 31.



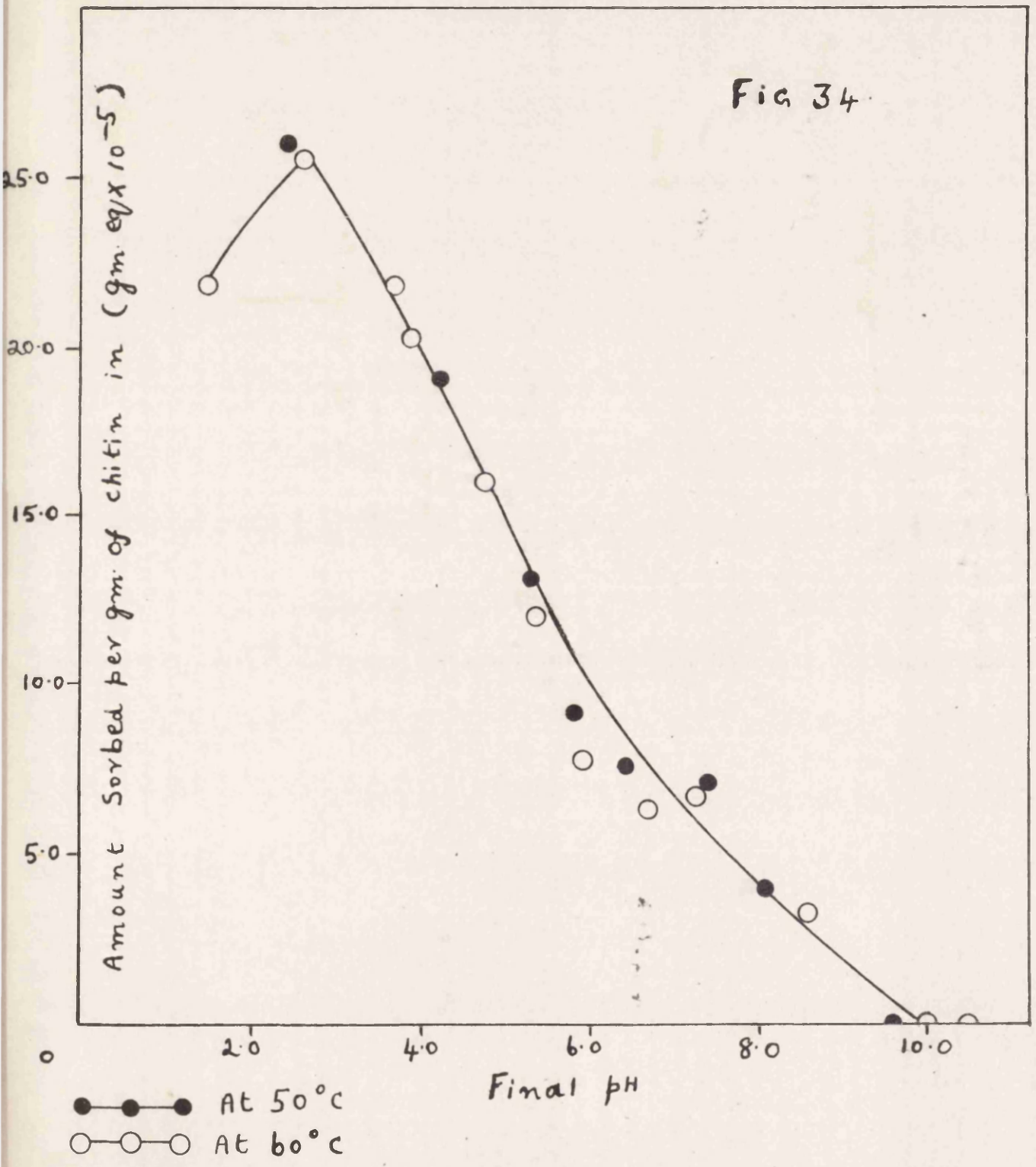
Sorption of benzene azo-2-naphthol-3:6-di sulphonic acid



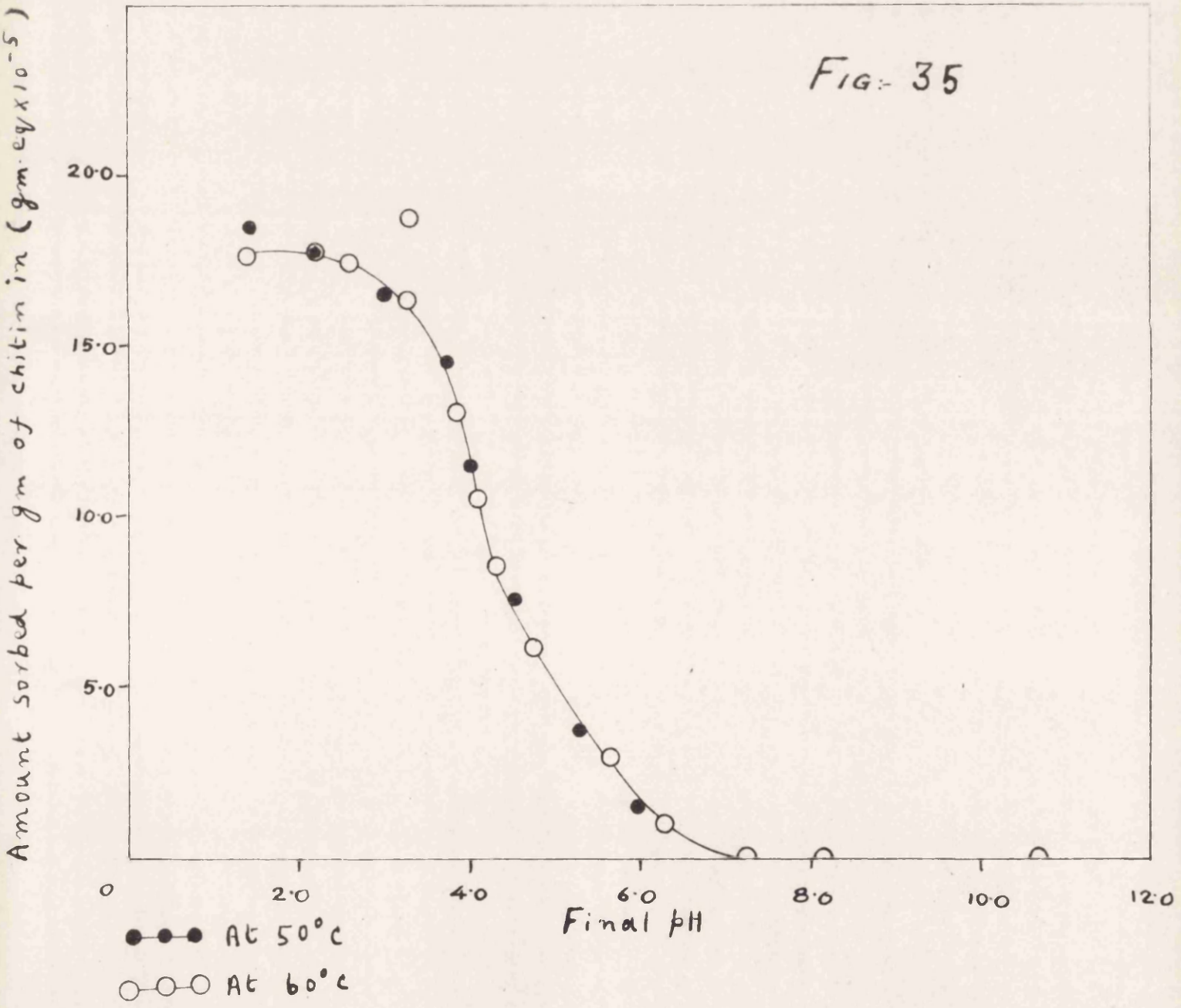
Sorption of benzene-4-Sulphonic acid azo-2-naphthol -6-Sulphonic acid



Sorption of naphthalene azo-2-naphthol-3:6-disulphonic acid.

