STUDIES IN THE MECHANISMS OF ADSORPTION FROM SOLUTION

I. ADSORPTION AT EQUILIBRIUM

II. HYDROGEN-BOND FORMATION

BY

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Publications

The work described in this thesis has been included in the following papers.

Part I, Section I.

"Studies in Adsorption. Part XI. A System of Classification of Solution Adsorption Isotherms, and its Use in Diagnosis of Adsorption Mechanisms and in Measurements of Specific Surface Areas of Solids", by C.H.Giles, T.H.MacEwan, S.N.Nakhwa, and D.Smith, J.Chem.Soc., 1960, 3973-3993

Section III

"Studies in Adsorption. Part XIII. Anomalous (Endothermic) Effects of Adsorption on Inorganic Solids" by C.H.Giles, J.J.Greczek, and S.N.Nakhwa, J.Chem.Soc., 1961, 93-95.

Section II

"Studies in Adsorption. Part XV. The Measurement of Specific Surface Areas of Solids by Solution Adsorption of p-Nitrophenol" by C.H.Giles and S.N.Nakhwa has been accepted for publication by J.Appl.Chem., some changes are at present being made according to a referee's suggestions.

Part II, Section I

"Studies in Hydrogen-Bond Formation. Part IX. Bonding between Esters and The Chloro-Group" by C.H.Giles and S.N.Nakhwa, J.Appl.Chem., 1961, 11, 197-201.

Summary

This thesis describes a series of investigations in the thermodynamics of solution adsorption, designed to throw light on the mechanisms of the process; these investigations include qualitative and quantitative studies of the specific hydrogen-bond forces responsible for some kinds of adsorption.

Solution adsorption isotherms are divided into four main classes according to the slope of the initial portion of the curve to the concentration axis, and thereafter into subgroups.

The four classes are: S Curves. The initial portion is convex to the concentration axis. They represent high affinity of the solvent for the solid substrate and low affinity of the solute; the surface becomes increasingly attractive with coverage; this is the case when molecules attract each other strongly so that they tend to orient vertically on the surface. L Curves. The normal or "Langmuir" isotherms, the initial portion is concave to the concentration axis. These curves usually indicate that the adsorbed molecules lie flat on the surface, but when competition from the solvent is weak (e.g. polar solutes on polar substrates from non-polar solvents)

and the intermolecular attraction is high, even vertical orientation can produce these curves. H Curves. ("High affinity"). (These commence at a positive value on the "concentration in solid" axis.) The solute has very high and the solvent low, affinity for the substrate. They are often given by solutes adsorbed as ionic micelles and by high affinity ions exchanging with low affinity ions. C Curves ("constant partition"). These are linear curves, given by solutes which penetrate into the solid more readily than does the solvent.

The sub-groups of these classes are those in which there is evident: (1) only an initial portion of the isotherm is obtained; (2) the first plateau indicating the completion of the first layer; (3) a plateau, followed by a further rising portion, caused by either adsorption on the top of the first layer or by further penetration of the solute into the accessible regions, or by reorientation of the molecules from the flat to the vertical position; (4) a second plateau, caused by completion of the processes given under (3); (mx) a maximum, followed by a decrease in adsorption, perhaps due to predominance of solute-solute attraction over solute-substrate attraction.

The measurement of specific surface area of solids has hitherto been the principal use of solution adsorption isotherms. p-Nitrophenol is one of the best solutes for this purpose because, it (i) is highly polar and therefore attaches to the whole surface of polar solids; (ii) has a hydrophobic benzene nucleus which enables it to be adsorbed by non-polar solids; (iii) has a small planar molecule and is often adsorbed as a vertically oriented close packed monolayer; (iv) is not highly surface active and therefore does not form three dimensional micelles at the solid surface; (v) is coloured and can be easily analysed; (vi) is soluble in water, but is also soluble in non-polar solvents so that it can be used with water-soluble solids.

p-Nitrophenol when adsorbed from water on (i) polar solids gives an S isotherm and the cross-sectional area occupied by each p-nitrophenol molecule is 25 A^2; on (ii) non-polar solids gives a L curve and the area occupied per molecule is 52.5 A^2. From non-polar solvents it gives a L curve and when vertically oriented its cross-sectional area is then 15 A^2.

p-Nitrophenol is anionic and is not readily adsorbed by acidic solids such as silica and titania. An acid wool dye (C.I.62,055) is found to be more suitable in such cases. It is adsorbed readily on acidic substrates, and gives a S isotherm from water solutions. The area occupied by each dye molecule for edge-on orientation (S curve) is

87.1 A^2. The surface area values obtained either by p-nitrophenol or dye (C.I.62,055) adsorption agree well with those obtained by low temperature nitrogen adsorption.

Adsorption from solution, as is vapour phase adsorption, is exothermic. In the case of two dyes (C.I.26,115 and 44,090) on alumina and silica however it is endothermic. These dyes are highly aggregated in aqueous solution. From a dissociating solvent (methanol) the adsorption is normal. Normally when a solute is adsorbed from solution, it aggregates on the substrate because the solute molecules are brought closer together on the substrate. In the anomalous cases it appears that the solute is partly dissociated on adsorption from aqueous solution, hence the anomalous adsorption.

Orange I (C.I.14,600) also gives apparently anomalous isotherms, but this is actually due to decomposition of the dye at high temperatures.

The refractometric method is used to demonstrate hydrogen-bond complex formation between aromatic chloro-groups and the α methylene groups of ester residues. The bond between chlorobenzene and ethyl acetate has an energy ca. -3 kcal./mole in aqueous ethanol. Cellulose acetate strongly adsorbs chlorobenzene, but it does not adsorb benzene at all; this suggests that the bonding must be taking place at the chloro-group. This type of bond probably assists the adsorption of non-ionic dyes containing chloro-groups by cellulose acetates and related polymers and the plant growth-promoting activity of chlorophenoxyacetic acid derivatives.

A refractometric method designed to study the hydrogen-bond energies between solutes in aqueous solutions, is described, and some results of its use are given.

GENERAL INTRODUCTION

Adsorption.

The atoms or molecules constituting a solid are held together by different forces: electrostatic or Coulomb forces, exchange or homopolar valence forces, van der Waals forces, etc. In most solids several of these are operative, with one or the other predominating. An atom located inside the body of the solid is subjected to equal forces in all directions, whereas an atom in the plane of the surface is subjected to unbalanced forces: it is attracted inwards and to each side by its neighbours, but there is no outward attraction to balance the inward pull. Therefore the surfac of a solid is in a state of strain or unsaturation. When a solid is in contact with any gas or solution a significant amount of material may be removed from the main body of the fluid and concentrated on the surface of the solid. Atoms or molecules of the concentrated substance saturate some of the unbalanced forces of the surface, thereby decreasing the free energy or the surface tension of the solid. A substance is said to be "adsorbed" if the concentration of the substance in a boundary region is higher than in the interior of the adjoining phases (gas or solution and solid). The solid that takes up the substance is called the "adsorbent" and the substance which is taken up the "adsorbate". A substance becomes adsorbed by a process of "adsorption", or accumulation in the boundary region.

Interfaces.

A system is an assembly of phases. The boundary between adjacent phases comprises an 'interface'. The interfaces formed by two phases are of several types: the liquid-gas; the liquid-liquid; the solid-gas; the solid-liquid; and the solid-solid interfaces. An important feature of the interface between two phases is that its depth or thickness is ordinarily molecular in dimension (say 100 A, or less) while its extent (length and breadth) is macroscopic in dimension. The area and the thickness of the interfacial region are of importance in adsorption phenomena.

Interfaces may be classified in two ways: as mobile and as immobile. Mobile interfaces include liquid-gas and liquid-liquid interfaces. These are characterised by an effective interfacial tension[1] under which the surface always tends to contract spontaneously. The molecules in mobile interfaces are continually being shuffled by the normal molecular motions of the fluid phases. The final state of the interface is thus a compromise: an equilibrium state in which the orienting forces of the interface are balanced by the shuffling effect of the molecular motions.

This leads to the observable fact that the mobile interfaces are usually homogeneous in directions parallel to their surfaces.

Immobile interfaces, on the other hand, are constrained by the rigidity of the solid phase, which forms at least one of the interface components. They include solid-gas, solid-liquid, and solid-solid interfaces. There are interfacial tensions here, but the interfaces may not contract because of their high viscosity. The opportunities for orientation in these interfaces are greater than those in mobile interfaces, for the solid phase contributes less fluidity, though even in solids, there may be considerable molecular vibration and rotation. The immobile interface is further distinguished by the fact that it may be grossly inhomogeneous. It may differ in properties in different directions, as on the surface of anisotropic crystals; and it may be inhomogeneous in directions parallel to the phase surfaces.

Adsorption takes place in the interface. The substance adsorbed may originate in one or more contiguous phases. The molecules of adsorbate pass from one phase into the interface, where they remain for a period of time. In a reversible process, the molecules can return to the phase from which they came or can reversibly pass into another phase, their place in the interface being taken by other molecules. At equilibrium the number of molecules entering the interface in a given period of time is the same as the number of molecules leaving the interface. The requirement for adsorption is, according to the definition, that the concentration of the substance in the interface be greater than that of the substance in the contiguous phases.

Only solid-liquid interface is important from this thesis point of view.

Solution-solid interface:

Whenever a solid adsorbent is introduced into a solution the components of the solution will compete for the interface. Williams[2] was apparently one of the first to call attention clearly to the role played by adsorption of solvent. He said: "The tendency has been to regard the solvent as a 'space' in which the solute has play", and he pointed out that this introduced errors in adsorption calculations in which the adsorption of the solvent was not evaluated. These errors were small with dilute solutions, but became important with increase in concentration of solute. Studies with adsorbents and mixtures[3] showed that at the ends of the concentration ranges the component present in smaller amount is usually preferentially adsorbed.

The factors that may be involved in the simple adsorption of a substance A from a solution in B on-to a solid surface are considered here. The factors operating: (1) from the solution side of the interface, (2) from the adsorbent side, and (3) within the interface, have to be considered. In each case the direction of influence of the factor toward or against adsorption is weighed.

1. Factors from the solution side of the interface.

(i) When a molecule is adsorbed from a solution it moves out of a three-dimensional region into a two-dimensional one, with attendant restrictions on its freedom. According to the calculations of Broda and Mark[4] and following the statement of Baum and Broda[5] the degrees of freedom corresponding to vibration of adsorbed molecules "are partly frozen, and do not contribute fully to the phase volume". Other things being equal, the state in which a greater number of degrees of freedom are active is the more probable. Accordingly, this factor, operating from the side of the solution, so to speak, works against adsorption.

(ii) If there are any interactions between the molecules of A and B that tend to cause them to adhere; if there are any hydration effects; or in general, solvation effects, where the term is used loosely and does not imply any special theory; then such effects would tend to hold the molecules of A in solution with B. Such interactions would operate against the escape of the molecules from solution whether into the vapour phase or into the interface. They would decrease adsorption[6].

Cassidy[7] studied the adsorption of fatty acids on charcoal from ligroin and petroleum ether. The acids showed lower adsorption in ligroin, in which they are more soluble.

Bhatnagar et al.[8] found the order of adsorption of benzoic acid on a dried phenol-formaldehyde resin from different solvents to be, methanol $<$ benzene $<$ ethanol $<$ acetone $<<$ carbon tetrachloride $<$ carbon disulphide $<<$ water. The order of solubility is methanol $>$ ethanol $>$ acetone $>>$ benzene $>$ carbon disulphide $>>$ carbon tetrachloride $>>$ water.

Bartell and Fu[9] discussed the role of solubility in adsorption and concluded that the influence of solubility upon extent of adsorption can be determined legitimately only if the solvents being used have the same interfacial tension against the adsorbent in question. Thus, benzene and carbon tetrachloride show approximately the same adhesion tension against silica, indicating that the interfacial tension must be of comparable magnitude. One would then be justified in comparing results obtained with these two liquids. They came to the same conclusion as regards solubility and adsorbability.

If the accumulation in an interface is considered as a manifestation of the escaping tendency of the adsorbate from the solution phase, then less soluble substances should tend to be adsorbed to a greater extent than more soluble ones.

(iii) If the molecules of A are not very compatible with those of B; if for example, they tend to associate; or if B itself tends to associate and exclude A, then such behaviour might make A less soluble in B than expected. This would, in effect, tend to "squeeze" the molecules out of solution and into the interface. Such effects would tend to increase adsorption[6].

Bakr and McBain[10], in studying the adsorption of toluene and acetic acid on sugar and animal charcoals found that acetic acid is less adsorbed at high temperatures. At 245°C practically no acetic acid, but considerable toluene was adsorbed. This was related by these authors to the known effect of high temperature in dissociating the acetic acid dimers.

Heymann and Boye[11] suggested that the adsorption of benzoic acid from nitro-benzene on to charcoal is greater than that from acetone or nitromethane because benzoic acid is exceedingly strongly associated in nitrobenzene.

(iv) If molecules of A dissociate in solution to form ions (as a salt may do) or free radicals (as many organic compounds do, such as hexaphenylethane) or two or more molecules (as some of the hydrocarbon picrates may do), this behaviour may lead either to decreased or increased adsorption. There is evidence, for example, that non-ionized molecules of fatty acids are much more effective in lowering the surface tension at the air-solution interface than are ionized molecules[12]. The acids were compared with their salts at equivalent concentrations. Here the increased dissociation brought about by some means would decrease the adsorption, whereas decreased dissociation would bring about a condition favourable to adsorption.

Landt and Knop[13] found that the adsorption of fatty acids, acetic through valeric and succinic, glutaric and adipic, from water on to ash-free charcoal is decreased by the presence of 0.02 N HCl. The adsorption curve for oxalic acid from HCl solution crossed that from water, being below it at low concentrations, where the relative amount of HCl was high. Gyani and Ganguly[14] found that adsorption on Patrick's silica gel at 25°C from 0.01 M alcohol solutions increased in the order, acetic, chloroacetic, dichloroacetic, trichloroacetic acid; this is the same order, they point out, as that of increase of the dissociation constant.

It seems generally to be found that ionization of an adsorbate decreases its surface activity. This may be because the (organic) ion, which usually differs in constitution only slightly from the undissociated molecule, with its envelope of solvent is much more soluble than the unionised molecule, and so shows less tendency to escape from solution. Phelps[15] finds evidence that on pure charcoal the unionized form of dibasic acids is the most strongly adsorbed, the singly ionized less so, and the doubly ionized acid is probably not adsorbed at all. Phelps and Peters[16] find a correlation between the amount of undissociated acid present and the amounts adsorbed, with simple fatty acids, which indicates that the undissociated form is generally adsorbed. They also found that most amino-acids are not adsorbed on charcoal; this may perhaps be due to these acids existing in the 'zwitterionic' form, with both amino and carboxyl groups dissociated. Many highly ionized surface-active substances are known, however, so that the extent of ionization itself cannot be a sole controlling factor[17].

If a single substance when dissolved in water dissociates or hydrolyses and if either anion or cation is preferentially adsorbed, then such a phenomenon is termed 'hydrolytic adsorption' by Bartell and Miller. That charcoal (and textile fibres, when dyestuffs are adsorbed) may change the pH of a solution of an electrolyte from which it adsorbs the solute has been long known[18]. Bartell et al.[19] Miller[20], and Kolthoff[21] obtained the results showing hydrolytic adsorption. E.g. there was some effect on solutions of inorganic salts, but the most striking effects of hydrolytic adsorption were found with salts of organic acids, in a few cases of organic bases also. The salts of basic dyes became acid in solution owing to the adsorption of large organic base; those of acid dyes became alkaline. Miller[22] showed that the solutions of salts of several simple organic acids become alkaline in the presence of charcoal, and that if charcoal is then removed and extracted with a neutral, organic solvent the adsorbed acid is dissolved off in amount quantitatively equivalent to the alkali set free during adsorption in the aqueous solution. The charcoal adsorbs organic acid, probably in the undissociated form, though it is just possible that some adsorption of anion also takes place, with the hydrogen ion attracted near the surface as the aqueous half of the double layer.

2. The factors from the adsorbent side.

From the adsorbent side of the interface the forces which might influence the adsorption per unit area of the interface are possibly quite numerous.

Solid adsorbents are usually classified chemically as polar and non-polar. The polar solids are those which interact attractively with molecules mainly through forces due to "segregated" electric charges and in which the relative intensity of the dispersion interaction is not great compared with the other (dipolar, etc.) type[23]. Polar solids may be crystalline or amorphous. Some few examples are quartz, barium sulphate, titanium dioxide, alumina, silica gels, glass, organic ion-exchange resins, and zeolites. In non-polar solids the interactions due to dispersion forces preponderate over those due to dipoles. Examples of non-polar solids are certain charcoals, paraffin, graphite, and a number of organic resins and plastics. It is impossible to draw a sharp distinction between polar and non-polar adsorbents; one can correctly speak only of more or less polar adsorbents. The chemical nature of the surface may be changed by appropriate treatment, for example by coating the adsorbent with organic substances[24], or with metals[25]. It may also be changed by other chemical treatments. For example, Bartell and Lloyd[26] showed that by changing the conditions of activation of purified charcoal it was possible to alter the behaviour of the charcoal. Organophilic charcoals could be prepared, by high temperature activation, which preferentially adsorbed benzene from benzene-ethanol solutions. The same charcoal activated at a low temperature in a highly oxidising atmosphere became hydrophilic, and adsorbed alcohol preferentially from benzene solution. Intermediate degrees of behaviour could also be produced.

(i) The chemical nature of the adsorbent may tend to increase adsorption, or actively to oppose it, depending on the chemical nature of the adsorbate and the temperature.

(a) If the surface of the adsorbent consists of dipolar molecules and the molecules of A also contain dipoles, then the molecules may be free to equilibrate themselves about a position in which their dipoles are opposed (as regards sign) to those of the adsorbent. There exists between them an attractive force (coulomb form). Such an interaction would favour adsorption[27]. Arnold[27b] observed that in isomeric molecules containing different numbers and kinds of functional groups, those with larger dipoles are more strongly adsorbed on polar media. Picric acid is more strongly adsorbed on alumina from petroleum ether than o-nitrophenol; the same is true for 2,nitro-4,methylphenol. It would be opposed by increase in temperature for this would increase the motion of the molecules and decrease the period of favourable orientation.

(b) If the surface of the adsorbent contains permanent dipoles and the molecules of A are polarisable, then an interaction may occur in which, on the approach of a molecule to the surface in the proper manner, a dipole is induced in A by the dipole present in the adsorbent. This type of interaction favours adsorption[27]. A corollary of this would be the case in which A contains a permanent dipole and the adsorbent molecules are polarisable. This interaction decreases with increase in temperature.

Arnold[27b] attempted to correlate relative intensity of adsorption on alumina (in a chromatogram) with dielectric properties of molecules and concluded that where no permanent dipoles exist in molecules those with higher polarisabilities would be more strongly adsorbed. The diphenylpolyenes were cited as examples, i.e. $C_6H_5-(CH=CH)_n-C_6H_5$. For n = 1 to 4, adsorption increases with the number of double bonds. (The polarisability increases with the number of conjugated double bonds.) Chromatographic studies of the separation of condensed ring hydrocarbons[28a] indicate that the more polarisable the molecule, the more adsorbable it is on to alumina from non-polar solvents. The following order of adsorption was found: benzene $<$ naphthalene $<$ anthracene $<$ naphthacene. The order of polarisability is the same.

Many attempts have been made to correlate dipole moment of the adsorbate with adsorbability. Heymann and Boye[11] looked for such a correlation on the hypothesis that it would be demanded by the electrostatic theory of adsorption[28b], which postulates that a dipole in the adsorbate polarises the lattice of the adsorbent, producing a mirror image of itself and thus an attractive interaction. Sata and Kurano[29] concluded, with others[30], that the dipole moment of the adsorbate plays no great role in adsorption from solution, but is outweighed by other influences.

Heymann and Boye[11] pointed out that the data found for molecules in the gas phase are not applicable for molecules in solution because of the strong interactions produced in the condensed state between solvent, solute, and adsorbent. They argue that even in favourable cases such complicated behaviour is being dealt with that only qualitative relations can be expected. Adsorption of benzoic, picric, and acetic acids, and iodine, from a wide variety of solvents on to deashed beechwood charcoal yielded results difficult to interpret in terms of dipole and polarisability effects. For example, the adsorption isotherms crossed.

(c) If any two molecules approach each other, there comes into importance within certain distances the attractive interaction, which is designated by London as the dispersion force. The motion of the electrons in one of these molecules modifies that of the electrons in the other, so that they tend on the average to move in phase[31]. This produces an attractive force proportional to the inverse seventh power of the distance between the molecules. It has been suggested that this force may be an agent in the process of adsorption. This interaction is additive. The more unlike are the molecules involved in this interaction the less likely are their electrons to move in phase.

(ii) The physical composition of a solid may be expected to play a role in the adsorption.

The solid state of matter is distinguished by the more or less rigid form which it assumes. In all fluids molecules are free to move relative to one another. Liquids are distinguished from solids by their fluidity. The effects of this limited mobility, on the surface properties of solids, are of two principal kinds. In the first place, those properties of liquid surfaces which are due to the free motion of the particles are absent, or very much less conspicuous, in solids. Thus solid surfaces do not contract spontaneously as a general rule, and liquids do not spread over the surface of solids to form surface films, nearly as easily as they do on liquids, even when the attraction of the liquid for the solid is great enough for such a film, once spread, to be very stable.

In the second place, the non-mobility of the surface particles of a solid results in the surface being extremely uneven, unless special means such as polishing have been employed to smooth out the irregularities. The atoms in a solid stay where they are placed when the surface is formed and this may result in no two adjacent atoms or molecules having the same properties.

Solids are divided into two classes, crystalline and non-crystalline. Only the former have reproducible properties such as a sharp melting point. Ice when pure always melts at 0°C ; in contrast, the properties of non-crystalline solids are highly dependent on their previous history and so tend to be variable and indefinite. Glasses, for instance, do not possess a melting point but only a softening range; a typical soda glass begins to soften at about 500°C and becomes progressively more plastic until at about 1500°C it is entirely molten: but no one temperature could be named as the melting point.

In crystalline solids, the constituent particles are arranged in a definite pattern, or space lattice; the whole crystal is built up from a single repeat unit or 'unit cell', comprising a small number of particles. In a non-crystalline solid the lattice may be regarded as badly distorted, whilst in a truly amorphous substance almost all trace of order is lost and the particles show random arrangement.

The surface of a solid may be homogeneous or heterogeneous in nature. It may contain regularly placed functional groups (ions, etc.), which form orderly patterns over the surface, as found on clean metal surfaces and clean crystalline surfaces. Such surfaces may be homogeneous in one direction and homogeneous but different in structure in another (anisotropic surface).

(a) In the case of crystalline surfaces with faces, corners and edges in large numbers, it would seem that even though the adsorbent is a single pure substance there will be sites of different kinds where adsorption may occur. In the plane face of a crystal any molecule or ion is surrounded on all sides, except the interfacial side, by other molecules or ions of the substance. Along the edges of the crystal the molecules are more exposed, and hence show more residual attractive forces. At the corners of the crystal the molecules are most exposed, and so are most reactive. One might rank such locations according to the energies of the molecules present[32], corners > edges > faces. The energies of molecules and ions at different locations in the surfaces of crystals have been calculated and discussed by Jones and Taylor[33] and others.

(b) On a plane crystalline, chemically homogeneous surface, the disposal of sites at which adsorption can occur will, as Langmuir has pointed out, be in a regular pattern. The spaces available on a plane crystalline surface may be of several kinds, but the regularity of surface may lead to some sort of stoichiometric relation in the adsorption of different substances[34].

Even on perfectly formed crystals, some faces adsorb very much more than others. A crystal will sometimes adsorb one dye on one set of faces, and another on a second set, no adsorption of the first occurring on the second set of faces or vice versa. Thus lead nitrate adsorbs methylene blue on the 110 faces, another set of faces adsorbing none of this dye, but easily adsorbing picric acid. If the crystals are grown from a solution containing both dyes, one set of faces develops with a blue colour, the other with a yellow. Bunn's[35] very exact work led him to the conclusion that adsorption takes place on those faces of the original crystal which have the same, or very nearly the same, interatomic spacings as one face of the normal crystal of the adsorbate.

(c) The phenomenon of catalysis depends on the heterogeneous character of a solid surface. The catalytic properties of a surface depend on the state of strain in certain atoms in the surface. About thirty-five years ago it began to be realised that all parts of a solid surface have not the same power of adsorbing. There is now universal agreement that most solid surfaces consist of patches of widely different activity, ordinary surface reactions on solids probably going on mainly at localised 'active patches' on the surface, which form a small part only of the whole surface[36].

That some degree of irregularity in a surface is often necessary for catalytic activity was shown by Palmer[37], who found that electrolytically deposited copper is inactive in dehydrogenating alcohols to aldehydes, whereas copper formed by reduction of the oxides was active. Constable[38] has extended this work, showing that a polished surface of a copper foil and copper mirrors, are inactive; commercial copper gauze is practically inactive, but copper produced by a rapid condensation of a vapour or formed by the rapid decomposition of various copper compounds, is always active. It would seem that copper is only catalytically active, if it is not arranged in a regular space lattice, or closely packed in the amorphous polished layer.

(d) If the surface contains capillaries and fissures, then the adsorption may be favoured for small molecules that can enter the capillaries, for here they would tend to condense under the pressure of the doubled attraction of two nearby walls or under the pressure of a curved meniscus[3c]. Thus "bulk liquid" might well be formed in these pores or fissures. Larger molecules might be unable to enter the capillaries and thus because of their size, they would be excluded from considerable adsorption surface.

Bruns[39] studied the adsorption of fatty acids, from one to six carbon atoms in chain length, on sugar charcoal from water solutions. The adsorption decreased with increase in chain length. According to 'Traube's[40] rule' adsorption should increase regularly for the members of a homologous series with increase in number of CH_2 groups, in the chain. Upon reduction in size of the charcoal particles by mechanical grinding, however, the adsorption of the higher members of the fatty acid series increased more than that of the lower members. According to Bruns this behaviour showed that the reversal of Traube's rule is due to the presence of pores, which are not accessible to molecules with large volume, and which are opened by mechanical particle size reduction of the charcoal.

With porous solids, the rate at which equilibrium is established may vary considerably with chain length. Baum and Broda[5] studied the adsorption of acetylated carbohydrates of different viscosities (different molecular weights) on alumina and charcoal. Equilibrium was not established even after several months. The establishment of adsorption equilibrium required less time for shorter chain compounds (which diffused more rapidly) than long chain compounds.

(e) If the surface of the adsorbent contains impurities these may markedly affect its chemical nature, but it is often very difficult to tell whether a given effect is due to impurities or to some special arrangement of the molecules of the adsorbent or to some other physical circumstance. Heymann and Boye[11] found that the adsorption of fatty acids on gold powder from water was decreased after boiling the gold with nitric acid, though no gold appeared in the solution and only traces of silver and iron. In separating a number of coal tar dyes on columns of alumina (in chromatography) it was found that the adsorptive properties were improved by washing with distilled water containing a little lime, or even with very hard tap water[41].

3. The factors within the interface:

In the region of the interface itself a number of factors may play a role in adsorption.

(i) An important factor must be the competition between molecules of A and B for the interface. This occurs because the interface is limited in extent, and non-expandable (in the cases under discussion) and so differs very much from the bulk liquid phase. More molecules of A added to the liquid phase may increase its volume (of course they may not, if interactions occur that lead to no change - or even contraction in volume) or at least present the opportunity for increase in volume, while molecules of A introduced into the interface generally displace other A molecules or molecules of B. The adsorption will favour that molecule the adsorption of which occurs with greater molecular decrease in free interfacial energy, other things being equal.

(ii) The area occupied by the molecules in the interface will play a part in the adsorption because a molecule that covers many active spots, for example, a chain molecule, will be more adsorbable than the monomer. This is because the tendency of molecules to remain in the desorbed state diminishes with increase in chain length[4,5]. Here both size and shape play a part.

(a) A large molecule may displace several small ones; or a large molecule may block off, without occupying, several sites where adsorption might otherwise occur. The adsorption of small molecules may not be appreciably affected by the presence of large ones if the small ones can reach areas of the surface inaccessible to the large.

(b) Molecules of certain shapes, i.e., chains with several anchoring groups distributed along their length, may be adsorbed in lesser quantity than those with the polar groups all at one end, or with a single polar group at one end, for the former lie spread on the surface, occupying an area approaching their lengthwise curled cross-section, while the latter may pack vertically and occupy an area approaching their smallest cross-section.

(iii) The mutual interactions between adsorbed molecules which may cause them to adhere laterally may influence the quantity adsorbed by allowing the adsorbed film to bridge roughness and fissures in the adsorbent[42].

SECTION I

A System of Classification of Solution Adsorption Isotherms, and its Use in Diagnosis of Adsorption Mechanisms.

The Adsorption Isotherm.

When an aqueous solution of a dye is shaken with charcoal, the colour intensity is lowered. The property possessed by charcoal of removing colouring matter from solution, i.e. of "adsorbing" it, was known at least as far back as 1785 (T.Lowitz). Usually the dye adsorbed can be extracted again by a suitable liquid and shown to be unaltered, thus proving that it was not destroyed or transformed into an insoluble compound. When the liquid phase contains two components, e.g. when it is made up of two miscible liquids A and B or is a solution of a solid A in a liquid B, in general A and B will be adsorbed to differing extents so that the concentration of A relative to B will change in the bulk of the solution. It is easy to measure the concentration of A before and after adsorption and, from this difference, to deduce the amount adsorbed; this is only the apparent adsorption, because some of the solvent B, has been adsorbed along with the solute. Results are conveniently expressed as an adsorption isotherm, in which the amount x of component A adsorbed is plotted as a function of the final concentration of A in the solution.

Apparent and Absolute Adsorption:

Suppose that initially each gram of solution contains

a_o gram of A and b_o gram of B and that after the adsorption the amounts are a' and b' respectively, the initial weight of the solution being W grams. (Thus $b_o = (1 - a_o)$ and $b' = (1 - a')$). Now the adsorption of A has to be calculated from the change in concentration of the solution and so is given by $x' = W(a_o - a')$; this is only the apparent adsorption and it is less than the true adsorption x because some of the solvent B, say z gram, has been adsorbed along with the solute and has thus had the effect of raising the concentration of A remaining in solution. The difference between x and x' is equal to the number of grams of A which were associated with the z gram of solvent, viz.

$$z \cdot \frac{a'}{b'} \quad \text{or} \quad z \cdot \frac{a'}{1 - a'}$$

We thus have

$$x - x' = z \cdot \frac{a'}{1 - a'}$$

or

$$x' = x - z \cdot \frac{a'}{1 - a'} \quad \ldots\ldots(1)$$

Now the true adsorptions of both solute and solvent, viz., x and z, will increase continuously as their respective concentrations increase, consequently as a' increases x will increase and z will diminish. Unfortunately z cannot be determined independently so that the equation (1) cannot be tested directly. In practice dilute solutions are much used, where the correction factor of equation (1) is negligible. This does not mean that the adsorption of the solvent is negligible - on the contrary, it is very large because b' is large - but rather that the difference between the true and apparent adsorptions is negligible[41].

Various methods have been devised to take account of the adsorption of the solvent. In Williams' method[2] the adsorbent is exposed to the vapours of the solution of known initial concentration in an evacuated desiccator until constant weight is reached. It may require a period of one hundred days to reach equilibrium. The solution is then analysed. The solid (the "adsorbent") is now mixed into the solution, and after equilibrium is reached the solution is again analysed. The concentration on the adsorbent can be determined from the change in concentration of the solution in the first step and the weight of both components adsorbed in the second step.

Pinkus and de Brouckere[43] studied the adsorption of HCl, LiCl, KCl, $CuCl_2$ and $NiCl_2$ on $BaSO_4$. After equilibrium was reached, $BaSO_4$ was removed from solution and washed with pure water repeatedly. They assumed that the adsorbed layer adhered to the adsorbent to the point of resisting washing, which only removed entrained solution.

Dobine[44] adsorbed acetic acid from water over the entire concentration range on moist and dried charcoal and from the curves of the two, with certain assumptions, calculated the adsorption of solvent and solute.

Jones and Outridge[45] determined the volume of the liquid taken up by the adsorbent in two ways: one from equilibration with the vapour of the liquid, one from immersion in the liquid. The former is the Williams Method. For determining the amount of the liquid adsorbed, Jones and Outridge used Bachmann's immersion method. The adsorbent (silica gel) was immersed in the solution (n-butanol in benzene) and allowed to come to equilibrium. Then it was removed from the solution and quickly dried with filter paper and weighed. The weight of liquid divided by its ordinary density at the temperature of the experiment gave the volume of the liquid adsorbed.

But the objection to these methods (except the method of washing the adsorbate) is that, when an adsorbent, saturated with a solvent, is immersed in a solution, solute is bound to displace some of the solvent from the sites occupied by it (solvent), unless the solute is adsorbed on the sites not previously occupied by the solvent, which will not always be the case. Hence, the volumes of the pure solvent and the solution adsorbed will be different.

The method of washing the adsorbent with a pure solvent after the adsorption is over is justifiable, if the solute (the "adsorbate") has a strong affinity for the adsorbent, but in some cases, such as cationic dyes on silica or *p*-nitrophenol on alumina, the whole of the adsorbate can be almost completely removed by washing a few times.

In one special case, however, adsorption of solvent can safely be neglected, and that is when the solute is chemisorbed on to the surface, i.e., is fixed by ordinary valency bonds acting between the solid surface and the molecules of adsorbate. This might be expected, for instance, where an organic acid is adsorbed from solution on to a solid having fairly basic properties (in a chemical sense)[46]. A study of the adsorption of a number of fatty acids on nickel and platinum catalysts - each probably covered with a film of chemisorbed oxide - illustrates the point. The adsorption was irreversible, for the acid could not be washed off by treatment with the solvent; with a given catalyst the number of molecules of acid adsorbed remained constant over a wide range of solute concentrations (cf. Fig.3Hc) in a variety of solvents, and moreover was unaffected by increasing the length of the carbon chain by steps from 10 to 22 atoms.

Isotherm Types.

Two types of isotherm are encountered in the literature: (a) In adsorption of binary liquid mixtures, if both components (A and B) of the solution are liquids, the isotherm can be determined for the whole range of concentrations, that is from 100% A + 0% B to 100% B + 0% A. Fig.1 shows an example of such a curve. Its abscissa represents the molar fraction of one component in its mixture with the other and the ordinate the amount of the same component adsorbed per gm. of the adsorbent. (b) If one of the two components is solid, the whole isotherm cannot be determined, and often only a part of the isotherm is measured, even when both ingredients are liquids.

Present Work.

This is a study of the relation between solute adsorption mechanisms at solid surfaces and the types of isotherm obtained. It describes a system of classification of all solution adsorption isotherms (of type b mentioned above), and suggests how their form can be used to diagnose the adsorption mechanism, to obtain information regarding the physical nature of the solute and the substrate surface, and to measure the specific surface area of the substrate. The last-mentioned has hitherto been the principal use of solution adsorption isotherms, but it has been hampered by lack of information on the detailed meaning of the curves*

Possibly the first attempt at a general classification of adsorption isotherms was that made in 1922 by Ostwald and de Izaguirre[3b], who described curves for adsorption from binary solutions over wide concentration ranges. They found two of the curves included in the present system (cf.Fig.2, footnote). Brunauer[48] later defined five types of isotherm that are observed in vapour-phase adsorption (cf.Fig.2, footnote). An outline of the present system of classification has already been given[49]; but the conclusions then drawn and the classification have been modified and developed as a result of later investigations.

Classification System.

The present system divides all isotherms into four main classes according to the initial slope, and sub-groups are described for each class, based on the shapes of the upper parts of the curves. The four main classes (Fig.2) are named the S, L (i.e., "Langmuir" type), H ("high affinity") and C ("constant partition") isotherms, and the variations in each class are divided into sub-groups.

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* The work recorded here and the conclusions reached are based on the results of several investigators who worked in this laboratory over the past few years. Examples are also cited from the literature, supplemented with the result of the writer's experimental investigations.

The L curves are the best known; indeed the L2 curve occurs in probably the majority of cases of adsorption from dilute solution and few cases of other types appear to have been previously recorded.

This work has already been published as a paper[50], wherein 166 isotherms falling under the four classes mentioned above are given. In Table I some selected isotherms are reported and Fig.3 shows some of the isotherms considered in this survey. The other figures are the writer's own work, unless stated otherwise. For more details the original paper may be consulted. The present discussion is mainly taken from the paper[50].

Table I.

List of some isotherms classified under the present rules and discussed in this thesis.

Solute	Solvent	Substrate	Isotherm	Ref.
		S Curves		
Phenol	H_2O	Al_2O_3 (anodic)	S 1	64
p-Nitrophenol	H_2O	Al_2O_3 (chromatographic)	S 2, S 3	(Figs.4 and 40d)
"	H_2O	SiO_2	S 2	(Fig.6)
Quaternary ammonium surface-active agents	H_2O	Cellulose	S 2	51

Table I (cont'd)

Solute	Solvent	Substrate	Isotherm	Ref.
		S Curves (cont'd)		
Dyes:				
Cyanine (non-planar)	Emulsion in gelatin	Silver halide	S 2	53.
Monosulphonated(C.I.15,510)	H_2O	Al_2O_3 (anodic)	S 2	52.
Disulphonated (C.I.16,045)	H_2O	C (graphite)	S 4	54
		L Curves		
Resorcinol	H_2O	Al_2O_3(chrom.)	L 2	55
Terephthaldehyde	C_6H_6	" "	L 2	55
Sodium palmitate	H_2O	Cellulose	L mx mx	56
Sodium alkyl sulphate	H_2O	Wool	L mx	57
Octadecyl alcohol	C_6H_6	Ni	L 4	58
p-Nitrophenol	H_2O	Coal	L 3	(Fig.22)
p-Aminoazobenzene hydrochloride	H_2O	SiO_2	L 1	65
Alkyl sulphate esters (Na salts)	H_2O	Al_2O_3 (anodic)	L 2	64
		H Curves		
Fatty acid	C_6H_6	Pt	H special	46

Table I (cont'd)

Solute	Solvent	Substrate	Isotherm	Ref.
		H Curves (cont'd)		
Dyes:				
Azo, mono-, di-. tri-sulphonated	H_2O	Al_2O_3 (HCl treated)	H 2	55
Basic (various)	H_2O	SiO_2	H 2, H 3	65
Cyanine (planar)	emulsion in gelatin solution	Silver halide	H 2	53
Dodecylammonium chloride	H_2O (pH 6.3)	Al_2O_3	H 4	59
Dodecyl sulphate, Na salt	H_2O	$BaSO_4$	H 4	59
		C Curves		
p-Nitrophenol	C_6H_6	Nylon	C 1	61
Non-ionic disperse dyes (anthraquinone and azo-classes)	H_2O	Cellulose acetates (di and tri), Terylene	C 2	62, 66,67
Biphenyl	aqueous dispersion	Terylene	C 3	63
Chlorobenzene	50% aqueous C_2H_5OH	Cellulose triacetate	C 1	(Fig.62a)
Phenol	"	"	C 1	(Fig.62b)
Phenylazobenzene compounds (non-ionic)	H_2O	Wool	C 1	68

Experimental

Preparation of the substrates:

Wool - Commercially scoured but unfinished woollen cloth was cut into small pieces, which were refluxed for 4 hr. either with n-butanol or n-heptane (depending on the solvent used for adsorption experiments). Afterwards the excess of solvent was squeezed out from the pieces by hand and they were dried by filter papers. They were then oven-dried at 105°C for 24 hr. and stored in a desiccator over phosphorus pentoxide. Wool, when shaken with organic solvents, gives cloudy solutions and this hinders estimations by spectrophotometry and refractometry. It was to avoid this difficulty that the pieces were previously treated with the solvent.

Viscose rayon - Commercially scoured and finished viscose rayon cloth was treated with a 1% solution of a desizing agent at 45°C for 4 hr., to remove starch, etc. Freedom from starch was tested for by means of iodine solution. The cloth was then thoroughly washed with water and allowed to dry in air and used for experiments with water as a solvent. When benzene was used as a solvent the cloth was refluxed with benzene for 4 hr. and oven-dried at 105°C for 4 hr.

Grade I alumina - This was prepared by the writer's colleague, Mr.R.B.McKay, by roasting chromatographic alumina (Grade II) in a muffle furnace at 700°C for 5 hr. and drying in vacuo. Roasting reduced the weight by 5.9%.

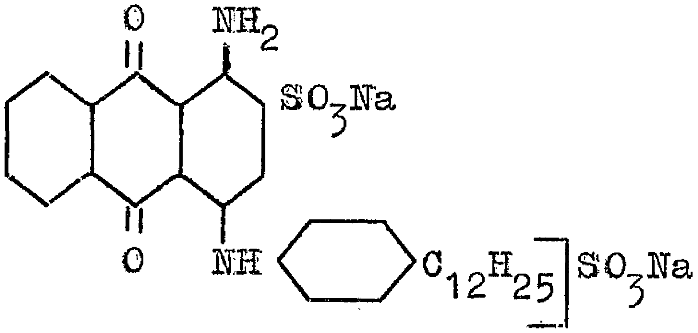
Silica (MSC brand) - Supplied by Messrs. Colin Stewart Ltd.

Silica (another variety) - Supplied by the Dust Research Laboratory in this Department. Both the varieties of silica were used without any pretreatment.

Cellulose acetate - Courtalds' 0.002" gauge cellulose (secondary) acetate film was used after cutting into small pieces.

Solvents and Solutes.

Distilled water was used for all aqueous solutions; p-nitrophenol was recrystallized from water; benzene of AnalaR quality was used; methanol was "specially dry", supplied by B.D.H.; Carbolan Blue B (C.I.62,075), - a batch (i.e. undiluted with salt) sample of this dye was supplied by I.C.I.;



(C.I.62,075)

Solway Ultra Blue BS, (C.I.62,055) a commercial sample was used; Solway Blue BN (C.I.63,010), a batch sample was supplied by I.C.I.; Orange II (C.I.15,510); and Naphthalene Red EA (C.I.16,045); samples purified in the laboratory were used; p-aminoazobenzene was recrystallized from water; n-heptane was commercial quality, and n-butanol was purified by distillation.

Adsorption procedure:

0.05 - 2.0 gm. samples of the solid substrate were weighed in soda glass test tubes and a series of 5-10 c.c. aliquots of adsorbate solutions of increasing concentrations were introduced, and the tubes sealed in a flame. The tubes were then fixed by spring clips to an electrically driven horizontal shaft, revolving at 35 r.p.m., under water in a thermostat tank. This apparatus and technique is described by Clunie and Giles[69].

To ensure sufficient time for equilibrium to be established in the system during the tests, it was necessary to measure the rate of adsorption, which was done by placing several sealed tubes with substrate and solution of one concentration in the thermostat and removing them at various time intervals. The solutions were separated from the substrates and analysed. The time after which there was no increase in adsorption was taken to represent the attainment of equilibrium.

After adsorption some substances, e.g. alumina and fibres, settled very quickly and the supernatant liquid was decanted and used for analysis. Silica (MSC brand) settled with difficulty; in this case, the solutions were centrifuged for about 15 minutes, then filtered through glass wool and used for analysis.

Analytical Techniques.

The amount of solute adsorbed was calculated from the difference in initial and final concentrations of the solution. The solutions were analysed either by a refractometer or a spectrophotometer.

Refractometric method:- Bellingham and Stanley, and Zeiss (both Pulfrich type) refractometers were employed with sodium light. The square of the refractive index, when plotted against concentration gave a straight line calibration curve, which was used to determine the concentration of the solutions. Water in butanol and methanol in benzene were analysed by this method.

Spectrophotometric method:- The Unicam S.P.500 photoelectric spectrophotometer was used. Light absorption spectra for the solutes in the solvents employed in the adsorption tests were first obtained and subsequent readings taken using light of the wavelength most strongly absorbed by the solute. A calibration curve (straight line) was obtained by plotting optical densities against concentrations and this was used in analysing the solutions.