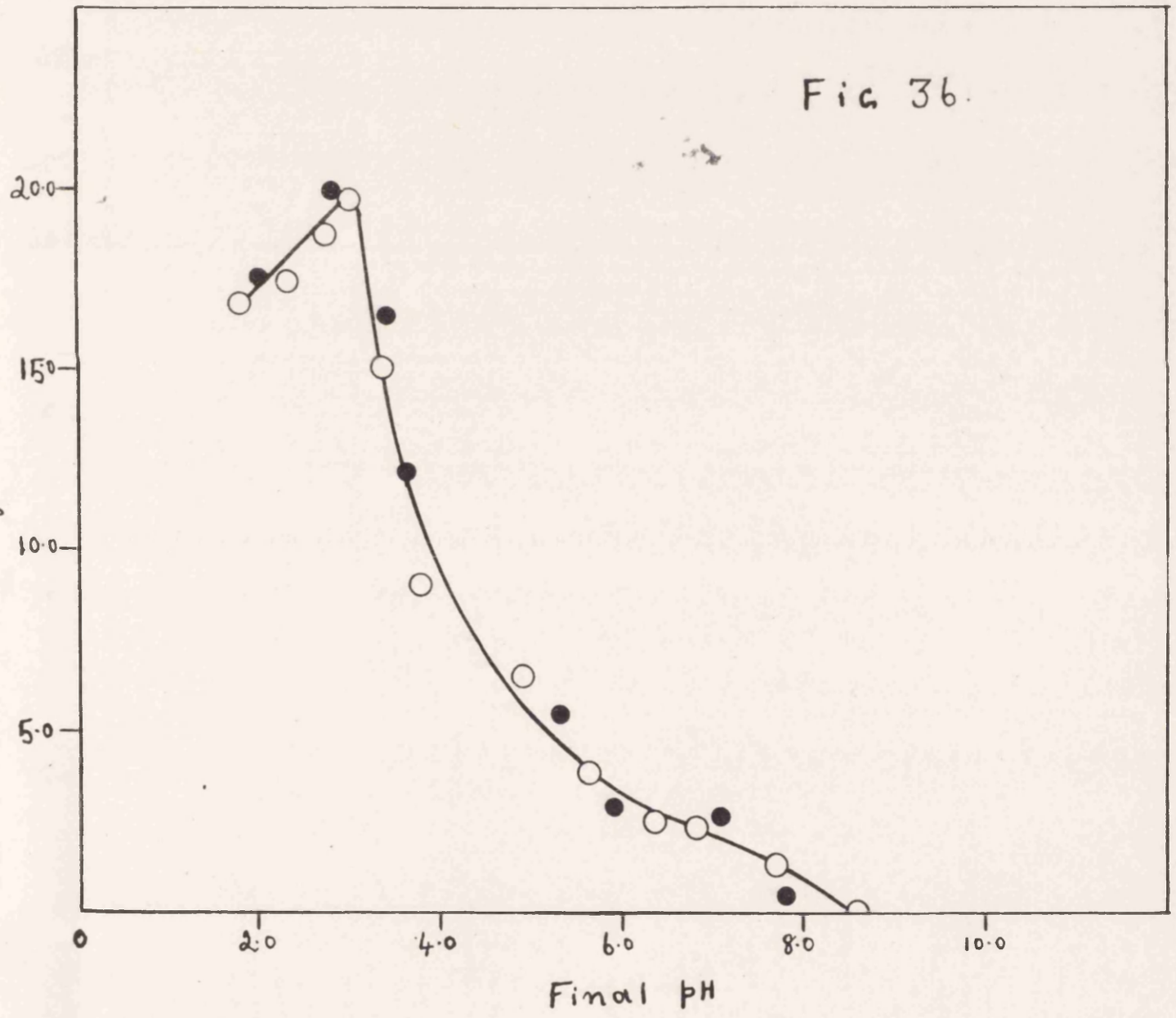


Sorption of naphthalene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid



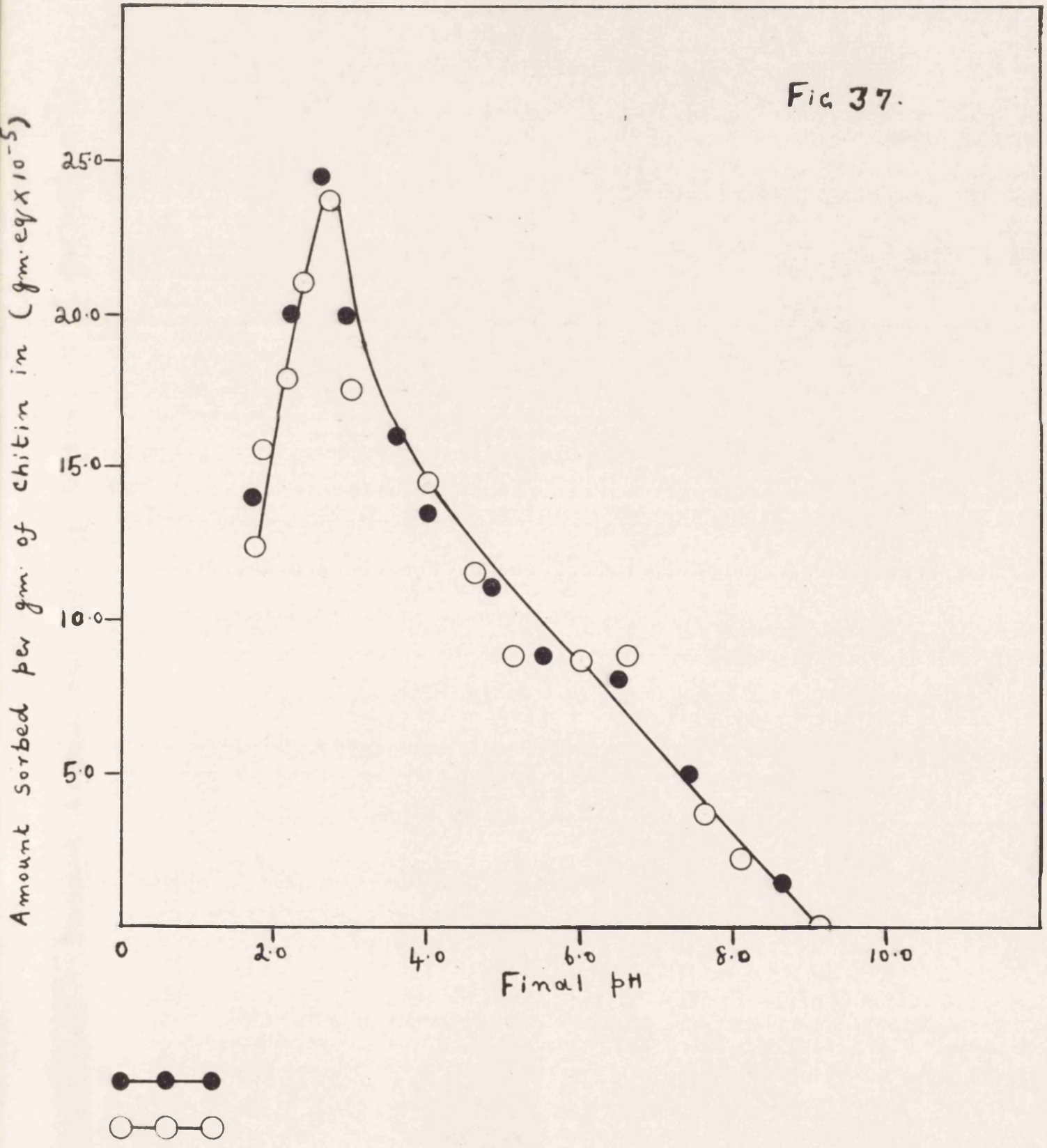
Sorption of benzene-2:5-disulphonic acid azo-2-naphthol—6—sulphonic acid

Fig 36.



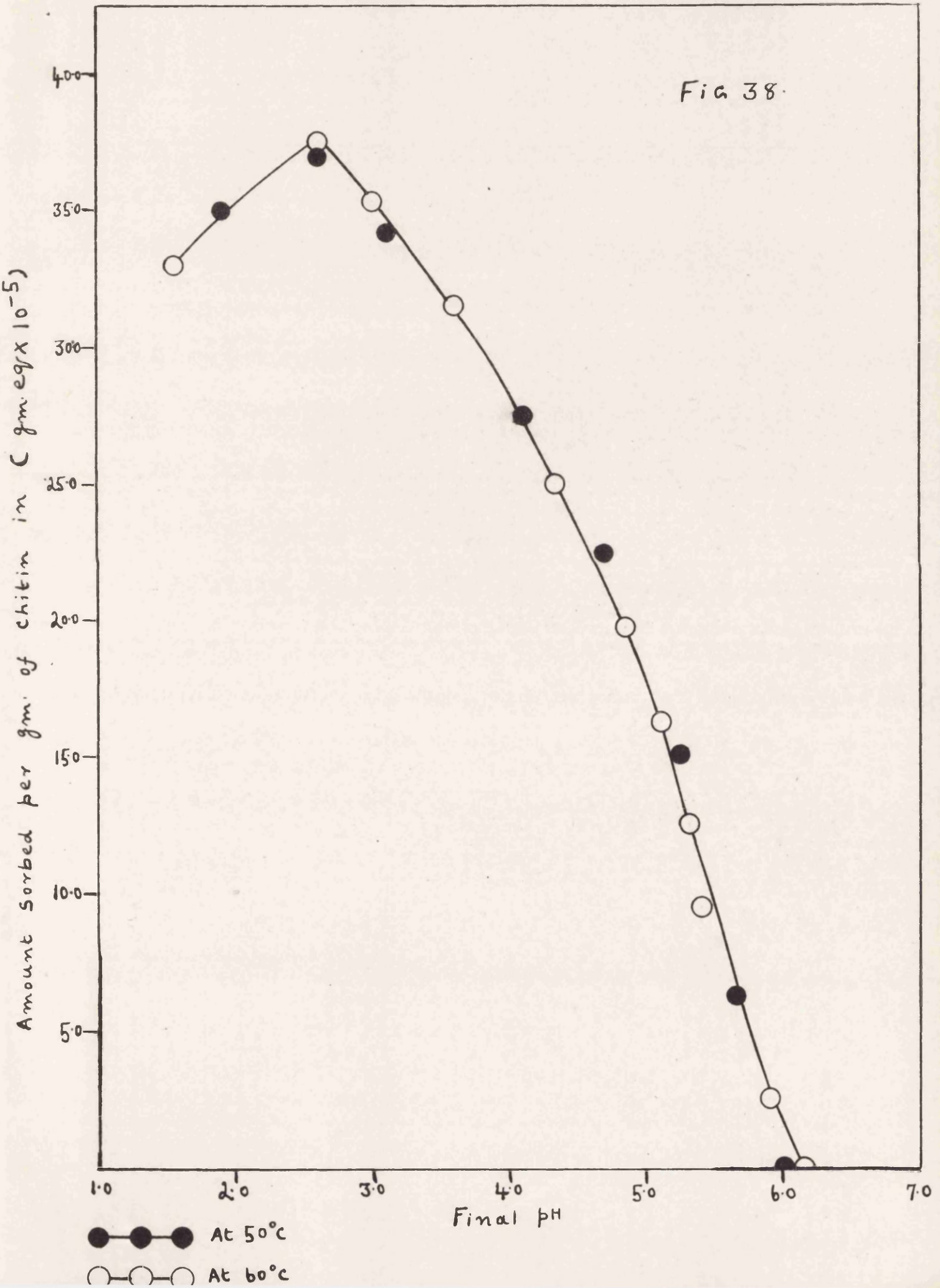
Sorption of benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid

Fig 37.