Plotting of the Isotherms:

In all the cases, the abscissa represents the final concentration of the solution in the bath in mmole/l. and the ordinate the apparent adsorption in mmole/kg.

Discussion:

Initial Slope of Isotherm - If conditions causing adsorption remain constant, one would expect that doubling the concentration of an adsorbate would also double the amount adsorbed, since twice as many molecules would now be reaching the surface. This holds good in the case of C curves, where the availability of sites remains constant at all concentrations up to saturation. In most cases however adsorption increases either faster or slower than concentration, and the isotherm is either convex or concave to the concentration axis. This means that conditions causing adsorption change, in one or the other direction, as adsorption proceeds. In general, if one adsorbed molecule renders the surface less attractive to the next one, the isotherm will be concave to the concentration axis. This is the case, for example, if a few most active spots of the surface are first occupied, when there is less chance that a subsequently bombarding solute molecule will find a suitable site for adsorption; i.e., to cause adsorption of a given additional amount of a solute, the external solution concentration must be raised by ever increasing amounts. This applies to the normal L curves and to the later stages of the S and H curves. On the other hand, under reverse conditions when the surface becomes increasingly attractive with coverage, the isotherm becomes convex to the concentration axis. This is the case when molecules attract each other so that they tend to bunch on the surface. This has been called "co-operative adsorption"[53].

The probable causes of these effects will now be described and illustrated.

The S Curve

The initial direction of the curvature shows, as just explained, that adsorption becomes easier as concentration rises. In practice, the S curve usually appears when three conditions are fulfilled: the solute molecule (a) is monofunctional, (b) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition, for substrate sites, from molecules of the solvent or another adsorbed species. Thus, monohydric phenols usually give S curves, especially when adsorbed on a polar substrate, e.g., p-nitrophenol on alumina or silica from a polar solvent such as water, but not from a non-polar solvent such as benzene or hexane (cf.Figs.4 to 6 and 44), which does not compete for the adsorption sites. So also do aqueous systems of non-planar cyanine dyes on silver halide, and surface-active quaternary ammonium salts on cellulose, and many monosulphonated dyes on anodic alumina (cf.Figs.3Sa,b and c). This isotherm thus apparently indicates a tendency for large adsorbed molecules to associate rather than to remain as isolated units (cf.Fig.7).

Monofunctionality.-

The definition of "monofunctional in this context is that the solute molecule has a fairly large hydrophobic residue ($>C_5$) and a marked localisation of the forces of attraction for the substrate over a short section of its periphery, and that it is adsorbed as a single unit and not in the form of a micelle. Thus, p-nitrophenol is monofunctional in its attraction towards a polar substrate, e.g., alumina, because the attraction arises from its hydroxy-group, but it is initially not monofunctional towards either graphite (graphon)(Fig.41) or pigments with larger planar assemblages of aromatic nuclei (Figs.28 to 31). With these it does not give an S isotherm, because its attraction for the substrate lies probably in non-polar forces operating over the whole p-nitrophenol nucleus.

Specific surface area measurements confirm the view that the molecules of monofunctional solutes are adsorbed edge-on or end-on to the substrate surface. Consider for example, adsorption of an anthraquinone dye, C.I.62,055, on silica (MSC brand) (Fig.43).

Monolayer adsorption	10.31 mmole/kg.
Cross-sectional area of a molecule for edge-on orientation (from a Catalin model)	87.10 A^2
Specific surface area of silica	5.37 $m^2 g^{-1}$

This agrees well with a low temperature nitrogen adsorption figure of 5.15 m^2/g.

All surface-active substances are monofunctional according to the above definition and should give S isotherms, but in practice they do not. Possible reasons are that they are either adsorbed as ionic micelles, or that their intermolecular attraction is very high.

Methanol adsorbed from benzene on normally dried cellulose gives S isotherms, probably as a result of competition for hydrogen-bonding sites by traces of firmly bound water not removed during the normal course of drying. Competition is reduced and adsorption promoted by methanol associating on adsorption; hence the form of the S curve. When the materials are intensively dried, competition from water is eliminated and the curves have the normal L shape (Fig.8).

The L Curve

Here the initial curvature shows that as the surface is getting covered, an incoming molecule finds it difficult to get a vacant site. This means either the adsorbed solute is not vertically oriented (on the argument used for S curve, cf. Fig.7) or there is less competition from the solvent for the substrate sites.

The systems which give L curves fulfil these conditions, (cf.Table I). They have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat, e.g. resorcinol (Fig.3La) and terephthaldehyde on alumina, or (ii) if adsorbed end-on, they suffer little solvent competition; examples of (ii) are (a) systems with highly polar solute and substrate, e.g., p-nitrophenol and alumina or silica, and a non-polar solvent, e.g., benzene or hexane; here the solvent benzene or hexane does not compete for the substrate sites and even though the solute is adsorbed edge-on the result is an L isotherm; while from a polar solvent like water we get S isotherms, (cf.Figs.4 to 6 and 44), and (b) systems in which monofunctional ionic substances with very strong intermolecular attraction, e.g. long paraffin-chain sulphate esters, are adsorbed from water by ion-ion attraction. It is possible that in these cases (systems b) the adsorbed ions may have become associated into very large clusters just before adsorption takes place.

The H Curve

This is a special case of the L curve, in which the solute has such a high affinity that in dilute solutions it is completely adsorbed, or at least there is no measurable amount remaining in solution. The initial part of the isotherm is therefore vertical. The adsorbed species are often large units, i.e., ionic micelles or polymeric molecules, e.g. cationic dyes on silica, but sometimes they are apparently single ions which exchange with others of much lower affinity for the surface, e.g., sulphonated dye ions which exchange with chloride ions on alumina, and cyanine dye cations adsorbed by ion-ion attraction on silver halides. (Fig.3Hb). In the most extreme form, the curve is a horizontal line running into the vertical axis. This was found for chemisorption of fatty acids on Raney nickel[46] (Fig.3Hc).

The C Curve

This is characterised by the constant partition of solute between solution and substrate, right up to the maximum possible adsorption, where an abrupt change to a horizontal plateau occurs. (The lowest part of the L curve is, of course, sometimes virtually linear, and some almost linear curves which are borderline cases, intermediate between S and L types, are occasionally found). This is the type of curve obtained for the partition of a solute between two immiscible solvents, and many authors consequently have used the term "solid solution" for adsorption processes which give it, but it is doubtful if the term is quite appropriate, though it is admittedly difficult to coin a more expressive one; "adsorption without solvent" may be suggested, for reasons given below.

The conditions favouring the C curve appear to be (a) a porous substrate with flexible molecules and regions of differing degrees of crystallinity, and a solute with (b) higher affinity for the substrate than the solvent has, and with (c) better penetrating power, by virtue of condition (b) and of molecular geometry, into the crystalline regions of the substrate.

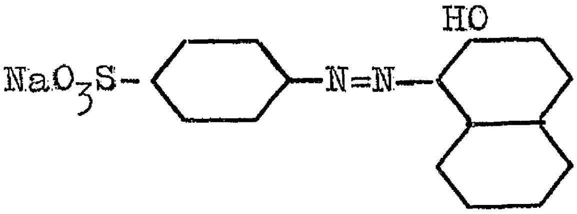
Fundamentally, the linearity shows that the number of sites for adsorption remains constant; i.e., as more solute is adsorbed more sites must be created. Such a situation could arise where the solute has a higher attraction for the substrate molecules than the solvent itself has. The solute could then break inter-substrate bonds more readily than the solvent could, and if its molecular dimensions were suitable, could penetrate into the structure of the substrate in regions not already penetrated by the solvent. This action is similar to the opening of a Zipp fastener, the fastenings representing the intermolecular bonds of the substrate, and the slider the first molecule or group of molecules to penetrate; this opens up the structure and allows more solute molecules to enter (cf. Fig.9). The action stops abruptly when more highly crystalline regions of the substrate are reached. In fact the isotherms usually do suddenly change direction to give the horizontal plateau. Thus a linear isotherm indicates that solute is penetrating regions inaccessible to the solvent.

Partition of a solute of limited solubility between two immiscible solvents is a special case of this behaviour; neither solvent penetrates between the molecules of the other but the solute penetrates both solvents.

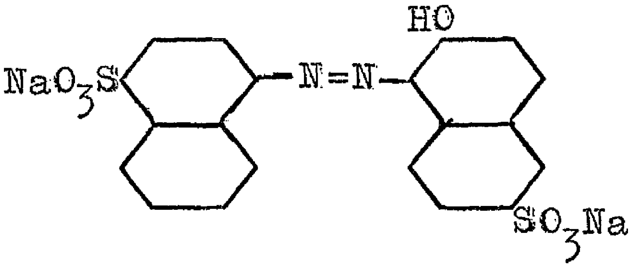
The isotherm has been found to occur in at least five types of system, though it has hitherto been known for only one ((i) below). The five systems are:

(i) Non- or mono-ionic aromatic solutes on hydrophobic polymers, e.g. cellulose acetate or polyethylene terephthalate (Terylene), from an "inert" liquid, i.e., one which does not readily swell the substrate, and may also be an indifferent solvent for the adsorbing solute. Systems under this description are the non-ionic ("disperse") dyes applied from fine aqueous dispersions (Table I; Fig.3Cc) or from carbon tetrachloride, and colourless aromatic substances ("carriers") used in aqueous solution or dispersion to assist the penetration of this type of dye into polyester fibres[63,70], (Fig. 62). (These substances are in fact found by physical tests, to be capable of penetrating into the crystalline regions of the fibre[70].)

Cf. Figs.10 and 11



C.I.15,510



C.I.16,045

Dye C.I.15,510 has only one sulphonate group and therefore is less solvated and able to penetrate the crystalline regions of secondary acetate and gives a C isotherm. Dye C.I.16,045 has two sulphonate groups and therefore is the more solvated in water. The accompanying solvated water prevents the necessary close approach of dye and secondary acetate chain, and 'dyeing' is confined to the amorphous regions[67]. Result: the L 2 isotherm.

(ii) Benzene in n-heptane (Fig.12) and water (as solute) in n-butanol (Fig.13) on wool. Butanol does not penetrate dry wool readily; presumably heptane does not, either.

(iii) Certain amino-acids and peptides, in water, on silica dust[60] (Fig.30a). The mechanism here is rather obscure. Probably it involves hydrogen-bonding of the amino-groups with silica in regions of the amorphous layer around the silica particles which are penetrated by the solutes but not by water.

(iv) Phenols, in water, on synthetic polypeptides (Fig.30b). The same solutes on wool give S curves (Fig.38). Presumably the highly crystalline structure of the synthetic products makes them less readily penetrable by water.

(v) Non-ionic phenylazobenzene derivatives adsorbed by wool from water[68]. In wool there are few crystalline regions[71] (10-15% inaccessible to D_2O) and the solutes must be adsorbed on these only, as they are adsorbed to a limited extent (saturation adsorption is one-tenth of that in cellulose acetate[68]). It seems probable that because of their weak hydrogen-bonding properties (cf. refs. 61,72,73) and stearic effects, these solute molecules cannot form a stable attachment to the fibre in the presence of water, but they can do so by hydrogen-bond and non-polar forces in some of the crystalline regions which are not penetrated by water. The system is thus essentially similar to other C-isotherm systems.

4-Aminoazobenzene on cellulose, however, gives the S isotherm (Fig.14). In this substrate the conditions are different: the cellulose molecule is planar, and can adsorb planar aromatic solute molecules from water by non-hydrogen-bonding forces[74], either oriented flat or edge-on (as probably in this case), in water-penetrated regions.

Abnormalities.-

Adsorption of biphenyl by polyethylene terephthalate (Terylene) fibre from hot aqueous dispersion appears to give the C 3a isotherm[63] (Fig.3Cd). The upper part of this curve must represent very deep penetration of the crystalline regions of the fibre, which appears to proceed without limit[70]. Some disperse dyes, especially of the anthraquinone class, give C3a isotherms, the upper portion rising more steeply if a second dye is present which has the effect of promoting adsorption of the one measured. Part of this steady increase in adsorption beyond the inflection is attributable to building-up of adsorbed dye on the outer surface of the fibres[75].

Unlike water, benzene (from n-butanol) on wool does not give a C-curve (Fig.15). Here the solvent has the higher affinity (by hydrogen-bonding), because of its large molecule, but normally penetrates wool only with great difficulty. It is completely miscible with benzene and probably penetrates better from the mixture than alone. The S-curve actually obtained indicates end-on orientation of adsorbed benzene.

Additional Characteristics

(i) Indications of the Monolayer.-

Nearly all sufficiently complete curves have either a plateau or an inflection ("knee"). Those that do not (sub-group 1) are clearly incomplete: saturation of the surface has not been reached, probably because of experimental difficulties. The plateau, or the beginning of the linear portion above the "knee" (Brunauer's "Point B", ref.48, p.287) must represent "first degree saturation" of the surface, i.e., the condition in which all possible sites in the original surface are filled and further adsorption can take place only on new surfaces. For convenience, this degree of coverage may be called the formation of a complete "monolayer", but this does not necessarily imply that it is a close-packed layer of single molecules or ions, as in a compressed monolayer on water. It may be so in some cases, and when it is, specific surface area determinations can readily be made. Generally, however, the layer may (a) contain solvent as well as solute molecules, or (b) consist only of isolated clusters of solute molecules adsorbed on the most active sites, or (c) consist of ionic micelles, either packed closely or well separated.

(ii) Solvent in the Monolayer.-

Adsorption tests with p-nitrophenol give some indication of the likelihood of the presence of solvent in an adsorbed monolayer. Table II shows that estimates of specific surface area of alumina made by using two solvents agree well if it is assumed that the adsorbed monolayer is a condensed one and does not contain benzene, but does contain water, when these solvents are used. The value of (a) 15 A^2 and (b) 25 A^2 for the cross-sectional areas of p-nitrophenol agree with estimates from a model assuming

Table II

Adsorption of p-nitrophenol by chromatographic alumina (Grade I) at 20°C

Solvent	Benzene (Fig.5)	Water (Fig.4)
Isotherm class	L 3a	S 2
Monolayer adsorption:		
mmole/kg.	425	260
estimated from	"Point B"	plateau
Assumed cross-section of adsorbed molecule (A^2)	15	25
Specific surface area (m^2/g.)	39.3	39.0

end-on orientation, with respectively (a) close-packing (b) packing with one water molecule sandwiched between each pair of phenolic groups (cf. the value of 24 A^2 for p-alkylphenols in condensed monolayers on water[76]).

As a working hypothesis, it is suggested that (1) no solvent is present in adsorbed monolayers on solids of opposite degree of polarity to the solvent, i.e., monolayers on polar solids in non-polar liquids, and probably also not in monolayers on non-polar solids in polar liquids; and (2) a molecule adsorbed from water occupies the same cross-sectional area on a solid polar surface as it would do in a condensed monolayer, at zero compression, on water.

(iii) Adsorption of Isolated Clusters of Molecules, and of Ionic Micelles. Differences in Monolayer Capacity.-

In some systems, e.g., cationic dyes on positively charged alumina (Figs.45 and 46) or p-nitrophenol on silica (MSC brand) from water (Fig.6), the amount of solute taken up at the "monolayer" stage is much less than the surface capacity, estimated by other methods. In these cases adsorption probably takes place only on a few highly active sites. On the other hand the cationic azo-dye Janus Red B (C.I.26,115), which is very colloidal in solution, is adsorbed on silica (MSC brand) at 38° in about 3.5 times the amount theoretically required to form a condensed monolayer (Fig.50a,b). It is probably adsorbed as ionic-micelles.

In all adsorptions of large organic molecules, in fact, there is the possibility that association of the adsorbed ions or molecules may occur, because at the adsorbing surface they are brought close together. Association may thus occur just before or just after the moment of adsorption. Association of dyes in the adsorbed state has been detected by a variety of indirect means[77] and by a direct method, with use of electron micrography[78]. By this method a number of (water soluble, sulphonated) direct cotton dyes are seen to be present in cellulose as dense clusters of minute particles or microcrystals (size $>$ 40 A). There is as yet no certain evidence of the stage at which these aggregates are formed, but there are some indications of their formation during adsorption[77].

(iv) Significance of Plateau Length or "Point B" Slope Change.

In practice the precision of the value of the "monolayer" capacity determined from the curve varies widely. At one extreme there are curves with a long flat plateau (e.g., Figs.52e,f), and, at the other, those with only a very small change of slope at "Point B". Indeed, in some cases the position of this point is not very clear (cf.Fig.42); these can be considered special cases in which the plateau is very short.

The significance of a long plateau must be that a high energy barrier has to be overcome before additional adsorption can occur on new sites, after the surface has been saturated to the first degree. The solute has high affinity for the solvent, but low affinity for the layer of solute molecules already adsorbed. It is perhaps significant that the adsorptions of ionic micelles give curves with long plateaux; in these cases the surface of the solid, when covered, will tend to repel other micelles holding the same charge.

A short plateau must mean that the adsorbed solute molecules expose a surface which has nearly the same affinity for more solute as the original surface had. Consider the isotherms of p-nitrophenol adsorbed on alumina from water (Fig.4) and from benzene (Fig.5) respectively. The first (S 2) has a well-marked plateau, the second has the L 3a form, without plateau. The calculations of specific surface area, just discussed, indicate that the "monolayer" probably contains solvent in the first case, but not in the second. It is assumed, therefore, that all the p-nitrophenol molecules adsorbed from water are attached to the alumina by the -O ····· HO- bond, and therefore the outer surface they expose after adsorption consists largely of nitro-groups and benzene nuclei and has less affinity for molecules of phenol from solution than the original surface had. The nitrophenol molecules adsorbed from benzene, however, appear to be close-packed, and the surface they expose after adsorption has almost as high affinity for additional phenol molecules as the original surface has. Further, the isotherm beyond "Point B" rises steadily without inflection to a level representing adsorption several layers deep. These facts could be explained by assuming that the adsorbed phenol molecules have their hydroxy groups alternately facing up and down, i.e., in contact with the external solvent and with the alumina. This is equivalent to adsorption of the solute as dimers in which the two individual molecules are face-to-face, but reversed end-to-end, i.e. each OH group lies against the NO_2 group in the other molecule. The adsorbed layer then has an exposed surface with a high concentration of hydroxy-groups, which have high affinity for more phenol molecules. If the molecules in each subsequent layer are oriented as they are in the first, the affinity of the outer surface for an additional layer of phenol will remain almost constant, no matter how many layers are already present. This could account for the long and nearly constant slope of the isotherm.

(v) Second Rise and Second Plateau.

These (cf. sub-groups 3 and 4) are attributed to the development of a fresh surface on which adsorption can occur, the second plateau (sub-group 4) representing the complete saturation of new surface, though this stage is not always realisable, and the curve then appears as in sub-group 3.

The fresh surface may be: (a) the exposed parts of the layer already present (e.g., basic dyes adsorbed from water as ionic micelles, on graphite, curve H 3a, cf. Fig.3Ha); this will be the case, of course, only if there is room for a second layer (e.g., Fu, Hansen, and Bartell[79] obtained curves with a second rise for phenol adsorption on several types of highly porous carbon, but on sugar charcoal, which had very small pores, only a single plateau was obtained); or (b) new, probably more crystalline regions of the substrate structure into which the solute begins to penetrate*, or (c) part of the original surface.

Thus, under (c) a portion of the original surface may be uncovered by re-orientation of the molecules already adsorbed. This may apply to the adsorption of p-nitrophenol from water by pigments (Figs.28 to 32), where the appropriate measurements are consistent with complete coverage in flat orientation at the first plateau, and complete coverage in vertical orientation at the second. A similar phenomenon was noted by Daniel[58] in the adsorption of fatty alcohols on metal powders (cf.Figs.16 and 3Ld). Alternatively, the second plateau may apparently in many cases represent a second condensed monolayer formed on top of the first; examples are certain monosulphonated aromatic compounds on graphite, from water (curve S 4), and some cyanine dyes on silver halide (L 4).

It is observed that adsorption of ionic micelles seldom produces a rise in the isotherm beyond the first plateau. Possibly the mutual repulsion of the charged layer and micelles in solution, already mentioned, prevents this.

---

* E.g., certain sulphonated dyes on (chromic acid) anodic film on aluminium, where the penetration is so complete that the substrate eventually crumbles away when excess dye is present.[64] The same phenomenon is observed on wool, once its capacity for adsorbing acid dyes is satisfied, further adsorption results in a decrease in tensile strength of the fibres[75].

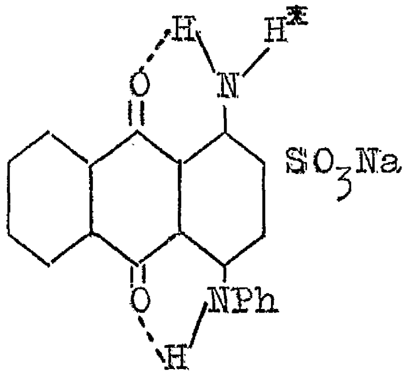
(vi) Maxima

Occasionally a fall in slope occurs after the first inflection, i.e., the isotherm has a maximum (sub-group mx). This is probably due to association of the solute in solution, i.e., with increase in concentration, the solute-solute attraction begins to increase more rapidly than the substrate-solute attraction.. Examples are adsorption of p-nitrophenol on alumina (Fig.40b,c), methanol on nylon[61], anionic detergents on wool etc. Often there is a minimum after the first maximum, and the curve thereafter rises again (Fig.3Lc). Aickin[57], while studying the adsorption of sodium alkyl sulphates by wool and other fibres, observed that the amount of detergent adsorbed increases until a certain concentration is reached, then it decreases to a temperary minimum and then increases slowly again as the concentration rises. By surface tension experiments with the same adsorbate, he has come to the conclusion that the initial adsorption up to the maximum is due to single ions, and once the concentration, at which micelle formation begins is reached, the adsorption starts to fall and reaches a minimum (due to micelle formation); then adsorption rises again (this time the micelles are adsorbed and not the single ions).

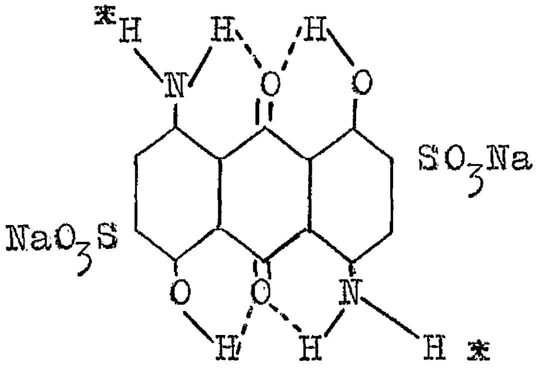
Changes in Isotherm Shape with Change in Adsorption Variables.

Sometimes a small change in some variable can change the isotherm class. Adsorption of p-nitrophenol is an interesting example; p-nitrophenol gives: S curves from polar solvent on polar substrates - alumina (Fig.4), silica (Fig.6), wool fibre (Fig.38); L curves on carbons from water (Figs.21 and 22) or on polar substrates, viz. alumina (Fig.5), silica (Fig.44), or wool (Fig.39) from non-polar solvents; and a C curve on nylon from benzene (Fig.3Cb) (which has a low swelling power for this polymer). The reasons for these variations will be apparent from the discussion above.

A particularly useful example to consider is that of the difference between certain anthraquinone dyes on silica.



(C.I.62,055)
I



(C.I.63,010)
II

* Probable hydrogen-bonding centres

From water, on silica I gives the S curve but II gives the L-curve (Fig.17). This suggests that I is close-packed vertically in the monolayer and II is adsorbed flat. The >NH groups presumably form hydrogen bonds with the silica surface. Dye I has only one H-atom free for bonding hence packs vertically and gives an S curve, while II is attached to the surface at two points and gives an L-isotherm.

We have not encountered any evidence that change of temperature causes changes in the class of the adsorption isotherm, though of course the position of the isotherm is usually altered.

Determination of Specific Surface Area -

This is discussed in more detail in a later section.

Section II

The Measurement of Specific Surface Areas of Solids by Solution Adsorption Methods.

The industrial uses of materials in powdered form are very extensive. There are some industries whose entire product is in the powder form, involving huge tonnages of material, e.g., pigments and building cements; there are other materials, such as rubber, plastics, bituminous road materials, paper, etc., where large quantities of powders are used as fillers. The pharmaceutical, insecticide, ceramic, and cosmetic industries handle large quantities of materials in the powder form. Powder metallurgy is an industry by itself. Fine coal is essential for certain applications such as pulverised fuel, carbonization, and the production of smokeless briquettes from low rank coal.

For[80] most industrial control purposes three characteristics of a powder are important: (1) size frequency (2) particle shape and (3) specific surface. Size frequency data give the frequency of occurrence of particles of the various groups of sizes present in the powder. From the nature of these data, a curve is generally the most convenient form of presentation.

The definition of particle shape is complex; it is inevitably so, since the general term "shape" implies two distinct characteristics, namely, geometrical form and the relative proportions of length, breadth, and thickness. The quantitative correlation between process or product control in industry and particle shape appears never to have been attempted. The particle shape is a characteristic of some importance in practice; e.g., to give some typical examples, the durability of paints, the porosity of a bed of powder, the viscosity of a suspension, etc. are dependent on it.

The specific surface is defined as the surface area per unit weight or per unit volume of the powder; the definition based upon weight being the most generally useful. It is particularly useful for routine control of manufacturing processes in which a knowledge of the complete sizing analysis for every sample is unnecessary.

Quantitative assessment of the results of crushing and grinding - specific surface as a measure of the degree of comminution[81].

Grinding is the most important process of powdering. For any comparison to be carried out, whether between materials with regard to the "grindability" or between grinding equipment with regard to "efficiency", one must be able to measure the results of grinding in an objective and adequate way. The mean particle sizes at successive stages of a grinding operation will be found to form a series of decreasing values; but since, due to the homogenizing effect of grinding, the size range also decreases from one stage to the next, a measure is needed which would take into account both these effects. Such a measure is the specific surface of the particles, since it depends on both the mean particle size and size distribution.

Methods for determination of surface area:

Various methods[82] have been proposed for the determination of specific surface. They determine a factor which is proportional to the specific surface of the powder and are useful for routine control. They have been devised to obtain numerical characteristics of the average fineness of the powder or dust, and include: (1) adsorption of gases; (2) adsorption of solutes from solution; (3) X-ray examination; (4) air permeability measurement; (5) radioactive tracer techniques; (6) light extinction measurement; (7) heat of wetting measurement; (8) determination of the rate of solution of the powder in a solvent; (9) tinting strength measurement; and (10) the use of microscopy - optical and electron. The general principles on which these methods are based are described below; for detailed accounts the original references should be consulted.

(1) The Gas adsorption method:

This method depends upon the evaluation of a quantity known as the "monolayer capacity" of the powder. This is the quantity of gas which is adsorbed in forming a complete layer of single molecule thickness on the surface of the powder.

If the monolayer capacity, x_m , is expressed in moles per gm. of the powder; A is the area of powder surface occupied by a single molecule of adsorbate, then S, the specific surface of the powder,

$= x_m NA$, where N is the Avogadro Number. ....(2)

For determination of monolayer capacity the volumes of a gas adsorbed per gm. of the solid at equilibrium over a range of pressures and at a constant temperature are measured. Then an isotherm, - showing volumes against pressures, is plotted. Brunauer, Deming, Deming and Teller have described five types of isotherm (ref.48,p. 150), but in practice their Type II isotherm is usually obtained.

The equation[83] of the isotherm is

$$\frac{p}{V(p_o - p)} = \frac{1}{Vm\ C} + \frac{(C - 1)p}{Vm\ C\ p_o} \qquad \ldots\ldots\ldots(3)$$

(known as the BET equation, after Brunauer, Emmett, and

Teller, who first proposed it), where V = volume of gas adsorbed at pressure p at a temperature at which the vapour pressure of the liquified gas is p_o; Vm = volume of the gas required to form a monolayer, and C = a constant related exponentially to the difference between the heat of liquefaction of the adsorbate and its heat of adsorption.

Plotting $p/V(p_o-p)$ against p/p_o yields a straight line whose slope represents the quantity (C-1)/VmC, and whose intercept on the $p/V(p_o-p)$ axis represents the quantity 1/VmC. Hence both Vm and C are determined and can be evaluated. Dividing Vm by the weight of the powder in gm., we obtain the volume of the monolayer x_m per gm., and substitution of the value (x_m) in equation (2) gives the specific surface.

In some cases the adsorption isotherm is of the Langmuir type, where the quantity of gas adsorbed asymptotically approaches a saturation value q_o which is assumed to represent the completion of the monolayer. In these cases the Langmuir equation is most conveniently employed in the form

$$p/V = \frac{1}{a_1 \, Vm} + \frac{p}{Vm} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where a_1 is a constant characteristic of the system;

p/V plotted against p gives a curve whose slope is 1/Vm.

Popular adsorbates are nitrogen or a rare gas, at liquid air temperature, or benzene or carbon tetrachloride at 25°C.; the adsorbate must be inert, i.e., it must not react with or dissolve in the solid.

(2) Adsorption of a solute from solution:

The principle of this method is the same as in gas adsorption. The solid is shaken up with a known volume of solution at constant temperature until there is no further change in concentration, and then the supernatant liquid is analysed. In order to draw the isotherm it is necessary to carry out a series of adsorption determinations with a range of initial solute concentrations. The highest adsorption may persist over a wide range of concentrations, giving a plateau, which by analogy with the Langmuir isotherm for gas adsorption has often been taken to denote completion of the adsorbed monomolecular layer. By assuming a value for the area occupied per adsorbed molecule the total surface area may then be evaluated. Dyestuffs[84], long-chain fatty acids[85] and many other solutes have been suggested as adsorbates, together with aqueous and non-aqueous solvents.

(3) X-ray examination; Low angle scattering technique (ref. 41, p.227).

In this method monochromatic X-radiation is passed through a thin layer of the solid under examination and the scattered radiation is collected on a photographic plate; in addition to an intense black spot in the centre, where the undiffracted radiation hits the plate, there is a diffuse surrounding black patch, and from the intensity distribution of this patch the average particle size can be calculated. Experiments with a number of solids, such as ferric oxide, alumina and nickel oxide, have shown that the surface area calculated from this particle size agrees satisfactorily with that obtained from gas adsorption.

(4) The Permeability method: (Lea and Nurse method[86])

If a gas or a liquid flows through a bed of a fine-grained solid, it has to pass through a series of fine but tortuous channels; ultimately, this amounts to flow through a capillary tube, which is determined by the length and the radius of the tube, and so, indirectly by the surface area of its walls. With a bed of solid these walls constitute the external surface of the material.

In this method air or another gas is passed under pressure through a bed of solid and the drop in pressure across the bed is noted by means of a manometer connected to pressure points above and below the bed. Specific surface is calculated by the application of the formula:

$$S = \frac{14}{\rho} \cdot \frac{p^{3/2}}{(1 - p)} \sqrt{\frac{A\ h}{Cf} \cdot \frac{Hm}{Hf}} \qquad \text{..........(5)}$$

where S = the specific surface in cm.^{2}/gm.; ρ = the density of the powder; p = the porosity of the bed; A = the cross-sectional area of the bed; h = the height of the bed; Cf = the flowmeter constant; Hm = the monometer reading; and Hf = the flowmeter reading.

p, Cf and $^{Hm}/_{Hf}$ are determined by separate experiments;

$$p = \frac{Va - V}{V} \qquad \text{..........(6)}$$

where Va represents the apparent volume of the powder, and V is the actual volume (i.e. the weight of sample taken divided by its specific gravity).

Air is passed through the apparatus when empty and the flow rate (Q) and the corresponding flowmeter reading (Hf) are noted. The flowmeter constant (Cf) is given by

$$Cf = \frac{Q \cdot \eta_{air}}{Hf\ \rho_s} \qquad \text{..........(7)}$$

where η air is the viscosity of air in c.g.s. units and ρ_s is the density of the flowmeter liquid. The value of Hm/Hf is obtained by passing air through a bed of solid at several flow rates and noting the corresponding manometer (Hm) and flowmeter (Hf) readings. A graph of Hm against Hf is a straight line passing through the origin and the slope of the graph gives the ratio $^{Hm}/_{Hf}$.

The permeability method can be used successfully for the determination of the surface areas of powders which have coarse particles, i.e. an average particle size greater than 10 μ. On the other hand the method cannot be used at all for very fine powders. Carman[111] estimated that the theoretical lower limit of the validity of the method is in the neighbourhood of 0.1 μ.

(5) The Radioactive indicator method:

This was first used by Paneth and Vorwerk[87] for the determination of the surface area of lead sulphate. They shook up a very slightly soluble lead salt with a saturated solution of the same salt, containing, besides ordinary lead, a small quantity of radioactive isotope (Thorium B). During the shaking, there was an interchange of atoms between the surface of the powder and the solution, Thorium B atoms sharing in this interchange just like the inactive atoms. Equilibrium was rapidly set up, and finally, of course, the proportion of active to inactive atoms was the same both in the surface and in the solution. Hence the following equation holds,

$$\frac{\text{radioactive lead in surface}}{\text{radioactive lead in solution}} = \frac{\text{total lead in surface}}{\text{total lead in solution}} \quad \ldots\ldots (8)$$

Of the four quantities in this equation, the amount of radioactive lead in the powder and the solution can be determined by an electroscope, and the total lead in solution can be found by chemical analysis, so that the total number of lead atoms in the surface can be found by calculation.

One weak point in this method appears to be that it is not certain that it is the surface layer only which takes part in the interchange of atoms; at true equilibrium, the radioactive material would penetrate throughout the whole solid powder. This criticism is less serious than appears at first sight, because a nearly steady state is found to be established in less than a minute, only a slow change going on after this time. It is probably at the end of this initial period that the equilibrium is established as regards the easily accessible surface. Cracks in the solid material, as well as diffusion within the solid, may account for the further slow interchange.

This method gives the number of lead atoms on the surface, and this was converted into square cm. by assuming the density of the surface layer to be identical with that of the lead salt in bulk, and also that the area of the molecules in the surface layer is the same as if they were cubes with known volume of the molecule.

In the case of lead salts the areas deduced by the radioactive method are of the same order of magnitude as those found by microscopic examination; the discrepancies may, however, reach 100 or 200 percent. The method is only directly applicable to solids which have an element with a radioactive isotope. Kolthoff and O'Brien[88] used artificially radioactive bromine for estimating the surface of silver bromide. It is necessary in this case to have an adsorbed layer of dyestuff to restrict exchange with the interior.

(6) The light-extinction method[89].

The method depends upon the application of the Lambert-Beer law. For a system in which the solid particles are dispersed in a fluid medium the law may be written in the general form

$$I_1 = I_o e^{-\frac{\epsilon C l}{d}} \qquad \text{............(9)}$$

where I_o = intensity of light transmitted by pure fluid; I_1 = intensity of beam after passing through the suspension; ϵ = a constant (the extinction coefficient); C = mass concentration per unit volume (gm./c.c.); l = length over which absorption of light takes place (cm.); d = diameter of particles (microns).

Equation (9) may be rewritten

$$\log_e \frac{I_o}{I_1} = \frac{\epsilon C l}{d} \qquad \text{..........(10)}$$

The law thus demands that for a suspension of a given powder the ratio $\log_e \frac{I_o}{I_1}$ should be directly proportional to the concentration of particles and to the length of the light path.

It will be evident that equation (10) is of no help in obtaining a measure of particle size unless the extinction coefficient ϵ be known, which is not usually the case. For this reason, several workers have used a somewhat different form of the equation, thus

$$I_1 = I_o e^{-A C l} \qquad \text{..........(11)}$$

$$\text{or} \quad \log_e \frac{I_o}{I_1} = A C l \qquad \text{..........(12)}$$

where A = projected area (sq.cm.) per gm. of particles, in the light beam.

Equation (12) differs from equation (10) in that it is assumed the particles are absolutely opaque and that the light cut off by the particles can be equated to their projected area, irrespective of particle size. Further, ϵ in equation (10) is a comprehensive constand and takes into account any light passed on, in a forward direction, by reflection from one particle to another. This is of necessity ignored in equation (12), in which there is also an additional assumption made, that the extinction due to particles of a certain size is unaffected by the presence of particles of size other than that under consideration.

It has been shown by Cauchy that for irregularly shaped solids (only for convex bodies), randomly oriented,

$$A = {}^{1}/_{4}\ S \qquad \ldots\ldots\ldots\ldots\ldots(13)$$

where S is the specific surface, the surface area in $cm.^2$ per gm.

Accordingly, Heywood has used the following form of the light extinction equation,

$$S = \frac{4}{C\ l} \log_e \frac{I_0}{I_1} \qquad \ldots\ldots\ldots\ldots\ldots(14)$$

The use of equation (14) enables S to be calculated readily, I_0 and I_1 being most conveniently measured by means of a photo-electric cell. It is, of course, essential to the above treatment that the beam of light should be parallel, or as nearly so as can be achieved in practice. Furthermore, the relation expressed by equation (14) is valid only for the particles of size greater than the wavelength of visible light (0.4μ to 0.7μ).

It will be realized that there are so many inherent errors in the method that its application for absolute measurements is very uncertain. Nevertheless the method is attractive on account of its convenience, use of only a small sample and the great precision of the optical instruments.

(7) The heat of wetting method[90]:

The heat of wetting of a powder in a given liquid is the heat evolved when 1 gm. of the powder is immersed in excess of the liquid; if h is the heat evolved by 1 cm^2 of the surface when wetted, then the heat of wetting (H) per gm. is $H = h\,S$, where S is the specific surface of the solid.

The factor h is a function of both the solid and the wetting liquid, both chemical and physical factors being involved, and its value must be determined for each combination. Hence for absolute determinations it is necessary to calibrate with samples of the material of known surface area measured by an appropriate method, usually nitrogen adsorption. H is a measure of the total area reached by the molecules of liquid, so unless the molecules are very large it will include an appreciable proportion of the internal area; and if the molecules are small, such as those of methyl alcohol, the liquid will reach most of the internal surface.

Even for fine powders, the heat liberated per gm. of powder is very small, of the order of 0.1 cal. and so the measurement of heat evolved is difficult. This in practice restricts such standard determinations to porous or extremely finely divided solids.

The solid must be thoroughly outgassed, otherwise the heat measured will be the true heat of immersion less the heat of displacement of the impurity; moreover, the displacement process will greatly reduce the rate of approach to equilibrium and therefore of evolution of heat. The wetting liquid must be pure. The presence of water, particularly in a non-polar solvent, is especially deleterious, e.g. Harkins et al.[91] found that 0.01% water in benzene nearly doubled the heat of immersion of titanium dioxide. The liquid must neither react chemically with the solid nor dissolve it.

The method has the advantage of requiring only a single observation for the calculation of specific surface. Because of its complexity, it has not enjoyed the popularity it deserves, though it gives quite accurate surface area values.

Harkins et al.[91] have given a number of values of heat of immersion h per cm^2. of various solids in various liquids.

(8) Rate of solution of a powder in a solvent:

This method depends for success upon the provision of a solvent which has a uniform reaction, at a reasonable rate and capable of easy and accurate measurement. If W_1 is the weight of a sample of surface area S_1 dissolved in a certain solvent in a certain time, and W_2 is the weight of a sample of the same substance, but with a different surface area S_2, dissolved in the same solvent under identical conditions, then weights and areas are related by the equation,

$$\frac{W_1}{S_1} = \frac{W_2}{S_2} \qquad \text{.................(15)}$$

W_1 and W_2 are calculated by weighing the powders before and after the dissolution, then if S_1 is known, S_2 can be calculated.

The disadvantages of the method are: (i) the surface area of the powder used as a standard must be known; (ii) a suitable solvent may be difficult to find; (iii) if there is a wide range of particle sizes in the powder, some of the finer particles may dissolve completely during the experiment.

This method was much used for the determination of specific surface areas of various glass powders by Schmidt and Durau[92], and Schelte[93]. In spite of the above objections the method was successfully used by Palmer and Clark[94] for surface area determination of vitreous silica powder by measuring the rate of solution in hydrofluoric acid.

(9) Tinting strength method[95]:

Theoretical studies of the optical properties of black pigments show that they must give minimum white reflectance and this condition is favoured by the smallest possible particle sizes, preferably well below the wavelength of visible radiation. The particles of enamel blacks are between about 0.01μ and 0.1μ in diameter and so are well below the wavelength of visible light, which covers the range of about 0.4μ to 0.7μ.

The measurement of size characteristics of these fine blacks is a problem of extreme difficulty. These materials are difficult to disperse in most fluids and are difficult to analyse by other methods owing to the small particle sizes involved.

The tinting strength of a pigment is an operational concept. It depends upon the method used, and thus upon the implied definition. As a rule, tinting strength is expressed relative to a standard. One method consists in mixing the test pigment, say a certain kind of carbon black which has been suspended in linseed oil, with a specified amount of zinc white. The same is done with a carbon black that is serving as a standard. The tinting strength ratio is the ratio of the weights of test black and standard black which give the same shade with one and the same amount of zinc white.

(10) The microscope method:

A method for estimating the surface areas of irregularly shaped particles by microscopy was suggested by Kenrick[96]. A photomicrograph of the particles on a microscopic slide is taken and projected on a screen. The outlines of several hundred particles are traced on the screen, and the areas of the outlines are measured with a planimeter. Particle surface area is related to projected area by the equation:

$$\text{average particle surface} = \frac{4\sum A}{n} \qquad \text{..........(16)}$$

where $\sum A$ represents the summation of areas of the projected images of n convex particles mounted in random orientation. If there are N particles per gm. of the powder then the specific surface (S) is:

$$S = N \cdot \frac{4\sum A}{n} \qquad \text{..........(17)}$$

A variation of this method is suggested by Pidgeon and Dodd[97]. Use is made of the camera lucida. A prism arrangement is fitted in the eyepiece of the microscope by which the image of the particle is projected downwards on the table on which the microscope stands. The outline can now be easily traced with pencil on paper. Alternatively, a graticule is fixed in the eyepiece of the microscope, which enables the observer to express the areas of the particles in terms of calibrated circles, opaque or transparent, on the graticule.

A special technique is needed to get a random orientation of the particles on a slide and count the number of particles in a certain weight of the sample.

The lower limit of particle size that can be resolved by the microscope using visible light is of the order of

0.2 μ. Many industrial powders contain a high proportion of particles smaller than 0.2 μ in diameter; for them the electron microscope is used, which resolves particles of 0.005 μ in diameter. Electron microscopy requires specialized techniques for specimen preparation and because of the very small field of view available a large number of plate exposures must be made in order to count a sufficient number of particles for an accurate analysis. Electron microscopy is not suitable for routine analysis.

In addition to the above ten methods of surface area determination, the method of surface silvering has been used for researches on finely ground silica particles;[98] also, for metals, electrolytic[99] and interference[100] methods, and for general use, a heat conductivity method[101] has been used.

Scope of surface area methods:

Particles of many powders possess in addition to their external visible surface an internal surface. In compact bodies such as powdered quartz or crystalline alumina the internal surface is only small, whereas in porous bodies such as clay, cement, coal, starch, etc., the internal surface may be considerably greater than the external surface; indeed, a difference factor of the order of 100 times is not unusual. Whether the external or the total surface is required depends on the purpose for which the powder is to be used and this purpose must be borne in mind in selecting a suitable method. Thus for applications connected with resistance to flow of gases and packing problems, the external area is relevant, whereas in problems such as the application of carbon blacks in rubber reinforcement, the use of catalysts in the chemical and oil industries, and the study of adsorbent and ion-exchange materials the total surface is required, of which the internal part is usually by far the greater proportion.

Measurement of the total surface can only be made either by heat of wetting or adsorption methods. Other methods give the external area of the particles and are also limited to measurements in size ranges coarser than about 0.1μ (except the electron microscope).

Comparison of Adsorption Methods:

As described above there are two adsorption methods, adsorption of a gas and adsorption of a solute from solution. The results of the two methods may agree for dense, non-porous particles, but often there is serious disagreement if the particles have considerable pitting or porosity.

Gas adsorption requires a complex apparatus and the complete degassing of the sample. The experiment is carried out at a temperature near the condensation point of the adsorbate. Nitrogen gas is the most popular adsorbate and the temperature used in practice is $-195.8^{\circ}C$, the boiling point of liquid nitrogen. In spite of these objections, it is the only accepted method for absolute specific surface area determinations. A number of workers have compared surface areas on specially selected samples determined by gas adsorption with those calculated from other methods such as microscopic count, electron microscope, air permeability, and adsorption from liquids. The agreement obtained justifies workers in accepting with confidence the results of the gas adsorption method.

The solution adsorption method is much more rapid, since no pretreatment of the sample is required, the experiment is carried out at room temperature, the equilibrium is usually reached rapidly and the analysis of the residual adsorbate may be accomplished easily. Dyestuffs are popular adsorbates, for they can be rapidly and accurately determined by a colorimeter. It is assumed that there is complete coverage of all areas accessible to the solute; however the competition of the solvent adsorbed at some sites may make this assumption incorrect for certain systems. Another difficulty is the uncertainty of the value of the surface area occupied by each adsorbate molecule. The dye molecules are very asymmetrical, whereas the gas molecules are reasonably symmetrical and so variations of estimated specific surface would be expected to be larger with the method of dye adsorption than with gas adsorption. For comparison of specific surfaces of large numbers of samples, however, these effects are immaterial. With judicious absolute calibration by low temperature gas adsorption the method may speed up comparison in a routine control of a production process.

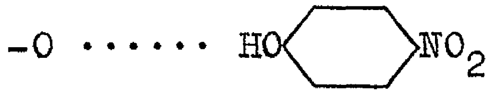
Giles and collaborators[54,65] have cautioned against the use of dyes, since they are often adsorbed as ionic micelles. A more reliable method is the adsorption of a surface-active compound, e.g., a fatty acid from an organic solvent[85,102]. An accurate estimate of the surface area covered per adsorbed molecule can be obtained from independent monolayer measurements on water.

In order to overcome some of the objections against adsorption from solution, such as uncertainties of orientation of the adsorbed molecules, their cross-sectional area, the extent of competition from the solvent, etc., a method based on adsorption of p-nitrophenol from solution has been developed.

From the present knowledge of the forms and significance of solution adsorption isotherms, presented in Part I, Section 1 of this thesis, the following requirements are necessary for a solute to give reliable specific surface area measurements. It should be: (i) highly polar, to ensure strong attachment to the whole surface of polar solids; (ii) partly hydrophobic, to ensure adsorption by non-polar solids; (iii) of small molecular size, preferably with a planar molecule, and likely to be adsorbed with its molecules stacked together end-on to the surface, to ensure accurate estimates of the area covered per molecule; (iv) not surface-active, to avoid the formation of three dimensional micelles at the surface; (v) coloured, for ease of analysis; (vi) readily soluble both in water and in non-polar solvents. p-Nitrophenol (PNP) satisfies these requirements.

Orientation and Area occupied by PNP on the substrate:

This solute is normally adsorbed end-on at polar surfaces from polar solvents by hydrogen bonding between -O atoms on the substrate and the OH groups in the PNP molecule, thus -



As the solvent also competes for the substrate sites, the isotherm is of S 2 type. Examples are, adsorptions from water on silica (Fig.25), alumina (Fig.19), wool (Fig.38) etc. The effective cross-sectional area for end-on adsorption at room temperature is ca.25 A^2. This is very close to that for surface-active p-alkylphenols in monolayers on water[76]. Presumably the p-nitrophenol molecules are separated by about the thickness of one water molecule and the adsorbed layer consists of mixed water and p-nitrophenol.

On surfaces composed of aromatic nuclei, e.g., graphite or pigments, the adsorption is by van der Waal's forces between the benzene nucleus of p-nitrophenol and the aromatic nuclei of graphite and therefore p-nitrophenol lies flat on the surface and gives L 2 or H 2 type isotherms, The effective cross-sectional area in such cases is ca. 52.5 A^2 (calculated from Catalin models). p-Nitrophenol molecules presumably occupy the whole substrate with very little water between them. Usually these L 2 and H 2 isotherms give a second plateau about twice the height of the first with increased concentration. This second plateau probably represents a re-orientation to the end-on adsorption with increased concentration. The area occupied at this second plateau is ca. 25 A^2 per molecule. Examples are adsorptions on yellow azo pigments (Figs.28 to 31).

Non-polar solvents such as benzene or hexane do not compete for polar substrate sites and hence the isotherms from these solvents are of L or H type. Apparently in this case the whole surface is covered by _p_-nitrophenol molecules tightly packed. The end-on cross-sectional area measured from a model, is _ca_. 15 $Å^2$ and this is the value obtained for adsorption on alumina from benzene (Fig. 5). Examples, are adsorption on silica (Fig.44), cement (Fig.23), and sugar (Fig.37).

With extremely finely divided substances such as Neo Spectra carbon black, there is no clearly defined plateau, only a "point B" (ref.48, p.287) inflection (Fig. 20), and presumably the monolayer is complete at that point and the area occupied by _p_-nitrophenol is 52.5 $Å^2$ per molecule because of flat orientation (L type isotherm).

Effect of temperature on area occupied by the PNP molecule:

The effect of change of temperature upon the apparent cross-sectional area of adsorbed solutes is important in calculating surface areas. The adsorption of _p_-nitrophenol, like nearly all solution adsorptions, is exothermic, and the amount adsorbed consequently increases with fall in temperature. Reduction of temperature causes a fall in the apparent cross-sectional area of the surface-active molecules in monolayers on water[103] and the same effect would be expected in solution adsorption.

Tests made with p-nitrophenol from water on alumina (Fig.40) show that the apparent cross-sectional area does in fact seem to decrease a little with fall in temperature, but complications in the measurements are introduced by a sharp fall to a minimum in the curves, due probably to the association of the solute in the solution of highest concentration. On a graphite surface, the solute is adsorbed flat and the surface is non-polar, so that there will be a lower proportion of water in the adsorbed layer at room temperature; thus little change occurs when the temperature is lowered (Fig.41).

Thus, if the adsorption temperature is about 18°C the molecular area is 25 A^2 for the S-curves (end-on orientation) and 52.5 A^2 for the L-curves (flat orientation) from water. From benzene on polar solids the value is 15 A^2, with probably little or no change if the temperature varies a few degrees on either side of 18°C.

A Rise or Fall in p-nitrophenol Isotherms:

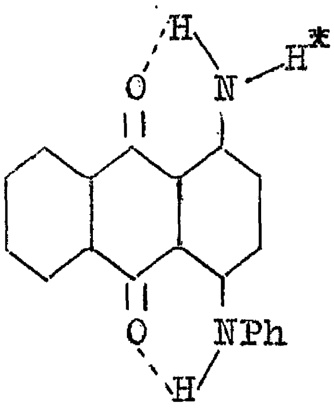
A glance at the p-nitrophenol S-isotherms shows that most of them are of either S 2 (Figs.19,26) or Smx (Figs.40b,c) shape. Usually during investigation, once the plateau was reached (i.e. an S 2 type isotherm obtained) the case was not investigated further. All solutes tend to aggregate in solution as the concentration increases and *p*-nitrophenol is not an exception to this rule, but this aggregation or association can occur on the adsorbent as well. So there is a competition between the adsorbent and the solvent for this association to occur. Solubility is another variable and it can favour the adsorbent or the solvent, depending on temperature. Once all the sites on the adsorbent are occupied, there is little competition from the adsorbent, association can occur in the solvent, and the isotherm then falls (i.e. the curve is Smx type). If the temperature is high, or if the concentration where solute-solute attraction predominates is not yet reached, then a further layer of solute can be built up on the one already occupied and an S 3 type of curve is obtained. This accounts for the various shapes of S curves. They are determined by the surface area of the adsorbent, the concentration of solution, and the temperature.

At present there is very little information about S 4 curves. With L curves it is definitely known that the first plateau corresponds to the molecules lying flat on the surface and as the concentration rises, these molecules stand up to accommodate the incoming molecules till the whole surface is occupied (e.g. *p*-nitrophenol on pigments). The above reasoning holds good for a fall in the L curves after a first plateau is reached.

The second rise after a minimum in the isotherm is due to adsorption of micelles as pointed out by Aickin[57].

Specific Surface Area of Silica.

The specific surface area values for finely powdered silica (MSC brand) are almost the same when measured by nitrogen adsorption and by p-nitrophenol adsorption from a non-aqueous solvent, or by adsorption from water of a mono-sulphonated anthraquinone acid wool dye (C.I.62055, Acid Blue 25). Refer Table III.



In the last mentioned case, the adsorption is probably by a >NH ····· O- bond at the free hydrogen atom marked by an asterisk, and is assumed to be end-on in a close-packed monolayer. (Molecular cross-section = 87.1 A^2, measured from a Catalin model). Any water in the monolayer can be accommodated between the dye molecules without interfering with their packing, because of the bulkiness of the sulphonate group.

The silica-dye combination in this case is of the nature of acid-base bonding, apparently with the whole surface of silica. The silica-p-nitrophenol combination in water is weaker, both components having acidic properties, (SiO^- and $^-O-C_6H_4-NO_2$), and the active sites for p-nitrophenol adsorption are limited to about 20% of the total surface. (Refer Table III, S.S.A. by PNP in water is ca. 1.0 $m^2 g^{-1}$ and by dye and N_2 it is ca. 5.0 $m^2 g^{-1}$). On addition of a little hydrochloric acid (to reduce the ionisation of PNP) or of sodium chloride (to decrease the solubility of PNP in water in the hope of increasing adsorption) to the solutions, adsorption actually decreased. This suggests that the active sites on the silica surface consist partly of ionised $-O^-$ groups.

Therefore, for potentially acidic solids that are likely to be negatively charged in water, the most reliable result will probably be given by using the dye C.I.62055 in water or p-nitrophenol in a non-aqueous solvent. The dye method is preferred because it uses water as solvent and the analysis does not need a u.v. spectrophotometer.

p-Nitrophenol in water gives a value for quartz that agrees with that obtained by use of the dye; this was not further investigated, but it would appear that the amount of grinding that MSC powder has received has affected the reactivity of the surface in water.

S.S.A. of Titania

Titania, like silica, is negatively charged in contact with water and repels negatively charged p-nitrophenol ions, dye (C.I.62,055) adsorption however gives values close to nitrogen (ref.Table III). Surface area values by p-nitrophenol adsorption from a non-polar solvent (xylene) agree with nitrogen, but only if it is assumed that the p-nitrophenol molecule lies flat (cross-sectional area 52.5 A^2) on the titania surface. The following hypothesis is suggested. p-Nitrophenol is attached to oxide surfaces by hydrogen bonding, in the case of titania this bond must be very weak because p-nitrophenol is not adsorbed either from water or chloroform (at least in the case of four titania samples examined), which themselves are hydrogen bonding agents. From non-polar solvents, p-nitrophenol can apparently form a hydrogen bond with the titania surface, but as the bond is weak, it is unable to hold the p-nitrophenol in a vertical position (end-on orientation) with the result that the p-nitrophenol molecule lies flat.

Alternatively forces acting over the whole of the benzene nucleus might be stronger than the hydrogen bonds, and hence would promote flat orientation. One way to check this hypothesis would be to find out if p-nitrophenol on titania from non-polar solvent gives the L 4 curve (the present curves are of L 3 shape) the first plateau corresponding to flat orientation and the second to vertical orientation, but unfortunately due to limited solubility of p-nitrophenol in non-polar solvents, the curves cannot be extended further. However, in this case, the use of the dye from water is more convenient and gives good results, so that it is not necessary to use p-nitrophenol and a non-aqueous solvent.

Surface area of fibres:

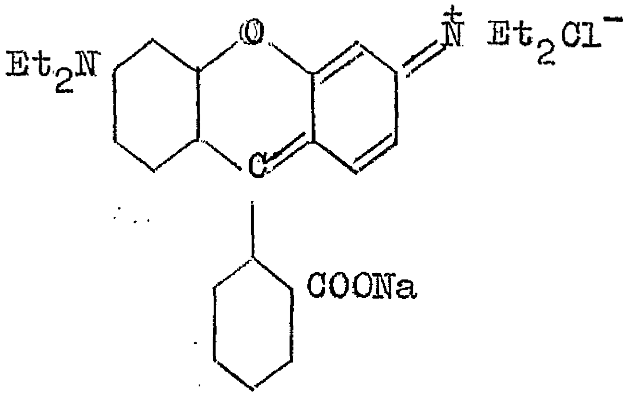
p-Nitrophenol from water solutions was used to measure the surface area of wool fibres, but the value obtained was much higher than the microscopic value, (by microscope, 0.13 $m^2 g^{-1}$; by p-nitrophenol, ca. 48 $m^2 g^{-1}$). This proves that p-nitrophenol penetrates the fibres. Water causes swelling of the wool fibres and p-nitrophenol can go in. (cf. Fig. 38).

The next step therefore was to choose a solvent whose molecules are bigger than the pores of the wool fibres, so that p-nitrophenol will be restricted to the surface. Speakman[104] found that alcohols of higher molecular weight than n-propanol are unable to penetrate dry wool fibres, so n-heptane, which has a larger molecule than n-propanol, was selected as a solvent. Even then it was found that the surface area value was higher than that given by the microscope, and it increased with time, showing there is the slow penetration of p-nitrophenol inside the fibres (cf.Fig.39).

To overcome this difficulty, surface areas were determined by adsorption for various lengths of time, say 1, 2, 3, 4 hours, and a graph of surface area against time was plotted. This gave a straight line. When this straight line was extrapolated to zero time, the value of S.S.A. obtained was in fair agreement with the microscopic value. At present this method is being developed in this laboratory; and it is found that if the adsorption is carried out for 10 minutes from n-heptane, the values of S.S.A. for fibres obtained by p-nitrophenol agree very well with the microscopic values.

Adsorption of Basic dyes on acidic Alumina.

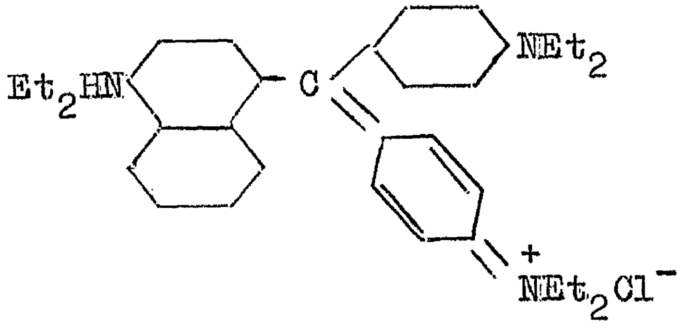
After the successful use of an anionic dye (C.I. 62,055) on the negatively charged silica surface, a cationic dye (C.I.45,170) was tried on a positively charged surface. The positively charged surface chosen was hydrochloric acid-treated alumina (preparation and properties described elsewhere).



Rhodamine B (C.I. 45,170)

This dye gave an L 2 isotherm (Fig.45) and considering flat orientation of the molecule on the substrate, the surface area of alumina was found to be 1.26 $m^2 g^{-1}$ as against 39.0 $m^2 g^{-1}$ by p-nitrophenol. (The molecular cross-section for flat orientation is 210 A^2, calculated from Catalin models). The reason for the low area given by the dye may be that the dye does not contain a proton donor group by which it can attach to the O-atoms on the alumina surface by means of hydrogen bonding, or the acid treatment has replaced all the OH groups by Cl and thus it cannot act as a proton donor.

Next a dye containing a proton donor group in the molecule (C.I.42,595) was selected, but even then the attempt was not successful.



Victoria Pure Blue BO (C.I.42,595)

It was expected that the dye would attach to the -O atoms in the surface through the HN- group and give a vertical orientation (S isotherm). It gave an L isotherm (Fig.46) indicating that either the molecule is too bulky and the vertical orientation is not possible or that the three N atoms in the dye molecule are attached to the -OH groups still present on the substrate and by this three-point attachment it lies flat on the surface. The cross-sectional area of the dye molecule for flat orientation, from Catalin models is 254 $Å^2$, and hence the surface area is 0.724 $m^2 g^{-1}$. The matter was not pursued further.

The rate of adsorption.

Adsorption involves three stages, namely: (1) diffusion of solute through the solution to the surface of the adsorbent, (2) adsorption of solute on the outer surface of the adsorbent, and (3) transport of this solute from the surface to the adsorbing sites within the adsorbent. The second of these steps, the actual adsorption process, is generally assumed to be so much more rapid than either of the other steps that it can be regarded as instantaneous. The measurable rate in the adsorbents is due to either of the steps (1) or (3), whichever is slower. The process indludes diffusion and convection and, therefore, is accelerated by stirring. Inside the adsorbent, convection is negligible and solute transport is not affected by external agitation. The rate of this transport, that is the velocity of diffusion inside the adsorbent, very often determines the overall rate of adsorption. As would be expected, it is larger the wider the adsorbent pores.

In the initial stages, adsorption is usually extremely rapid, but it decreases once the equilibrium state is approached. Apparently, the solute diffuses towards the least accessible sites of the adsorbent.

It will be evident from the time-adsorption curves

(Fig.47) that with active solids such as alumina or carbons equilibrium is rapidly established. Silica (MSC brand) (Fig.47c) takes about 15 minutes to attain equilibrium from a non-polar solvent (xylene), while it takes about 4 hr. from a polar solvent (water)[65]. This supports the view already put forward, that in water both silica and *p*-nitrophenol are negatively charged and therefore repel each other, while in non-polar solvents there is no ionization and adsorption is easy due to hydrogen bonding.

The case of zinc is rather an interesting one (Fig. 47d). It seems that for the first two hours *p*-nitrophenol lies flat on the substrate and then gradually stands up. This is not due to its making room for the incoming particles while the adsorption proceeds, because in that case, the adsorption of *p*-nitrophenol on zinc would have given an L curve and not an S curve (Fig.24a). *p*-Nitrophenol on alumina from water also gives an S curve, but it does not show this phenomenon (Fig.47e); perhaps in this case the orientation is so rapid that it is not detected.

Experimental

p-Nitrophenol, dye adsorption and bulk density experiments were done by the writer; nitrogen, air permeability and microscope values were determined elsewhere.

Preparation of the substrates:

All the substrates, except wool, were used without any pretreatment.

Chromatographic Alumina - Supplied by Savory and Moore Ltd. for chromatographic use.

Alumina Samples 'A', 'B' and 'H' - Supplied by Dr.K.S.W. Sing of Liverpool College of Technology, who also kindly provided the N_2 value for them.

Alumina - in Fig.40. A sample in the laboratory was used. The N_2 value was provided by Dr.K.S.W.Sing.

Neo-Spectra Carbon Black and Cabot 'ELF' 8 - Supplied by Dr.D.H.T.Spencer of the British Coal Utilization Research Association, who also kindly gave the N_2 and other vapour values.

Graphon. The sample and its nitrogen data were provided by Dr.J.J.Kipling of Hull University.

Coal powder and its s.s.a., obtained from the average particle size by sedimentation procedure, were provided by the Dust Research Laboratory in this Department.

Cement - Sample and air permeability figure were provided by the Dust Research Laboratory and N_2 data by Dr.K.S.W. Sing.

Metal powders - Supplied by Professor E.C.Ellwood, of the Metallurgy department in this College.

Silica (MSC brand) - Supplied, with air permeability value by Messrs. Colin Stewart Ltd., Nitrogen value provided by Dr.K.S.W.Sing. The second air permeability and nitrogen figures were supplied by Dr.Culfeather, late of this Department.

Silica - Supplied by the Dust Research Laboratory.

Quartz - A sample in the laboratory was used, microscopic value found earlier by Miss M.M.Allingham.

Titanium dioxide - Supplied, with N_2 values, by Mr.J.F. McVey and British Titan Products Co.Ltd.

Pigments - Yellow, blue and red pigment samples and their nitrogen values were supplied by Dr.D.M.Stead and James Anderson & Co. (Colours) Ltd.

Sugar - Commercial sugar was used.

Wool - Treated in the way as mentioned in Part I, Section I of this thesis.

Preparation of the Solutes:

1) p-Nitrophenol was recrystallized from water.

2) Dyes - C.I.62,055, Acid Blue 25, (commercial Solway Ultra Blue BS (I.C.I.)) was purified by crystallization from water-ethanol mixture (1:1 v/v) several times, until there was no increase in the optical density of a solution of a given strength.

Cationic dyes (C.I.45,170 and 42,595) - Samples purified in the laboratory were used.

Solvents:

Distilled water, commercial benzene, xylene and *n*-heptane were used.

Adsorption Procedure:

The same as described in Part I, Section I of this thesis.

The rate measurements were not made in all cases. Where not, the adsorption was carried out for about 16 hours and that equilibrium was attained during that time was taken for granted.

Analytical Techniques.

The solutions were analysed spectrophotometrically using a Unicam SP 500 instrument. p-Nitrophenol in water gives a pale yellow solution, which darkens in colour on addition of alkali. The solution can then be analysed at 4000 A. The water solution becomes colourless on addition of a little acid, the solution can then be analysed at 3200 A. n-Heptane and benzene solutions of p-nitrophenol are colourless and were analysed at 2860 A and 3000 A respectively. Xylene solutions of p-nitrophenol were carefully evaporated and the residual p-nitrophenol extracted with water and analysed by the addition of alkali.

The solutions of the dyes (C.I.62,055; 45,170; and 42,595) were analysed at 6000 A, 5500 A and 6100 A respectively.

Bulk Density.

This is the reciprocal of the volume occupied by 1 gm. of the dry sample. It was determined by adding 1 gm. of a pigment to a graduated tube and noting the volume occupied by the pigment. The graduated tube was tapped several times after the addition of the pigment.

In the beginning the volume decreased and reached a steady value after a fairly large number of taps. The reciprocal of this steady volume was taken as the bulk density.

The bulk densities are given in Table III A.

S.S.A. of sugar.

The density of sugar was found by using a specific gravity bottle with benzene as the liquid. Then a large number of (800) sugar cubes were weighed and their volume found by the formula, Volume = $\frac{\text{Mass}}{\text{Density}}$. Considering ordinary sugar particles as cubes, (volume = l^3; surface area of a cube of length l = $6\ l^2$; surface area of a cube = $6 \times (\text{volume})^{2/3}$;

$$\text{specific surface} = \frac{\text{Area of a substance}}{\text{Weight of the substance}}$$), then

$$\text{S.S.A. of sugar} = \frac{800 \times 6 \times (\text{mass/density})^{2/3}}{\text{Weight of 800 sugar cubes}}$$

Calculation of S.S.A.

In all the cases the isotherms - concentration on substrate (C_s) against concentration in bath (C_b) - were plotted, and the monolayer capacity determined from the first plateau of the isotherm or from "Point B".

Consider the curve 'b' Fig.41. The curve is of L type and from water therefore the area occupied by one molecule of p-nitrophenol is 52.5 A^2 (flatwise), so that

$$S = C_s \times A \times N = \text{s.s.a in cm}^2/\text{gm.}$$

where C_s = monolayer capacity in moles/gm. (In this figure 344 mmole/kg.)

N = the Avogadro Number (6.019×10^{23})

A = Area occupied by 1 mole of PNP in cm^2 (52.5×10^{-16} in this case).

As concentration on the substrate in the figure is given in mm/kgm., it must be divided by $10^3 \times 10^3$ to give concentration in moles/gm.

$$\therefore \quad S = \frac{344}{10^6} \times (52.5 \times 10^{-16}) \times 6.019 \times 10^{23}$$

$$= 108.7 \times 10^4 \text{ cm}^2/\text{gm. or } 108.7 \text{ m}^2\text{g}^{-1}$$

Table III

Specific Surface Area Measurements of solids by Solution Adsorption of p-nitrophenol, and other Methods.

Solid	Specific Surface area ($m^2 g^{-1}$) by various methods.					
	PNP* adsorption	Nitrogen adsorption	Air permeability	Optical microscope measurement	Dye (C.I.62,055) adsorption	PNP isother Fig. No
Inorganic						
Alumina						
Alumina chromatographic	39.0					4
" "	39.3(B)					5
" "	82	88				40c
" (type 'B')	39	206				19b
" (type 'A')	48	106				19a
" (type 'H')	55	139				19h
Carbon						
Carbon black ("Neo Spectra")	492	610-750†				20
Graphon	108	120±12				41b
Cabot 'ELF8'	108	112 ††				21
Coal powder	45.7$^{\gamma}$					22
Cement						
Cement	1.17(B)	<1	0.22			23
Metal powders						
Copper	2.62			0.02		24c
Iron	4.57			0.04		24b
Zinc	12.3			0.14		24a

Table III (Cont'd)

Solid	Specific Surface area (m^2g^{-1}) by various methods PNP* adsorption	Nitrogen adsorption	Air permeability	Optical microscope measurement	Dye (C.I.62,055) adsorption	PNP isother Fig.No
Silica	(1.0					6
Silica (MSC brand)	(5.35(B)	5.0, 5.15	1.08, 1.51		5.37 (Fig.43)	44
Quartz	0.086			0.08		25
Quartz	0.27				0.236(Fig.42)	26
Titania						
Titania Type 1	7.40(X)	6.8			8.1 (Fig.63-1)	27-1
" " 2	17.32(X)	15.2			16.72 (Fig.63-2)	27-2
" " 3	10.33(X)	10.8			11.24 (Fig.63-3)	27-3
" " 4	11.08(X)	11.2			12.54 (Fig.63-4)	27-4
Organic						
Pigments						
Yellow (azo) Sample 1	31.8	33.4				28
" " " 2	66.8	70.4				29
" " " 3	37.1	38.0				30
" " " 4	62.0	16.0				31
" " " 5	46.6	-				32
Red " " 1	24.4	11.6				33b
" " " 2	43.0	9.9				33a
Blue (phthalo-cyanine) " 1	72.4	53.2				34c
" " " 2	72.5	54.4				35
" " " 3	81.0	50.0				34b
" " " 4	85.0	59.2				36
" " " 5	116.5	-				34a
Sugar						
Sugar	0.018(B)			0.0076		37
Fibre						
Wool	0.15 (Hp)$^{\Theta}$			0.13		

* Solvent: water, except where shown otherwise (B = benzene; Hp = n-heptane; X = xylene)

≁ ca.230 by adsorption of benzene, ethanol, methanol, or n-heptane vapours.

≁≁ 100,102,105 by electron microscope,neon adsorption,and heat of wetting methods respectivel

ϒ 0.4 by sedimentation method.

Θ After Mr.S.D.Dandekar.

Table III A

Relation between Specific Surface Areas of Pigments by PNP and Nitrogen adsorption methods and their Bulk Densities.

Pigment	Specific surface area ($m^2 g^{-1}$) by PNP adsorption	Specific surface area ($m^2 g^{-1}$) by Nitrogen adsorption	Bulk density ($g.\ c.c^{-1}$)
Yellow (azo) Sample 1	31.8	33.4	0.0926
" " " 2	66.8	70.4	0.119
" " " 3	37.1	38.0	0.178
" " " 4	62.0	16.0	0.4166
Red " " 1	24.4	11.6	0.2
" " " 2	43.0	9.9	0.271

Comparison of results by different methods.

The question now arises as to the agreement between the results obtained by different methods. The determinations by the permeability and microscopic methods suffer from the fact that the finest cracks and crevices of the particles, the 'internal' surface, of porous material in the strict sense of the term, is not measured by them. This means that the fine structure, and with it the finest particles, do not enter into the determination, which must result in the surface area value found being too small.

With a porous material again, if some of the cracks in it are narrow, the fineness of the measuring device employed, determines whether or no it can penetrate into the finest cracks. This has been graphically presented by Emmett[105] (Fig.48) in a review of the problems met in measurements of adsorption and pore size of charcoals. Even the definition of what is meant by the real area presents difficulties in such cases.

It is therefore clear that the methods measure different entities and the errors are mainly due to differences in concept of the particle as a unit.

Results by PNP Method:

In practice, the values obtained with nitrogen measurements are taken as absolute. Table III shows that in most cases the method gives results that compare very favourably with those of nitrogen adsorption. Where values by nitrogen are higher than by p-nitrophenol the reason is almost certainly that the nitrogen molecule (cross-sectional areas of solid and liquid nitrogen are 13.8 A^2 and 17.0 A^2 respectively[106]) is smaller than p-nitrophenol and can penetrate smaller pores in the solid. For example, alumina in some cases gives higher values by nitrogen than by p-nitrophenol, and an electron micrograph of a dehydrated aluminium hydroxide crystallite shows evidence of a vast number of minute capillaries running inwards from the surface[107].

Where the values by nitrogen are lower than by p-nitrophenol the opposite is the case, i.e., p-nitrophenol can penetrate some small pores or interstices more rapidly than nitrogen. This occurs with some of the pigment samples, (Table III). All pigments contain aggregates consisting of clusters of primary particles, and in the case of precipitated pigments, these aggregates are formed during the process of manufacture. Researches carried out at the paint research station, Teddington, have shown that the main stage of aggregate formation is the normal drying process, and that the final grinding process, while it produces an overall reduction in size, does not regain the original fineness and freedom from aggregates of the precipitated material[108]. The nitrogen method is static, the powder stays as a pile in a bucket; the surface measured includes the outer surface of all such aggregates. In the p-nitrophenol method, the powder is continuously shaken with the liquid. This may break down the compound aggregates and thus increase the area measured. Bond and Spencer[109] have cited several examples, that suggest that nitrogen or argon does not possess sufficient energy at such low temperatures as -196°C to penetrate much of the internal structure and reach more than a small fraction of the internal surface of coal, in the time allowed for the experiment, which is usually less than a day. For a sample of coal, carbon dioxide at -78°C gave a value of 175 $m.^2g.^{-1}$ for the surface area, but the nitrogen value at -196°C for the same sample was 11 $m.^2g.^{-1}$. Other samples of coal gave a value of 200 $m.^2g.^{-1}$ by heat of wetting and vapour adsorption using methyl alcohol at room temperature; but nitrogen and argon adsorption gave values of only a few $m.^2g.^{-1}$ at low temperatures. One other sample of coal gave a value about 30 times higher with nitrogen and methane at room temperature than at low temperature with nitrogen.

Bulk densities (cf. Table III A) also confirm this view. Where the densities are low, nitrogen and p-nitrophenol values agree very well, but as the densities increase nitrogen gives low values.

In the case of the coal powder the values by p-nitrophenol and sedimentation methods are 45 $m^2 g^{-1}$ and 0.4 $m^2 g^{-1}$ respectively. In the sedimentation analysis, the average particle size was determined from the size frequency (weight percentage) curve and it was not extended to particles below 5 μ in diameter. The rate curve on the same sample of coal (Fig.22 inset), shows that p-nitrophenol takes six hours to reach equilibrium, showing it probably has a porous structure. These two facts account for the low value by sedimentation method.

Plotting of the isotherms:

As mentioned earlier, the monolayer capacity was calculated in each case from the first plateau of the isotherm or from the "Point B" inflection and the Langmuir reciprocal plotting method or B.E.T. equation mentioned under gas adsorption was not adopted. The B.E.T. equation if used by some authors[110], concentrations taking the place of pressures in the equation, and the maximum solubility of the solute is taken as the saturation solubility.

Section III

Anomalous (ENDOTHERMIC) Effects of Adsorption from Solution on Inorganic Solids.

Adsorption from solution is usually, like vapour-phase adsorption, an exothermic process. One would expect, therefore, an increase in temperature to cause a decrease in adsorption. This expectation has been amply verified by studies on the adsorption of solutes from solution.

In a few cases however change in temperature produces no change in adsorption, but so far all such cases are apparently ion-exchange adsorption[52,55,65], where one set of ions is replaced by another without the formation of new bonds.

Little is known of systems showing a reversed temperature effect, i.e., where rise in temperature increases the saturation adsorption: previously recorded cases include the adsorption of (i) two azo dyes (C.I. 14,600, anionic; C.I. 26,115, cationic) from water by silica[65]; (ii) butanol from its mixtures with water on carbon[112]; (iii) succinic acid from water or ethanol, by charcoal[113]; and (iv) long-chain sulphate esters by wool[57].

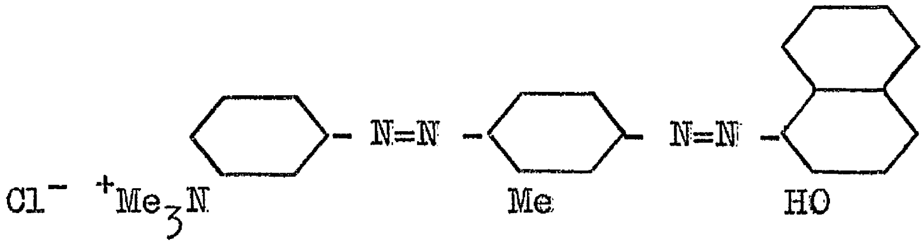
According to Bartell et al.[112] the temperature effect of adsorption from solution depends on two factors, (1) the adsorption proper and (2) change in the solubility of the adsorbate with temperature. Solubility and adsorption act in the opposite direction. The more soluble the solute, the less it is adsorbed and vice versa. The adsorption is an exothermic process, it must decrease with increase in temperature but the solubility may increase or decrease with temperature. If the solubility increases with temperature, then both the factors act in the same direction and the adsorption is decreased. If, on the other hand, the solubility of the adsorbate has a negative temperature coefficient, then the two processes act against each other, and the adsorption may show an increase or decrease depending on which factor is predominant. In the case of adsorption of butanol on carbon, the solubility effect overtakes the adsorption and the overall adsorption is increased with temperature.

In an adsorption from solution, the solvent competes with the solute for the substrate sites and thus the solute is deprived of some of the sites. A rise in temperature causes a decrease in both the adsorption of the solute and that of the solvent; if by any chance there is more decrease in the adsorption of the solvent with the rise in temperature, more sites will be available to the solute and its adsorption will increase. Heyne and Polanyi[113] have demonstrated this in the case of adsorption of succinic acid from its nearly saturated solutions in water and alcohol on charcoal.

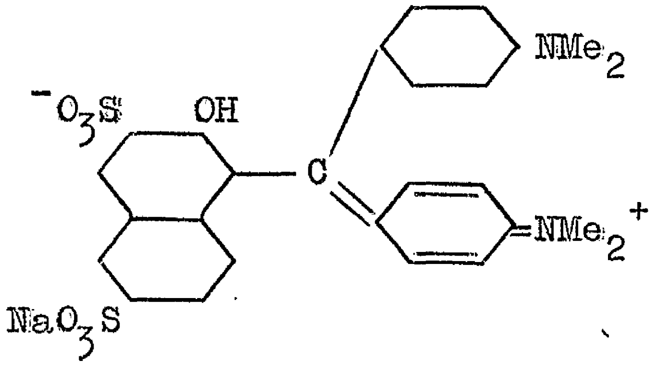
Aickin[57] comments that the secondary alkyl sulphates are better adsorbed at a higher temperature than lower on fibres.

Cause of the Anomaly:

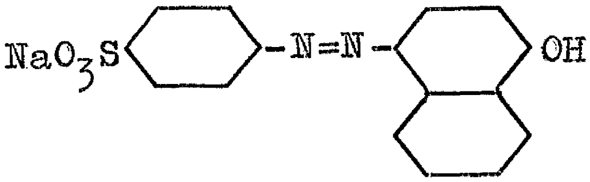
In the present work the adsorption of three dyes on various solids have been studied. None of the causes given above is applicable here.



Janus Red B (C.I. 26,115)



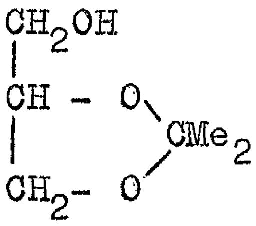
Lissamine Green BN (C.I. 44,090)



Orange I (C.I. 14,600)

In the first two cases, in which adsorption rises with temperature, there is good evidence that the dyes are highly aggregated in solution; thus the solutions do not obey Beer's law and show marked light-scatter. The dyes contain a free -OH group and they must be forming a dimer by the union of two such groups by hydrogen bonding.

So the first step in checking the cause of the anomaly, i.e. whether it is due to aggregation, was to select a disaggregating agent. A solvent known as 'Solketal' was used. This is a glycerol condensate and has the formula:



Even then the adsorption was endothermic. Refer Figs. (49a,b and 50a,b). The next step was to use another dissociating solvent (instead of water). Accordingly when methanol was used as a solvent, the adsorption was normal, falling with rise in temperature. The apparent endothermic nature of these systems is therefore a result of the aggregation of the solutes in solution, as will be shown in the discussion later.

Experimental

Preparation of substrate:

(1) Silica (MSC brand) was supplied by Messrs. Colin Stewart Ltd., and was used without any pre-treatment.

(2) Acidified alumina: The starting material was ordinary alumina powder supplied by Savory and Moore Ltd. for chromatography. In its original state it was alkaline (10 c.c.s of distilled water shaken with 0.5 gm. of powder at room temperature had pH 9.5). It adsorbed cationic dyes but not anionic ones, unless previously acidified. Acidification was done by shaking approximately 20 gm. of the substance with 50 c.c. of 2N hydrochloric acid solution for half an hour. The acidified alumina was then rinsed thoroughly with distilled water. It was then dried at 150°C for several hours. When 0.5 gm. of this compound was shaken with distilled water it gave a pH of 3-4.

(3) Graphite: Graphite was supplied in a pure state by the General Electric Co. Ltd.

Dyes

(i) Lissamine Green BN (C.I. 44,090). "Batch" sample (no added salt) was supplied by I.C.I.Ltd., and was used as such.

(ii) Janus Red B (C.I. 26,115). Commercial sample was recrystallised three times from 1:1 (v/v) ethanol-water, to constant molar extinction.

(iii) Orange I. (C.I. 14,600). Commercial Naphthalene Orange IS was recrystallised from water to constant molar extinction.

Solvents

(i) Distilled water.

(ii) Commercial methanol.

(iii) 1:1 v/v Solketal-water mixture.

(iv) 1:1 v/v glycerine-water mixture.

(v) 2.5% phenol (AnalaR quality) solution.

Adsorption procedure was the same as given in the earlier sections.

Aggregation in solution was checked (qualitatively) by means of a nephelometer, (EEL instrument). The galvanometer was set to full deflection with an aqueous aggregated solution of the dye of suitable concentration. A solution of the same concentration in the disaggregating solvent was next prepared and its reading noted. When this reading was zero or nearly zero the dye was considered to be disaggregated.

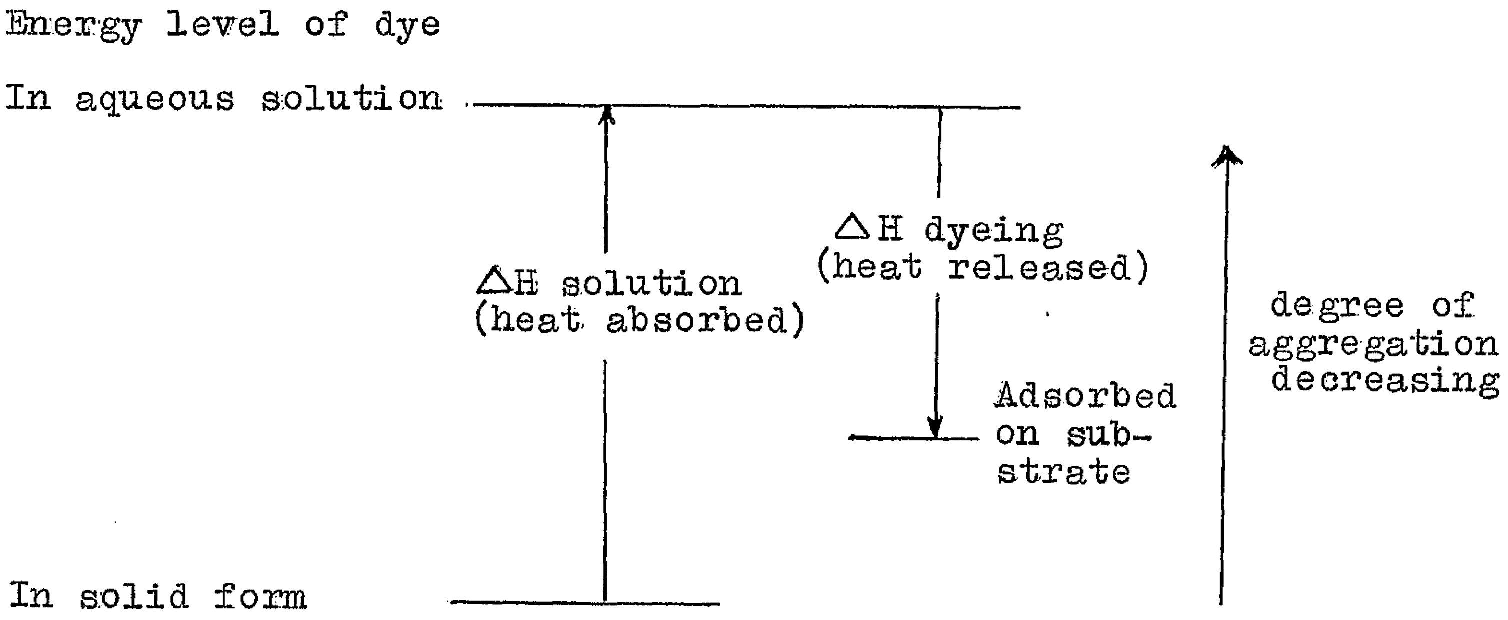
The nephelometer readings were taken by the writer's colleague Mr. J. J. Greczek.

Analyses.

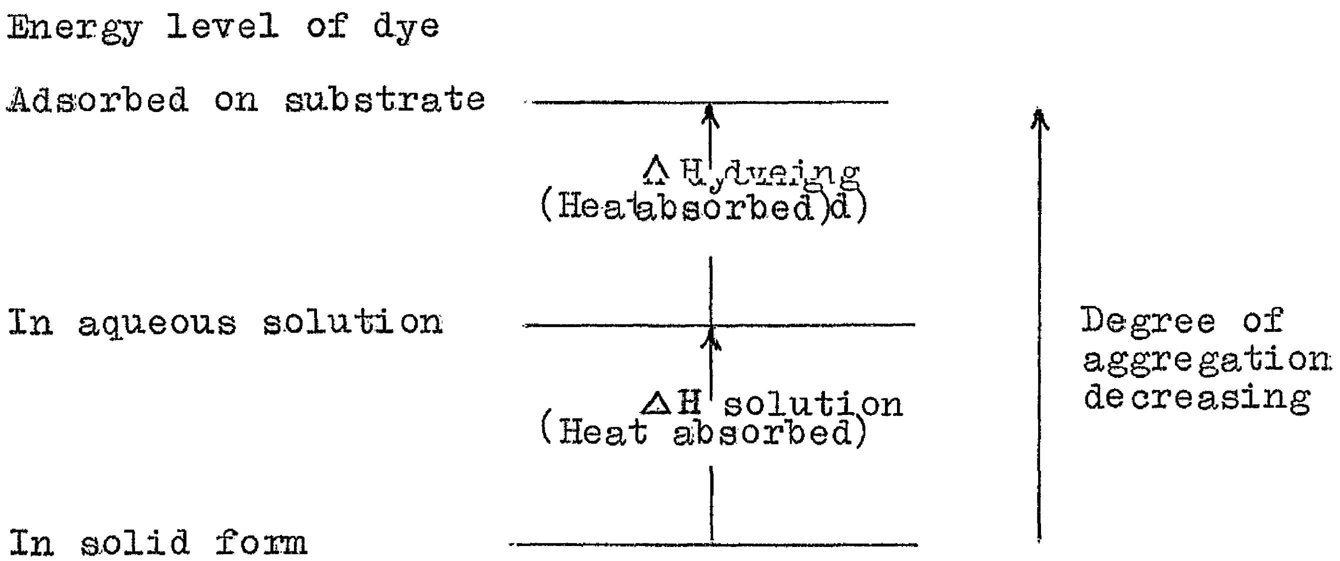
The solutions of the dyes, C.I.26,115; 44,090; and 14,600, were analysed spectrophotometrically using a Unicam SP 500 instrument at 5100 A, 6300 A and 4840 A respectively.