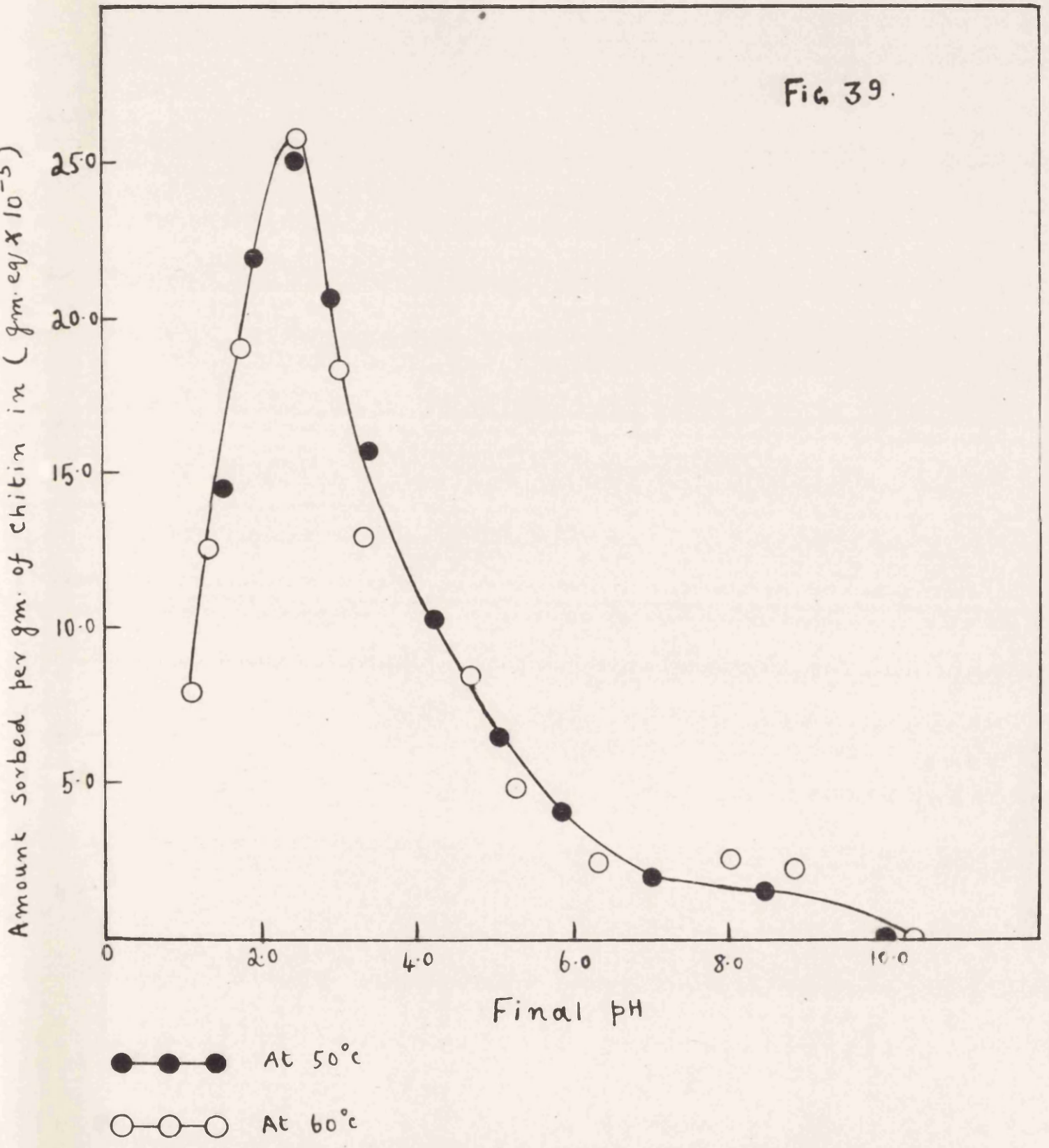


Sorption of naphthalene + ... disulphonic acid

Fig 38.

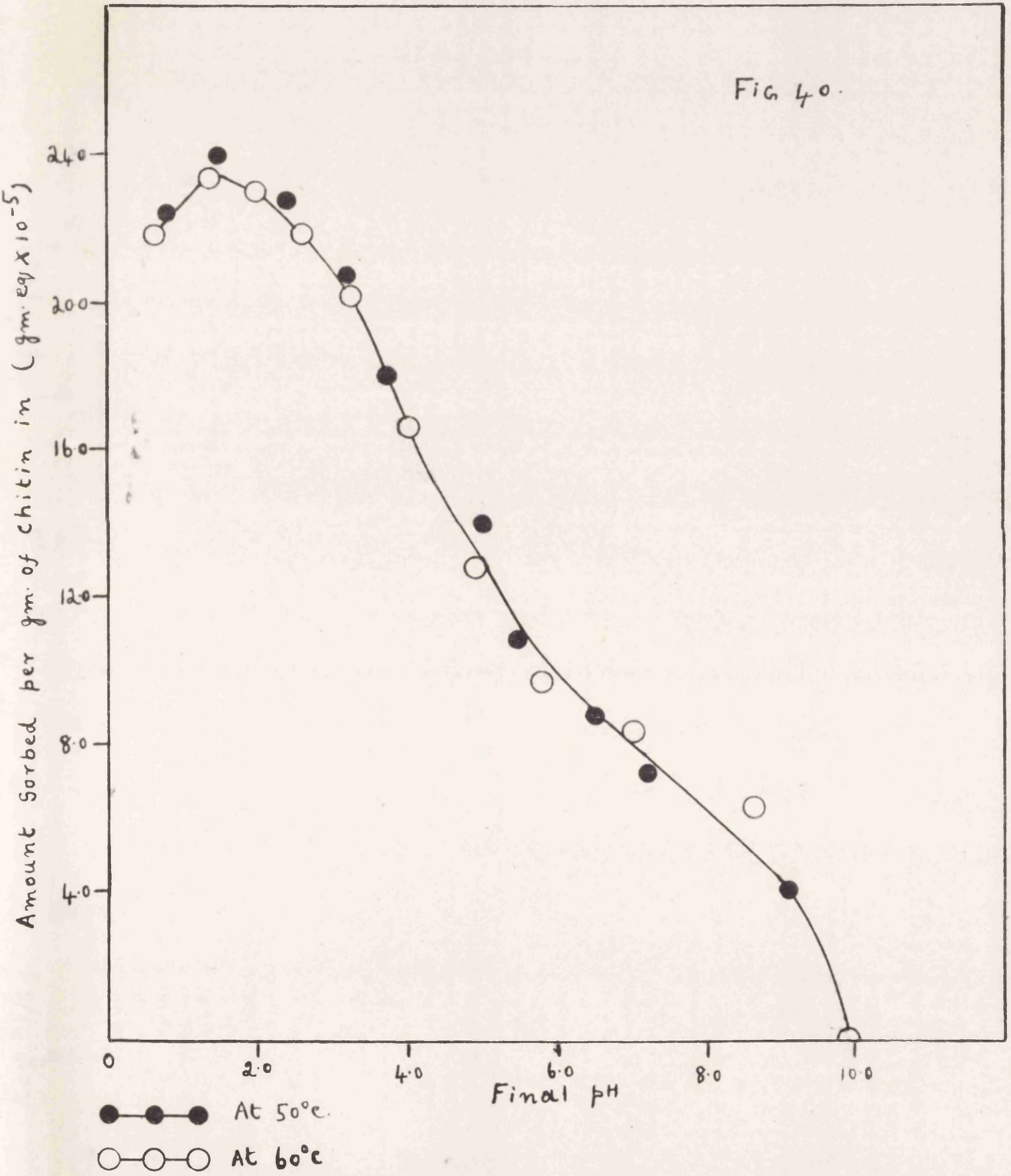


Sorption of benzene-2:5-disulphonic acid azo-2-naphthol-3:6-disulphonic acid.



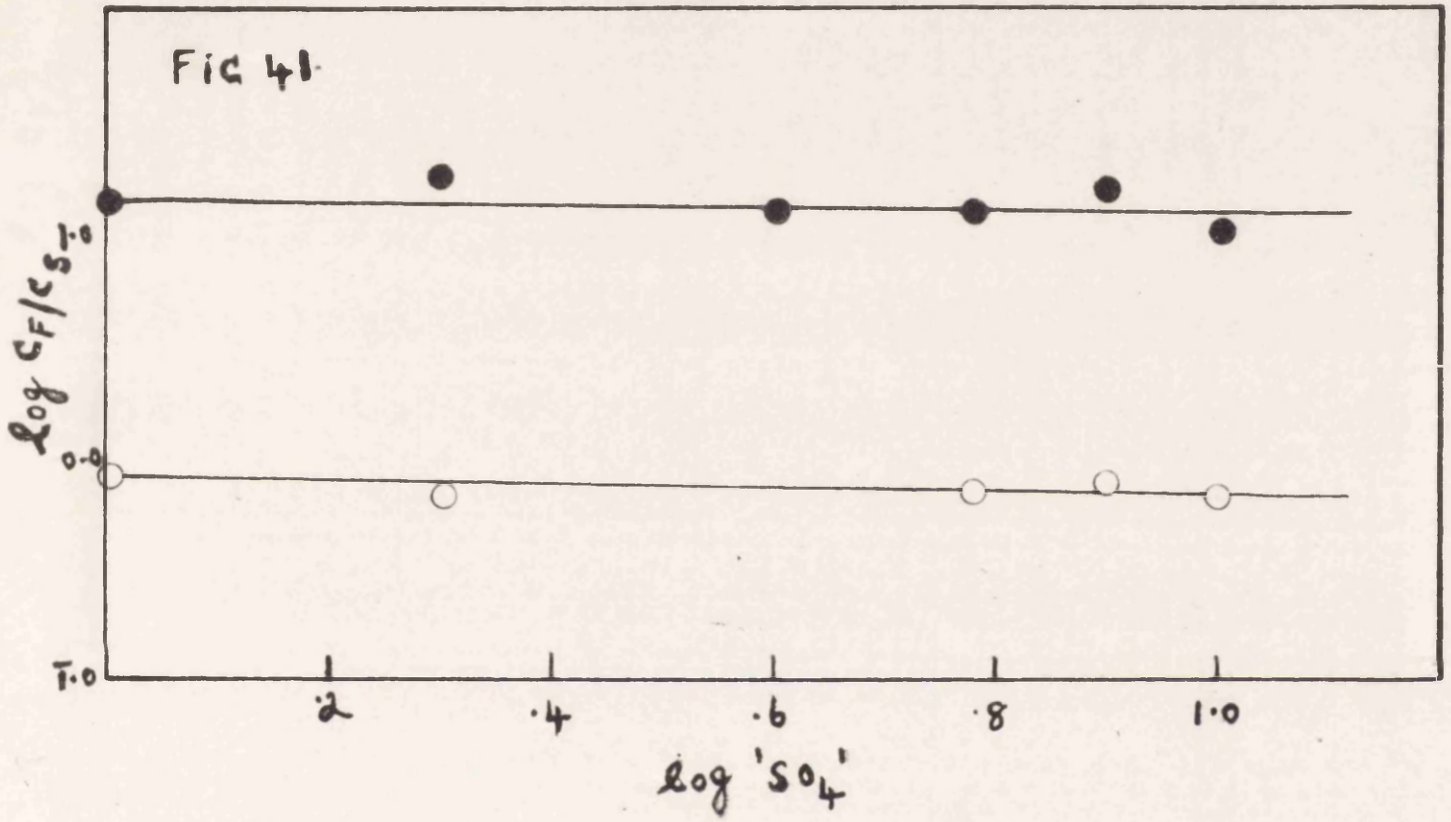
Sorption of **naphthalene**-3:6- disulphonic acid azo-2-naphthol -3:6- disulphonic acid