Discussion.

Majury[114], in connection with his work in determining heats of dyeing has drawn up a diagram which illustrates the various heats of reaction in dyeing. The following is adapted from his diagram.



The energy level of the dye on the substrate is lower than the solution level, thus heat has to be evolved for adsorption to occur. But supposing that a negative temperature coefficient existed, i.e. heat taken up in dyeing, then that can be explained by a new diagram as follows:



From the energy level diagrams it appears that the solute is partly dissociated on adsorption.

<u>Nature of Association on Substrate</u>:

Two facts indicate that the adsorbed layer of both dyes (even in methanol) consists of aggregated particles, and is not a true unimolecular layer: (a) the isotherms are of L 2 shape. Both the dyes contain OH (hydrogen bonding) group and from a polar solvent (methanol) on polar substrates (alumina and silica) the isotherms should be of S shape, following end-on orientation, and (b) the high "coverage factor" (i.e., the amount of dye adsorbed to fill a "monolayer" divided by the amount calculated for a unimolecular layer) which is <u>ca</u>. 50 for Janus Red B at 16°C and <u>ca</u>. 2 for Lissamine Green BN at 19.5°C.

It is well known that dyes aggregate in solution in water and the degree of aggregation falls with rise in temperature. In a disaggregating solvent (e.g. methanol) the dyes are molecularly dispersed. It is especially interesting that aggregates can apparently be adsorbed under conditions (high temperature in disaggregating solvents) in which the dyes must be molecularly dispersed. Giles et al.[77,115] have already expressed the view that aromatic solutes in water are associated at a solid surface during adsorption, either immediately before or at the moment of attachment to the surface. The above findings confirm this view.

Orange I.

This dye also gives anomalous isotherms on silica[65], so before trying Solketal as a disaggregating agent, phenol was used as a disaggregating agent. Phenol is a powerful hydrogen bonding agent, it forms a complex with the dye molecule in water and thus disaggregates the dye, but it did not act so here (refer Fig.51a,b). When Solketal was used as a disaggregating agent, a strange effect was noticed. The solutions after adsorption slowly decolourised. It was suspected that some impurity in Solketal (perhaps a reducing compound) was causing reduction of Orange I. Therefore Solketal was replaced by another disaggregating agent -

glycerine, and surprisingly enough when adsorption tests were made on graphite from a glycerine-water mixture, the isotherms were of normal type (Fig.51c,d).

However, adsorption from aqueous pyridine (another disaggregating agent) or from methanol is anomalous. These unexpected results were found to be due to slow decolourisation of the dye solutions at high temperature, presumably owing to decomposition of the azo-group (either by hydrolysis or reduction). Orange I in 1:1 water-glycerine (v/v) does not decompose. The solutions of Lissamine Green BN and Janus Red B do not decompose at high temperature and Solketal does not reduce them. Thus Orange I behaves in a normal way, but due to decomposition at high temperature, the anomalous adsorption is observed.

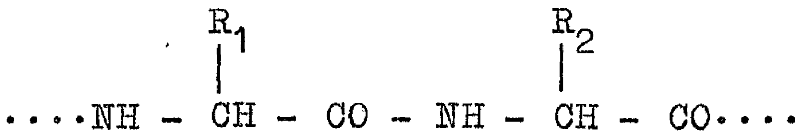
O'Connor, Johansen and Buchanan[116] have studied the electro-kinetic properties of corundum (naturally occurring alumina) before and after treatment with solutions of acids, alkalis and salts. Normally the zeta-potential of alumina powder in water is positive, which these authors attribute to the presence of a layer of $Al(OH)_3$ formed from chemically bound water; this releases hydroxide ions into the diffuse layer and the oxide has then a surface of positively charged Al atoms. Treatment with hydrochloric acid apparently produces a surface consisting of both covalently bound and ionized chloride, by the following mechanism:

$$\begin{tikzcd}
>Al - OH + \overset{+}{H}Cl^{-} \arrow[r, shift left, "(i)"] & >Al - Cl + H_2O \arrow[l, shift left] \arrow[d, shift right] \\
& >Al^{+} \quad Cl^{-} \arrow[u, shift right, "(ii)"']
\end{tikzcd}$$

Reaction (ii) (formation of ionized chloride) is favoured by increase in acid concentration. The substrate in this condition will be able to behave as an ion-exchanger, chloride ions exchanging with anions in the applied solution.

Giles et al.[55] have studied the adsorption of anionic dyes on acid-treated alumina which shows that adsorption in these cases is very rapid, and since the isotherms obtained have a well defined plateau (H 2 type) it is suggested that a monolayer is formed on the outer surface of the alumina particles with no penetration of the internal structure. The shapes of the isotherms indicate that the anions have a much higher affinity for the substrate than has the solvent (water). The isotherms for different temperatures are almost identical, i.e. the apparent heat of adsorption of the anionic dyes is very low, ($<$ *ca*. 0.25 kcal./mole). This independence of temperature appears to be characteristic of several ion-exchange adsorptions, e.g. cationic dyes on (negatively charged) silica[65].

Wool and silk are important protein fibres. The proteins consist essentially of polypeptide chain molecules, with various side groups R pendant to the polypeptide chain:



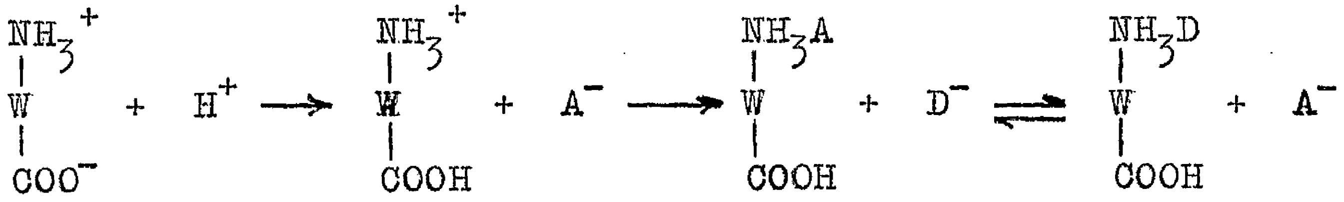
$$\cdots\mathrm{NH}-\underset{}{\overset{\overset{\displaystyle R_1}{|}}{\mathrm{CH}}}-\mathrm{CO}-\mathrm{NH}-\overset{\overset{\displaystyle R_2}{|}}{\mathrm{CH}}-\mathrm{CO}\cdots$$

Some of these side groups are basic and some acidic in character and they are very largely ionized in the neutral substance; thus a wool protein molecule can be written as:

$$\mathrm{NH_2 - W - COOH} \quad \text{or} \quad \mathrm{\overset{+}{N}H_3 - W - COO^-}$$

where W is the wool residue.

The most important dyes for protein fibres are acid dyes, which are anionic. They are normally applied to wool from acid solution, and the mechanism of dyeing is as follows[75]:

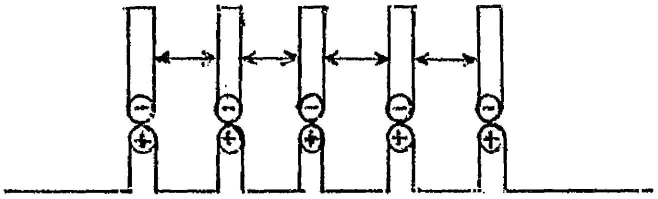


$$\begin{array}{c} NH_3^+ \\ | \\ W \\ | \\ COO^- \end{array} + H^+ \longrightarrow \begin{array}{c} NH_3^+ \\ | \\ W \\ | \\ COOH \end{array} + A^- \longrightarrow \begin{array}{c} NH_3A \\ | \\ W \\ | \\ COOH \end{array} + D^- \rightleftharpoons \begin{array}{c} NH_3D \\ | \\ W \\ | \\ COOH \end{array} + A^-$$

D^- = dye anion, A^- = acid anion.

When the fibre is placed in acid solution, the very small hydrogen ions diffuse rapidly into it and neutralise the negatively charged carboxyl ions. The fibre is thus left positively charged and anions will be attracted to the positively charged sites. The small acid anions diffuse into the fibre and are initially adsorbed to the amino-groups but they are largely replaced by the more slowly moving dye anions afterwards. This greater affinity for the dye molecules arises from the interaction of dipoles, hydrogen bonding and van der Waals forces, which do not exist in the case of simple acid anions. These forces in general increase with increasing molecular weight and decreasing solubility of the dye.

The mechanism of dye adsorption, anionic dyes by alumina and wool and cationic dyes by silica (negatively charged) appears to be the same, viz., ion-exchange; then why is it that a temperature coefficient exists in the case of wool (at least in the few cases reported) and does not in the case of alumina[55] and silica[65]. Giles et al.[73] in reporting studies of reactions in monolayers suggest that there is an ion-ion association between the wool's cationic groups and the dye anions, as shown in the following diagram:



It is suggested that the heat of reaction is a measure of the intermolecular forces between adjacent hydrophobic residues of the dye anions. That there is no heat of reaction in the case of alumina can be explained by considering the substrate structure. Alumina has a very rigid surface which will hinder positively charged sites from being drawn together, thus keeping the dye anions apart and hindering intermolecular binding. Wool on the other hand has a flexible structure, which can accommodate the associated anions by bending and twisting of the fibre molecules.

The present investigation was undertaken as an attempt to check these hypotheses, i.e., to discover whether there is any evidence for the suggested form of inter-anion aggregation being preferred on the protein fibres and to check up on the temperature dependence of adsorption on alumina and protein fibres.

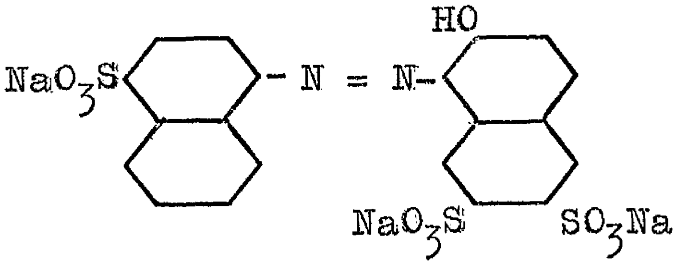
Experimental

(a) Substrates:

Acid alumina: Preparation is described in the present section.

Wool and Silk: Clean commercial cloth samples were used without any pre-treatment.

(b) Dye: This was Naphthalene Scarlet 4R (C.I.16,255).



C.I.16,255

Electrolyte-free material was supplied by I.C.I., and this was used without further purification.

(c) Solvent: Distilled water was used as a solvent. Acid alumina when shaken with distilled water gives a pH of about 3-4, so in the case of wool and silk this pH was adjusted by adding 0.5 c.c. of glacial acetic acid to 99.5 c.c. of dye solution.

Adsorption procedure and Analysis - The adsorption procedure was the same as described before. The solutions were analysed spectrophotometrically at 5040 A.

Discussion.

The isotherms are shown in Fig.52. The isotherms obtained at two different temperatures are identical, i.e., the apparent heats of adsorption are very low ($<$ ca. 0.25 kcal./mole). This is consistent with an ion-exchange mechanism of adsorption. This process consists of replacement of one set of ions by another, no bonds are broken or formed and the electronic system of the adsorbed ion is unaffected, hence no heat change occurs.

Naphthalene Scarlet 4R is a tribasic dye, it probably attaches to three points on the protein or alumina surface and lies flat, hence, there will be no intermolecular forces acting between hydrophobic residues of the dye and therefore no heat of reaction of the type postulated will be expected. Unfortunately it was not possible in the time available to determine if a dye such as Naphthalene Red J, which does not lie flat on the substrate, shows any heat effect.

The lack of experimental evidence necessary to establish the original hypothesis was due to the finding of an apparently endothermic reaction for the adsorption of Lissamine Green BN on acidified alumina (described earlier in this section), and therefore this work was put aside and an explanation for endothermic adsorption was sought instead.

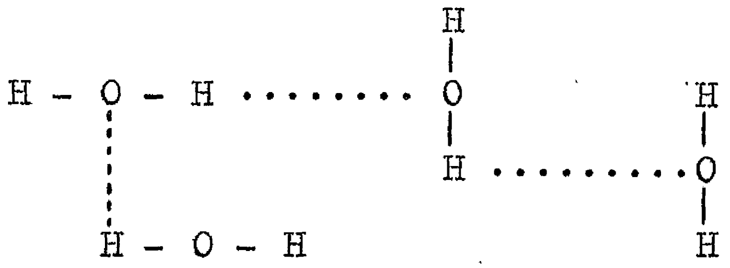
PART II

Section I

Hydrogen-Bond formation between Esters and the Chloro-Group

The Hydrogen Bond:

Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond.[117-119] The most obvious example of this bond is in ice:



The process of melting may be thought of largely as the breaking of a certain number of these bonds. The breaking of nearly all of them is associated with transition from the liquid to the gas phase.

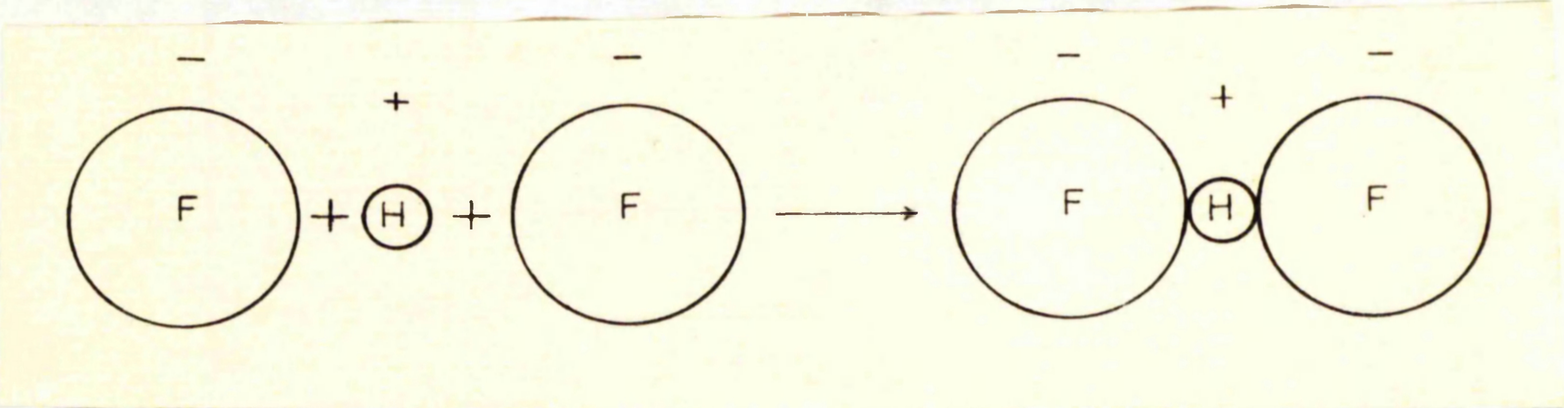
The first question that arises concerns the position of the H atom. Is it, as was at first supposed, at the mid-point of the atoms bonded or is it much more closely linked with one of the two atoms? Unfortunately there is at present no satisfactory method of determining experimentally the precise positions of the hydrogen atoms, but there are several methods by which their position may be inferred. The most striking evidence comes from infrared absorption. In the bonded system X-H ······ X′, the vibration frequencies corresponding to the X-H bond, and to the X'-H bond are found, and from this the strength of each bond is determined. An indirect argument then makes it possible to estimate where the H-atom is situated. The X'-H bond proves to be weak, and the corresponding frequency occurs far in the infra-red. On the other hand X-H is strong. The inference, therefore, is that the H atom is usually much nearer to the atom X, to which it is tightly bound, so that the bond is unsymmetrical.

Pauling[120] showed that a hydrogen atom, with only one stable orbital, cannot form more than one pure covalent bond, and that the attraction of two atoms observed in hydrogen bond formation must be due to ionic forces.

Cause of the Hydrogen Bond:

Effective hydrogen bonds occur only if the negative ions bonded have a high electron affinity (which may be used as a measure of their power to hold on to their electrons). The bonding power increases in the order $Cl < N < O < F$, which is the order of increasing electron affinity.

A simple physical explanation is advanced. The positive hydrogen ion is a bare proton, with no electron shell about it. The proton attracts an oppositely charged ion, but it can equally attract a second negative ion on its other side -



The proton thus forms a bridge between the anions, which would otherwise have repelled one another, being ions of like charge. Further, the proton is so small that it is tucked away between the two large anions; no other anion can get near enough to share it with them. This accounts for the experimental observation that a proton can only bond two anions. The model given above suggests that the tendency to form H-bonds may be associated with the proton affinity of the anions bonded. A high proton affinity coupled with high electron affinity of the anions would lead to powerful hydrogen bonds.

However, this discussion refers to an ideal case. The H-bond is formed by groups or molecules such as $-NH_2$, -OH, =NH, FH, in which the hydrogen atom is certainly not a bare proton, nor are the groups bonded simple anions.

Nevertheless these groups are polar, the distribution of charges in the -OH group being for instance $-\overset{-}{O}-\overset{+}{H}$, so that the group constitutes a dipole. The atoms, although they do not carry the full charge of the free ions, can interact in a similar way, i.e., the H-atom behaves in part as a proton and bridges negative atoms which behave in part as anions. In the typical bond =C=O ·····H-O-, e.g., the H atom remains attached to the hydroxyl oxygen by a covalent link, whilst it is attached to the negative oxygen atom of the carbonyl group by the attractions of positive and negative charges.

We can see why only hydrogen (or deuterium) will serve as the middle atom of the bond. In order that the electrostatic energy of interaction shall be greatest, it is desirable that the units should approach as close together as possible. In this respect the hydrogen atom possesses two favourable properties. Its atomic radius (0.3 A) is extremely small and it possesses no inner shell of electrons. As a result the adjacent molecule can approach very closely without the introduction of large repulsive energy terms. It is, of course, necessary to have an electropositive atom in the centre, but if, e.g. we tried to replace H by Na, the larger size of the Na atom (radius 1.54 A) and the presence of the complete inner

L-shell would open out the structure to such an extent that the energy of binding would be inadequate. It is also necessary to have an electronegative atom at either end of the system; here again the relatively small size of such atoms readily permits a close approach of the two molecules. The data in Table IV illustrate this argument, because it will be seen that the atoms forming the strongest hydrogen bonds have the smallest radii.

Table IV[118] - Covalent radii for atoms (A).

	H					
	0.3					
	Li	B	C	N	O	F
single bond	1.34	0.88	0.77	0.74	0.74	0.72
double bond			0.67	0.61		
triple bond			0.60	0.55		
	Na		Si	P	S	Cl
	1.54		1.17	1.17	1.04	0.99

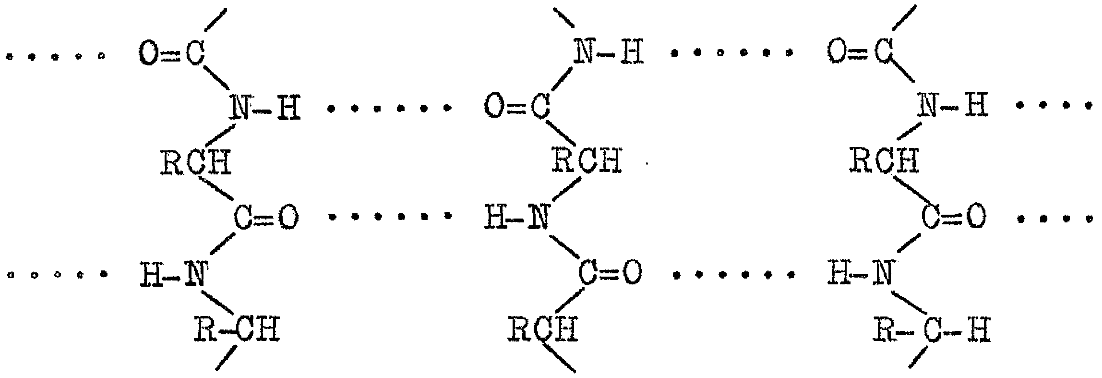
Energy of the Hydrogen Bond:

The hydrogen bond is not a strong bond. The bond energy lies in the range 3 to 8 kcal./mole. Since it is electrostatic in character, the strength of the bond depends upon (i) the electronegativity of the two bonded atoms and (ii) their interatomic distance. Referring to the electronegativity scale, we might expect that fluorine, oxygen, nitrogen and chlorine would possess this ability, to an extent decreasing in this order. It is found empirically that fluorine forms very strong hydrogen bonds, oxygen weaker ones, and nitrogen still weaker ones. Although it has the same electronegativity as nitrogen, chlorine has only a very small hydrogen-bond-forming power; this may be attributed to its large size (relative to nitrogen), which causes its electrostatic interactions to be weaker than those of nitrogen.

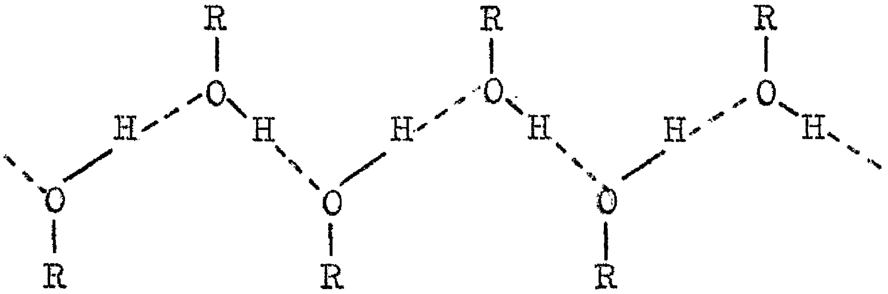
As expected, there is an inverse correlation (for bonds of the same type) between bond energy and interatomic distance, the sequences 4.5, 6.2, 7.1 kcal./mole and 2.76, 2.70, 2.67 A being observed for ice, alcohol and formic acid. The interatomic distance for bond formation lies between 2.26 and 3.38 A[117].

Intermolecular and Intramolecular Hydrogen Bonds:

Intermolecular hydrogen bonds are divided into two classes, (i) those extending over many molecules, as in proteins, crystalline alcohols, water etc.,

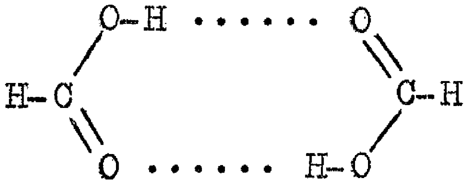


protein

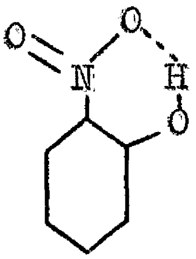


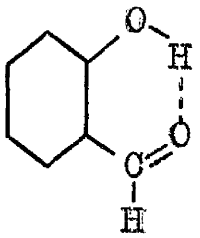
alcohol

(ii) those extending over two molecules, which form a dimer, e.g. formic acid, acetic acid etc.

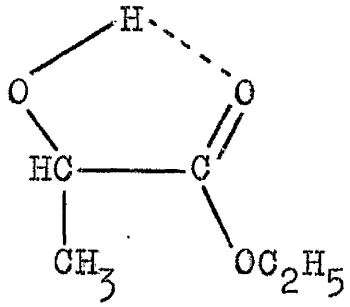


Intramolecular hydrogen bonds, in which the hydrogen is bonded to two atoms of the same molecule e.g. o-nitrophenol, salicyl aldehyde, etc.





In some substances, intramolecular hydrogen bond formation involves closing a six-membered ring, and the values of interatomic distances and bond angles may be such as to favour the formation of a strong hydrogen bond. On the other hand, a strong hydrogen bond is not formed with completion of a five-membered ring, the conditions being unfavourable, e.g. in ethyl lactate



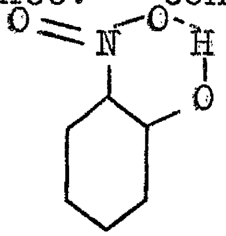
The Effect of the Hydrogen Bond on the Physical Properties of Substances.

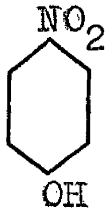
For the sequence of related substances H_2Te, H_2Se, H_2S, the melting points and boiling points show the decreasing course expected in view of the decreasing molecular weights and van der Waals forces. The continuation of the sequence in the way indicated would lead to the expected values of about -100°C and -80°C, respectively, for the melting and boiling points of water. The observed values of these quantities are very much higher; this is the result of the formation of hydrogen bonds, which have the extraordinary effect of doubling the boiling point of the substance on the absolute scale.

The melting and boiling points of ammonia and hydrogen fluoride are also considerably higher than the values extrapolated from the sequence of analogous compounds (SbH_3, AsH_3, PH_3 and NH_3; HI, HBr, HCl and HF.)

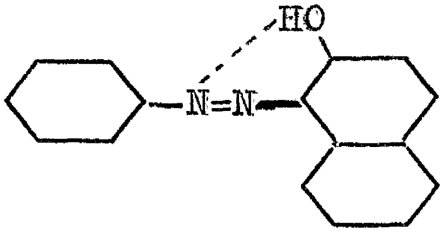
Substances such as water, ammonia, hydrofluoric acid, which polymerise through hydrogen bond formation show abnormally high dielectric constant.

Hydrogen-bond formation affects the solubility of a substance. Consider, e.g. o-and p-nitrophenols:-

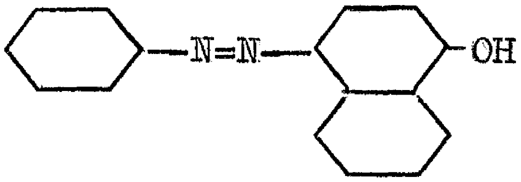




Due to intramolecular bond formation, o-nitrophenol is benzenoid in character, it is more soluble in organic solvents and non-ionic in nature; p-nitrophenol on the other hand is more soluble in water and is ionic. Consider again the compounds (III and IV) obtained by coupling diazotised aniline with ß- and α-naphthols:-



III



IV

(IV), because of the presence of a free OH group is soluble in alkali, while (III) is not.

Importance of Hydrogen Bonds

It is hard to exaggerate the importance of hydrogen bonding. Had it not been for the polymerisation of water due to hydrogen bonding its melting and boiling points, as just stated, would have been -100°C and -80°C and life would have been impossible. The regular arrangement of polypeptide chains in wool, silk and nylon, and the operations of the tanning of leather, chromatography, adsorption of dyes by textiles etc., all depend upon hydrogen bonding. The fact that nearly all biological processes seem to involve the hydrogen bond at some stage, shows that this type of bonding is outstandingly important.

Detection of Hydrogen Bonds

Infra-red spectrophotometry, electron and X-ray diffraction methods have been widely used for detecting hydrogen bonds[121]. Other methods depending upon changes in physical properties such as solubility, molecular weight, melting point, boiling point, dielectric constant etc., due to complex formation have also been used. Arshid et al.[122] have described a simple method of detecting hydrogen bond complexes between two solutes in aqueous and non-aqueous solutions by measurement of the refractive index. They have checked the results by comparison with many other independent methods, such as molecular weight determinations, infra-red spectrophotometry, and formation of monolayers on water. Their method has been used in the present investigation.

Use of Refractive-index Measurements

The method consists in plotting the refractive index* of solutions of binary mixtures of constant total molarity in which the relative proportions of the two components are varied over the range 0:100 to 100:0 . If no complex is formed a straight line is obtained (conversely, however, a linear plot does not necessarily indicate conclusively that a complex cannot be formed), because the square of the refractive index of dilute solutions is proportional to their concentrations, and is additive for mixtures of compounds if no interaction occurs (see Fig.53.),

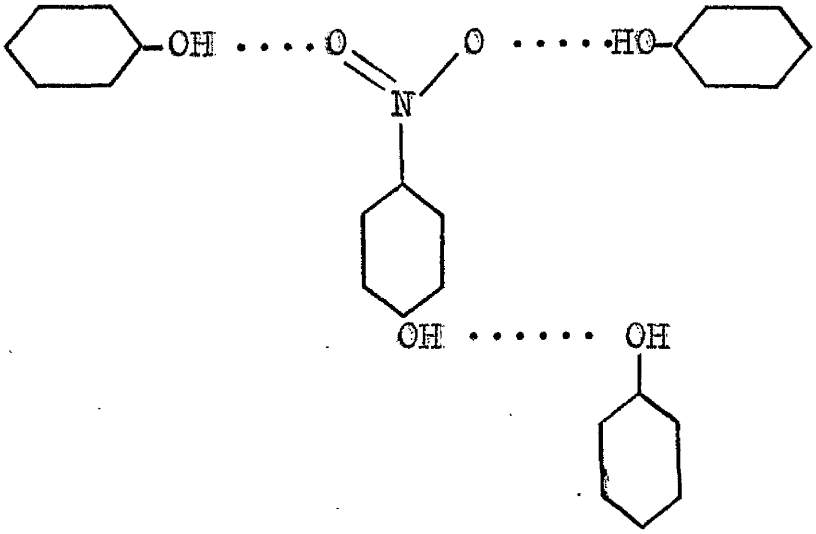
---

* Strictly the square of refractive index should be used to give a linear relation with concentration, but in practice the differences are so small that the index itself, or in the case of the Pulfrich instrument even the angle of the emergent beam, gives equally good results, and their use avoids tedious computations.

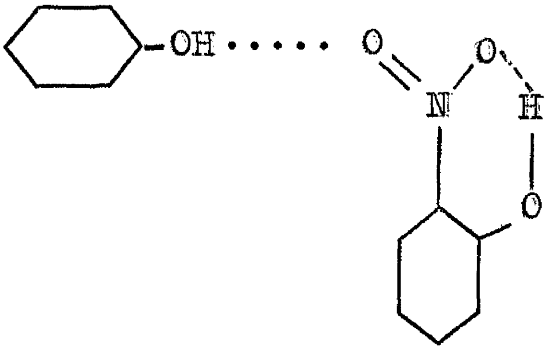
If the two components form a molecular complex, then the plot is a curve which may have a maximum or minimum at a point corresponding with the ratio of the two components in the complex. In practice, the curve approximates to two straight lines intersecting at the complex ratio point. In systems in which more than one complex exists, each may be represented by its corresponding maximum or minimum (see Fig.58).

Where a complex is detected, it is usually possible to specify with reasonable confidence which groups are interacting by inspection of the formulae of the components. The presence of a complex in aqueous solution means, of course, that the groups interacting can do so even in the presence of water, which will itself compete by combining with each group by hydrogen bonding.

It is found that even complexes which have quite low stability are readily detected. Some indications of the presence of intramolecular chelation may also be obtained in many cases, e.g., <u>p</u>-nitrophenol is found to form a complex V with three molecules of phenol, but <u>o</u>-nitrophenol, with only one (VI)



V

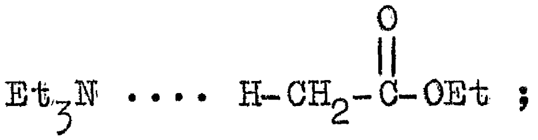


VI

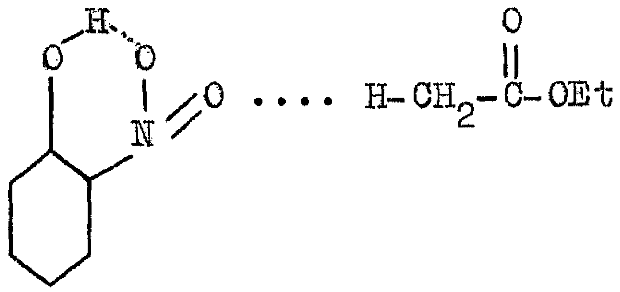
Previous work on Esters.

Esters can act both as hydrogen donors and acceptors[123,124,67], and can interact with electron donors, e.g. azobenzene, pyridine, or trimethylamine. It seems likely that this takes place through a -CH ····· O or

-CH ..... N bridge facilitated by the enhanced lability of the C-H bond adjacent to a carbonyl group[*]



$Et_3N \cdots\cdots H\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}OEt$;



The active C-H bond in some cases appears to be that attached α- to the -O-C=O-group (e.g., in ethylene glycol dibenzoate). The effect of a carbonyl group on adjacent atoms may be seen readily by the greater ionisability of the hydrogen atom in the carboxyl group than that in the alcoholic group. The activity of the methylene group situated between two carbonyl groups in acetoacetic ester is still greater. Rhodamine B (C.I.45,170) gives a red colour only in the presence of hydrogen donors, e.g. phenol or water, it is colourless in hydrocarbons. Toluene solutions of glycerol triacetate or pentane 1:5-diol diacetate give a red colouration, with Rhodamine B. These

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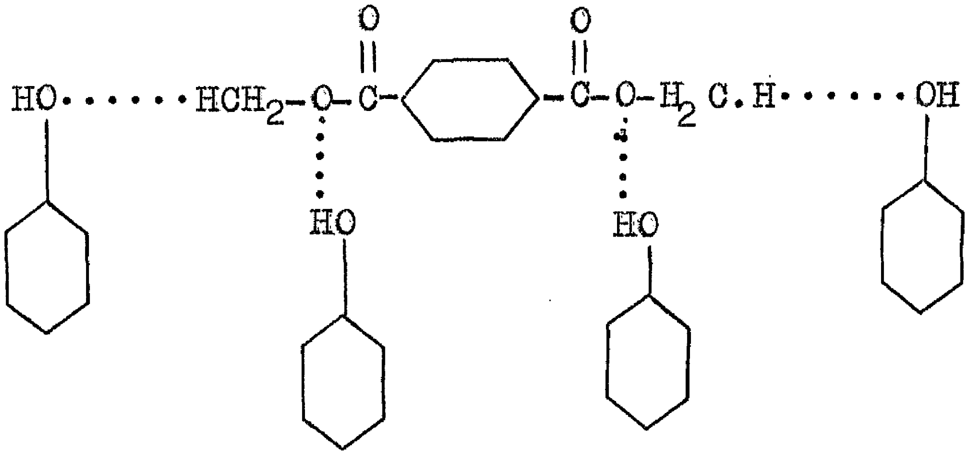
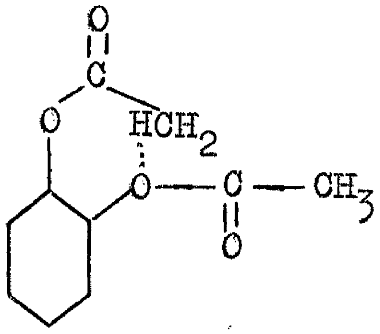
[*] (From the electronegativity scale the C-H bond would be attributed only a small amount of ionic character, insufficient to permit it to attract an adjacent negative atom with appreciable force. However, in compounds such as H-C≡N, resonance increases sufficiently the electronegativity of the C atom and the resultant positive charge on the hydrogen atom permits it to form C-H .... N- bonds. Pauling[117] has cited several instances of hydrogen bond formation with use of a hydrogen atom attached to a carbon atom of a halogenated hydrocarbon molecule, e.g. chloroform and similar substances with ethers and glycols.)

colourations are indicative of the presence of hydrogen available for bonding.

Esters can also behave as hydrogen acceptors, e.g. phenol forms a 4:1 - complex with dimethyl terephthalate in toluene solution. This can be represented as:



No definite evidence can be obtained that a -C=O group in any compound can form intermolecular bonds in water. A bond can form between phenol or alcohol and ether oxygen atoms (e.g. in dioxan) in water. Catechol diacetate forms an internal chelate ring:



When this compound was examined by infra-red spectrophotometry, it gave indications of changes in the $-CH_3$ and -O- groups, but not in the -C=O groups.

Present Work

This is concerned with the possible formation of hydrogen bond by esters of two broad types: plant growth promoters and cellulose acetates, etc.

Plant growth promoters - Many aryloxy-carboxylic acids, especially certain chlorophenoxyacetic acids have marked plant growth activity, which appears to require at least one free α-hydrogen atom and a given relation of this atom with aromatic nucleus and the carboxyl group, since it is stereo-specific[125].

From an inspection of formulae it appears that there might be some connection between hormone activity and ability to form hydrogen bond complexes and this work is concerned with tests made to check this hypothesis.

Cellulose acetates - Cellulose is built from cellobiose repeat units. Each cellobiose unit contains two linked ß-glucose residues, twisted through 180° relative to each other about their common axis. Chemical substitutions are restricted to the three hydroxyl groups per glucose residue. When these groups are fully acetylated we have cellulose triacetate. On partial hydrolysis of triacetate, we get secondary acetate. Secondary acetate contains an average of approximately $2^1/_3$ acetyl groups per glucose residue. Both tri- and secondary acetates are commercially important textile fibres.

Disperse dyes are commonly used for dyeing acetate fibres. These are mostly amino- or aminoazoanthraquinone derivatives, non-ionic in character, insoluble in water and applied to the fibre in the form of aqueous dispersions. The present investigations were carried out to discover the effects of chloro- and nitro-groups in the dye molecules on the dyeing behaviour of acetate fibres.

Terylene (polyethylene terephthalate) is another ester fibre. Its dyeing behaviour is similar to that of acetate, and so the conclusions reached here regarding acetate fibres may apply to Terylene also.

Experimental

The results recorded in Tables V to VII are the work of the author and his colleagues. Complex-ratio estimation by refractometry and adsorption tests were done in this laboratory, infra-red work was done elsewhere.

Materials:

The samples of phenoxyacetic acid derivatives were kindly supplied by Dr.C.H.Fawcett and Prof.R.L.Wain F.R.S., of Wye College. They were pure (all racemic mixtures). These acids are not soluble enough for tests to be made in water alone, so water-ethanol mixtures were used as solvents. When applied as growth-promoters, the concentration of the acids in the plant juices is probably much lower than that used here, though it may be raised locally at any active solid surface in the plant, by adsorption.

All the other solutes used were either of analytical reagent quality or were purified in the laboratory from commercial products.

'Specially dry' dioxan and benzene (B.D.H.) were used and toluene was dried over sodium.

Instruments:

Bellingham and Stanley (Pulfrich) and Zeiss (Abbe) refractometers were used. The source of monochromatic light was a sodium lamp.

Procedure:

The principle of the method has been already described[122]. The solutions of the two solutes to be examined were prepared, then mixed in different proportions giving 7-10 separate binary solutions of different molar ratios, and then stored overnight in ground-glass stoppered tubes for the completion of complex formation. The instrument readings were taken either at room temperature or at the temperature of tap water which was circulated through the instrument. As the complete set of readings can be taken within 60 minutes, there was hardly any variation of temperature during the experiment. A concentration of 0.1 M or 0.25 M was normally used, but in some cases where either very little material was available or solubility was low, lower concentrations have been used.

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

Infra-red spectrophotometry:

2,6-Dichlorophenoxypropionic acid (1% solution in CCl_4) was examined by infra-red spectrophotometry with no satisfactory result. The carboxylic acid dimer broad absorption band between 2.9 and 4.2 μ obscured the region where the C-H stretching frequency might be expected to appear, while the region of the $-CH_2-$ deformation is complicated by absorptions due to aromatic and carboxylic acid systems.

An examination of the infra-red spectra of thin films of chlorobenzene, nitrobenzene and phenyl acetate in pure liquid form, singly and in equimolar mixtures of the first two separately with the last-named, was also made. Again, no conclusive evidence of interaction by the acidic -CH group in the acetate could be obtained, presumably because of the known insensitivity to disturbance of the CH_3 group band (7.3 μ).

Adsorption tests:

Cellulose triacetate powder (acetyl value as acetic acid - 62.2%) was supplied by British Celanese Ltd. The procedure of the experiments was the same as described in earlier parts of the thesis. Chlorobenzene and phenol were analysed by spectrophotometry using a Unicam SP 500 instrument at 2640 and 2715 A respectively.

The results of refractive index work are given in Tables V, VI and VII and adsorption isotherms in Fig.62. Curves showing relation between either square of refractive index or instrument reading and component ratio in solutions are given in Figs.55 to 61.

Table V

Ratios of complexes (a:b) formed by nitrobenzene and chlorobenzene and derivatives, with proton donors.

Temperature: 10 - 24°C, maintained constant, in each test

(a)	Second solute (b)*							
	Aqueous solvent/		Organic solvents					
	Ethyl acetate	Phenyl acetate	Ethanol	EGDB	Ethyl acetate	GTA	Phenyl acetate	Concn.(M)
Chlorobenzene	1:1 //	1:1 //	1:1		1:1	1:1		0.1
				2:1(B)//			1:1(B)//	0.25
o-Dichlorobenzene					1:2$^{\gamma}$			0.1
p-Dichlorobenzene			1:2		1:2	1:2		0.1
o-Chlorophenol					* *	* *		0.1
Nitrobenzene		1:1						0.2
				(1:1;1:2) (B)//			1:1(B)//	0.1

*EGDB = ethylene glycol dibenzoate; GTA = glyceryl triacetate.
Solvent, toluene, except (B) = benzene

/ 50% (v/v) aqueous ethanol; γ Also in dioxan.

* * No complex detected. Data in parenthesis denote uncertain indications

// Work of the writer.

Table VI

Ratios of complexes (a:b) formed by 'inactive' carboxylic acids.

(a) Acid	Second solute (b) *					
	Aqueous solvent≠	Organic solvents				
	Chloro-benzene	Chloro-benzene	DIBK	Ethyl acetate	TEA	Conc. (M)
Acetic					1:1	0.1
Phenoxyacetic			1:1		1:1	0.1
Phenoxyisobutyric				1:2; 2:1 ≠≠		0.05
Phenoxypropionic				1:2; 2:1 ≠≠		0.04
α-4-Chlorophenoxyisobutyric					1:1	0.1
2,6 Dichlorophenoxyacetic					1:2	0.05
α-2,6 Dichlorophenoxy propionic			1:1			0.05
2,4,6-Trichlorophenoxy-acetic	1:1 ≠≠					0.01
			(1:1)		1:1	0.1
α-2,4,6-Trichlorophenoxy-propionic	1:1 ≠≠					0.02
		1:1	1:1		1:1	0.1
α-2-Methyl-4,6-dichloro-propionic	1:1 ≠≠					0.02
		1:1				0.1

* DIBK = di-isobutyl ketone; TEA = triethylamine

≠ 50% (v/v) aqueous ethanol

Data in parenthesis denote uncertain indication.

≠≠ Work of the writer.

Table VII

Ratios of complexes (a:b) formed by 'active' carboxylic acids

(a) Acid	Second solute (b) *						
	Aqueous solvent†	Solvent: dioxan					
	Chloro-benzene	Chloro-benzene	DIBK	Ethyl acetate	Phenol	TEA	Concn.(M)
4-Chlorophenoxyacetic	1:1;1:2††						0.03
		1:1;1:2	1:1		1:1		0.05
		1:1;(1:2)		1:4		1:1;1:2	0.1
α-4-Chlorophenoxypropionic	1:1 ††						0.02
		1:1		1:1;1:3		(1:1;1:2)	0.1
		1:1	* *		1:1		0.05
α-4-Chlorophenoxy-<u>n</u>-butyric	1:1;1:2††						0.08
		1:1;1:2	* *		1:1		0.05
						1:1;(1:2)	0.1
α-2-4-Dichlorophenoxy-propionic			1:1				0.05
2,4,5-Trichlorophenoxy-acetic	1:2 ††						0.025
		1:2	(1:1)	1:1;1:4	1:1	(1:1;1:2)	0.1
α-2,4,5-Trichlorophenoxy-butyric		1:1;1:2					0.1
α-2,4,5-Trichlorophenoxy-propionic	1:1 ††						0.01
		1:1	1:1	1:1;1:4		1:1	0.1
		1:1					0.005

* DIBK = Di-isobutyl ketone; TEA = triethylamine. † 50% (v/v) aqueous ethanol

* * No complex detected. Data in parenthesis denote uncertain indications.

†† Work of the writer.

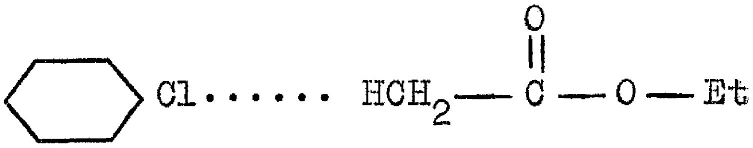
Results and discussion.

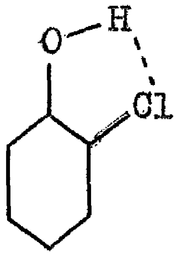
Satisfactory differentiation of properties between the phenoxyacetic acid derivatives depends upon suitable choice of the second solute as indicator for active <u>α</u>-hydrogen and chlorine atoms. Phenol, di-isobutyl ketone and triethylamine were first examined by the writer's predecessors for this purpose, but proved to be unsatisfactory, giving mainly the same complex-ratio (1:1) with any aliphatic or arommatic carboxylic acid. Ethyl acetate and chlorobenzene were found to be more satisfactory.

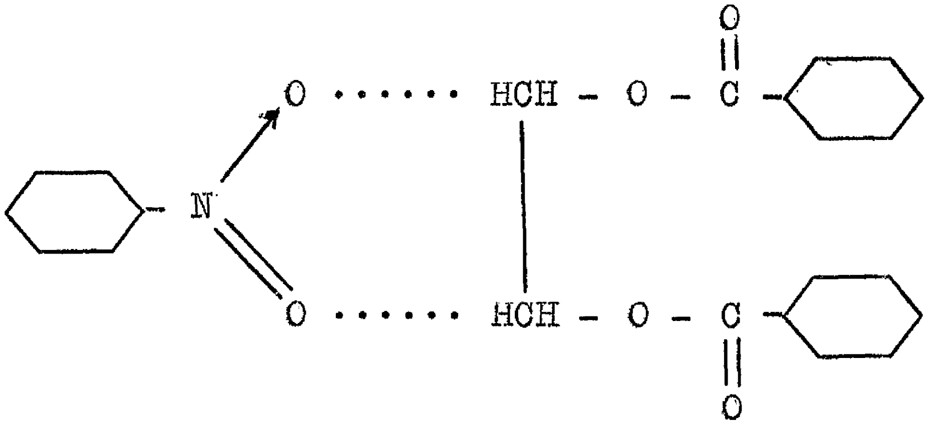
Ester-chloro-group bonding.

The present results may be interpreted thus:

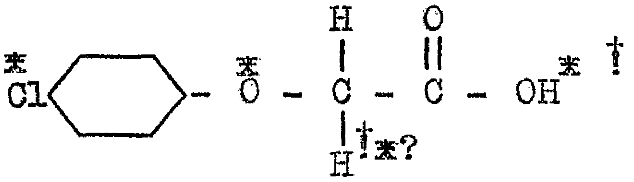
(i) The acetates form the CH ····· Cl bond with an unchelated chloro-group (not with the chelated-group in <u>o</u>-chlorophenol), and with each oxygen atom of the nitro-group.



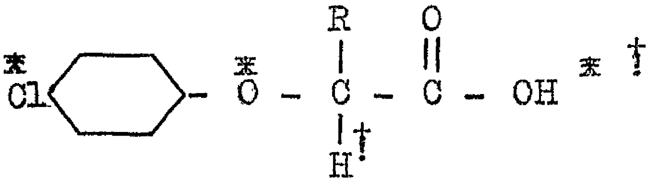




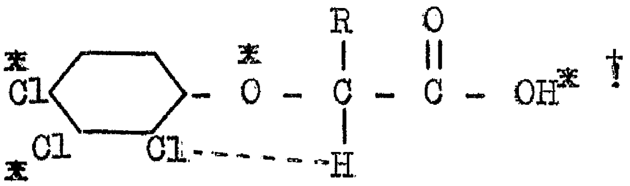
(ii) The chlorophenoxy acids VII - IX (R = Me or Et) form bonds with ethyl acetate at the positions marked ⁎ and with chlorobenzene at those marked † .



VII



VIII



IX

(iii) Each free chloro-group in the *ortho*-position to the ether oxygen atom in the aryloxy acids may perhaps interact with an *α*-hydrogen atom. If chelate rings are so formed they would probably be weak. (Infra-red spectra show that intramolecular -OH ...... Cl bonds are weak[126] and indeed it is suggested that these 'bonds' are due to the electrostatic effects by the adjacent polar group, and 'whether the term "hydrogen bond" should be used ...... is a matter of opinion'[126b]). The Cl ..... H separation measured from the molecular models in the 2,6-dichloroacetic acid compounds is $\sim$3 A (symmetrical position) and in the 2-chloro-compounds, $\sim$ 2.5 A.

There appears to be no difference in the complexing properties of any of the solutes examined, as between aqueous or non-aqueous media, respectively.

Relation of present results to dyeing and to plant-growth promotion phenomena.- The $>$CH .... bond formed by ester groups appears to assist adsorption of non-ionic solutes by cellulose acetates and related polymers, e.g. polyethylene terephthalate[67,123,124]. Dye adsorption increases with the number of proton-accepting groups in the dye molecule (cf. Table VIII). The present results give further evidence that this type of bond can form between an acetate group and a chloro-group in an aromatic nucleus. Consequently chlorobenzene would be expected to be adsorbed by cellulose triacetate. Experiment shows that it is in fact quite strongly adsorbed, more so even than phenol - (Fig.62). The difference is attributable to the lower solubility of chlorobenzene in water (chlorobenzene, 0.0488 gm./100 c.c. at 30°C; phenol, 6.7 gm./100 c.c. at 16°C; both compounds are completely miscible with ethanol); because of the lower solubility the competitive effect of the solvent will be reduced.

Table VIII

Relation between constitution of non-ionic phenylazobenzene dyes and their adsorption by secondary cellulose acetate data recalculated from Bird and Harris[127]

Substituents					Maximum adsorption (mmole/kg.) †
2′	4′	6′	3	4	
	NO_2			$NEt.C_2H_4.OH$	56
Cl	NO_2			$NEt.C_2H_4.OH$	61.5
Cl	NO_2	Cl		$NEt.C_2H_4.OH$	71
NO_2	NO_2			$NEt.C_2H_4.OH$	95
	NO_2			$N(C_2H_4.OH)_2$	41
	NO_2		Cl	$N(C_2H_4.OH)_2$	93
NO_2	NO_2			$N(C_2H_4.OH)_2$	119
	NO_2	OMe		$N(C_2H_4.OH)_2$	268

† The secondary acetate contains a proportion of unesterified hydroxy groups, but these do not appear to influence its adsorption properties; it is said that both the secondary acetate and the triacetate have the same affinity for a given dye, so that this affinity probably originates in the acetyl rather than the hydroxy-group[114].

In confirmation that the adsorption of these two solutes is mainly due to polar, rather than non-polar forces, it was found that benzene was unadsorbed when applied from the same solvent under the same conditions. The importance of hydrogen bonds in determining the attraction of cellulose acetate for solutes appears also to be shown by data given by White and collaborators[128]. They report that the cross-sectional swelling (%) of cellulose acetate fibres in pure liquids is: benzene, 7; carbon tetrachloride, 3.5; methanol, 45; butyl acetate $\geqslant$ 26; water, 20 (?). Thus the liquids capable of hydrogen bonding with the substrate are able to penetrate the fibre far more readily than the non-bonding ones, and benzene appears to have low penetrability and affinity.

The strength of the ethyl acetate - chlorobenzene bond in dilute solution in aqueous ethanol has been measured here by a refractometric method, which will be described later, and found to be about -3 kcal./mole; the phenol - chlorobenzene bond has a similar strength.

<u>Activity of plant growth-promoters</u>: As pointed out above, the necessary requirements of a promoter are at least one free <u>α</u>-hydrogen atom and a given relation of this atom with the aromatic nucleus and the carboxyl

group, since it is stereo-specific. Activity[125] is enhanced by presence of (a) a 2-chloro group, and markedly by a 4-chloro group, also by (b) a 2-methyl group; it is reduced or eliminated by (c) substitution at both 2- and 6-positions simultaneously (with chloro or methyl groups) and by 3,5-dichloro-substitution; (d) by replacement of both $\underline{\alpha}$-hydrogen atoms by methyl-groups; and (e) by absence of the phenoxy-oxygen atom (as in phenylacetic acid compounds) or its replacement by a weaker proton-acceptor, e.g. the -S-, or the -NH- group.

The stereo-specificity of the action shows that it must involve simultaneous formation of several bonds[125]. These bonds probably include (a) proton-acceptance at the ether oxygen atom (which would account for the activating-effect of a 2-Me group; the effects of replacement of H by CH_3 in the side-chain are very slight[125b], in agreement with the smaller effect that methyl substitution has on the acidity of an adjacent or a conjugated hydrogen atom in an aliphatic, compared with an aromatic, system); and (b) proton-donation by the $\underline{\alpha}$-CH group, which is more effective when the proton donating power is enhanced by 2- or 4-chloro-substitution in the aromatic nucleus. Any form of 2,6-disubstitution reduces the activity by restraining free rotation at the Ph-O- bond, and the $\underline{\alpha}$-CH group is deactivated by 3,5-dichloro-substitution. A possible chelate ring between a 2-chloro-group and an α-CH group does not appear to influence growth promoting activity; and this chelate bond is therefore weaker than the $\geqslant$CH ......substrate bond.

The properties of a few compounds are not explained by the above hypothesis, but these compounds have low activity[125b], and they may operate by a different mechanism. Fawcett et al.[125b] suggest that the behaviour of a few unexpectedly active compounds may be due to formation of traces of highly active substances during testing.

SECTION II

Hydrogen bond energies between solutes in solution.

In the present work a refractometric method is used to calculate hydrogen-bond strengths between solutes in solution. The physico-chemical basis underlying the method may be described as follows. Suppose A and B combine to form a complex AB

$$A + B \rightleftharpoons AB \qquad \ldots\ldots\ldots(18)$$

Then if we start with m molecules of A and n molecules of B and at equilibrium k molecules of each have combined to form k molecules of AB, then the equilibrium can be represented as

$$(m - k) + (n - k) = k, \qquad K = \frac{k}{(m - k)(n - k)} \qquad \ldots(19)$$

If Ra, Rb and Rab are the refractive indices of molar solutions of A, B and AB respectively, then the refractive index, Ro, of the mixture at equilibrium is

$$Ro = (m - k)Ra + (n - k)Rb + k\,Rab \ldots\ldots(20)$$

$$\text{hence,} \quad k = \frac{Ro - (mRa + nRb)}{Rab - (Ra + Rb)} \qquad \ldots\ldots\ldots\ldots\ldots(21)$$

Ra and Rb can be calculated by measuring the refractive indices of solutions of known strengths and from them, calculating the refractive index of a molar solution. To get the value of Rab, the following procedure is adopted. Suppose in eq.(18) one of the components, say B, is present in very large excess over the other, then the reaction can be assumed to be complete in the forward direction as follows

$$1\ A + 100\ B \longrightarrow AB + 99\ B \quad \ldots\ldots.(22)$$

$$2\ A + 100\ B \longrightarrow 2AB + 98\ B \quad \ldots\ldots.(23)$$

$$3\ A + 100\ B \longrightarrow 3AB + 97\ B \quad \ldots\ldots.(24)$$

Then eq.(24) - eq.(23) = eq.(23) - eq.(22) = AB - B

$$= Rab - Rb \quad \ldots\ldots.(25)$$

If we start with solutions containing quantities given on the left hand side of the equations (22), (23), and (24), we can find Rab, since Rb is known from the earlier experiments. Substitution of the value of Rab in eq.(21) gives the value of <u>k</u> and that in turn gives the value of the equilibrium constant, K, at the temperature of the experiment from eq.(19). The experiment is carried out at two different temperatures and by the application of the Clausius-Clapeyron equation, the heat of formation, $-\Delta H$, is calculated.

$$-\Delta H = \frac{2.303\ R\ T_1 T_2}{(T_2 - T_1)} \log \frac{K_1}{K_2}$$

Experimental

Solutes - "Analar" quality phenol was used. Chlorobenzene, ethyl acetate, n-butanol, dimethyl-formamide and acetonitrile were purified by distillation.

Solvents - 50% (v/v) Aqueous ethanol, xylene and carbon tetrachloride were used. 50% Aqueous ethanol was prepared by mixing equal quantities of distilled water and absolute alcohol. Xylene was dried over sodium. "Analar" quality carbon tetrachloride was used without further pruification.

Instrument - The Bellingham and Stanley (Pulfrich) refractometer was employed with sodium light.

Temperature - This was controlled to ± 0.1°C by water circulated from a thermostat tank through the cell jacket.

Procedure - To get the molar refractive index value for a pure solute in solution, solutions of 0.05 M to 0.25 M were prepared and their refractive indices measured, and from these the refractive index of a molar solution (Ra or Rb) was calculated.

To obtain the value of the refractive index of a molar solution of a complex (Rab), the solutions of the two components were mixed in such a way that the final concentration in a mixture of a solute (say B) was 0.5 M, while that of the other (A) varied from 0.001 M to 0.005 M, thus giving mixtures containing 1 unit of A + 500 units of B, 2 of A + 500 of B, ... 5 of A + 500 of B, and from the principle explained earlier the value of Rab was obtained*. 10 c.c. of a 0.2 M solution of each component was mixed with the other; this gave a mixture comprising 0.1 M solution of each component. The refractive index of this mixture was measured, then by the application of the formulae given in equation (21) and (19), the equilibrium constant K was obtained. Two sets of experiments were carried out, one at room temperature and the other at about 40°C, to get the equilibrium constants at two different temperatures.

The results are given in Table IX. All the pairs of solutes selected had been found to give a 1:1 complex when examined by earlier investigators, using the refractometric method in this laboratory.

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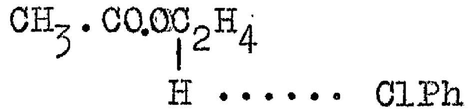
* This general method was developed by the author, following a study of a similar one described by Basu and Chandra[129], who used ultra-violet absorption spectral measurements.

Table IX.

	Components	Solvent	Temperatures °C t_1	t_2	Kt_1	Kt_2	$-\Delta H$ kcal/mole
1	Phenol, chlorobenzene	50% aqueous ethanol (v/v)	21.0	39.0	0.07615	0.05447	3.38
2	Ethyl acetate chlorobenzene	50% aqueous ethanol (v/v)	21.0	39.0	0.0705	0.05051	3.35
3	Phenol, n-butanol	carbon tetrachloride	17.2	42.8	0.636	0.3372	4.50
4	Phenol, dimethylformamide	xylene	21.0	39.0	0.233	0.1297	5.91
5	Phenol, acetonitrile	xylene	15.5	45.2	0.277	0.1508	3.72

The following are the probable formulae of the respective complexes:-

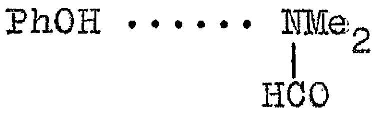
1. $Ph.OH \cdots\cdots ClPh$

2. 

$$\begin{array}{l} CH_3.CO.OC_2H_4 \\ \qquad\qquad | \\ \qquad\qquad H \cdots\cdots ClPh \end{array}$$

3. 

$$PhOH \cdots\cdots \overset{H}{\overset{|}{O}}-C_4H_9$$

4. 

$$PhOH \cdots\cdots \underset{HCO}{\underset{|}{NMe_2}}$$

5. $PhOH \cdots\cdots NC.CH_3$

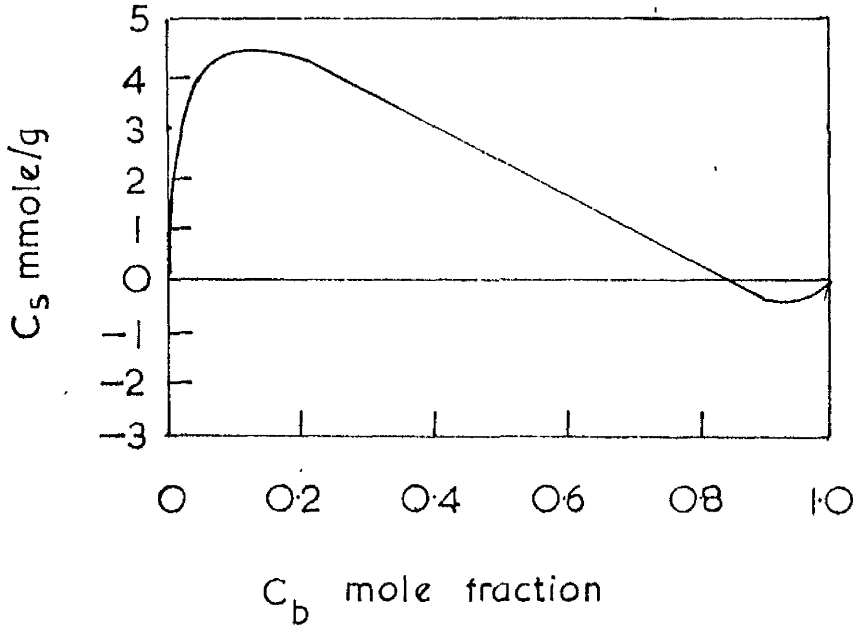


Fig.1. Adsorption of benzene-ethanol mixtures by silica gel.

Abscissa - mole fraction of ethanol in the mixture.

Ordinate - amount of ethanol adsorbed in millimoles per g. of adsorbent. After Bartel et al[47].

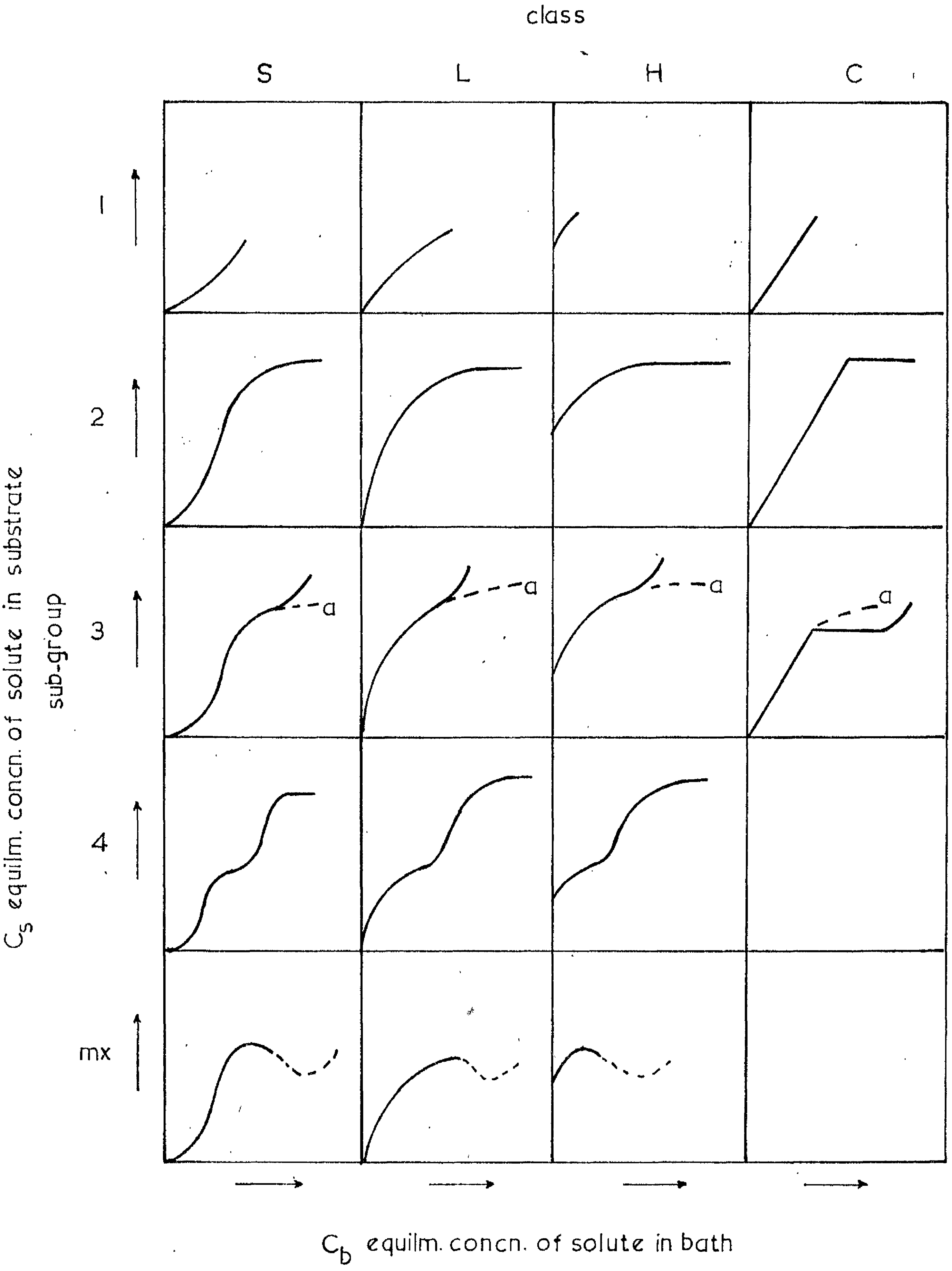


Fig.2. System of isotherm classification.

(Footnote)

Footnote to Fig.2.

Ostwald and de Izaguirre's two types of curve for adsorption from dilute solutions are classified as L 2 and C 1 here.

Brunauer's five types of vapour-phase (physical) adsorption isotherm (ref.48, p.150) are defined as H 2, L 3, S 1, L 4, and S 2 under the present system.

The present nomenclature is slightly different from that originally given[49].

The system can be readily adapted to describe curves with additional variations not shown above, e.g., the isotherm for p-nitrophenol adsorption on a pigment (Fig.28) has two inflections followed by a further rise and would be defined as L 5, and curves with two successive maxima (Fig. 3Lb) as Lmxmx.

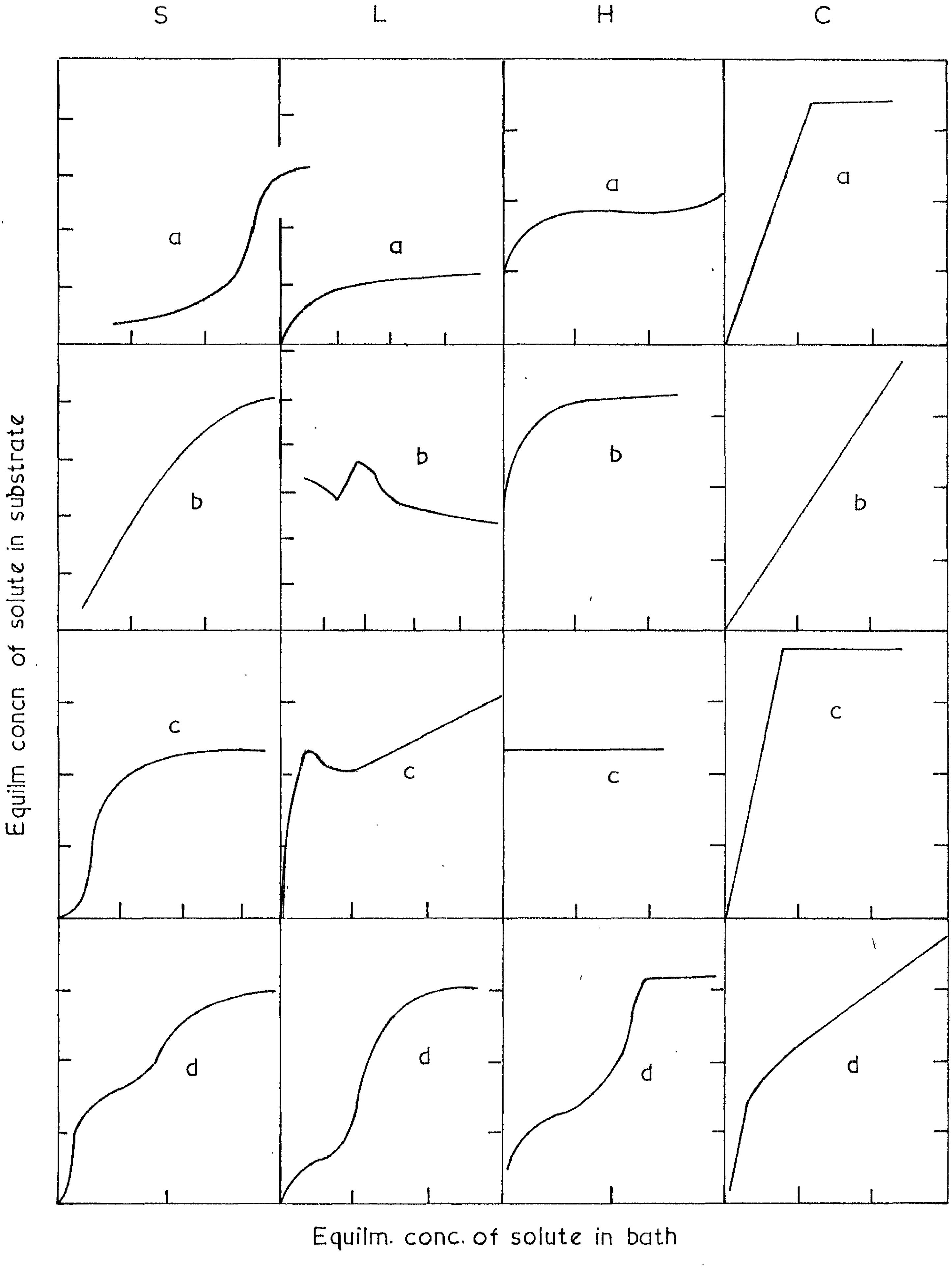

S
L
H
C
a
a
a
a
b
b
b
b
c
c
c
c
d
d
d
d
Equilm concn of solute in substrate
Equilm. conc. of solute in bath

Fig. 3

Fig.3. Examples of solution adsorption isotherms of the four classes. (From water, unless otherwise stated).

Curve and ref.	System	Scales (box limits)	
		Horizontal	Vertical
	S Curves		
a[51]	Cetyltrimethylammonium bromide on cotton at 25°C	0 - 1.0 (log) mmole/l	0 - 17.5 mmole/kg
b[52]	Monosulphonated dye (C.I.15,510) on anodic alumina at 50°C.	0 - 1.5 mmole/l	0 - 500 mmole/kg
c[53]	Cyanine dye on silver iodide at 40°C from 7% gelatin emulsion	$0 - 20 \times 10^{-3}$ mmole/l	$0 - 40 \times 10^{-3}$ mmole/kg
d[54]	Naphthalene Red EA (C.I.16,045) on graphite at 20°C.	0 - 2 mmole/l	0 - 20 mmole/kg
	L Curves		
a[55]	Resorcinol on chromatographic alumina at 58°C	0 - 80 mmole/l	0 - 400 mmole/kg
b[56]	Sodium palmitate on cotton at 75°C.	0 - 0.125% equivalent conc.	0 - 6 m equivalent/ 100 g.
c[57]	Sodium alkyl sulphate on wool at 40°C.	$0 - 6 \times 10^{-4}$ Normal	0 - 16 m equivalent/ 100 g.
d[58]	Octadecyl alcohol from benzene on nickel at 23°C	0 - 45 g/l	0 - 4 g/kg

Fig.3. (Cont'd.)

Curve and ref.	System	Scales (box limits)	
		Horizontal	Vertical
	H Curves		
a[54]	Methyl Violet 10 B (C.I.42,555) on graphite at 20°C.	0 - 0.18 mmole/l	0 - 8 mmole/kg
b[53]	Cationic cyanine dye on silver halide from 7% gelatin emulsion at 40°C	0 - 15 mg/l	0 - 80 mg/g
c[46]	Palmitic acid on Adams platinum catalyst from benzene solution	0 - 60 mmole/l	0 - 0.8 mmole/kg
d[59]	Dodecylammonium chloride on alumina at 20°C (pH 6.3)	0 - 20 mmole/l	0 - 400 mmole/kg
	C Curves		
a[60]	Glycine on silica (MSC brand) at 25°C	0 - 30 mmole/l	0 - 4000 mmole/kg
b[61]	p-Nitrophenol from benzene on nylon at 60°C	0 - 60 mmole/l	0 - 1200 mmole/kg
c[62]	Disperse dye (C.I.11,110) on cellulose diacetate from starch paste at 100°C	0 - 3 mg/g	0 - 20 mg/g
d[63]	Diphenyl on Terylene polyester fibre at 85°C from aqueous dispersion.	0 - 15 mmole/l	0 - 1200 mmole/kg

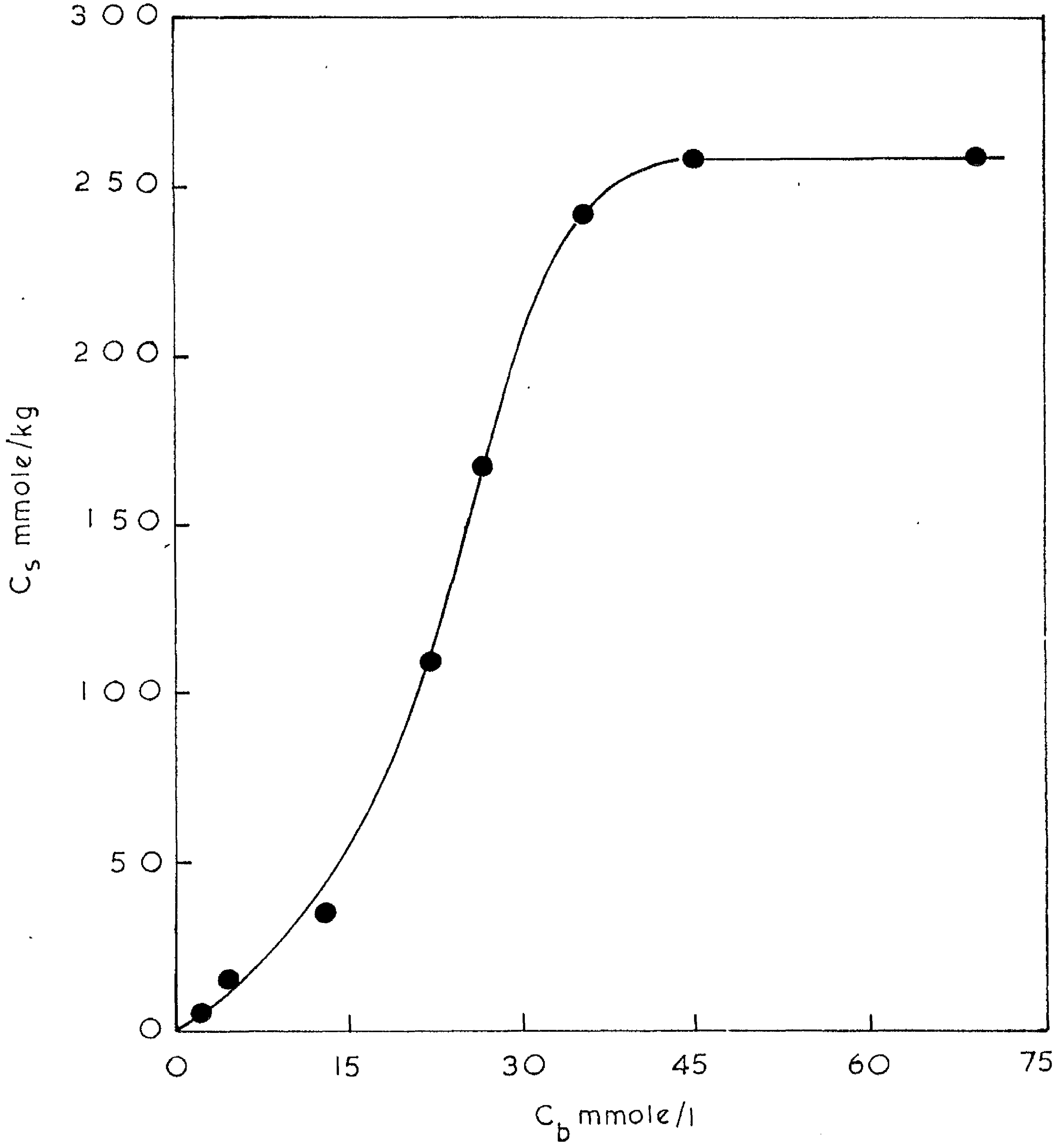


Fig.4. Adsorption Isotherm of p-nitrophenol on chromatographic alumina (Grade I) from water, at 20°C.

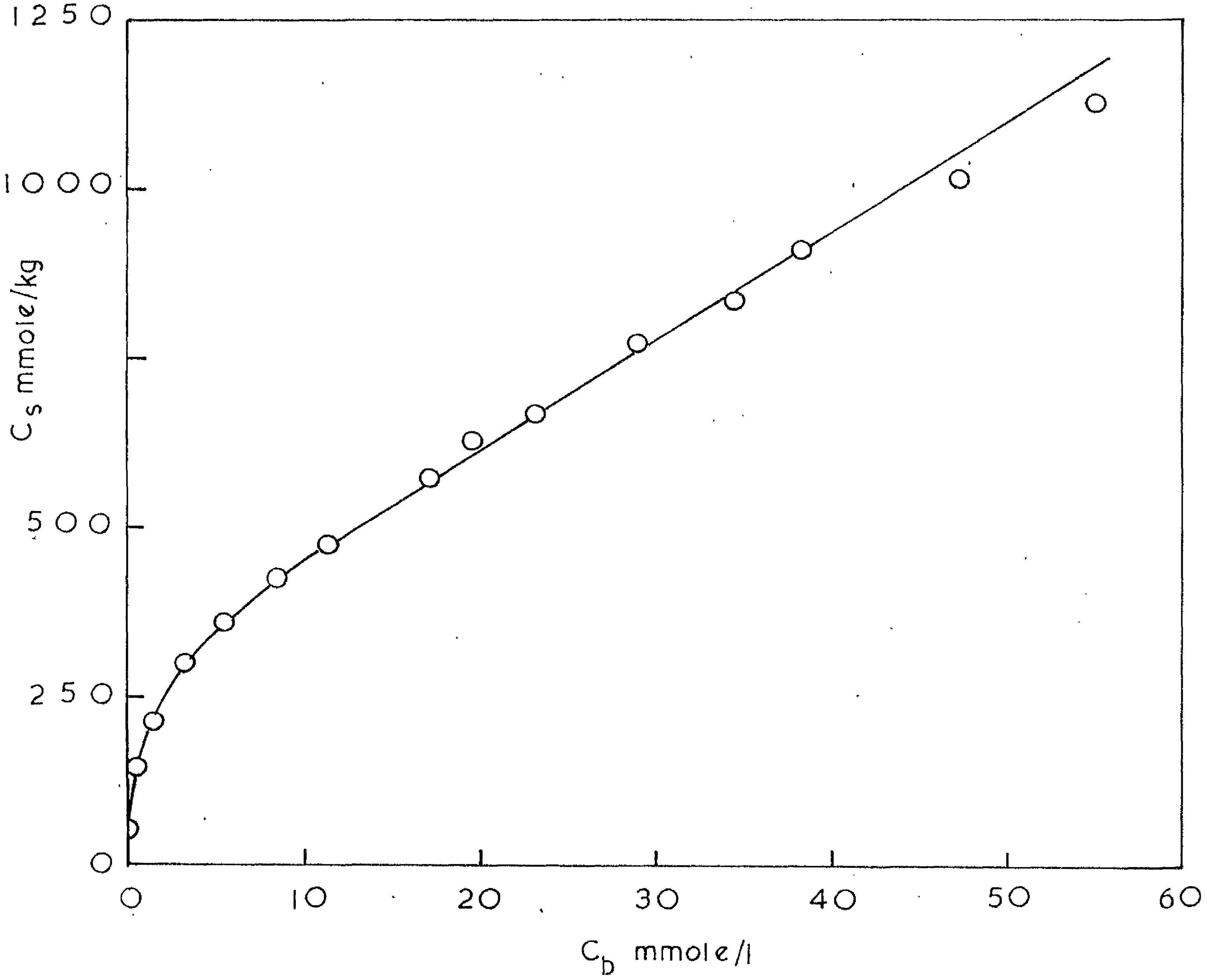


Fig.5. Adsorption isotherm of p-nitrophenol on chromatographic alumina (Grade I) from benzene, at 20°C.

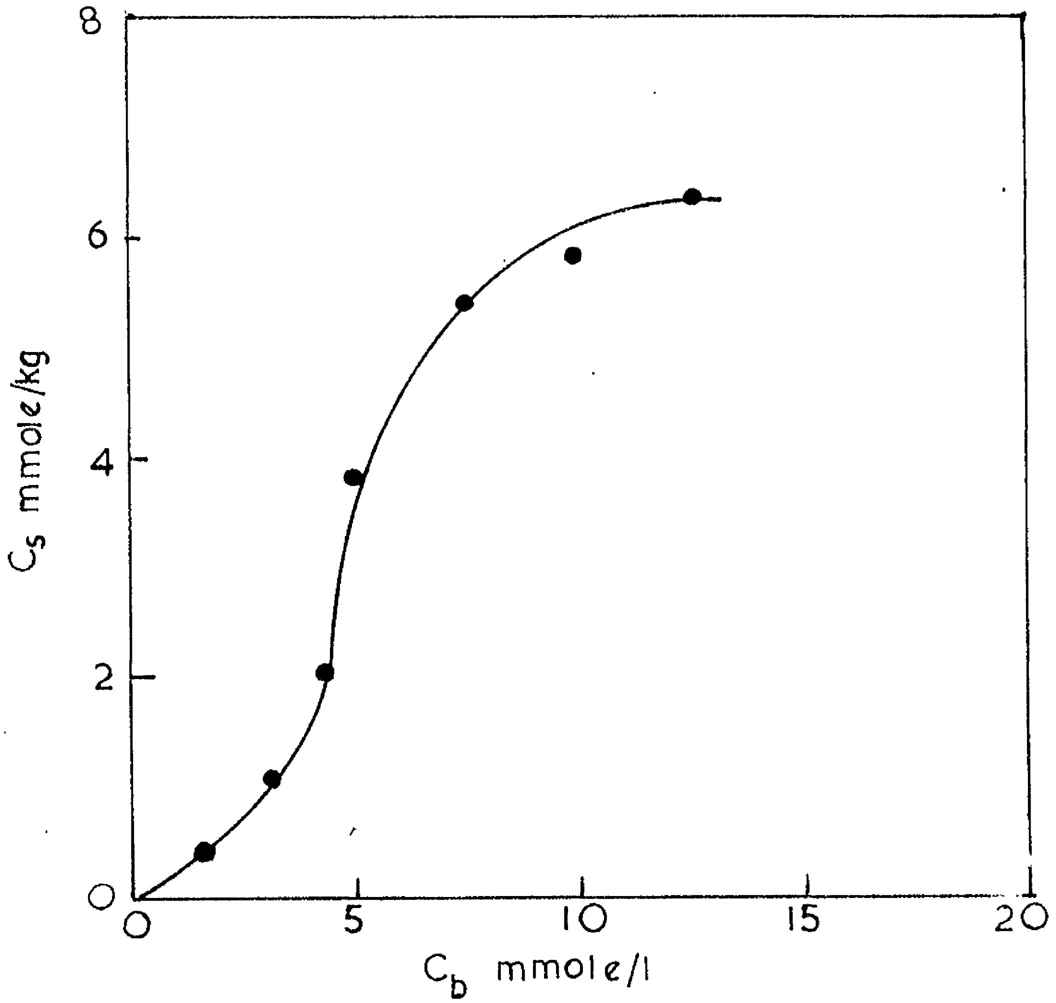


Fig.6. Adsorption isotherm of p-nitrophenol on silica (MSC brand) from water, at 15°C.

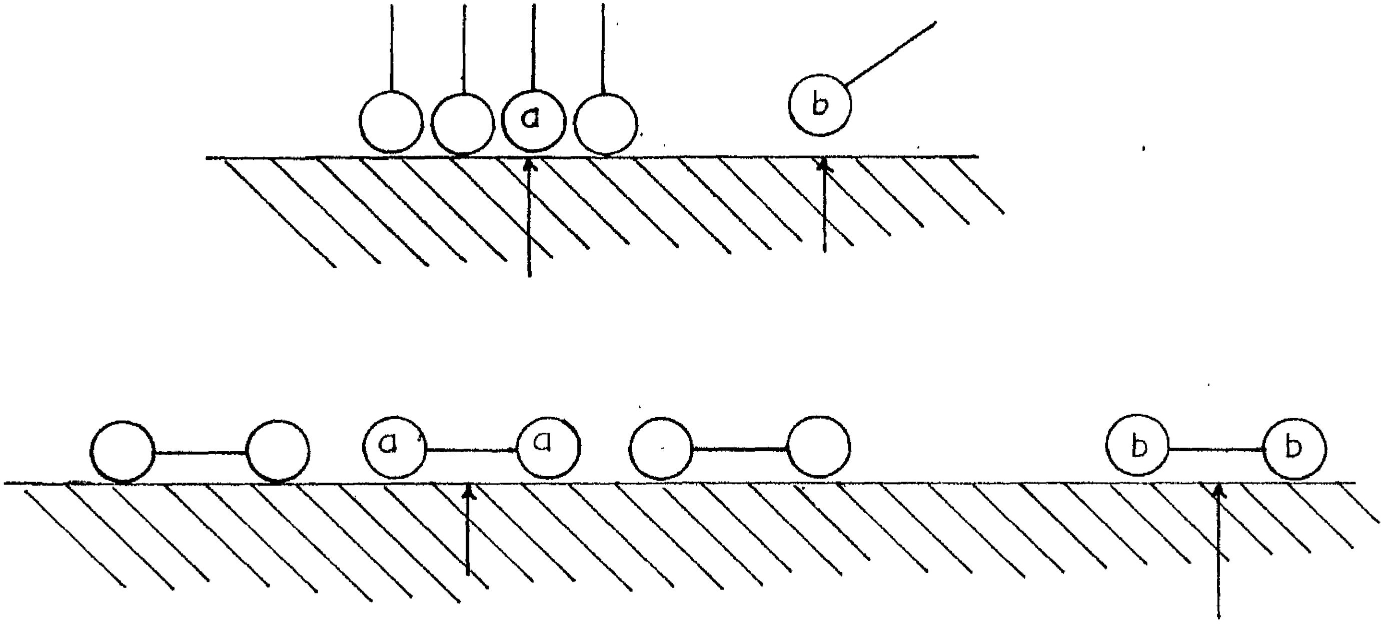


Fig.7. Schematic illustration of conditions favouring production of S and L isotherms.

Top: Monofunctional polar solute on polar substrate in polar solvent. A solute molecule is more stable when adsorbed at a, adjacent to other already adsorbed molecules, than in isolation at b. Result: S isotherm.

Bottom: A bifunctional solute molecule is equally stable when adsorbed at a as at b. Result: L isotherm.