Fig. 40.



●—●—● Naphthalene-4-sulphonic acid azo-2-naphthol

○—○—○ Benzene-4-sulphonic acid azo-2-naphthol



●—●—● Naphthalene azo-2-naphthol-3:6-disulphonic acid.

○—○—○ Naphthalene-4-Sulphonic acid azo-2-naphthol-6-Sulphonic acid

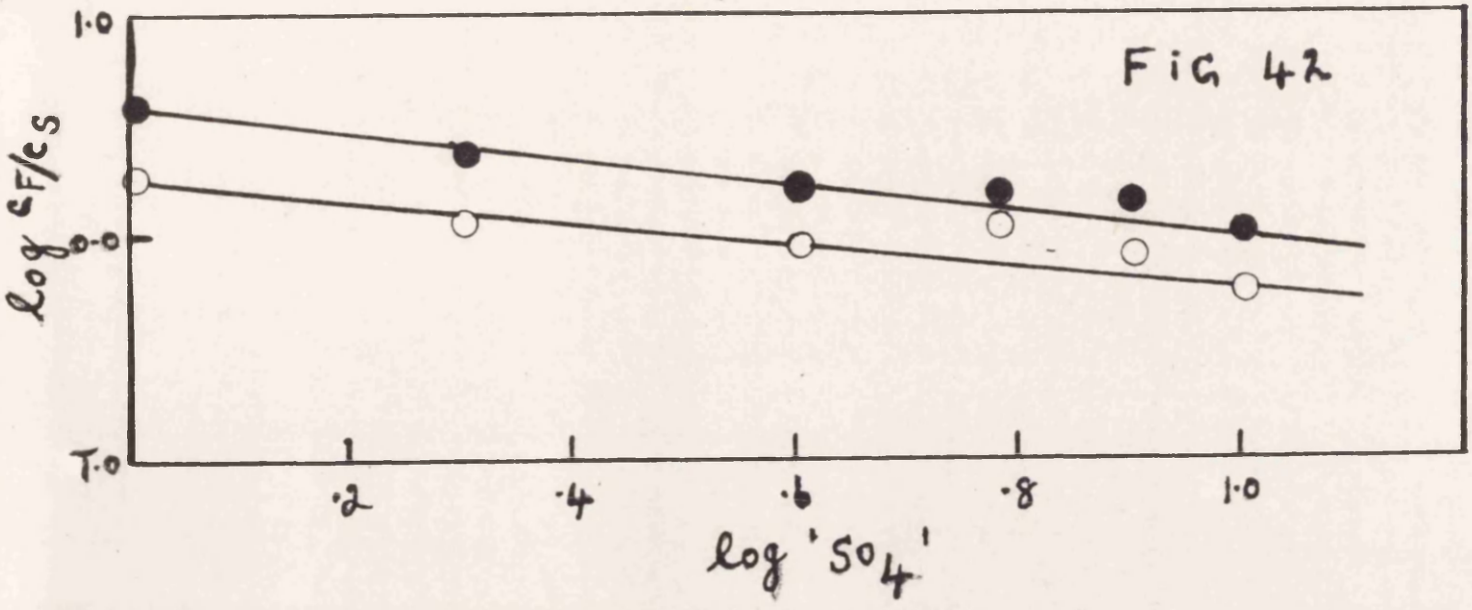
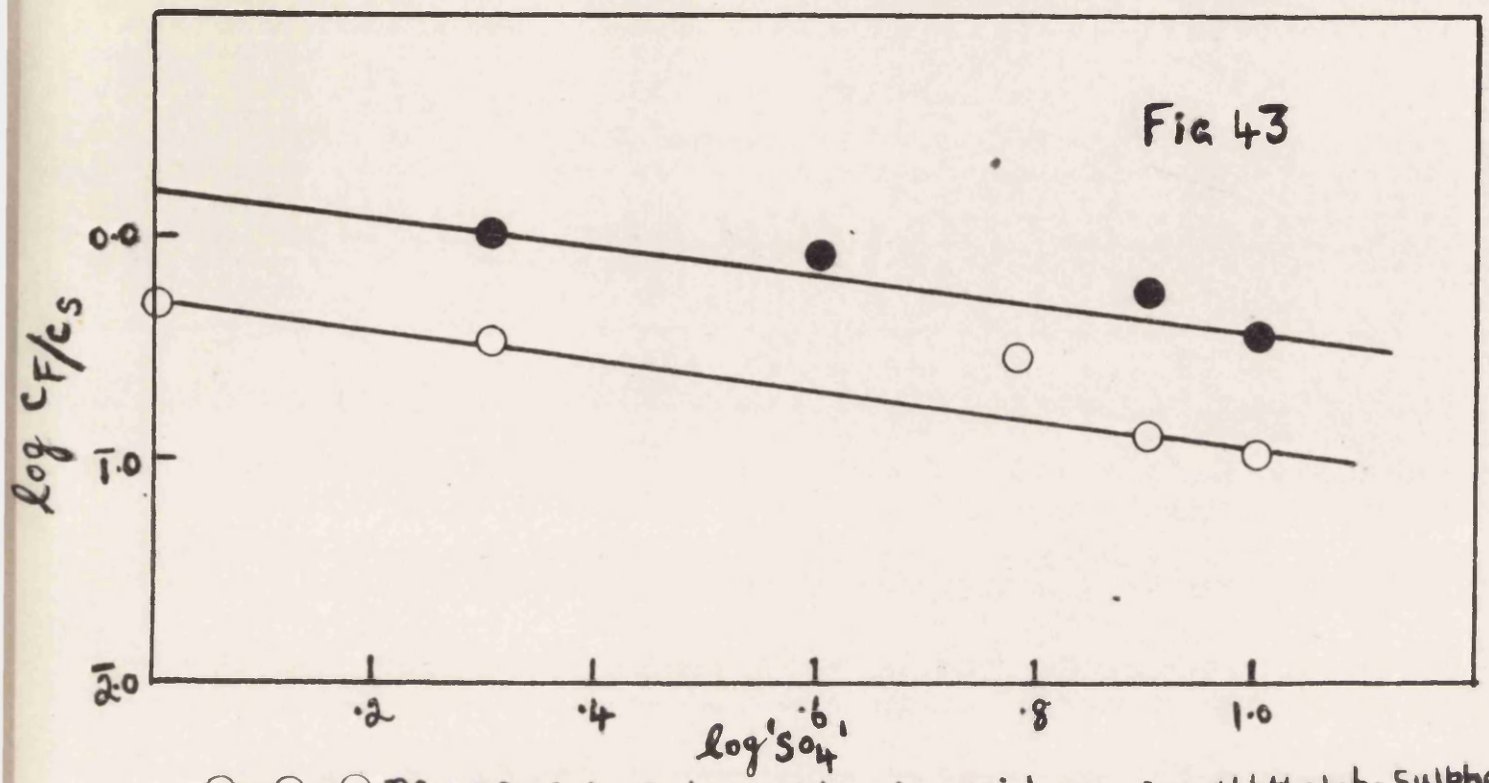