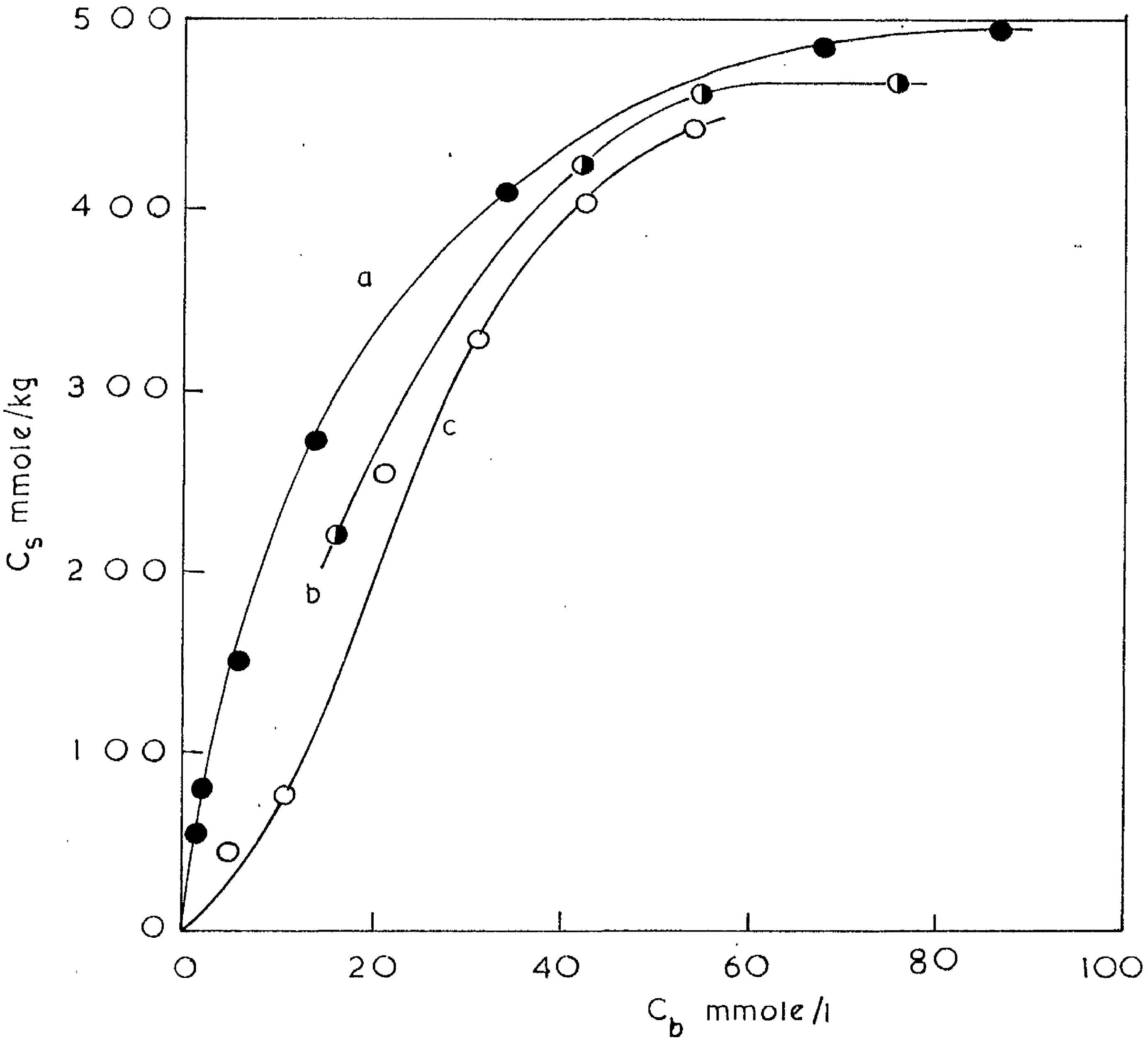


Fig.8. Adsorption isotherms of methanol in benzene on (a,b) intensively dried and (c) normally dried cellulose (viscose rayon) at 19°C, 23°C and 50°C respectively. (Curve <u>c</u> after Dr.A.S.A.Hassan).

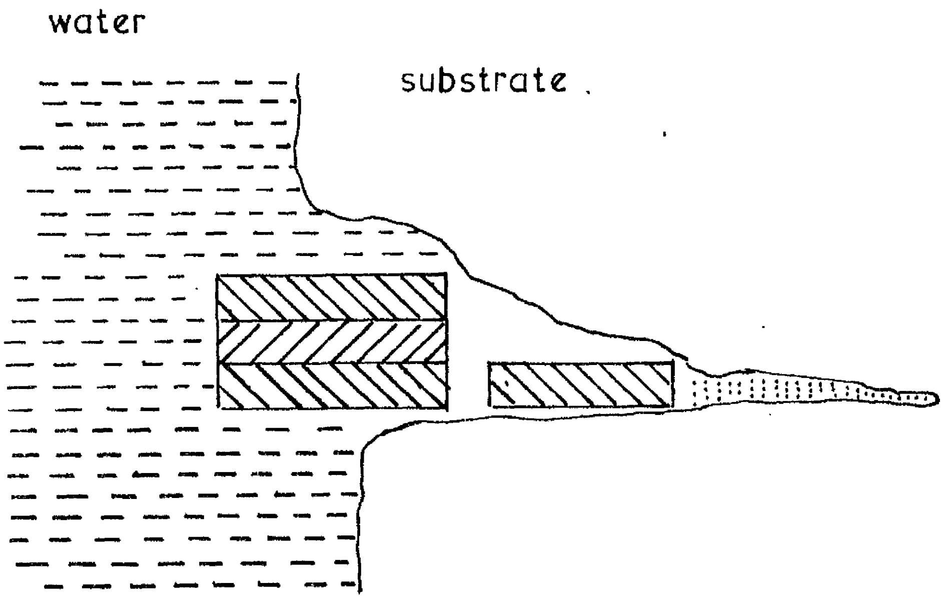


Fig.9. Schematic representation of conditions favouring the C isotherm. (Adsorbed molecules of a low solubility solute (e.g., a non-ionic disperse dye) in water, entering a hydrophobic substrate beyond the region swollen by water.)

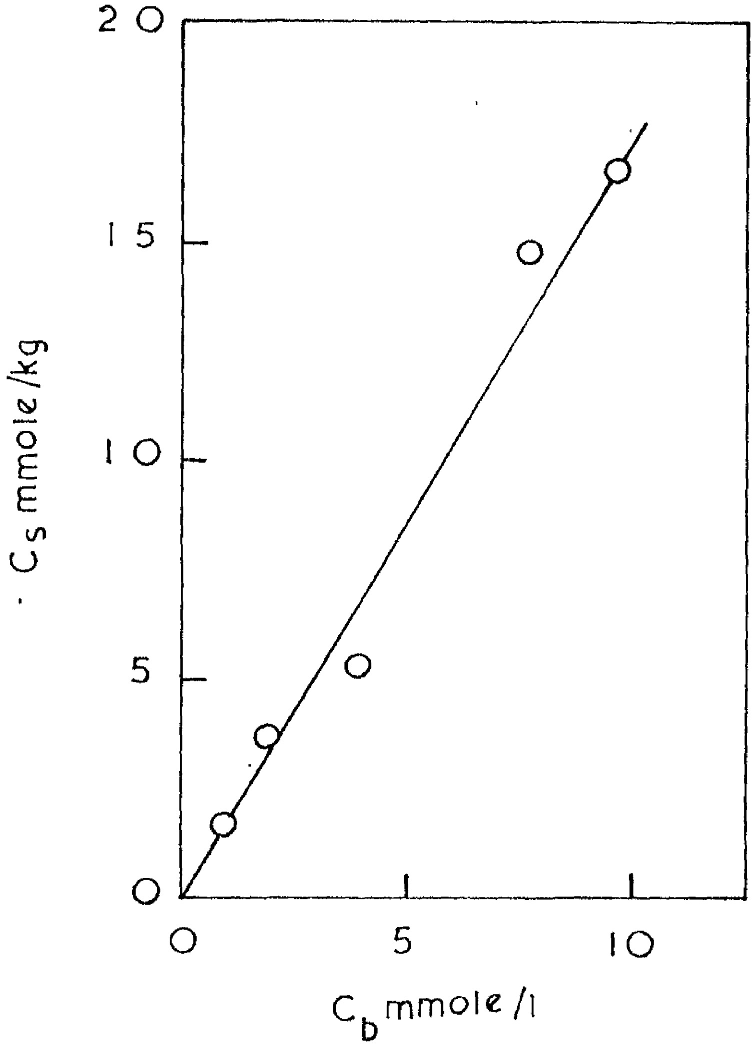


Fig.10. Adsorption isotherm of Orange II (C.I.15,510) on secondary-cellulose acetate from water at 50°C.

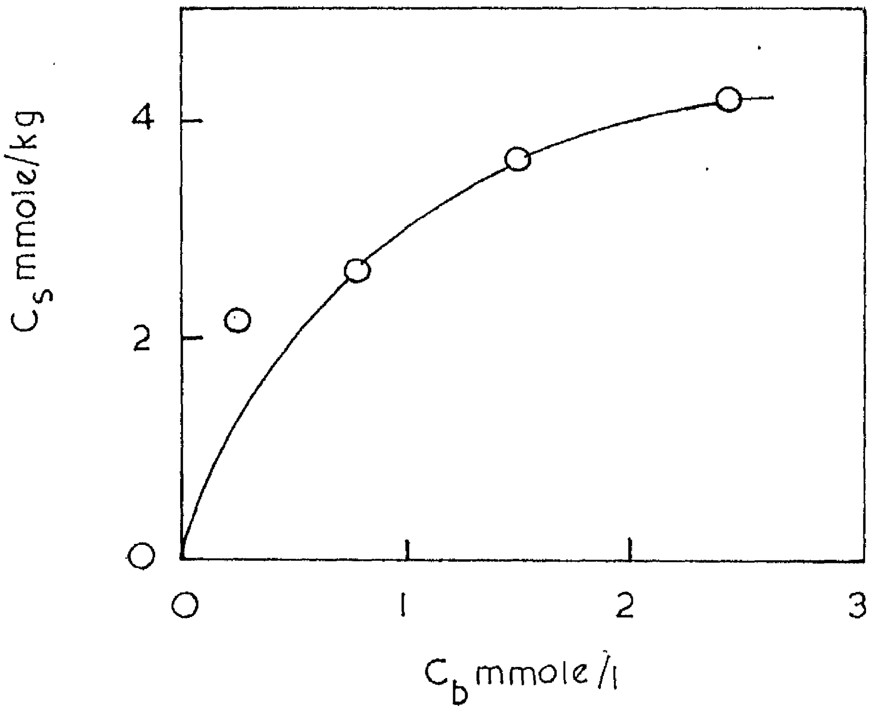


Fig.11. Adsorption isotherm of Naphthalene Red EA (C.I.16,045) on secondary-cellulose acetate from water at 50°C.

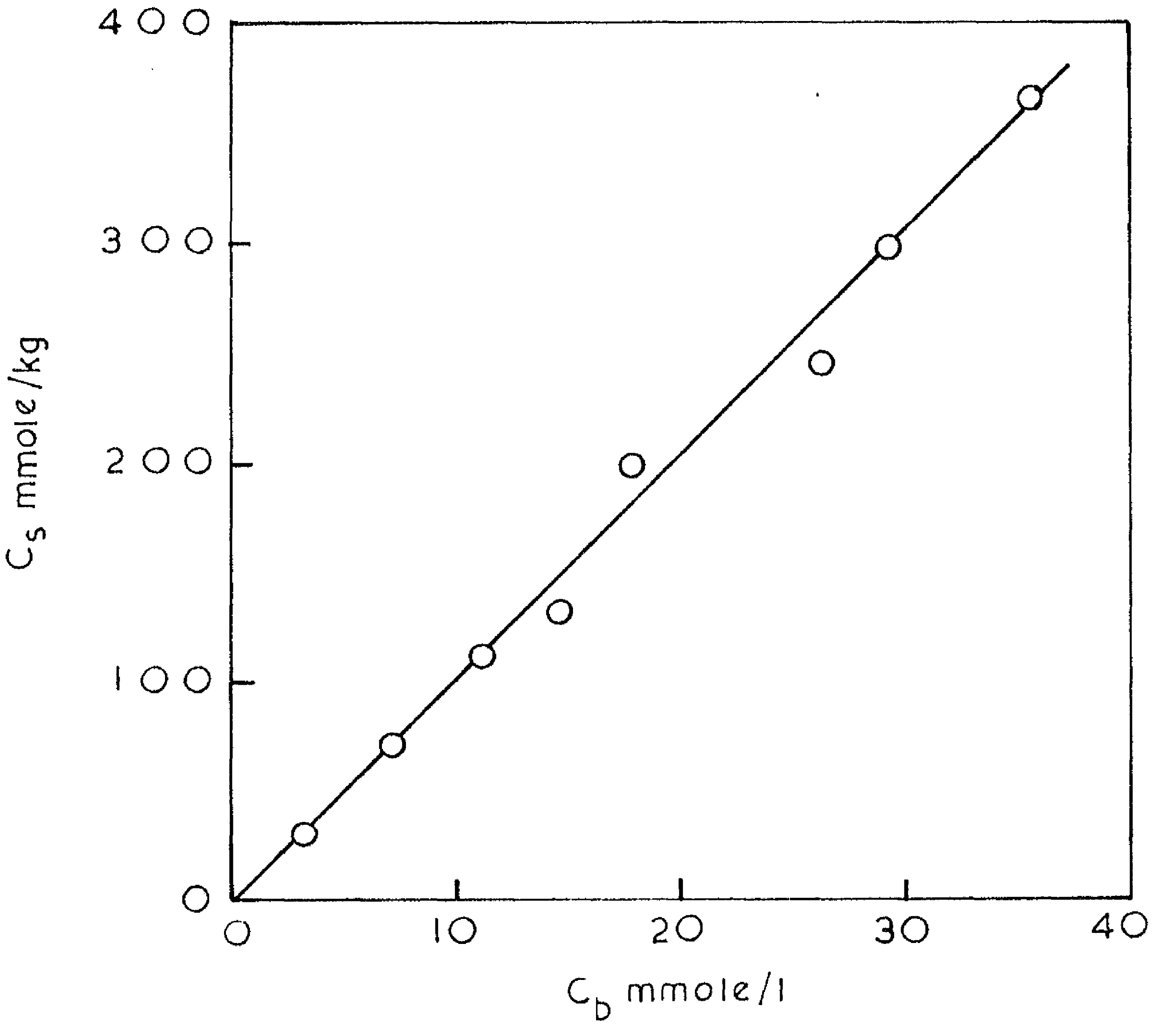


Fig. 12. Adsorption isotherm of benzene on wool from n-heptane at 19°C.

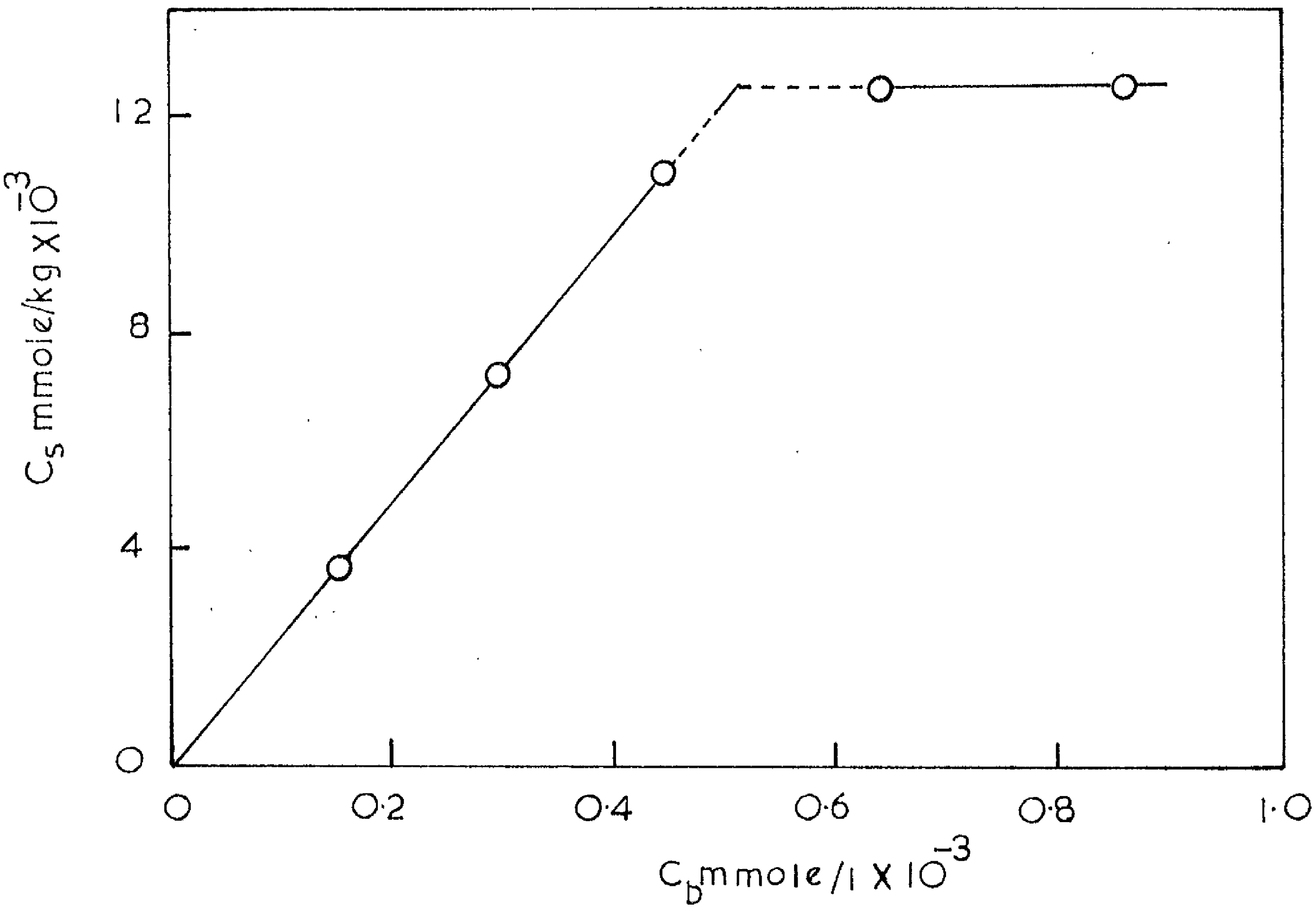


Fig.13. Adsorption isotherm of water on wool from n-butanol at 19°C.

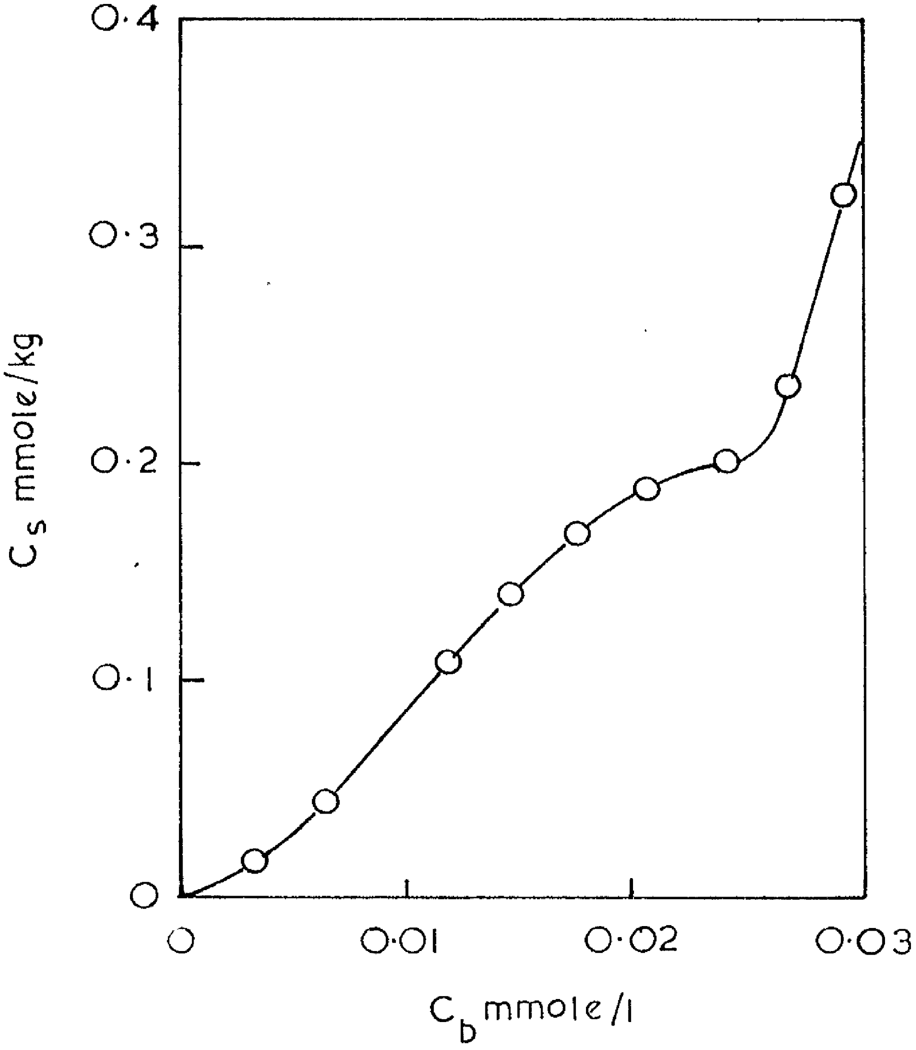


Fig.14. Adsorption isotherm of 4-aminoazobenzene on cellulose (viscose rayon) from water at 52°C.

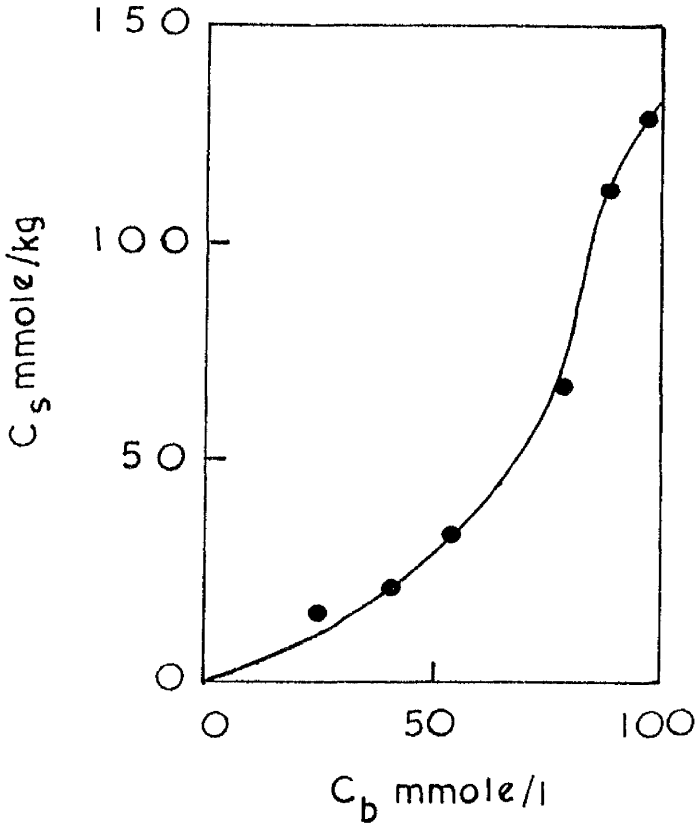


Fig.15. Adsorption isotherm of benzene in n-butanol on wool at 50°C.

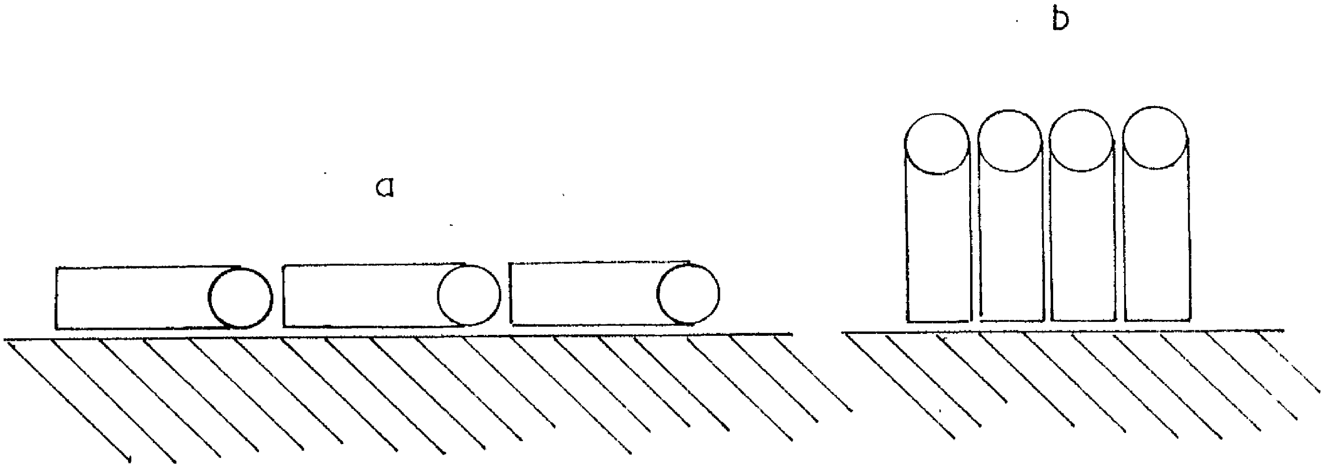


Fig. 16. Schematic representation of probable orientation of p-nitrophenol molecules on a pigment surface, from water. (a) Flat orientation at low concentration. (b) Vertical orientation at high concentration.

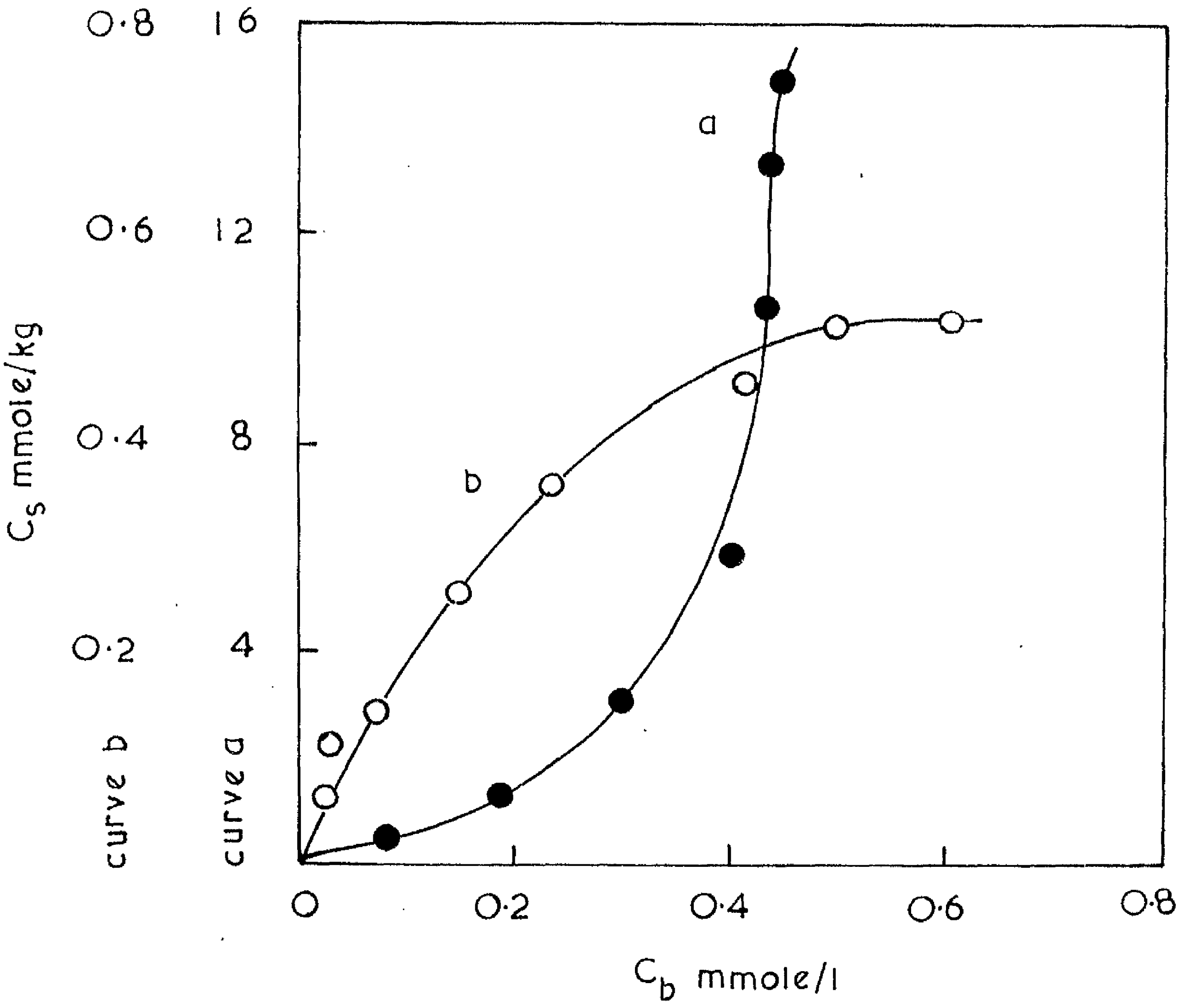


Fig. 17. Isotherms for sulphonated amonoanthraquinone dyes adsorbed by hydrogen-bonding on powdered silica from water. (a) Monofunctional (1-amino) dye (I); (b) bifunctional (1,5-diamino) dye (II).

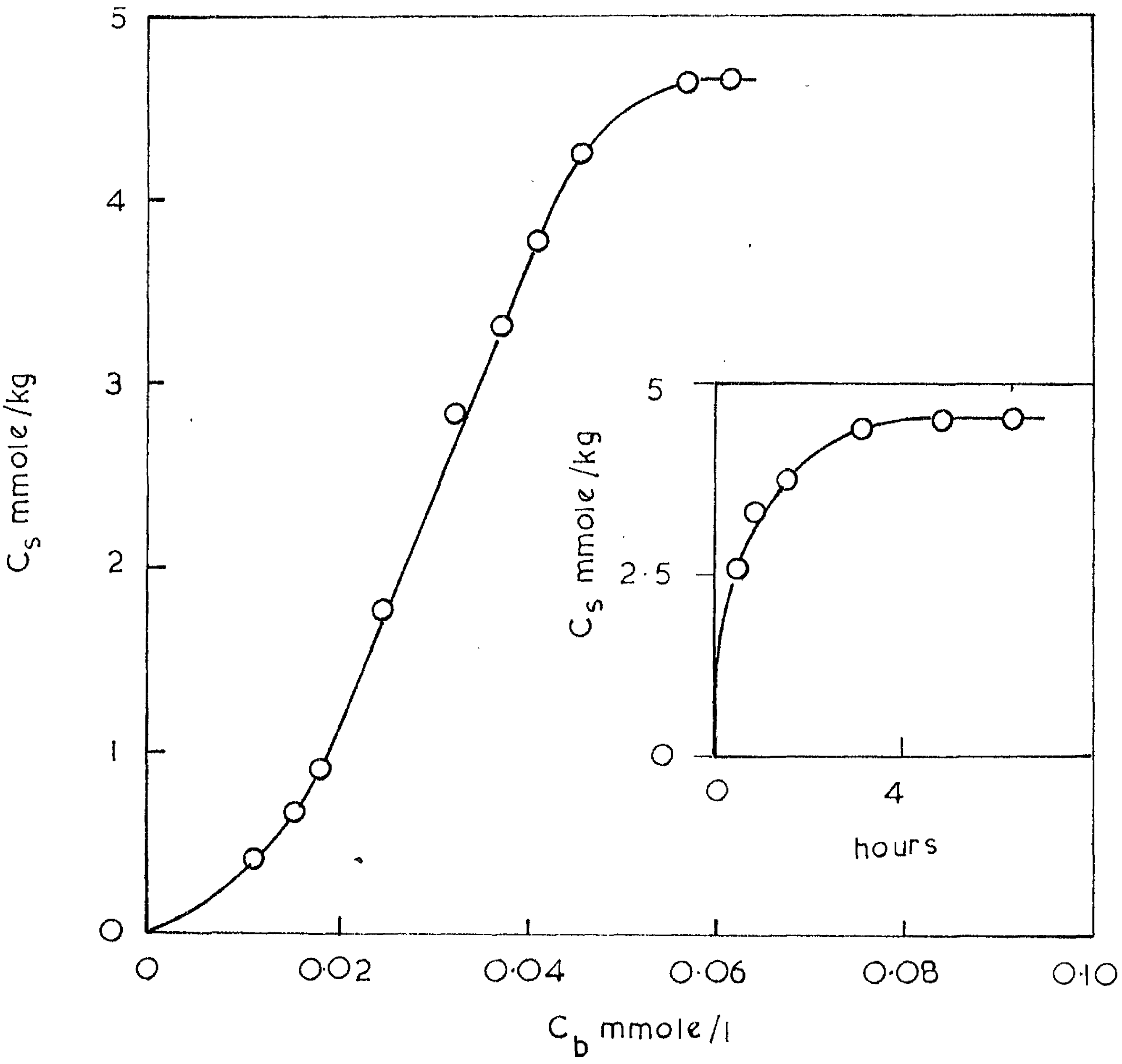


Fig.18. Adsorption isotherm of Carbolan Blue B (C.I.62,075) on silica (MSC brand) from water at 18°C. Inset - rate curve.

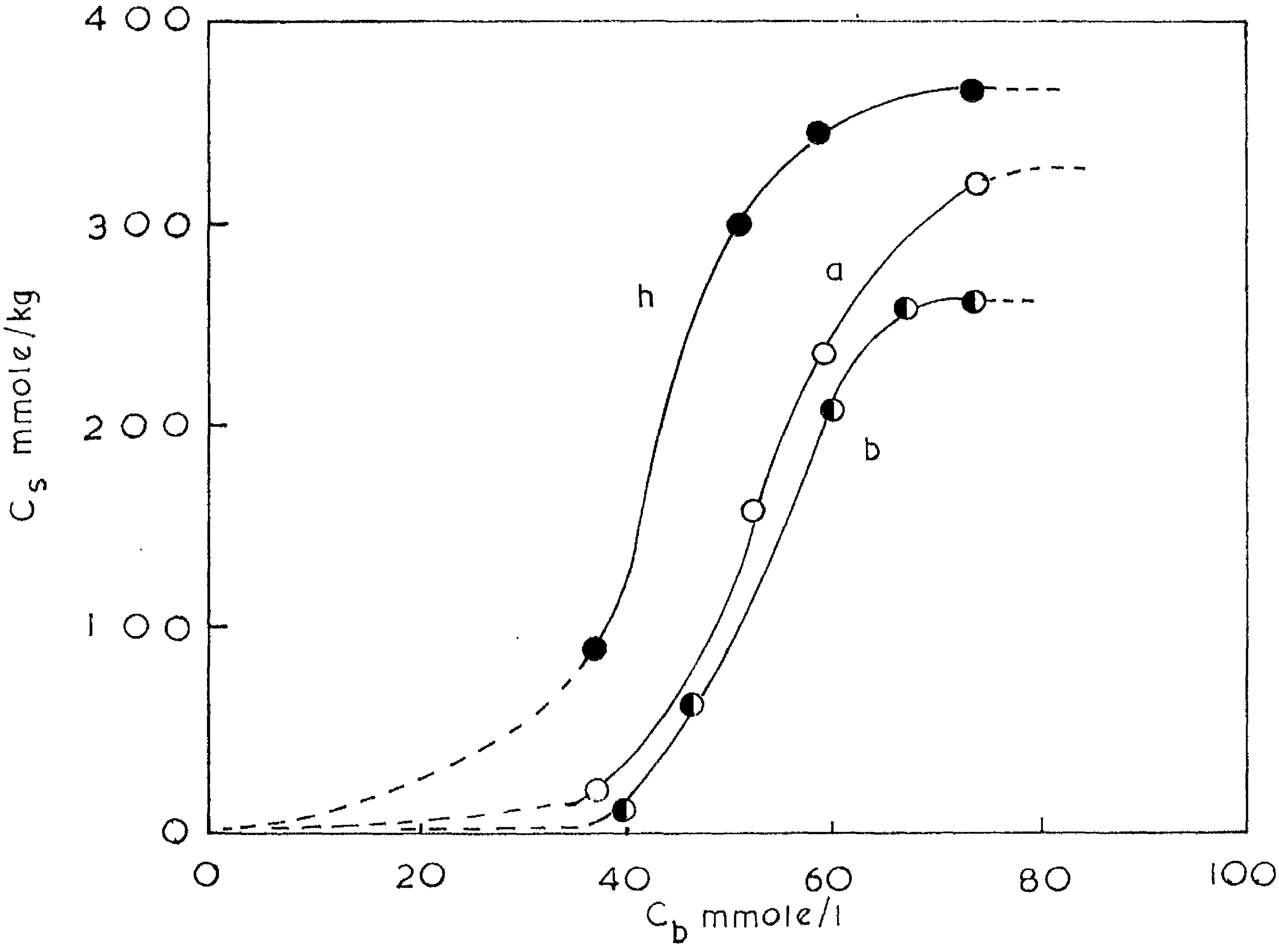


Fig.19. Adsorption isotherms of p-nitrophenol on three types of alumina from water at 20°C. (a) Type 'A'; (b) type 'B' (h) type 'H'

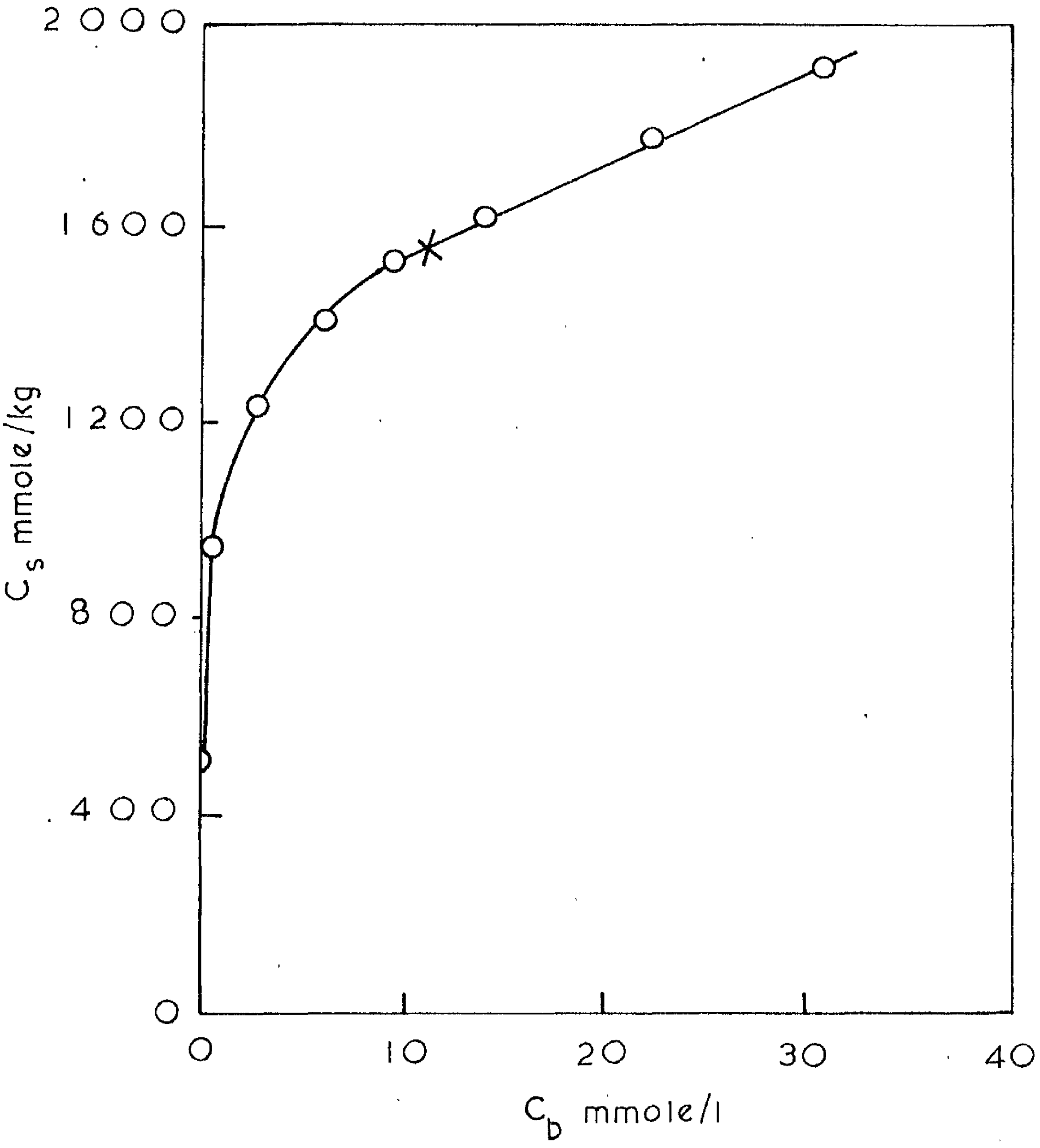


Fig.20. Adsorption isotherm of p-nitrophenol on "Neo-Spectra" Carbon black from water at 19.5°C.

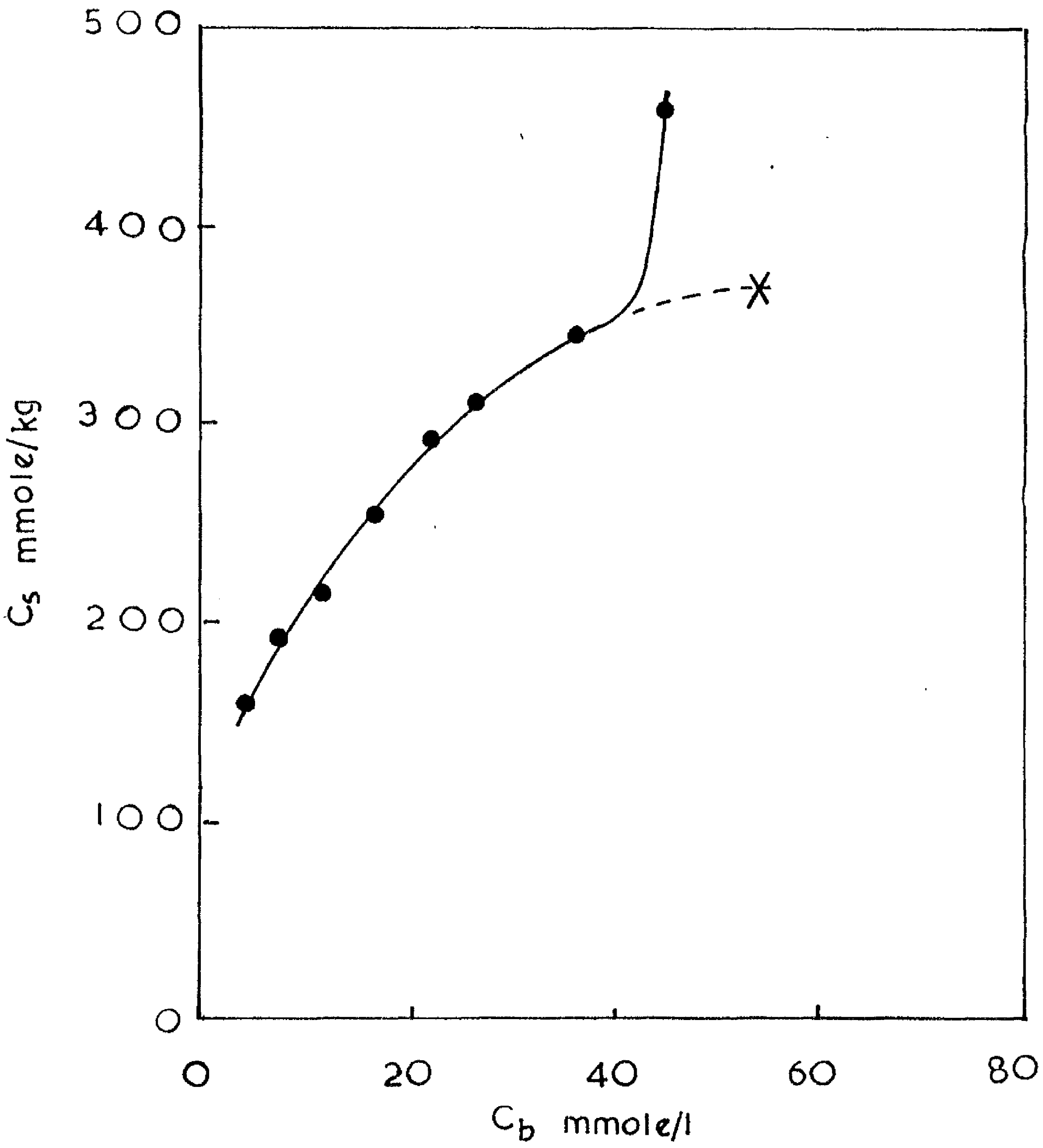


Fig.21. Adsorption isotherm of p-nitrophenol on Cabot 'ELF8' carbon from water at 18.5°C.