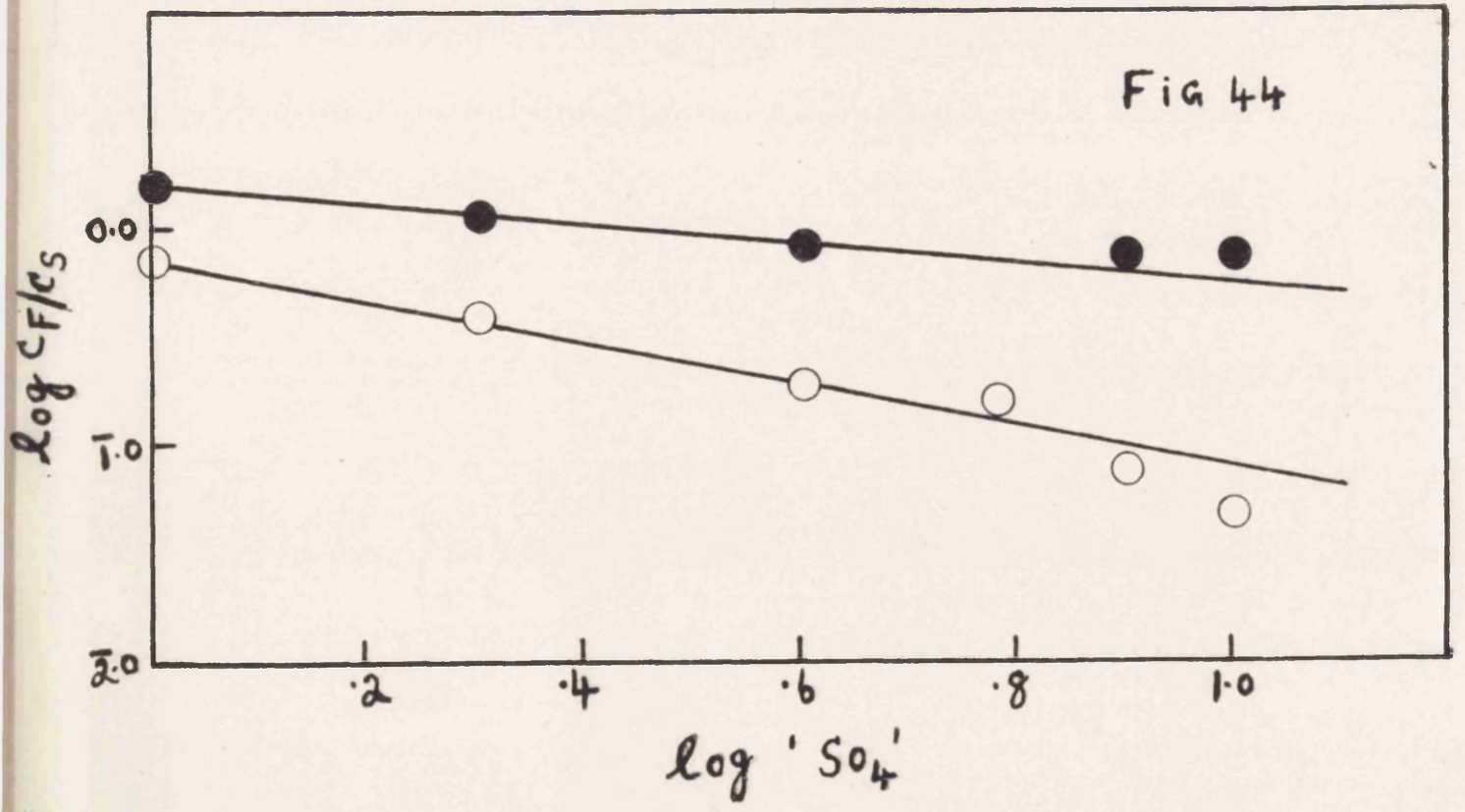
Fig 43



Benzene-2:5-disulphonic acid azo-2-naphthol-6-sulphonic acid

Benzene-4-sulphonic acid azo-2-naphthol-3:6-disulphonic acid

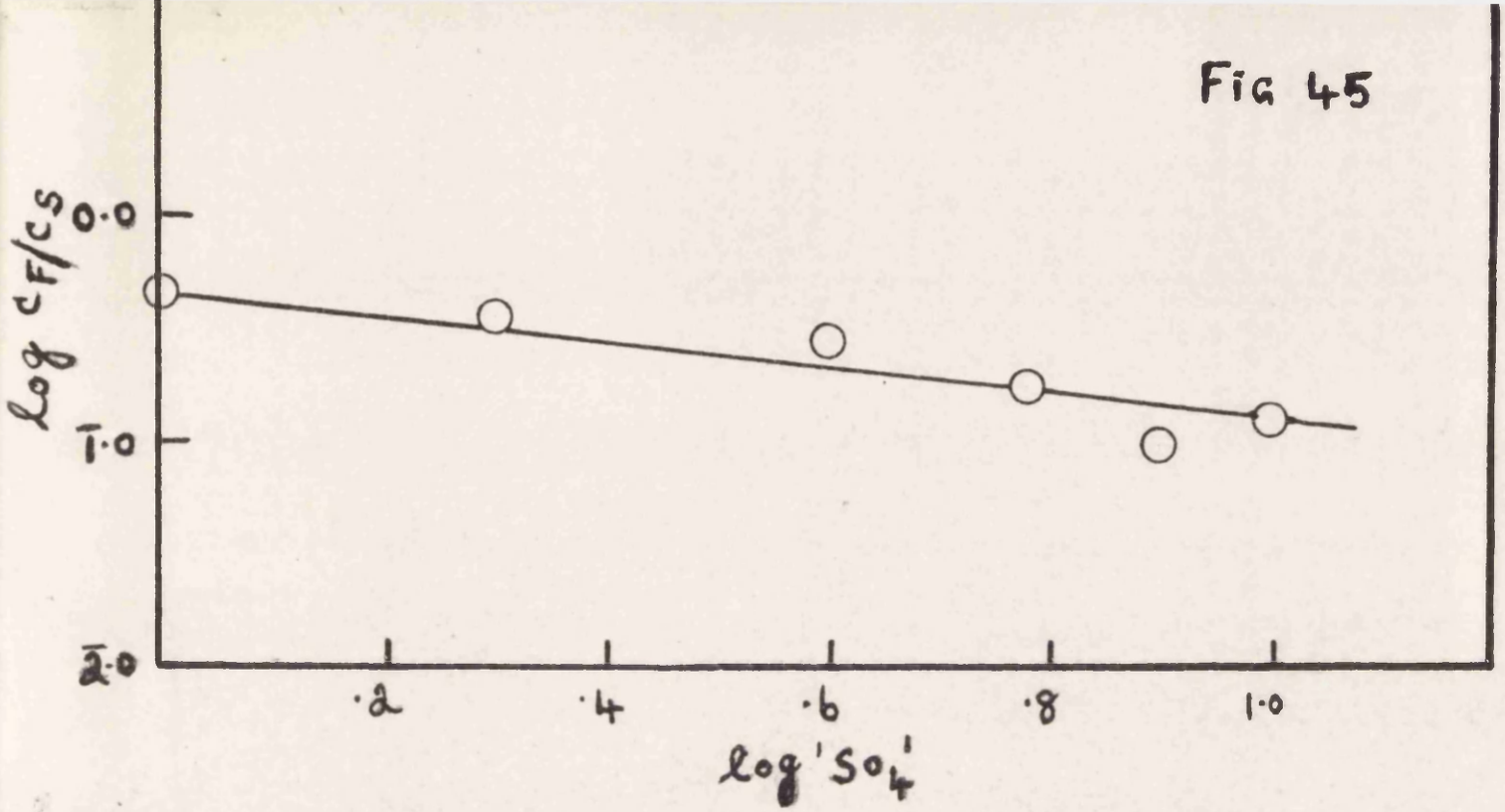
Fig 44



Benzene azo-2-naphthol-3:6-disulphonic acid

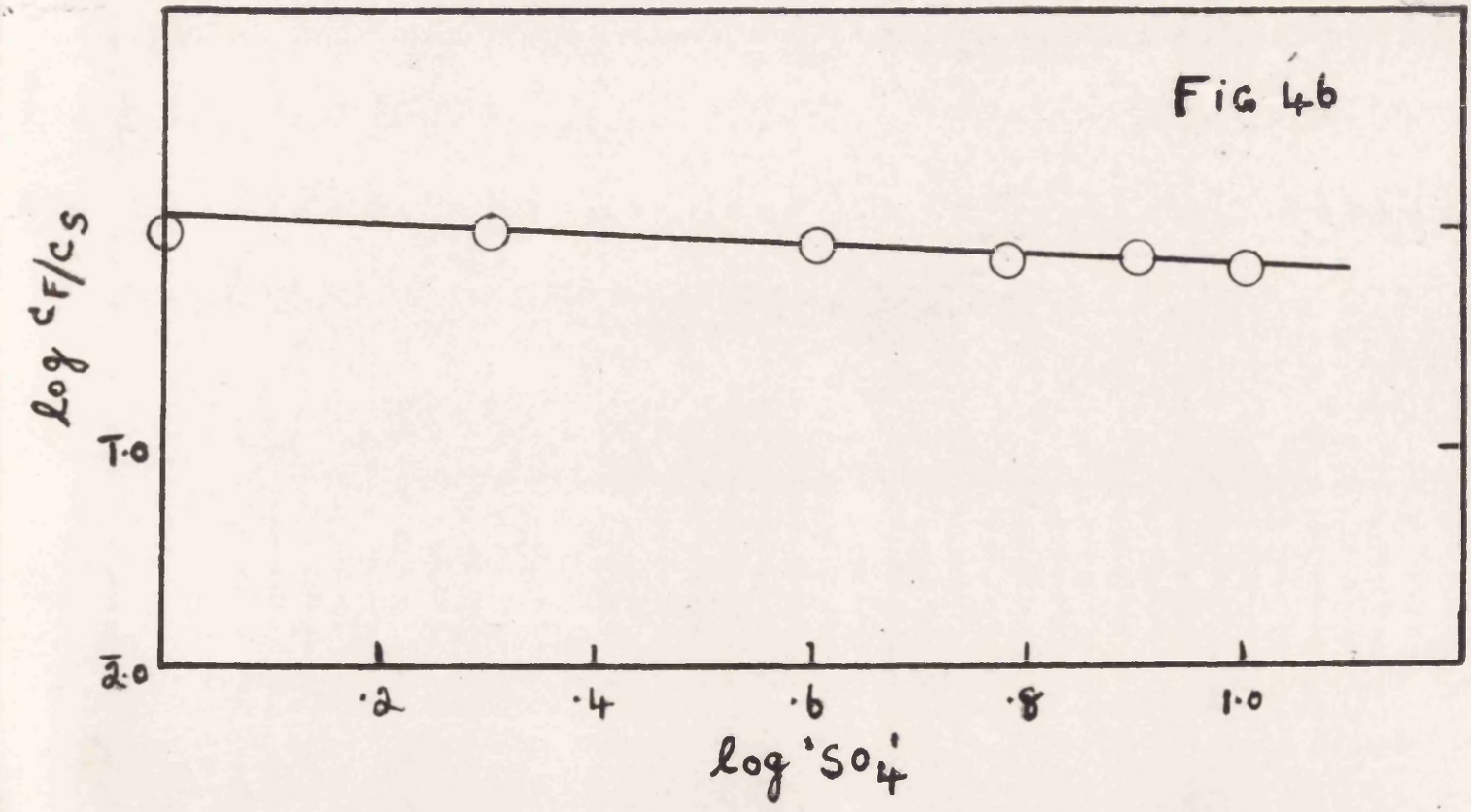
Benzene-4-sulphonic acid azo-2-naphthol-6-sulphonic acid

Fig 45

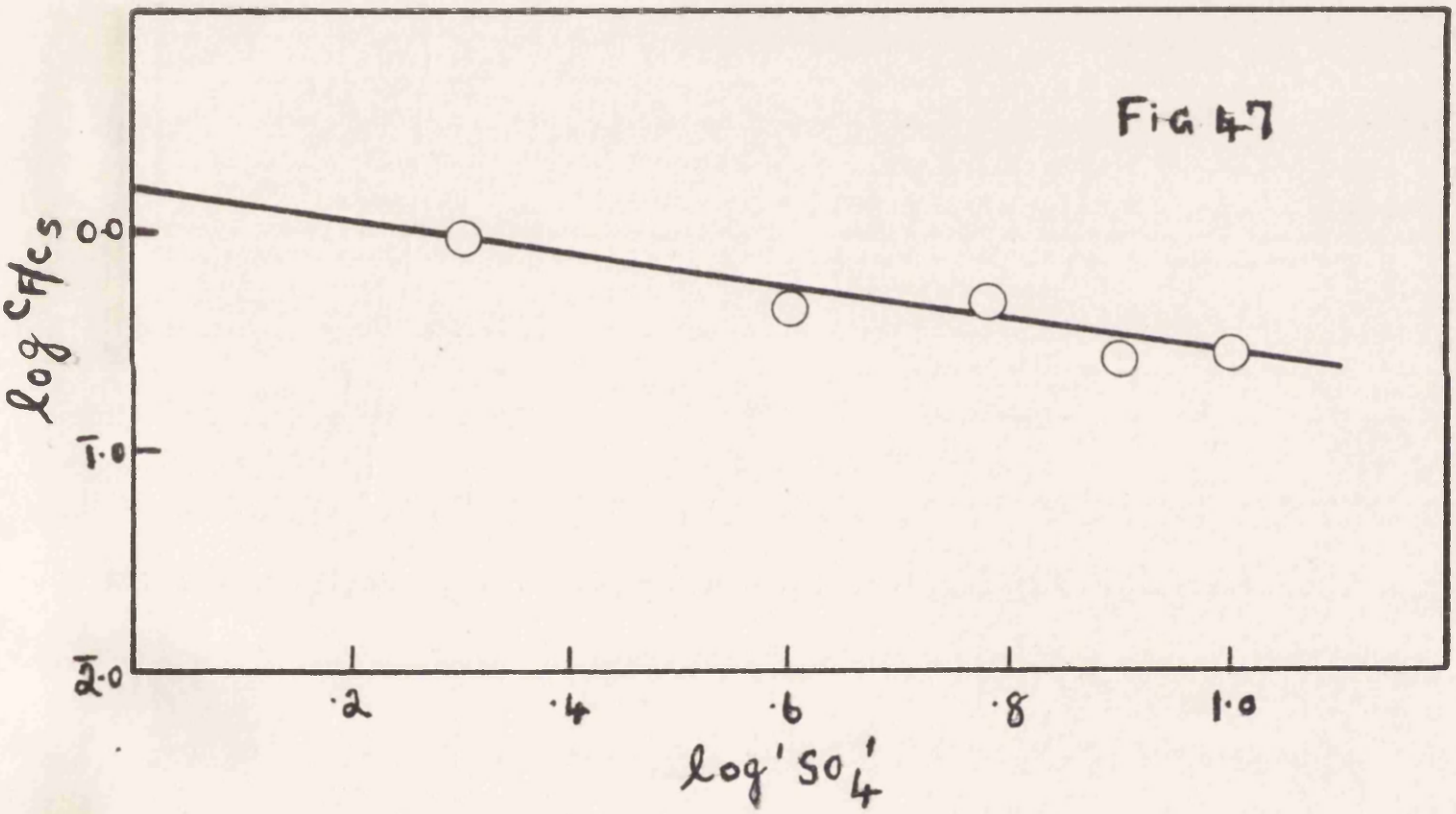


Naphthalene-4-Sulphonic acid azo-2-naphthol-3-6-di Sulphonic acid

Fig 46

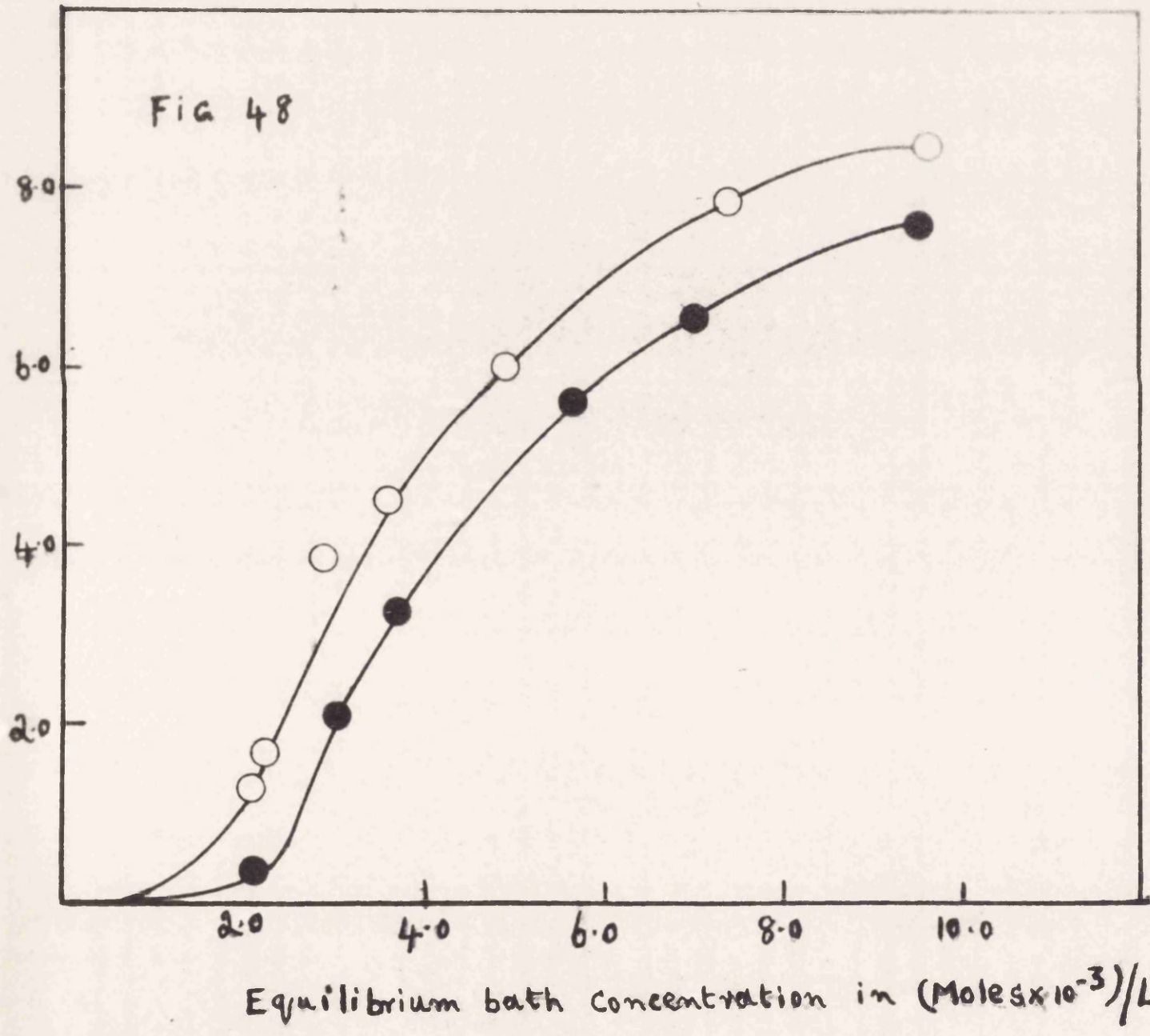


Naphthalene-3:6-di sulphonic acid azo-2-naphthol-3:6-di sulphonic acid



Benzene-2:5-disulphonic acid azo-2-naphthol-3:6-disulphonic acid