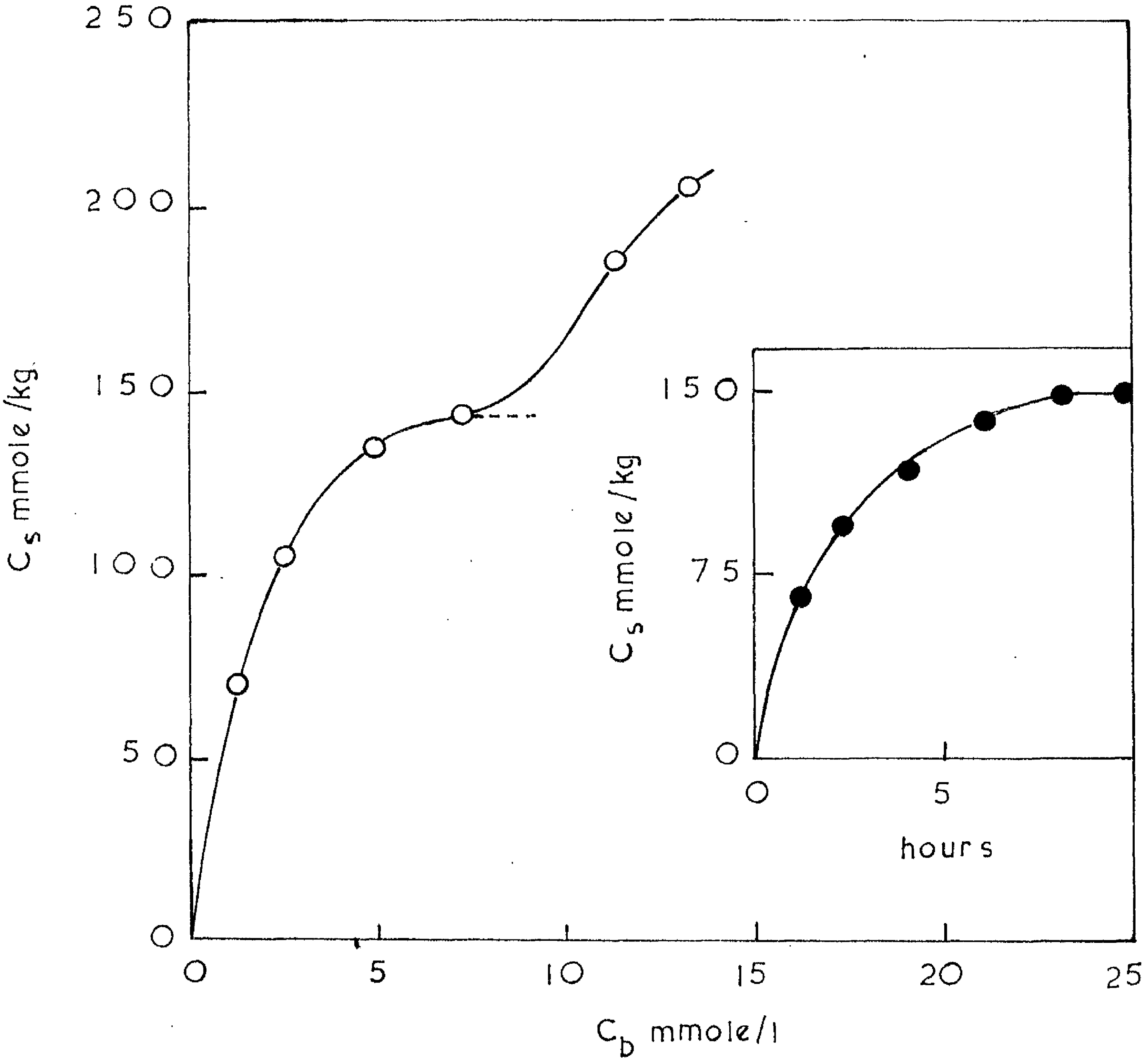


Fig.22. Adsorption isotherm of p-nitrophenol on coal powder from water at 20°C. Inset - rate curve.

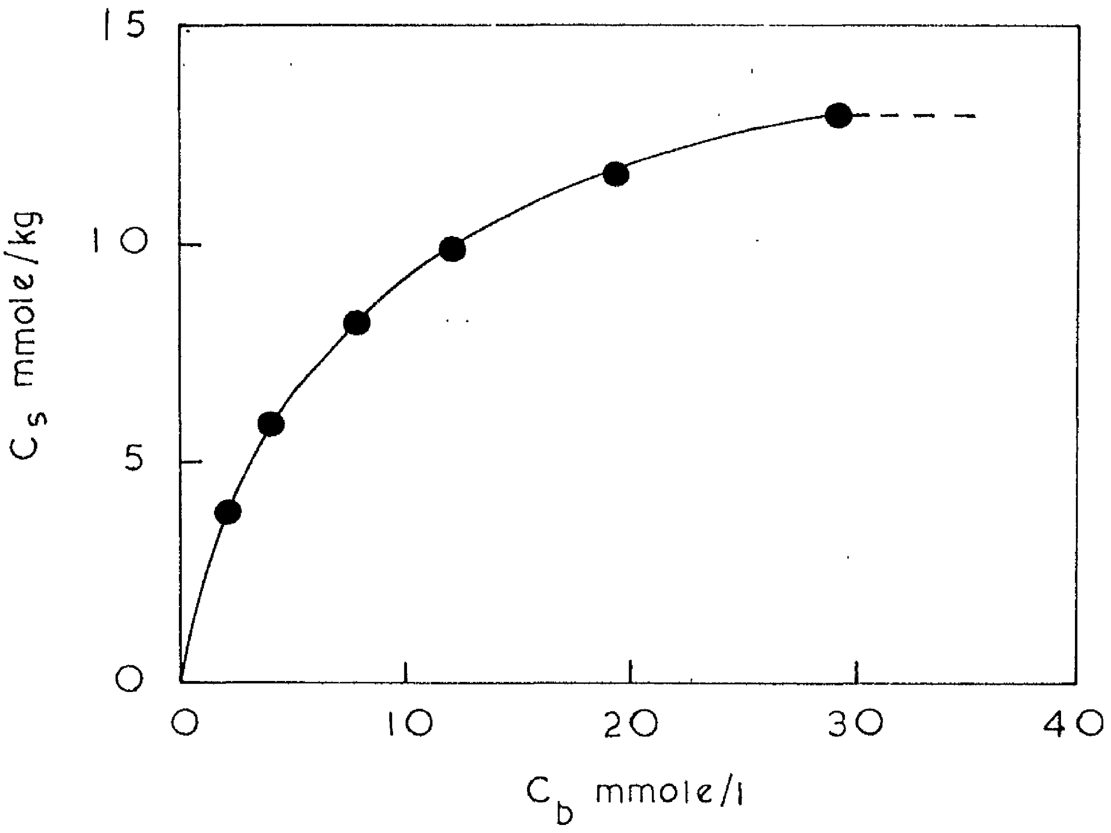


Fig.23. Adsorption isotherm of p-nitrophenol on cement from benzene at 17.6°C.

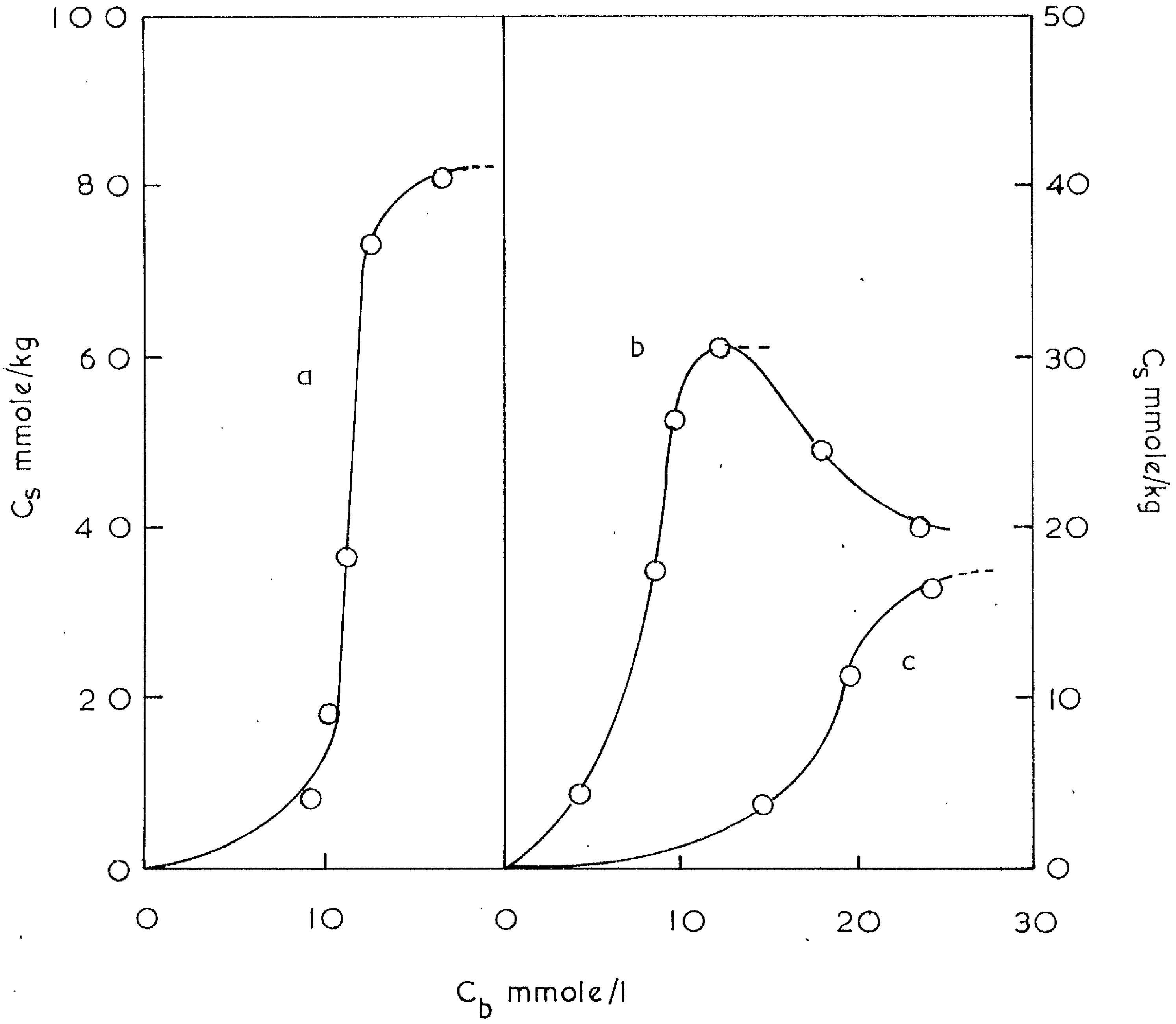


Fig.24. Adsorption isotherms of p-nitrophenol at 18°C on (a) zinc dust from water; (b) iron dust from water; (c) electrically deposited copper from 10% aqueous ethanol.

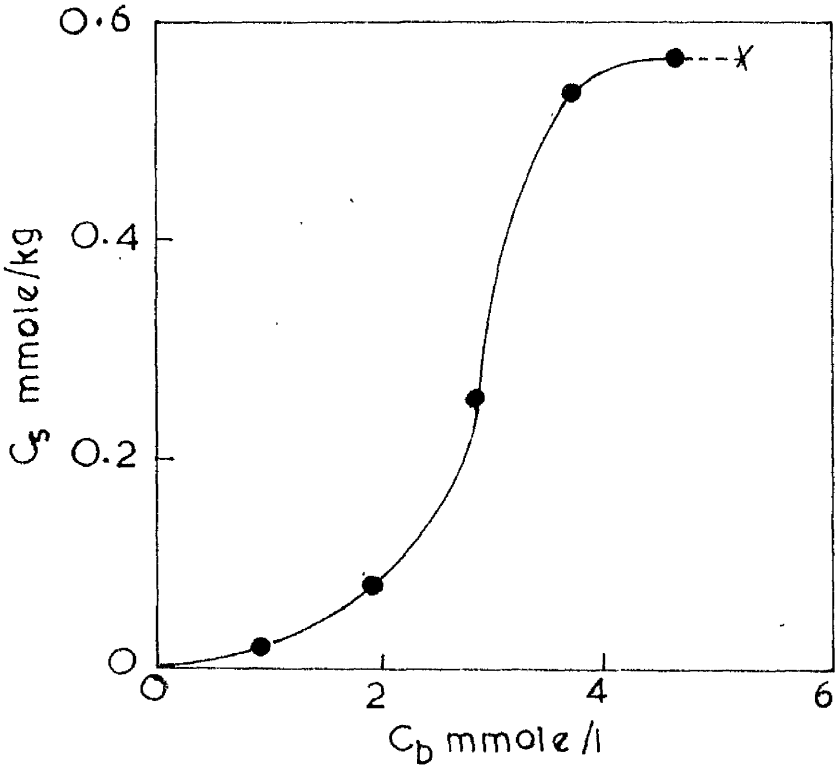


Fig.25. Adsorption isotherm of p-nitrophenol on quartz from water at 18°C.

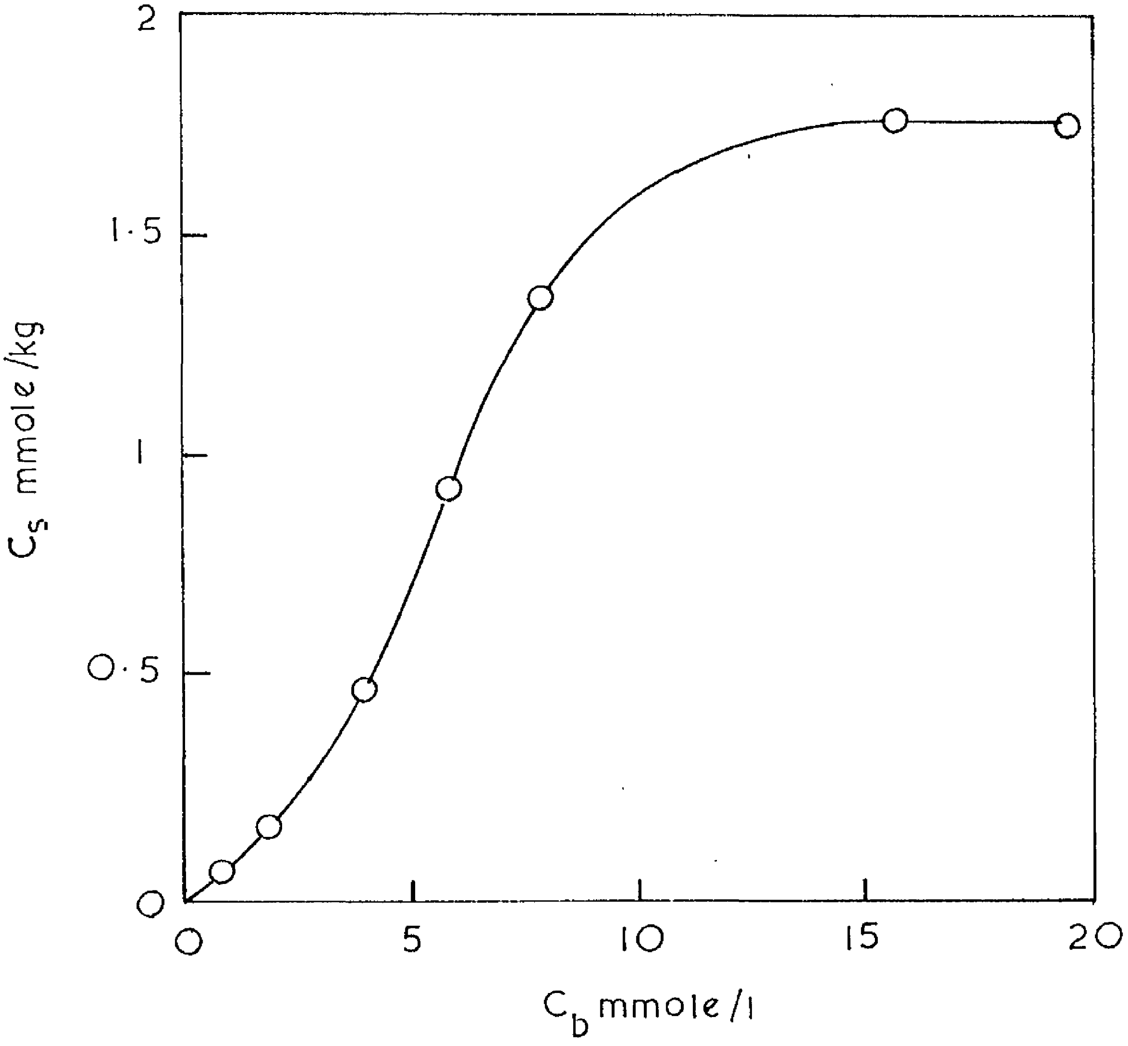


Fig.26. Adsorption isotherm of p-nitrophenol on quartz from water at 17°C.

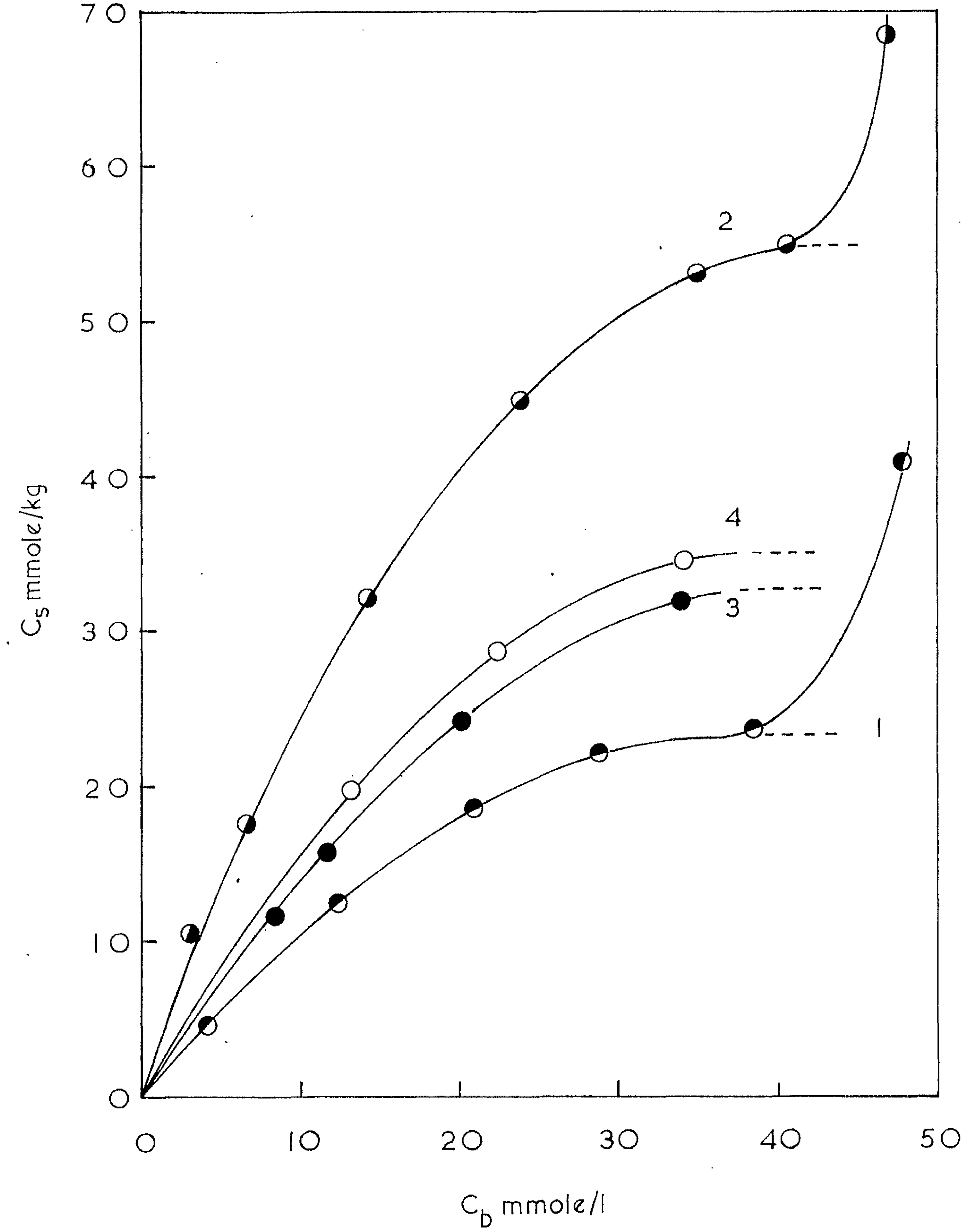


Fig.27. Adsorption isotherms of p-nitrophenol on types of TiO_2 from xylene at 19°C. (1) Type 1; (2) type 2;(3) type 3, and (4) type 4.

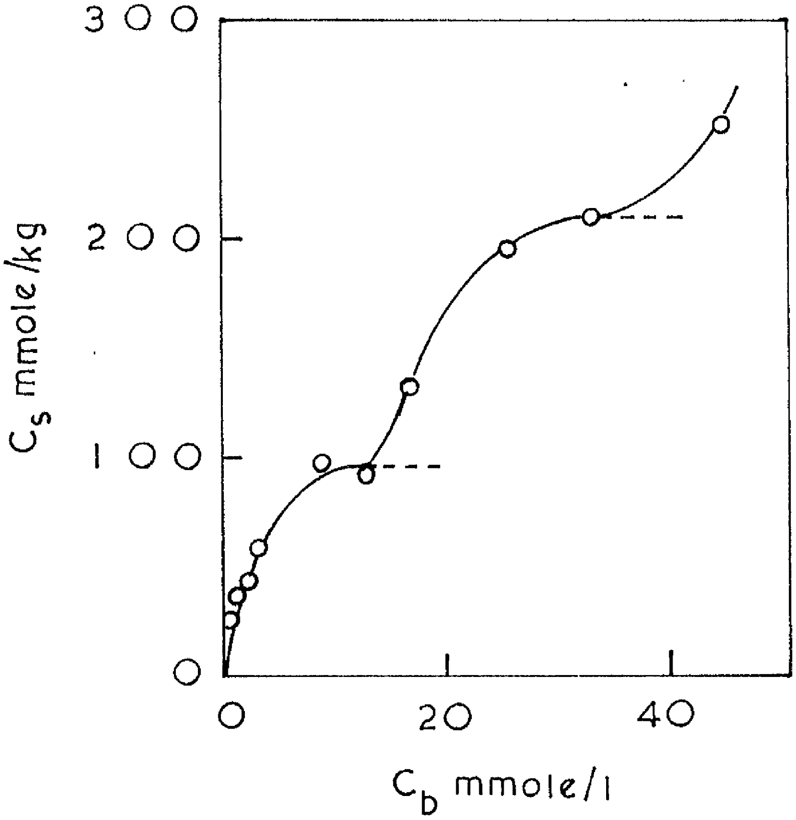


Fig.28. Adsorption isotherm of p-nitrophenol on a yellow azo pigment (Sample 1) from water at 19°C.

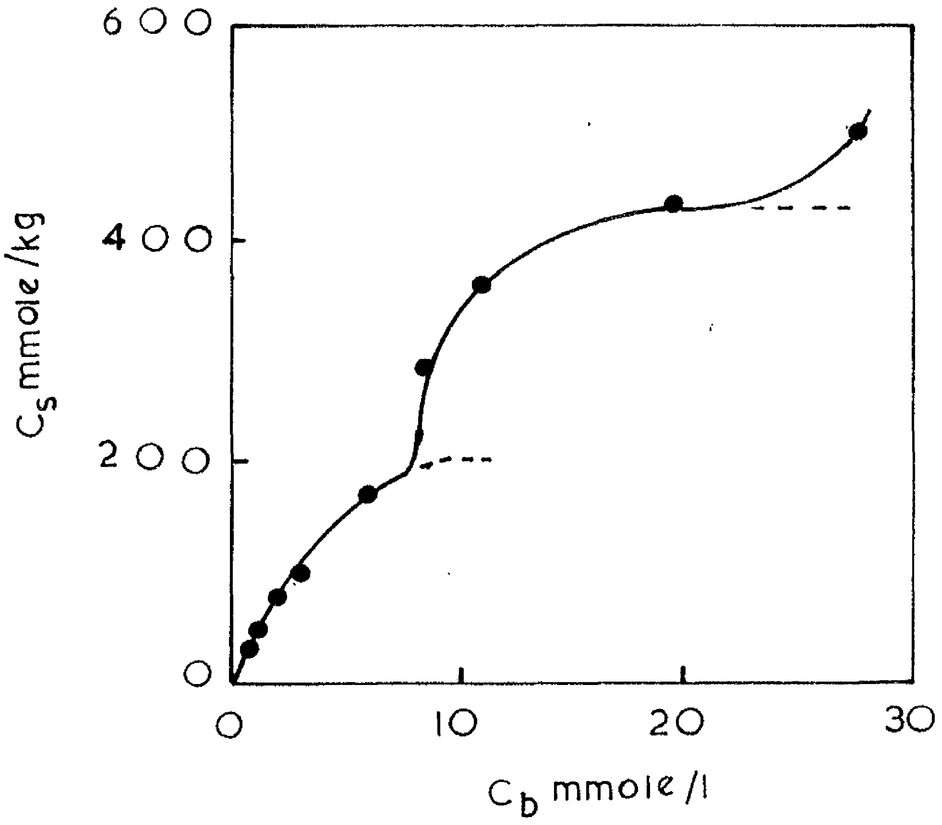


Fig.29. Adsorption isotherm of p-nitrophenol on a yellow (azo) pigment (Sample 2) from water at 19°C.

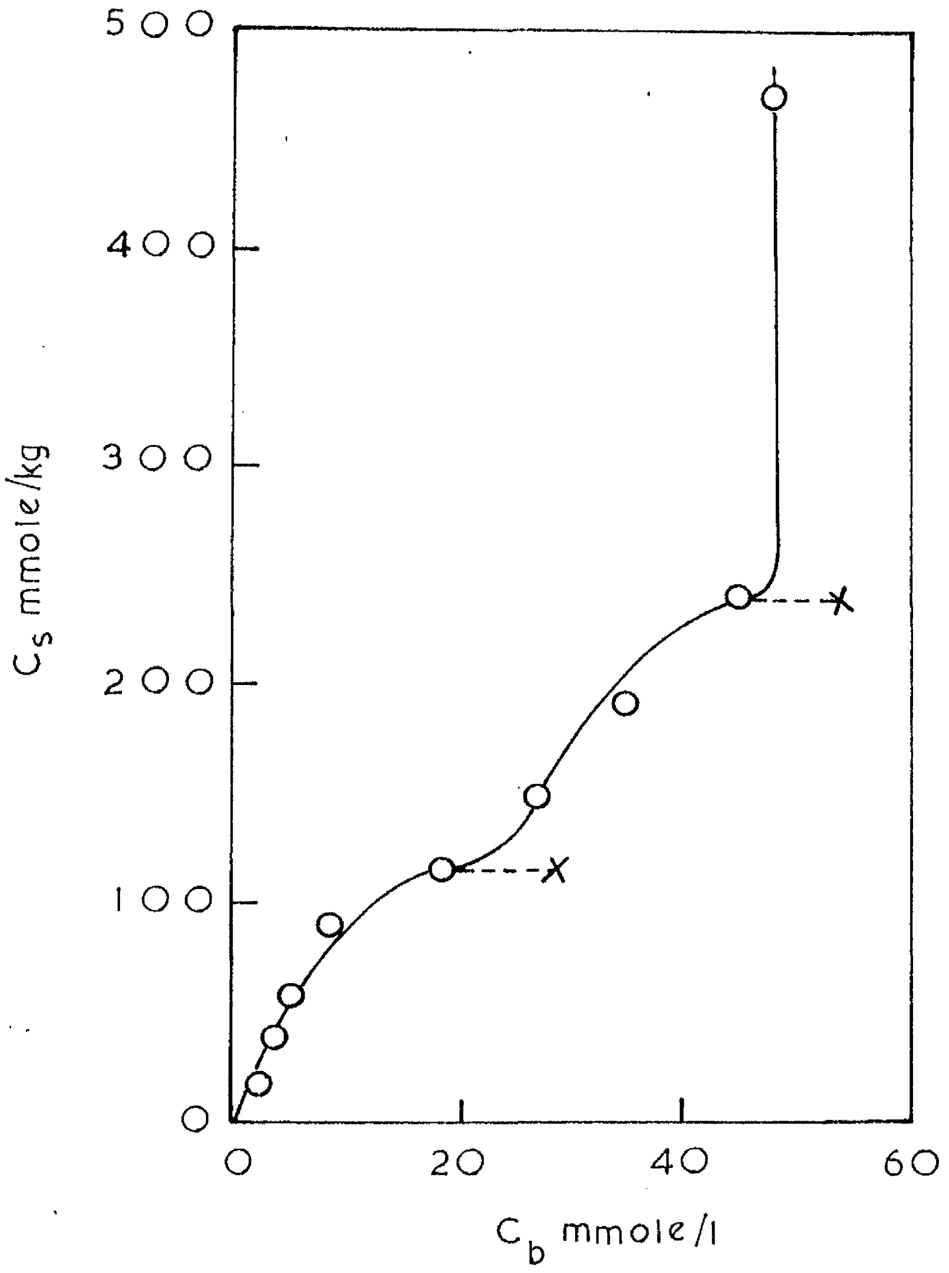


Fig.30. Adsorption isotherm of p-nitrophenol on a yellow (azo) pigment (Sample 3) from water at 19°C.

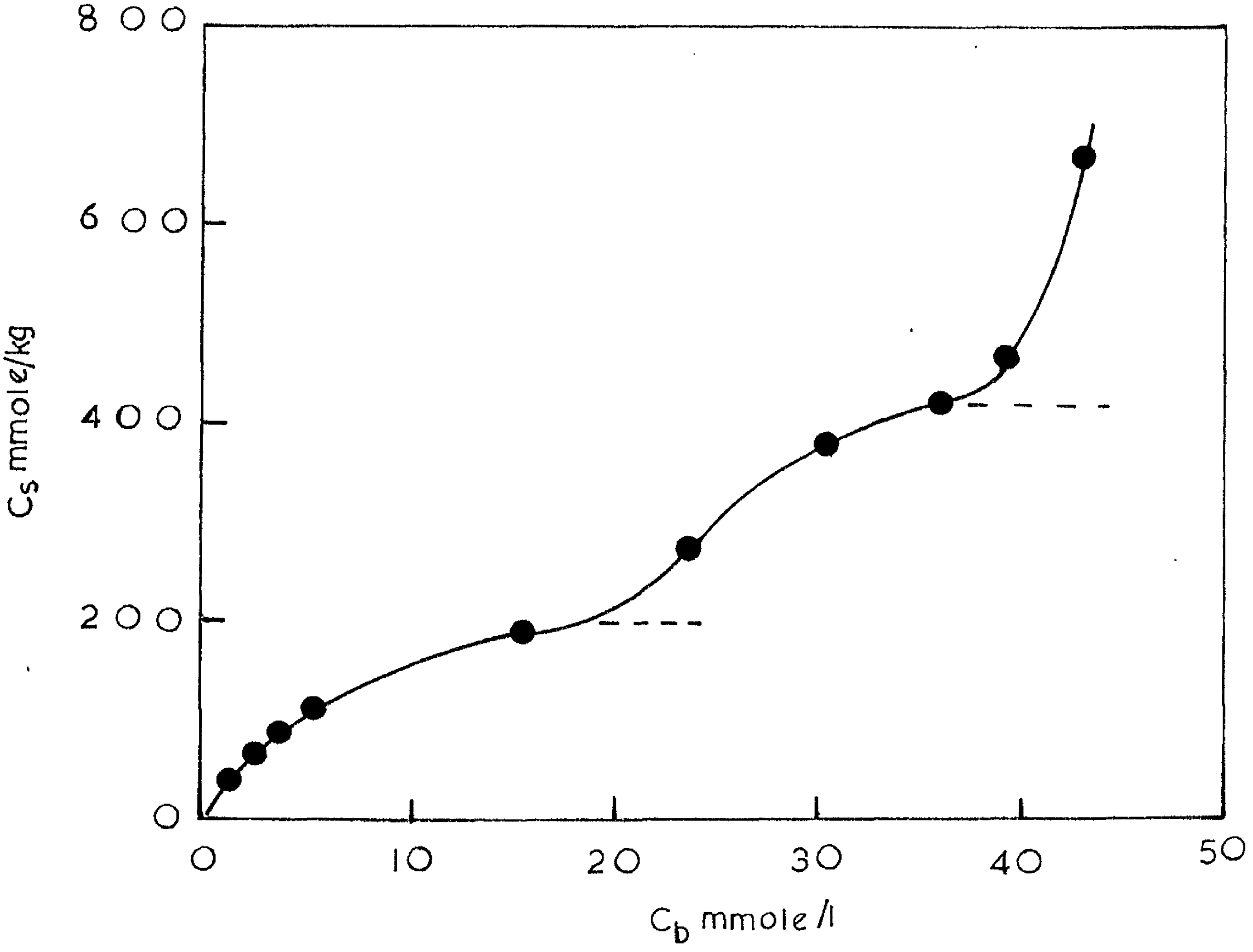


Fig.31. Adsorption isotherm of p-nitrophenol on a yellow (azo) pigment (Sample 4) from water at 19°C.

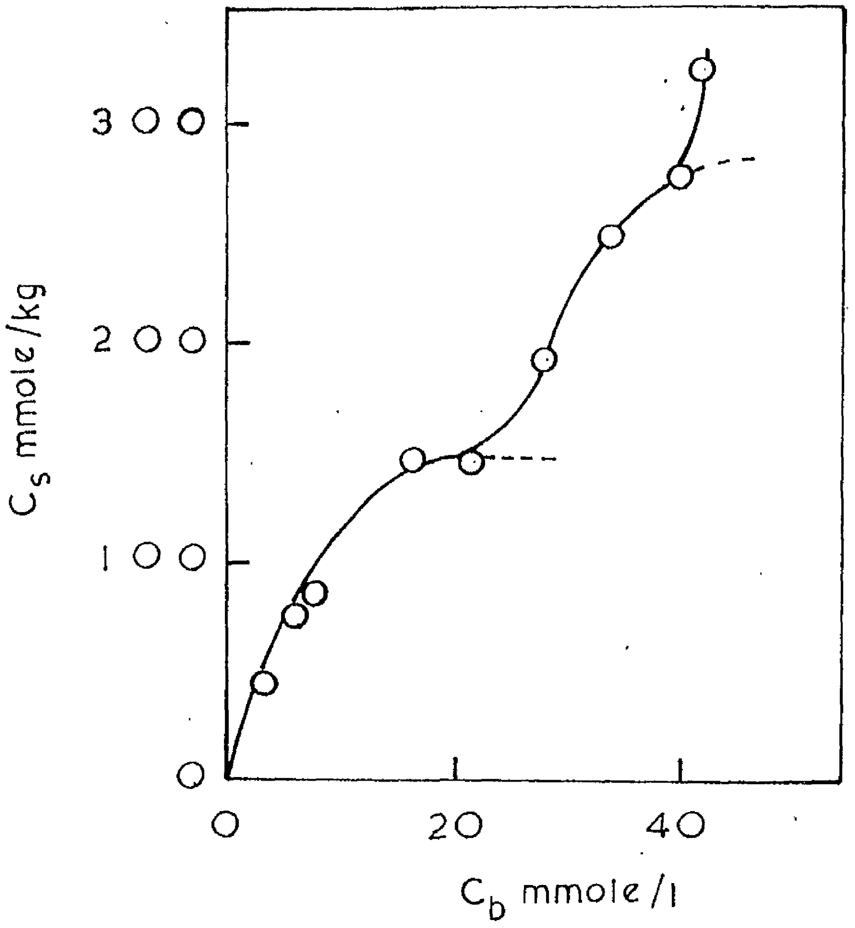


Fig. 32. Adsorption isotherm of p-nitrophenol on a yellow (azo) pigment (Sample 5) from water at 19°C.

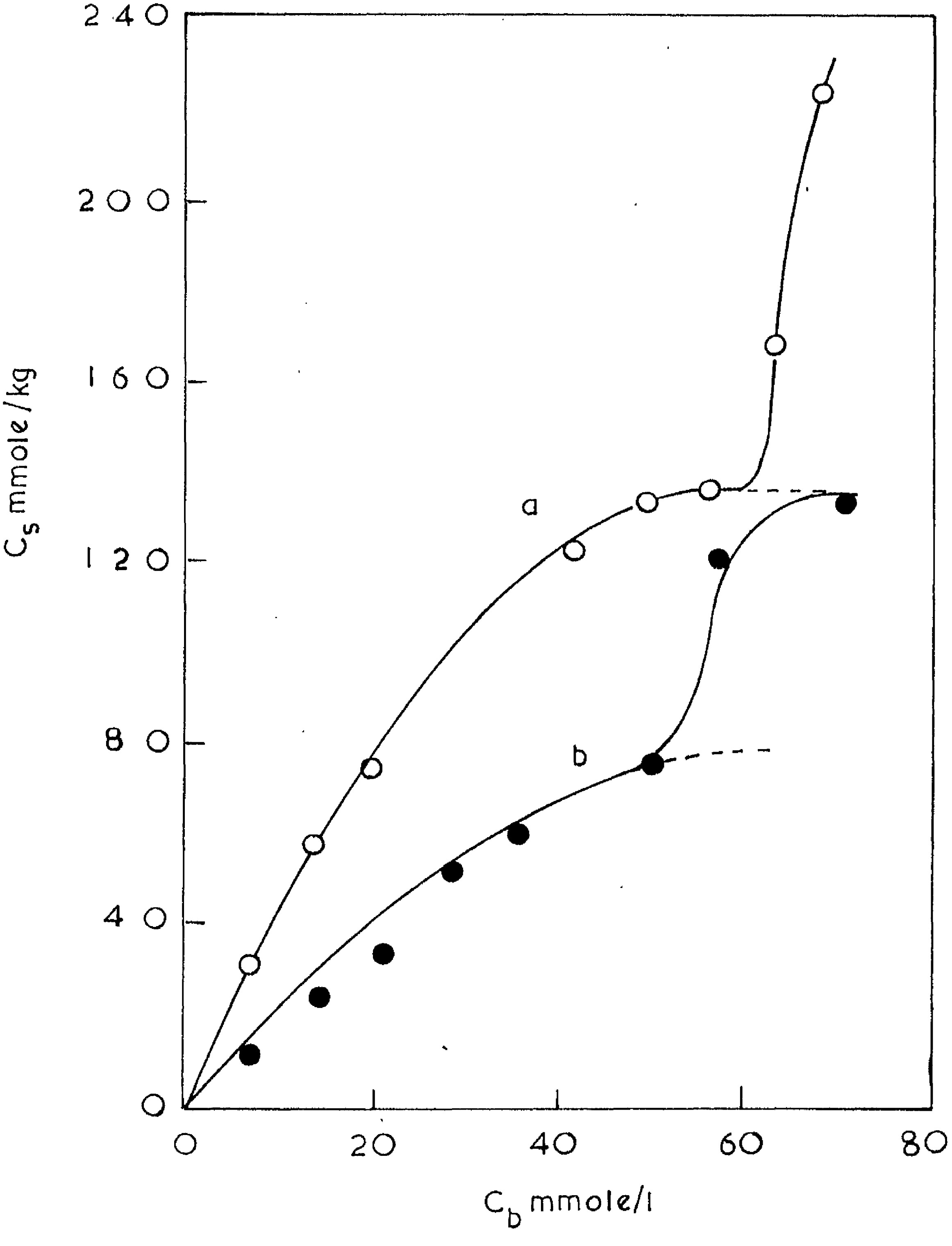


Fig.33. Adsorption isotherms of p-nitrophenol on red (azo) pigments from water at 20°C. (a) Sample 2; (b) Sample 1.

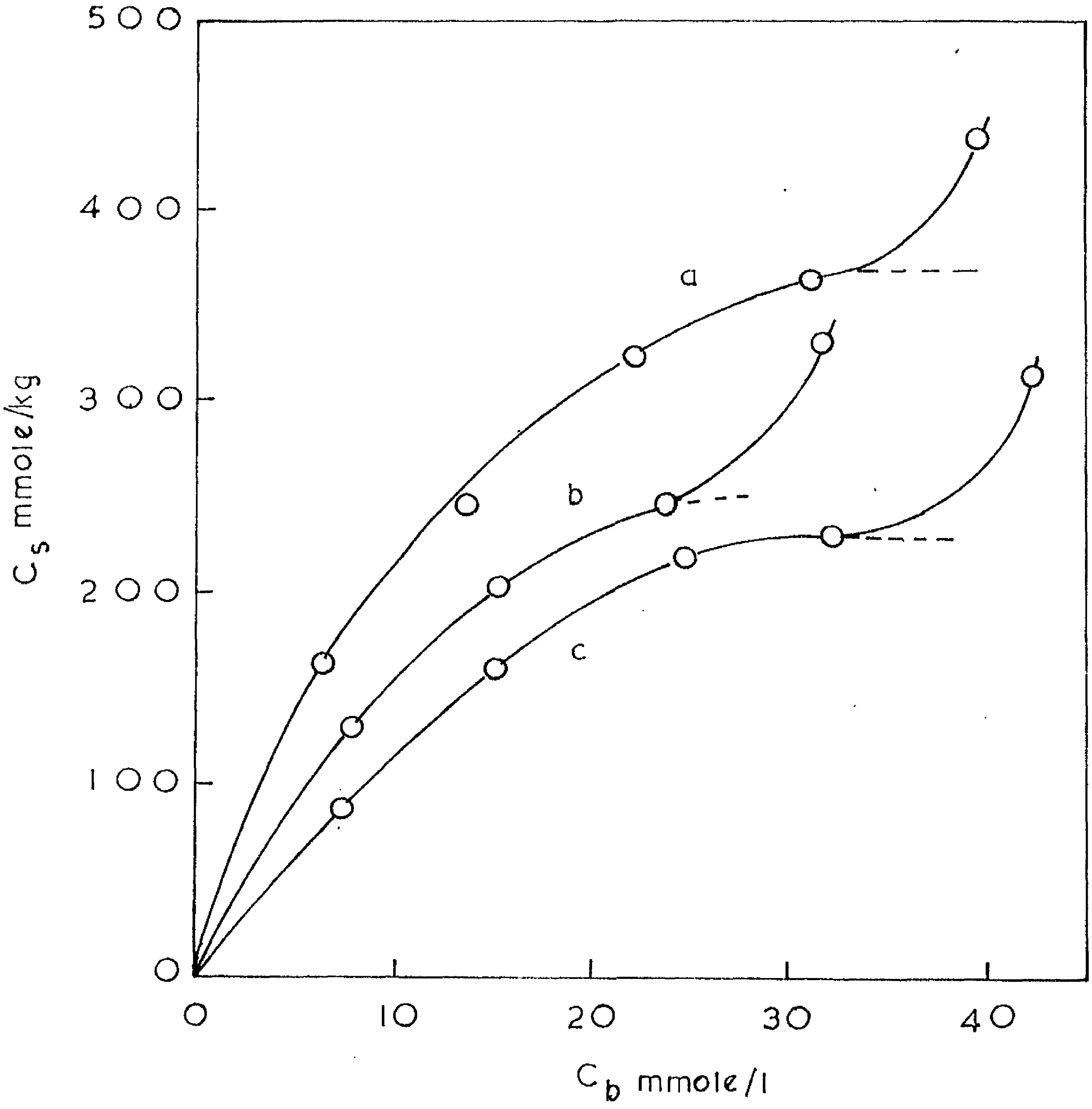


Fig.34. Adsorption isotherms of p-nitrophenol on blue (phthalocyanine) pigments from water at 15°C. (a) Sample 5; (b) Sample 3; (c) Sample 1.