Sorption of Phenol from aqueous solution



Sorption of Phenol from iso-octane

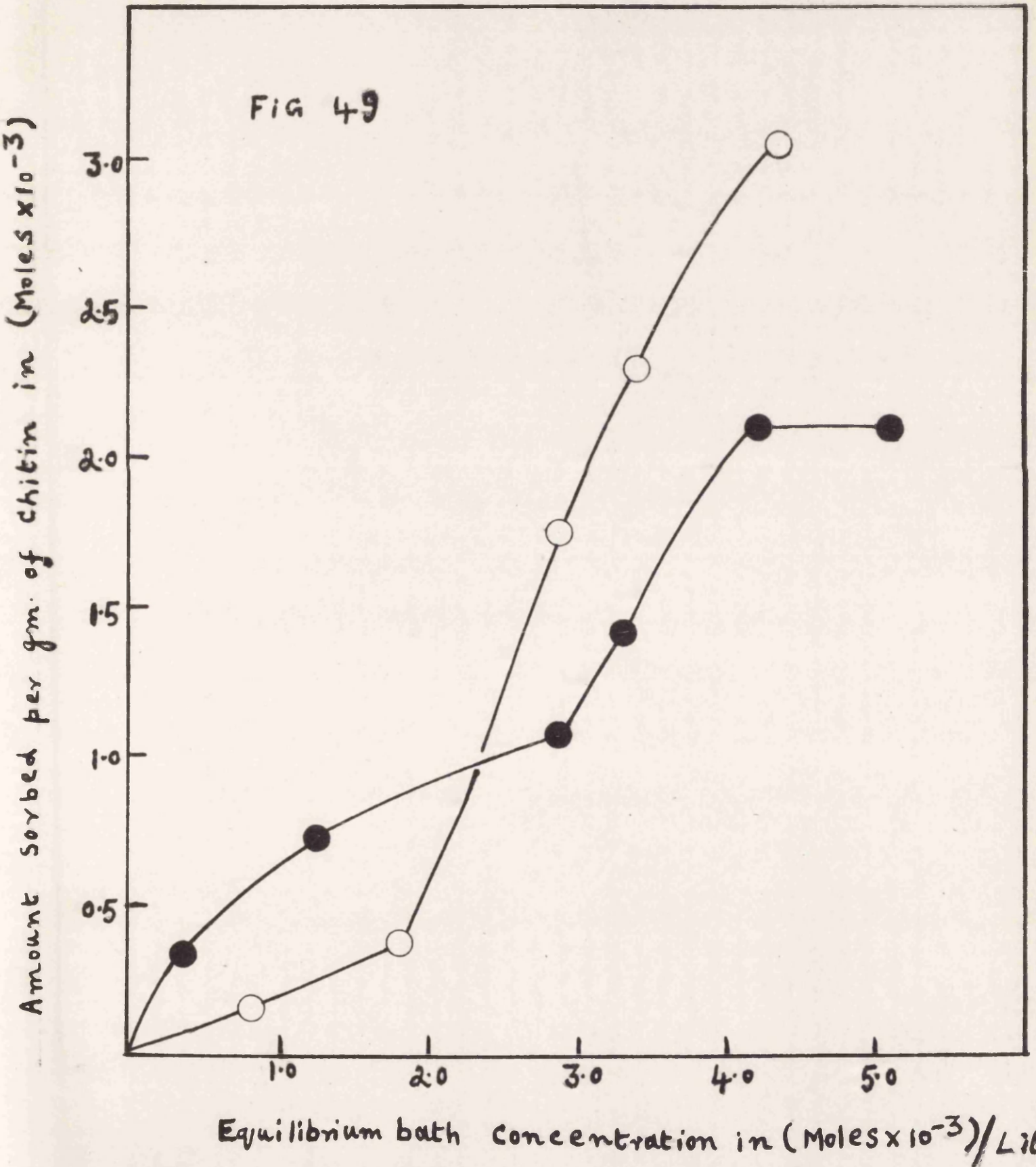
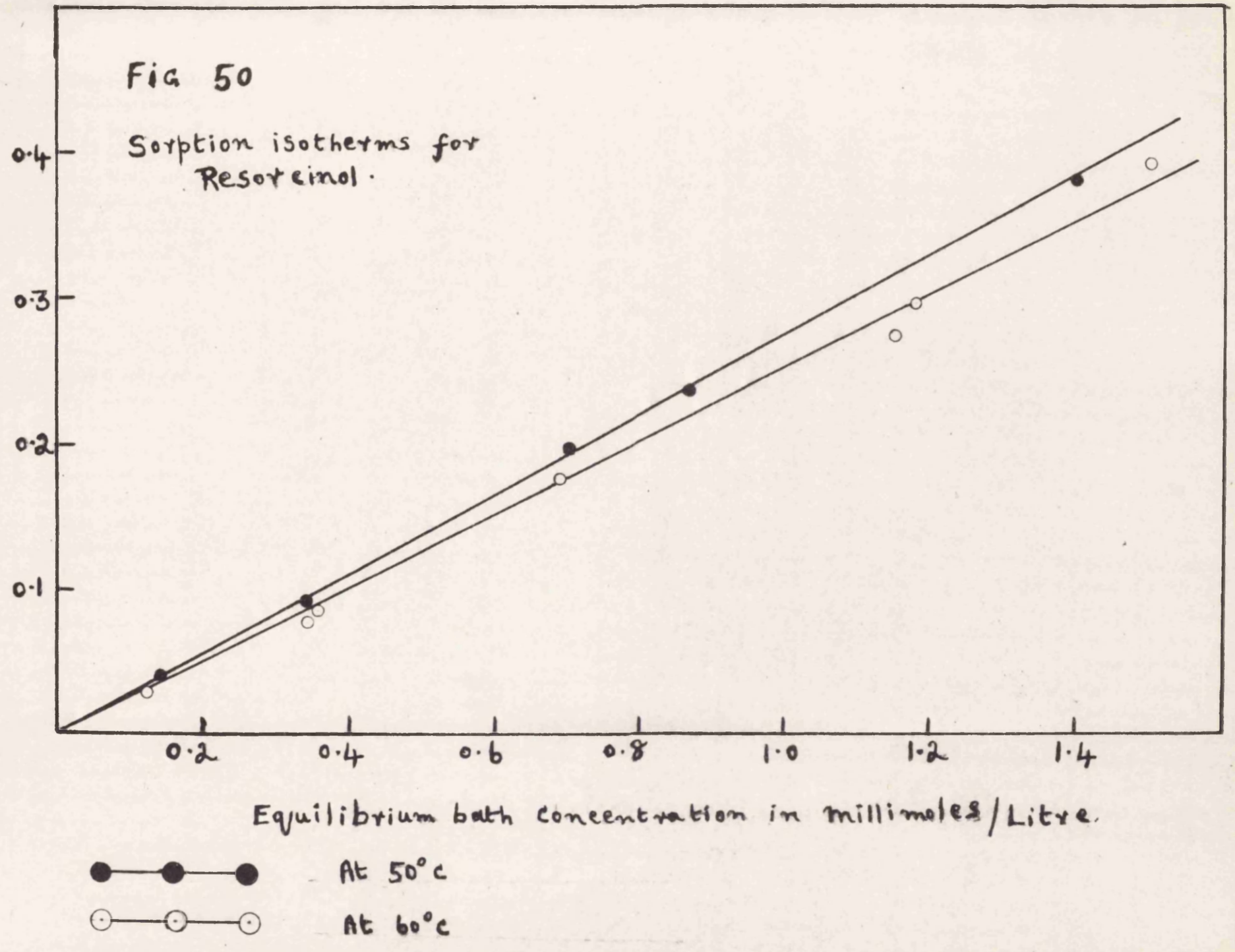
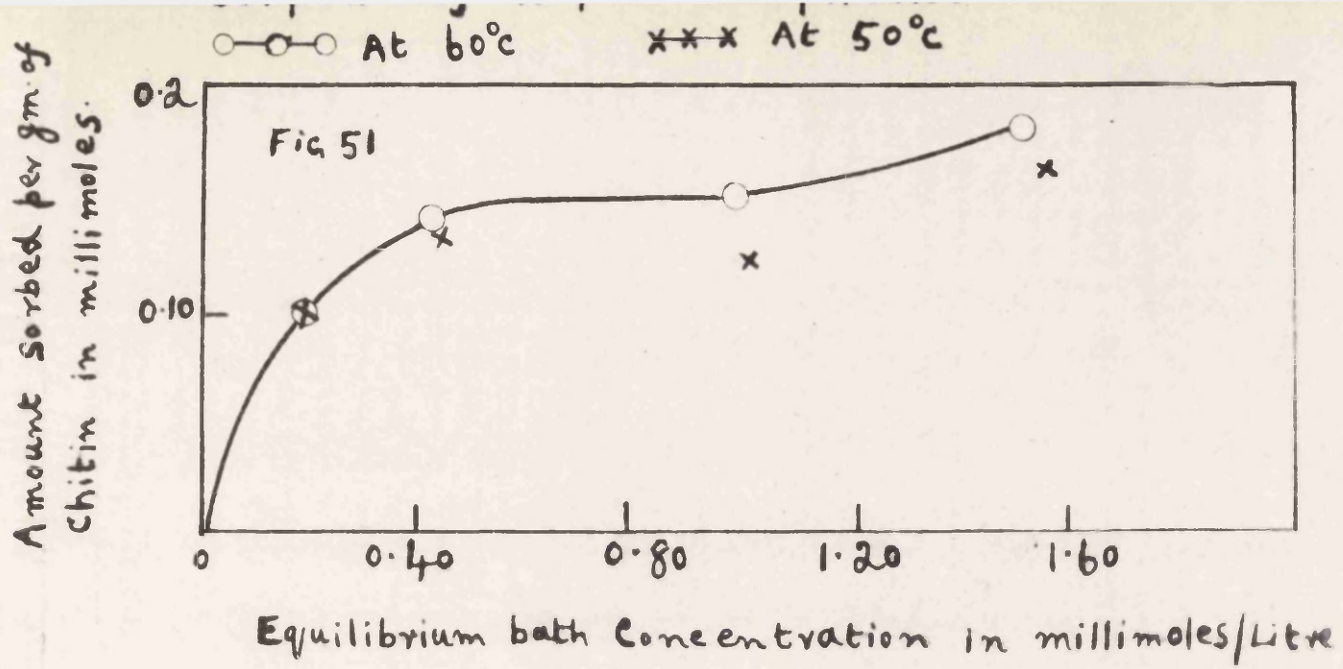
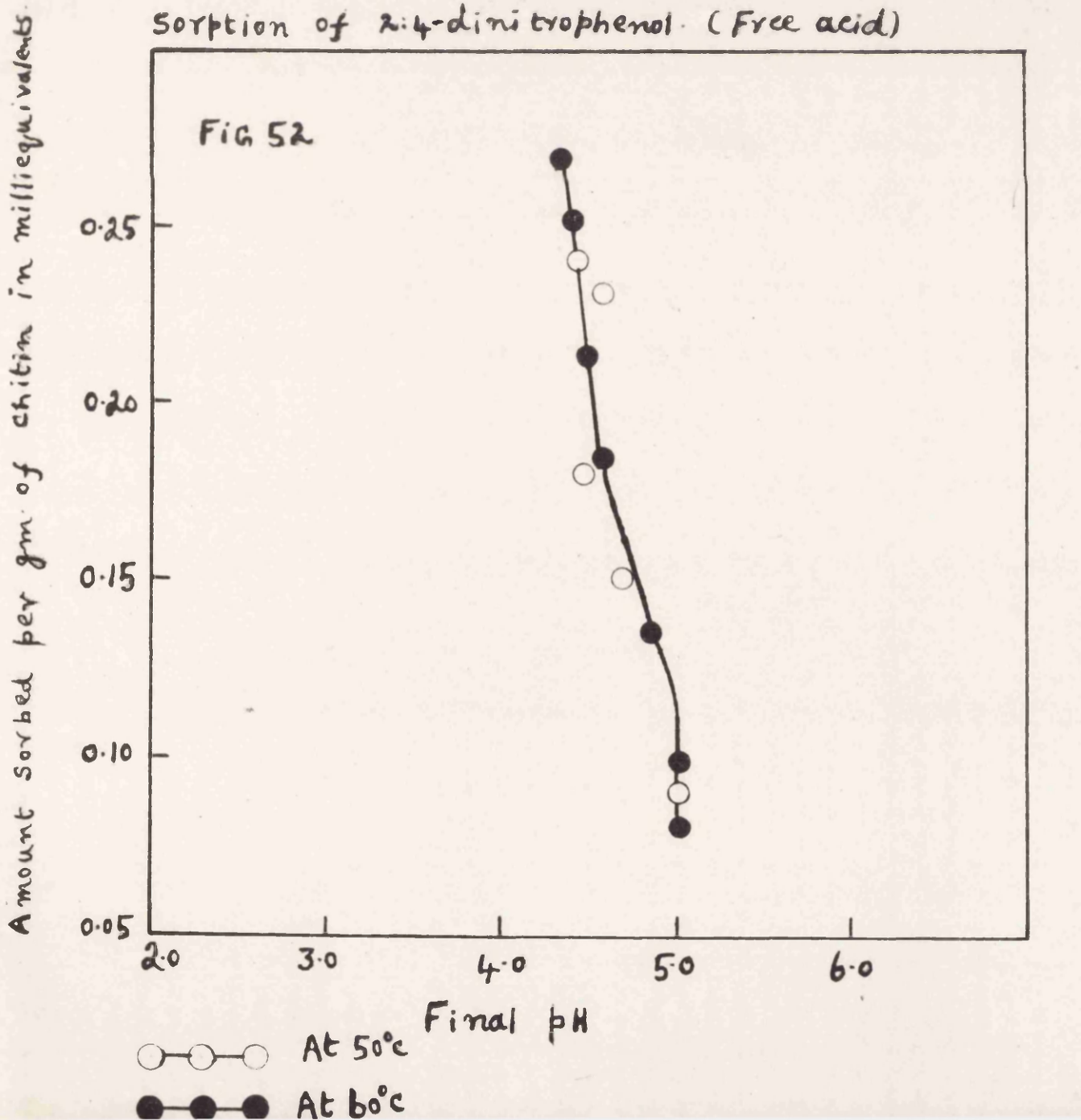


Fig 50

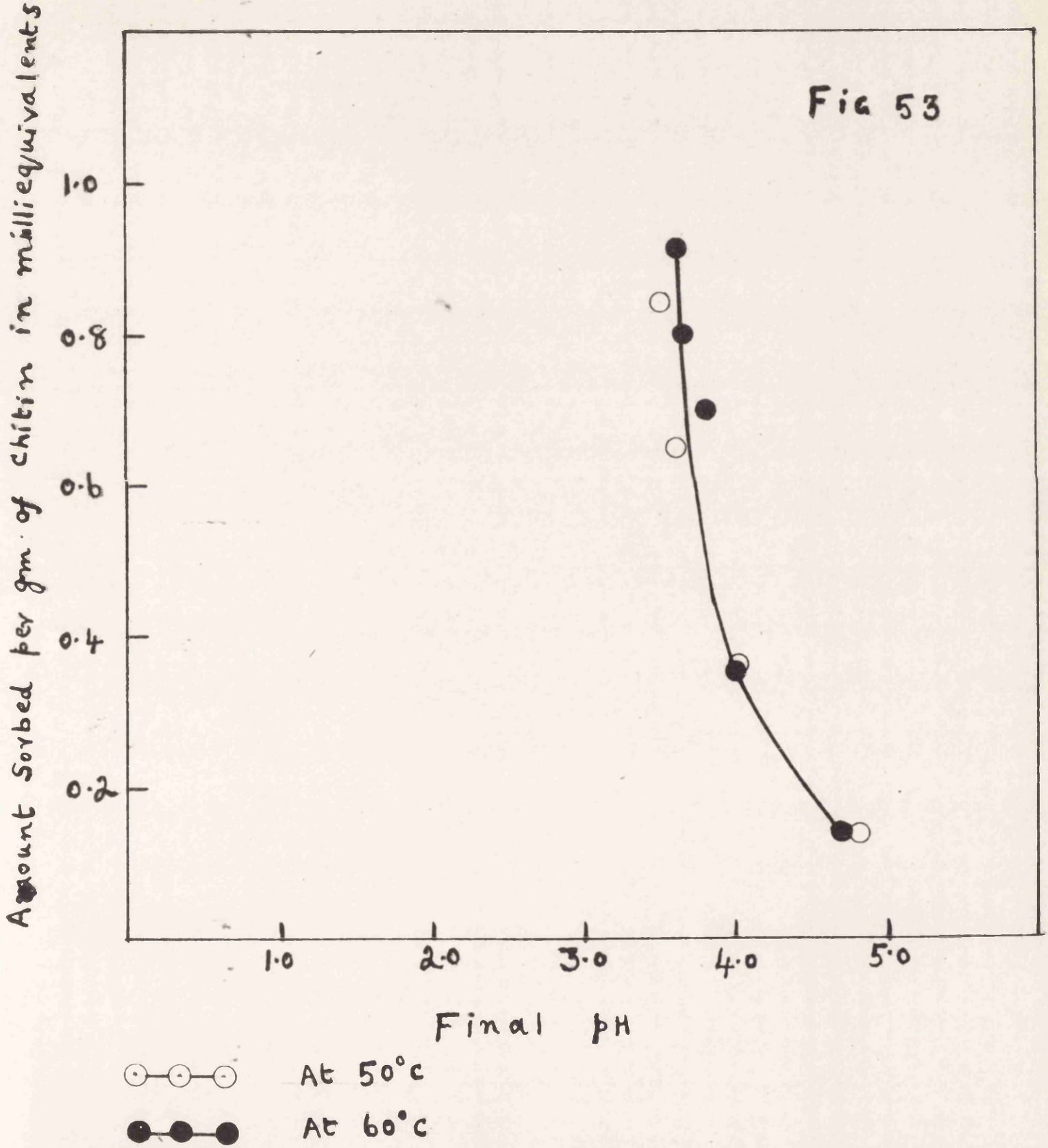
Sorption isotherms for Resorcinol.




At 60°c
At 50°c
Fig 51
Amount sorbed per gm of chitin in millimoles.
0·2
0·10
0
0·40
0·80
1·20
1·60
Equilibrium bath Concentration in millimoles/Litre


Sorption of 2:4-dinitrophenol (Free acid)
Fig 52
Amount Sorbed per gm of chitin in milliequivalents
0·25
0·20
0·15
0·10
0·05
2·0
3·0
4·0
5·0
6·0
Final pH
At 50°c
At 60°c

Sorption of 2:4:6-Trinitrophenol (Free acid)



APPENDIX

Attempted measurement of surface area of cellulose.

Both cellulose and chitin are known to develop a negative potential, when they come in contact with a neutral aqueous solution. Therefore, an attempt has been made to measure the surface area of cellulose through its adsorption of an oppositely charged ion, and it was hoped then to extend the method to chitin. The compound selected was the cationic surface-active agent, cetyltrimethyl ammonium bromide.

This attempt is based on the assumption that the negatively charged surface of the substrate would attract the oppositely charged ions, and knowing the nature of orientation of the solute towards the surface, the area of the same could be calculated from the amount of the compound adsorbed.

However, the results obtained tend to show that the amounts adsorbed correspond approximately to the carboxyl group content of the sample of cellulose investigated. Therefore, this line of attack on this particular problem has not been pursued further.

X-Ray and microscopic investigations on chitin.

The following investigations were carried out in an attempt to find out the degree of crystallinity in chitin.

First, X-ray photographs of the specimen were taken with copper radiation, using nickel filter. The nature of the photographs so obtained appears to indicate a fair degree of crystallinity in the substrate. The values of 'd' obtained for the different lines are given below.

Number of line	Nature of line	'd'
1	Strong line	3.401
2	Strong line	2.563
3	Weak line	2.391
4	Weak line	2.310
5	Strong line	2.086
6	Weak line	1.774
7	Weak line	1.697
8	Strong line	1.608
9	Weak line	1.408
10	Strong line	1.374
11	Weak line	1.241
12	Weak line	1.226

In addition, values for $Sin^2\theta$ have been calculated with a view to finding out whether the crystals are simple cubes, in which case, these values should be in the order of:-
1, 2, 3, 4, 5, 6, - 8, 9, 10, 11, 12, 13, 14, - 16, 17 etc.

But the values obtained for $Sin^2\theta$ have been tabulated below, which appear to show that the crystals in chitin are neither simple cubes nor body centred nor face centred cubes.

Number of line	$Sin^2\theta$
1	0.0514
2	0.0905
3	0.1039
4	0.1118
5	0.1366
6	0.1886
7	0.1974
8	0.2300
9	0.2993
10	0.3159
11	0.3859
12	0.3965

The powder sample was also examined under the microscope, using polarised light and with crossed nicols, the sample being mounted in a medium of refractive index 1.500. Here, the crystals were clearly seen, and they were found to be leaf-shaped in their pattern. No colour fringe was noticed, but four extinctions, each at 90^o were observed.

Therefore, the above results appear to indicate that the sample of chitin used has a fairly high degree of crystallinity. It is hoped to pursue these investigations further.

The author wishes to acknowledge his grateful thanks to Mr.Kabi, of the Metallurgy Department of this College for his invaluable assistance with the X-ray investigation.

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