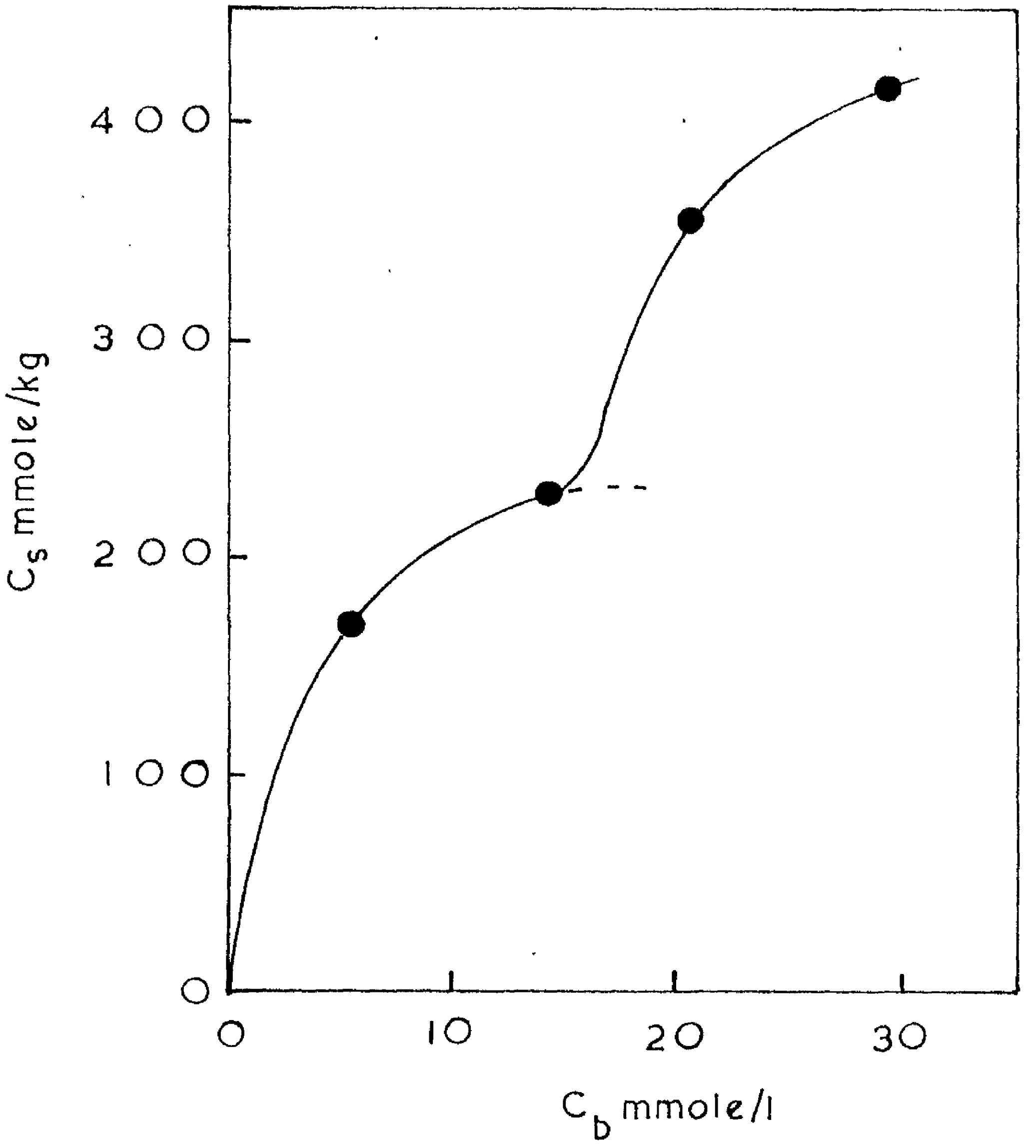


Fig.35. Adsorption isotherm of p-nitrophenol on blue (phthalocyanine) pigment (Sample 2) from water at 15°C.

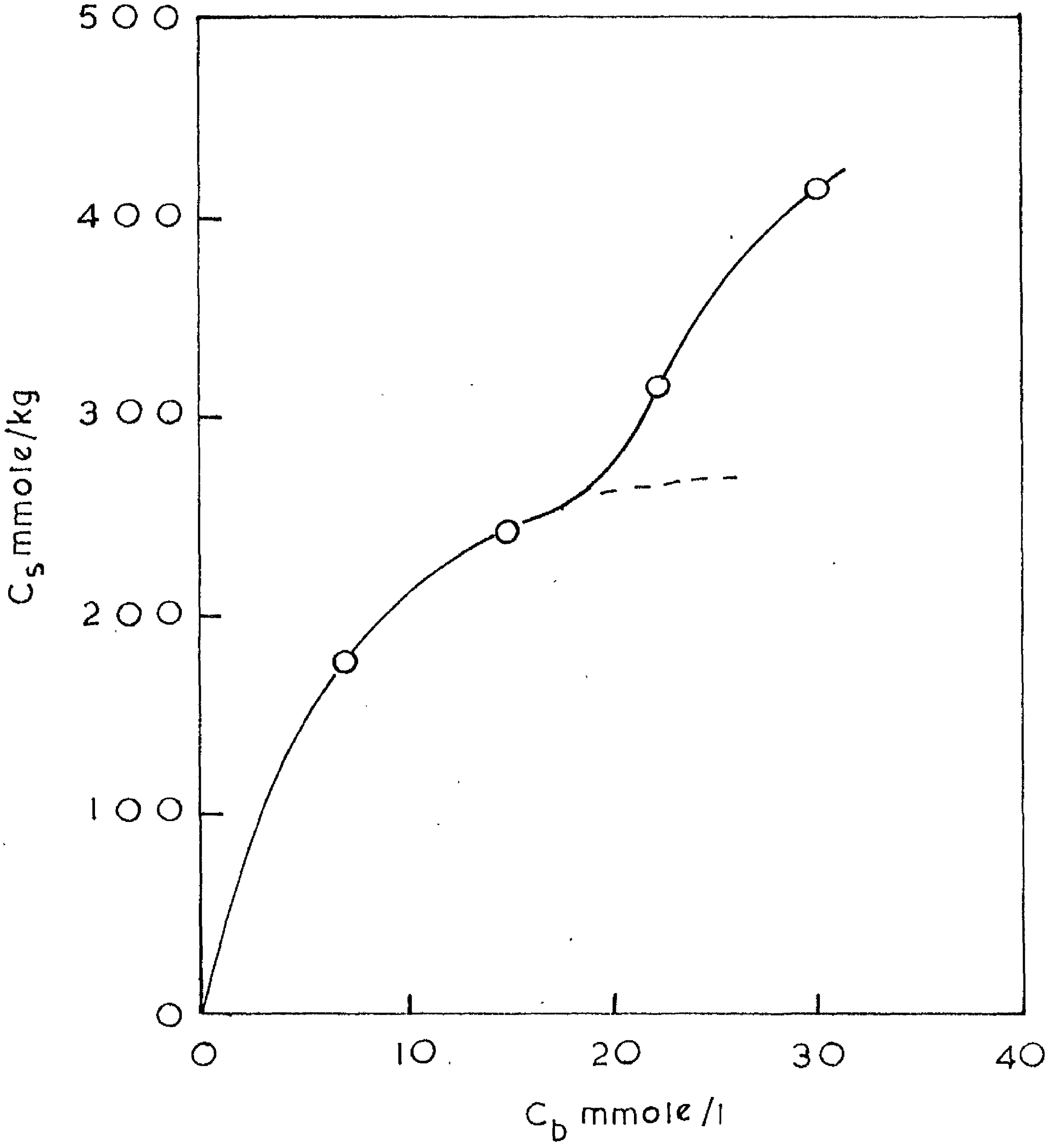


Fig.36. Adsorption isotherm of p-nitrophenol on blue (phthalocyanine) pigment (Sample 4) from water at 15°C.

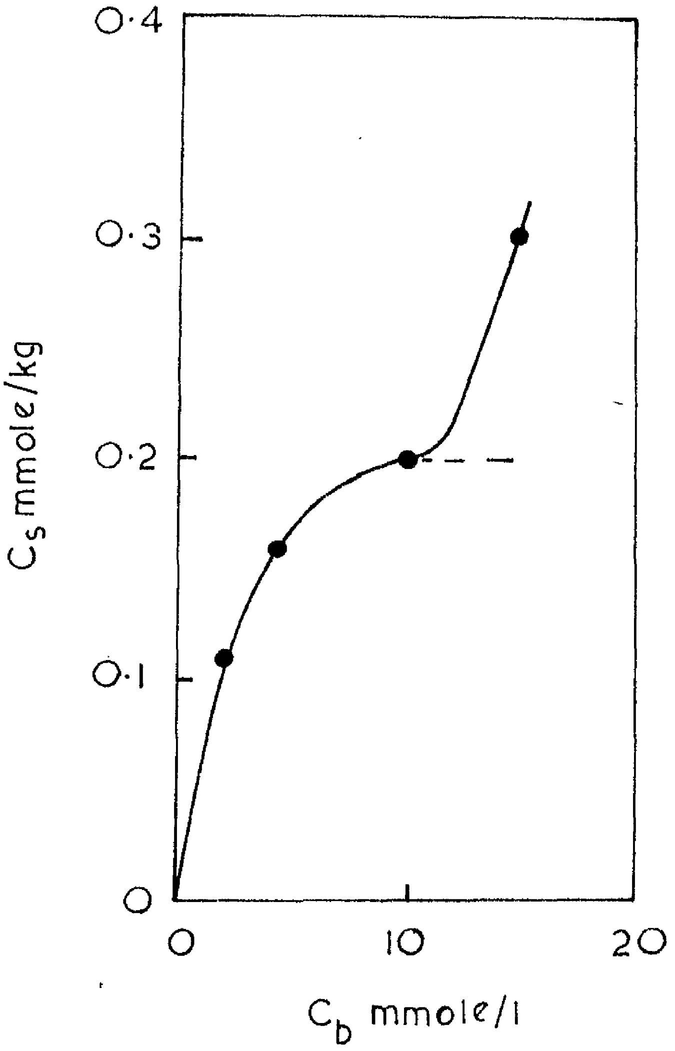


Fig.37. Adsorption isotherm of p-nitrophenol on sugar from benzene at 17°C.

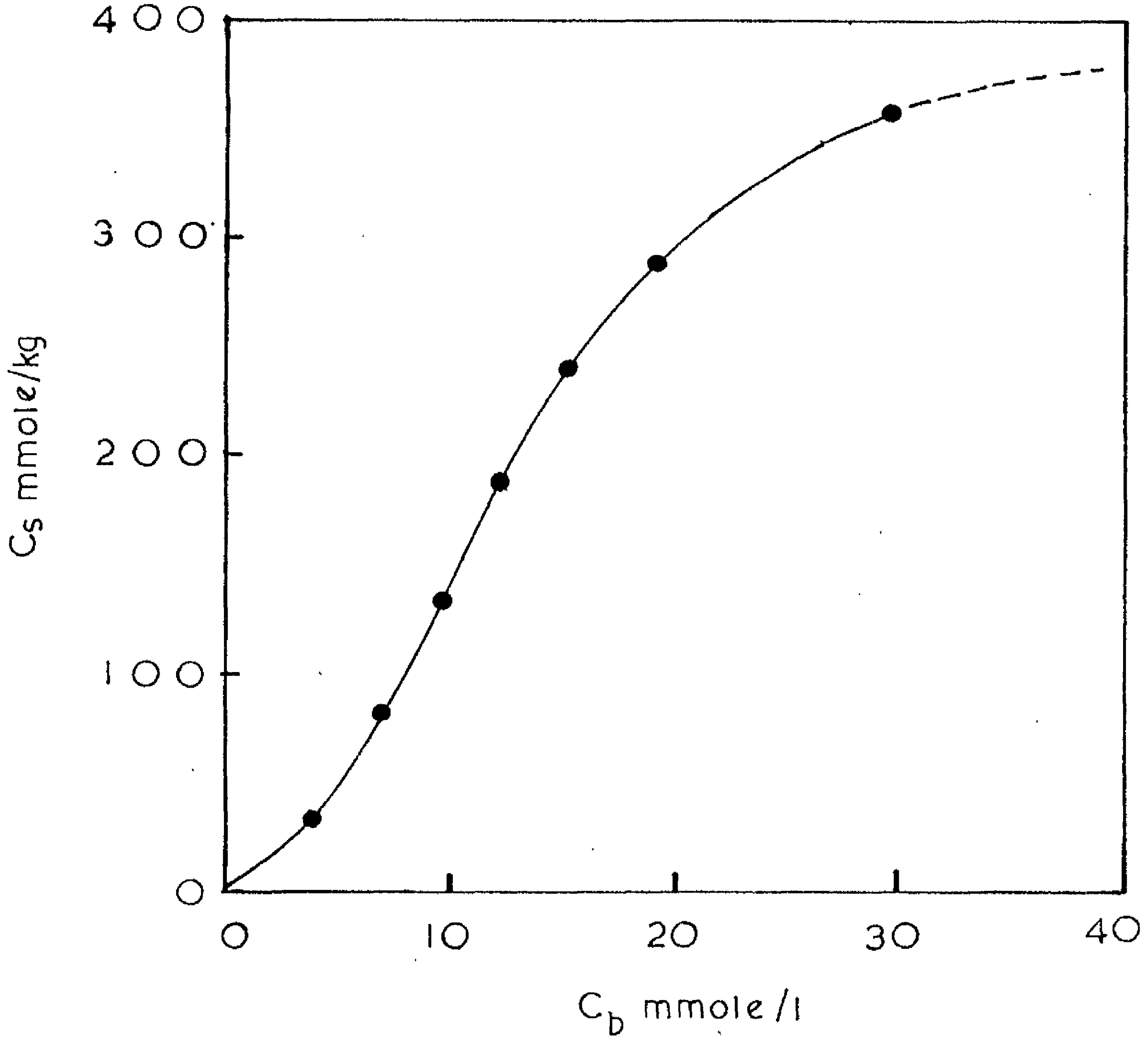


Fig.38. Adsorption isotherm of p-nitrophenol from water on wool at 18°C.

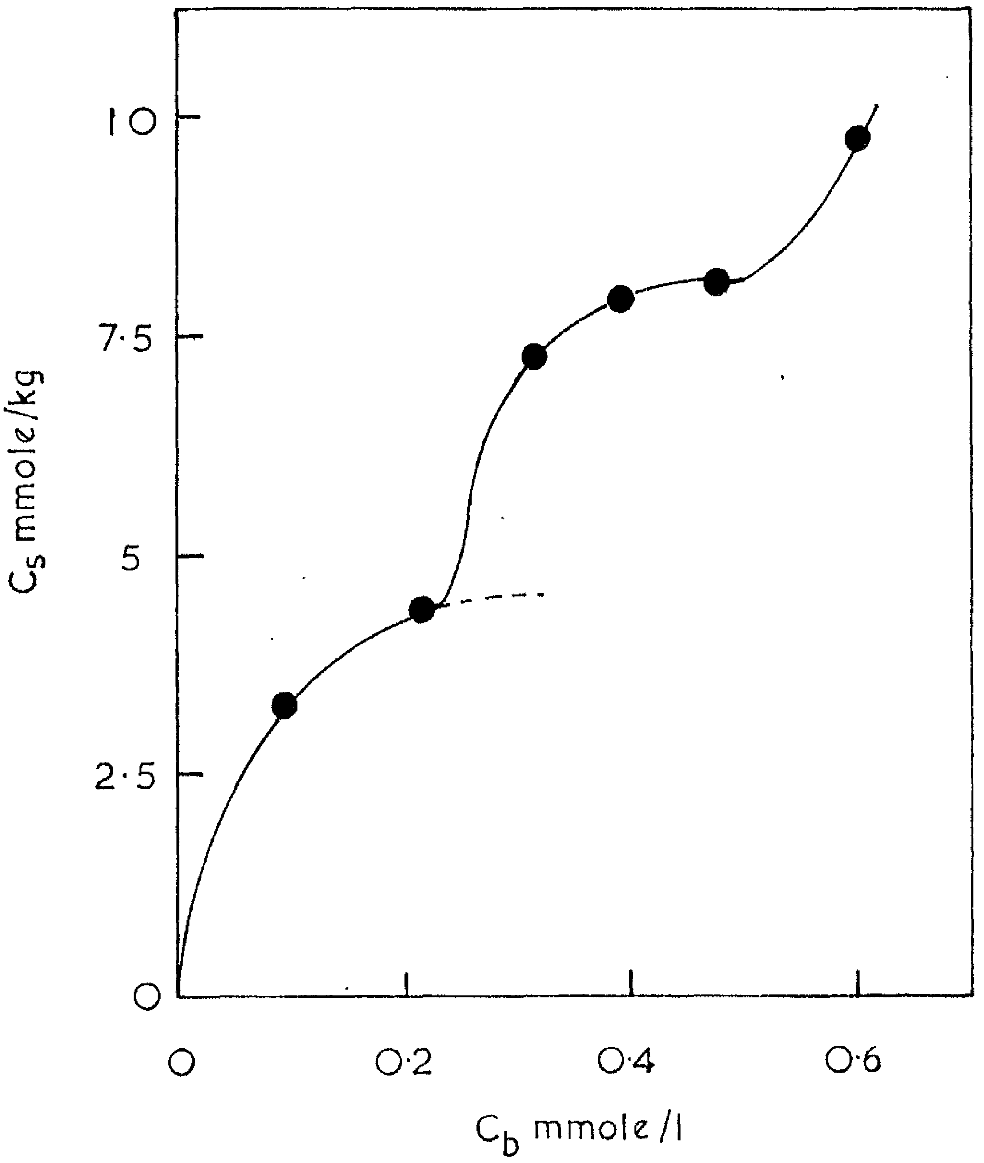


Fig.39. Adsorption isotherm of p-nitrophenol from n-heptane on wool at 17°C. Time of adsorption:- 4 hours. Specific surface area from the first plateau (dotted line) is 0.42 $m.^2 g.^{-1}$.

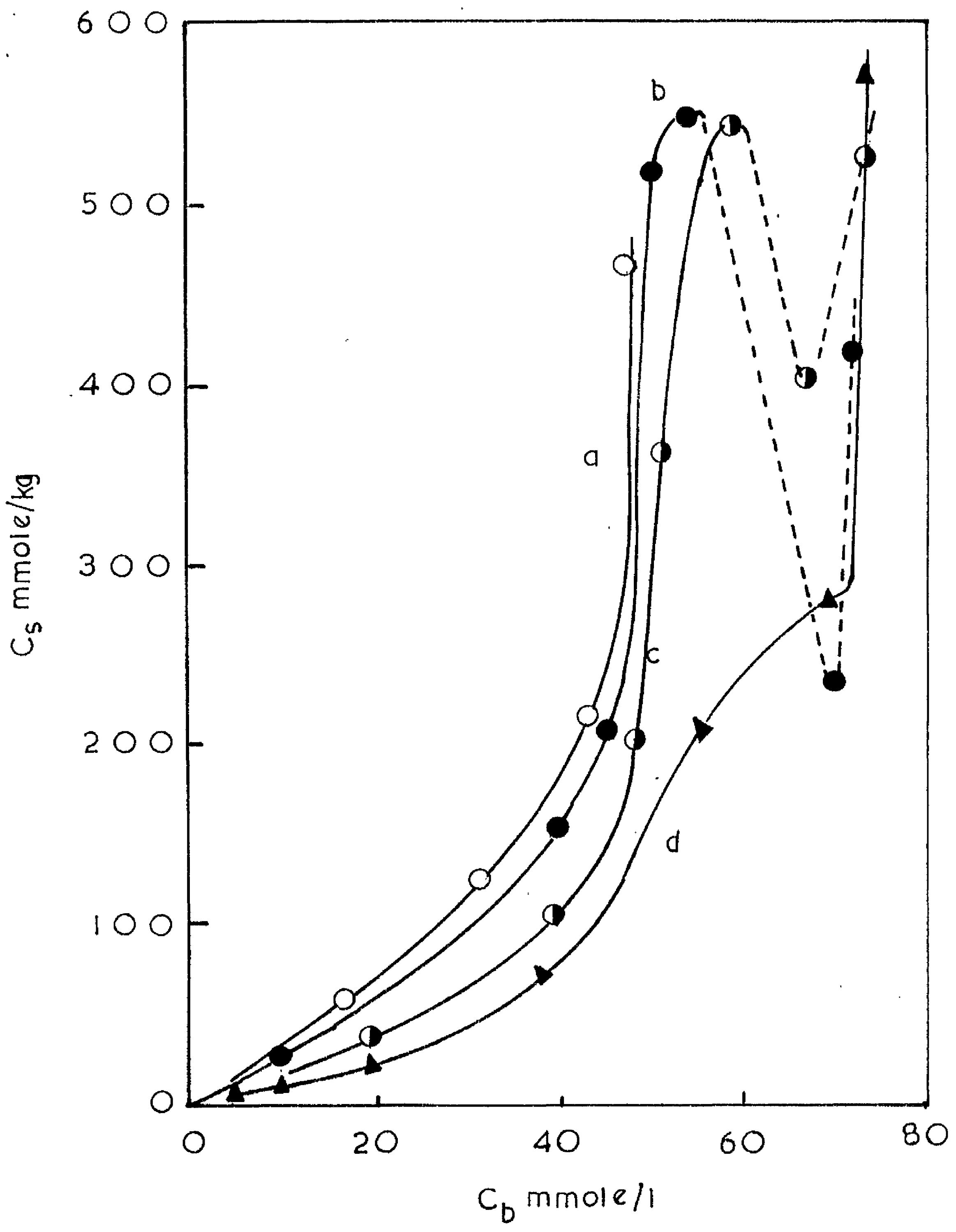


Fig. 40. Effect of reduction of temperature on p-nitrophenol solution adsorption isotherms on alumina (chromatographic). a, 2.0°C; b, 9.0°C; c, 19.0°C; d, 41.0°C.

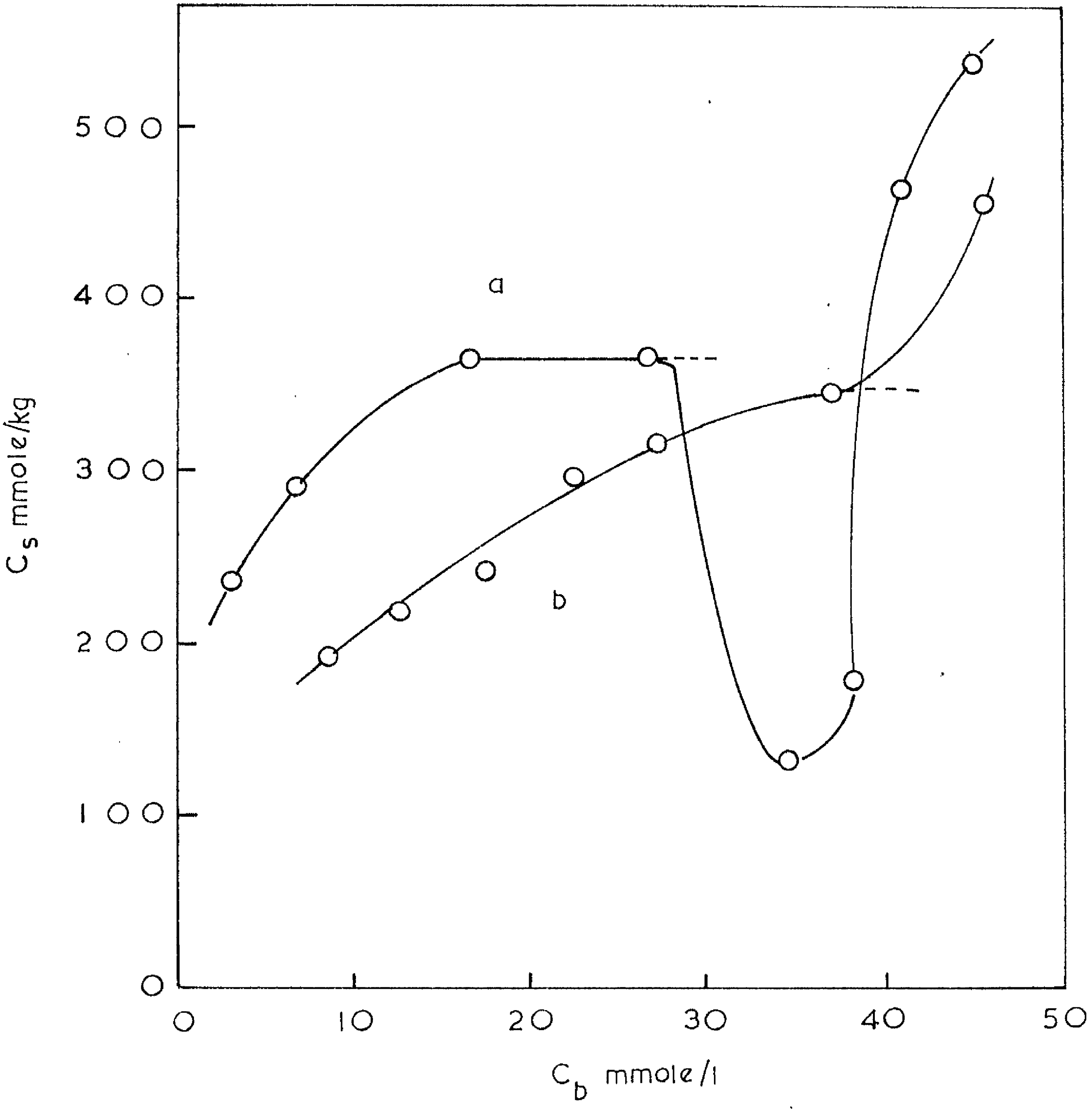


Fig.41. Effect of reduction of temperature on p-nitrophenol solution adsorption isotherms on Carbon ("Graphon"). a, 1.0°C; b, 18.5°C.

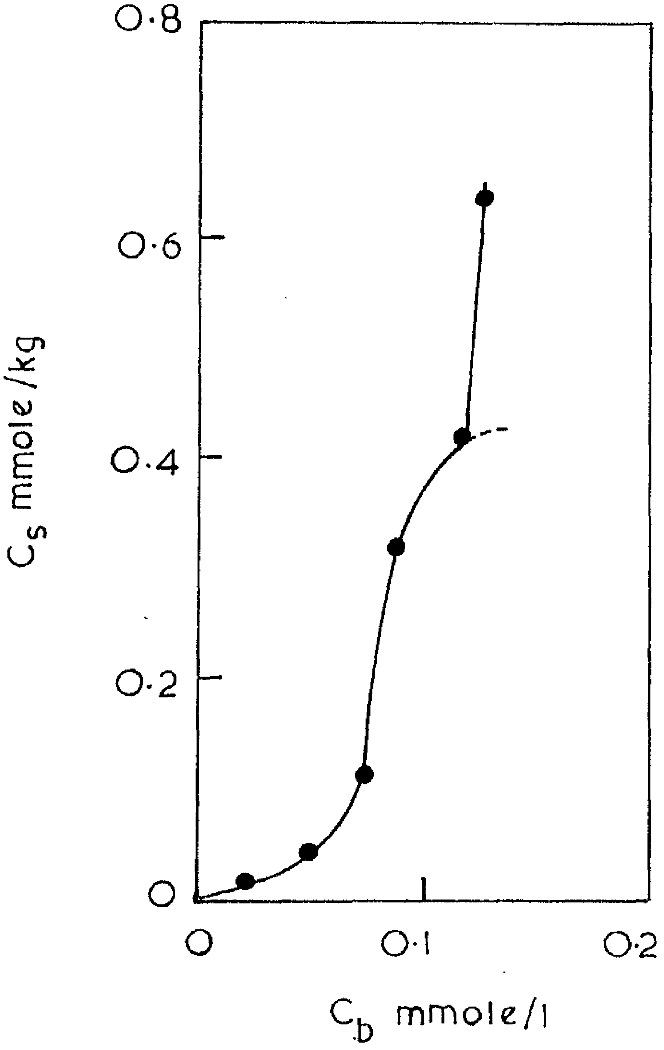


Fig. 42. Adsorption isotherm of acid wool dye (C.I. 62,055) from water on quartz at 16°C.

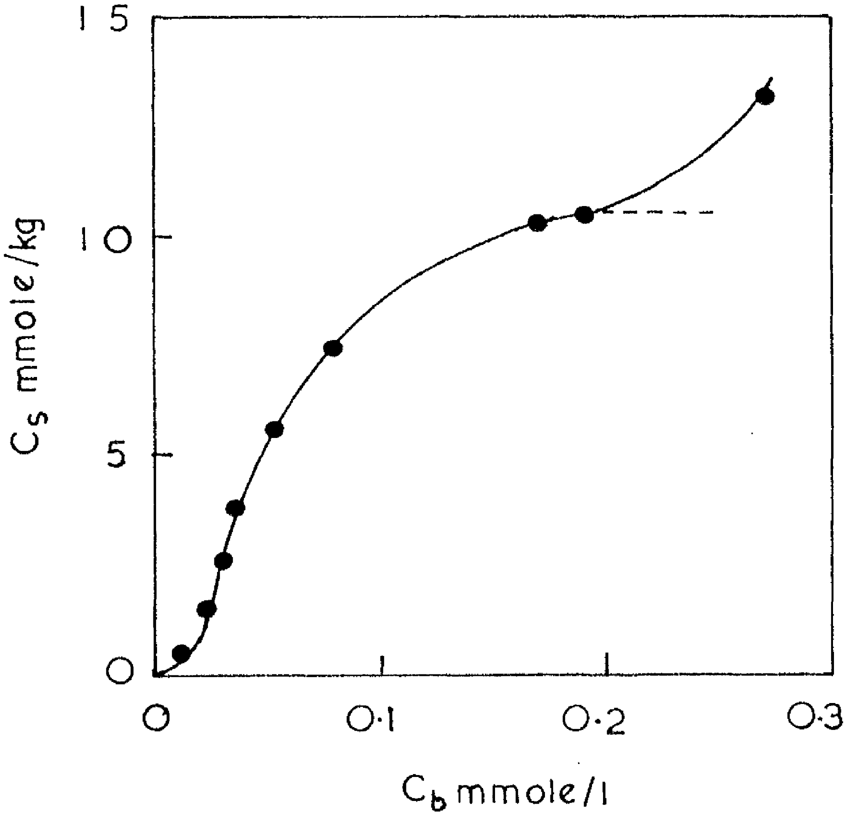


Fig. 43. Adsorption isotherm of acid wool dye (C.I. 62,055) from water on silica (MSC brand) at 17°C.

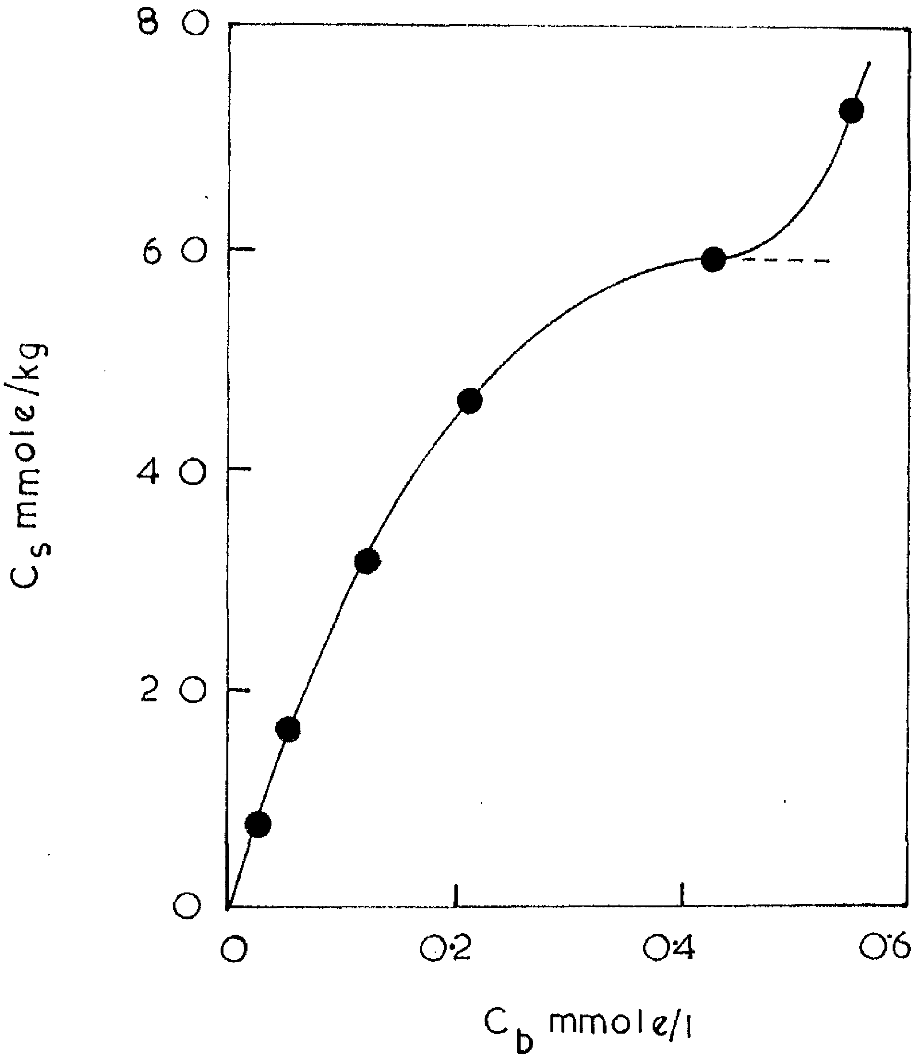


Fig.44. Adsorption isotherm of p-nitrophenol from benzene on silica (MSC brand) at 17°C.

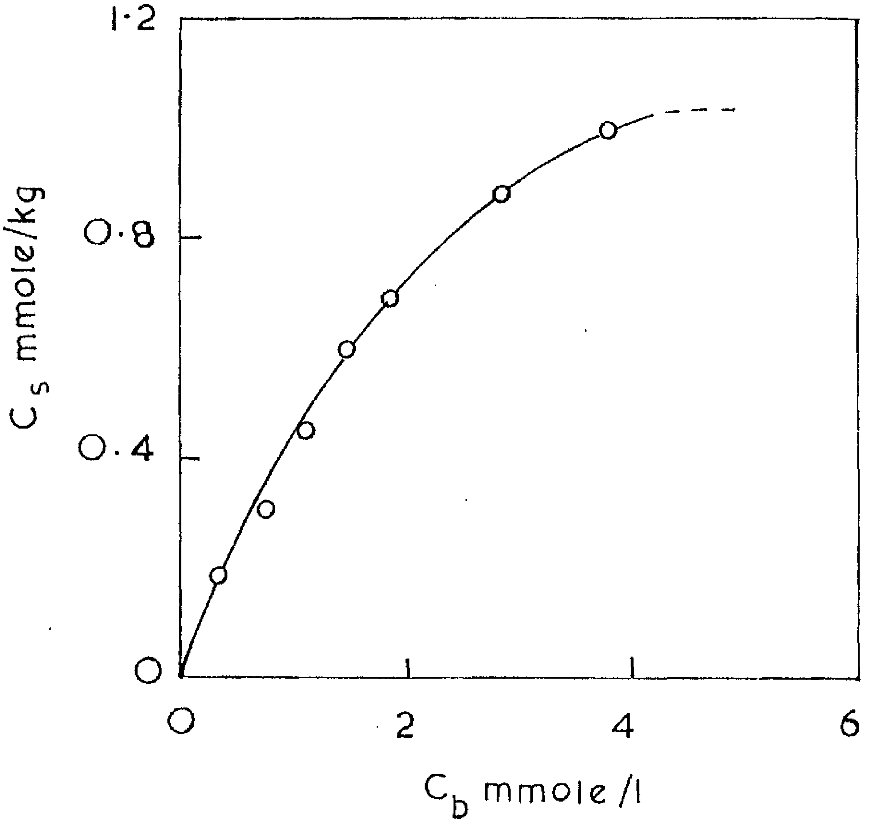


Fig.45. Adsorption isotherm of cationic dye (C.I.45,170) on acid-treated alumina from water at 19°C.

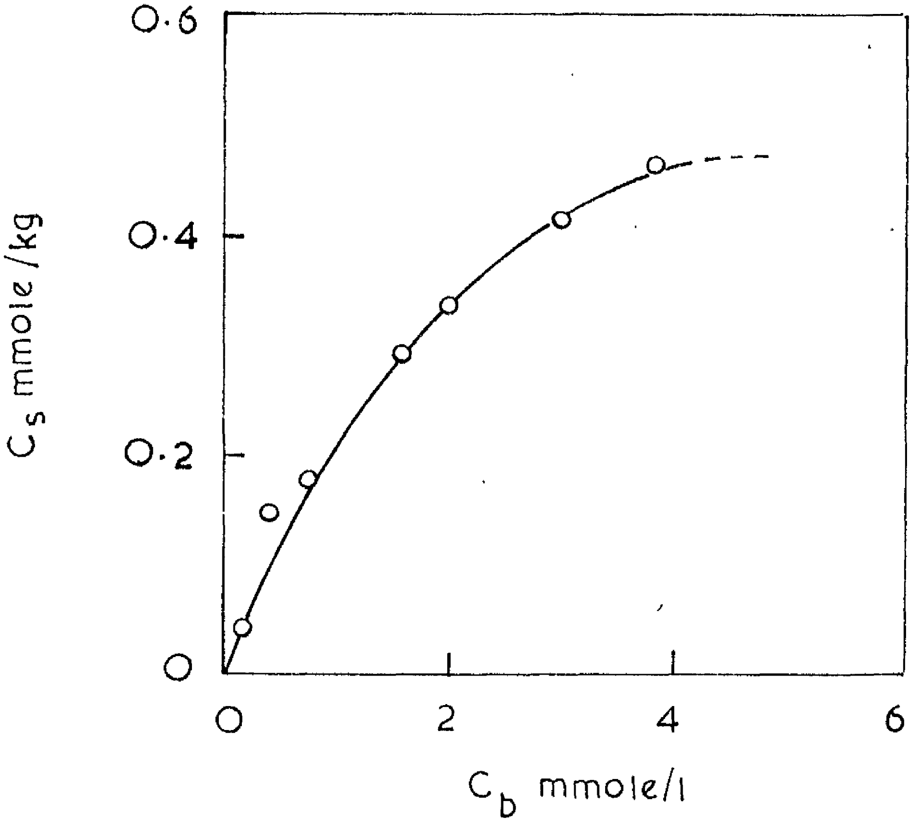


Fig.46. Adsorption isotherm of cationic dye (C.I.42,595) on acid-treated alumina from water at 19.7°C.

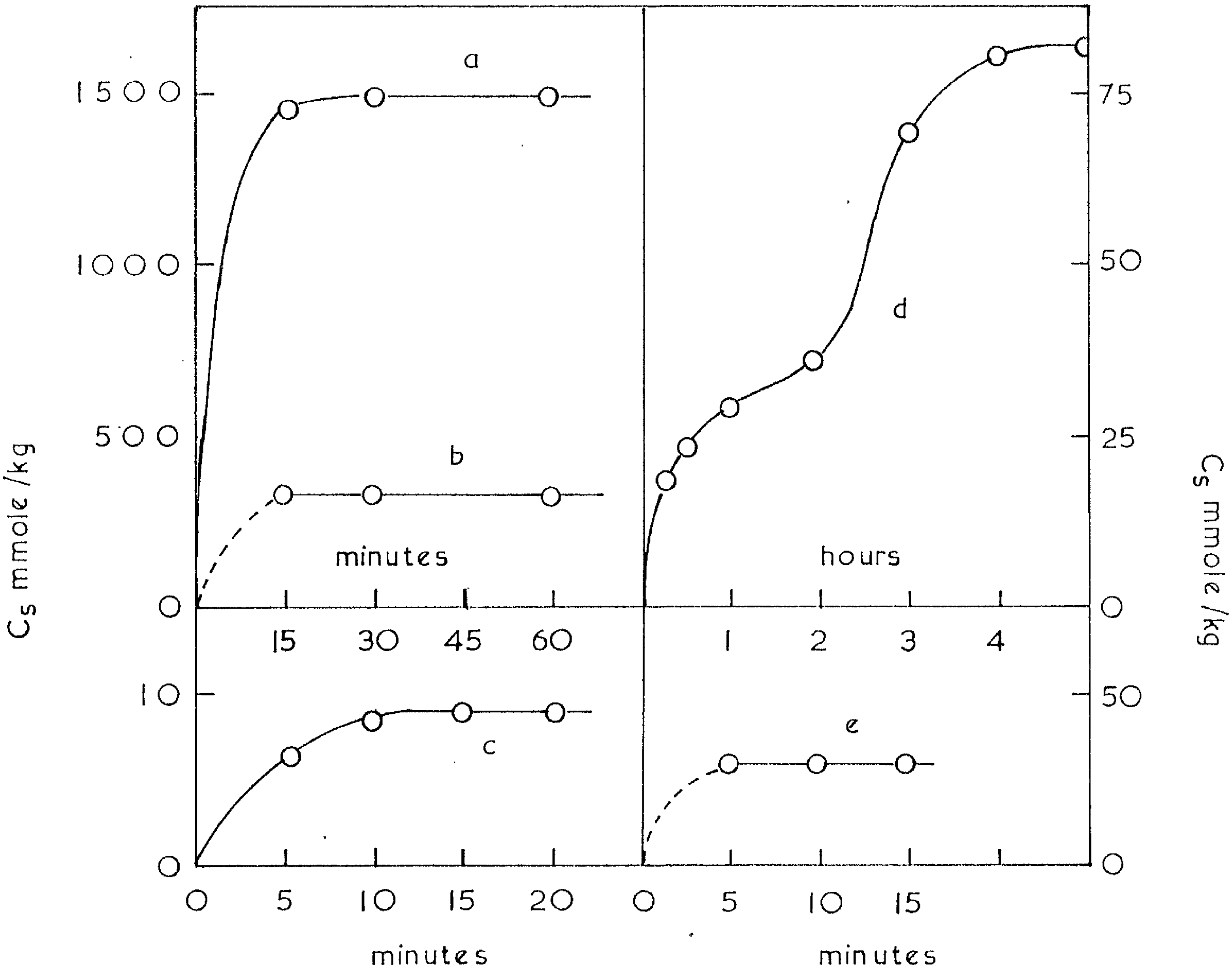


Fig.47. Rate of adsorption of p-nitrophenol on various substrates at 19°C from water (except c). a, "Neo Spectra" carbon black; b, Carbon ("Graphon"); c, silica (MSC brand) from xylene; d, zinc dust; e, alumina (Type 'H').

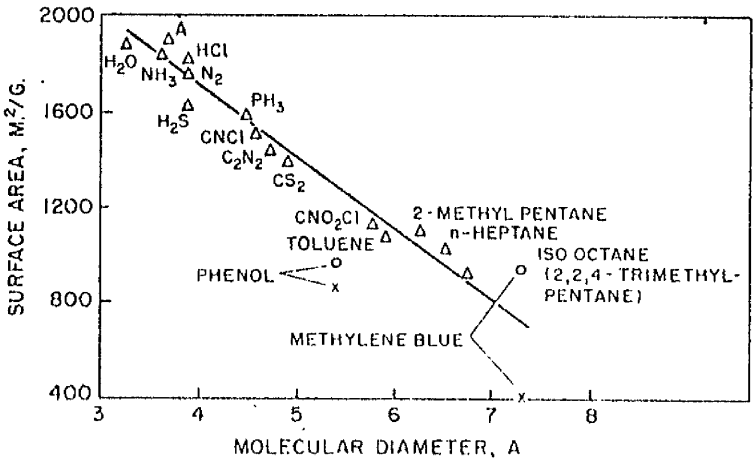


Fig.48. A plot of the surface areas of the charcoal calculated by means of various adsorbates against their molecular diameters. The points indicated by open circles are for the adsorption of phenol and Methylene Blue (C.I.52,015) from aqueous solution on crushed (100 mesh) charcoal samples; those marked X are for uncrushed samples. After Emmett[105].

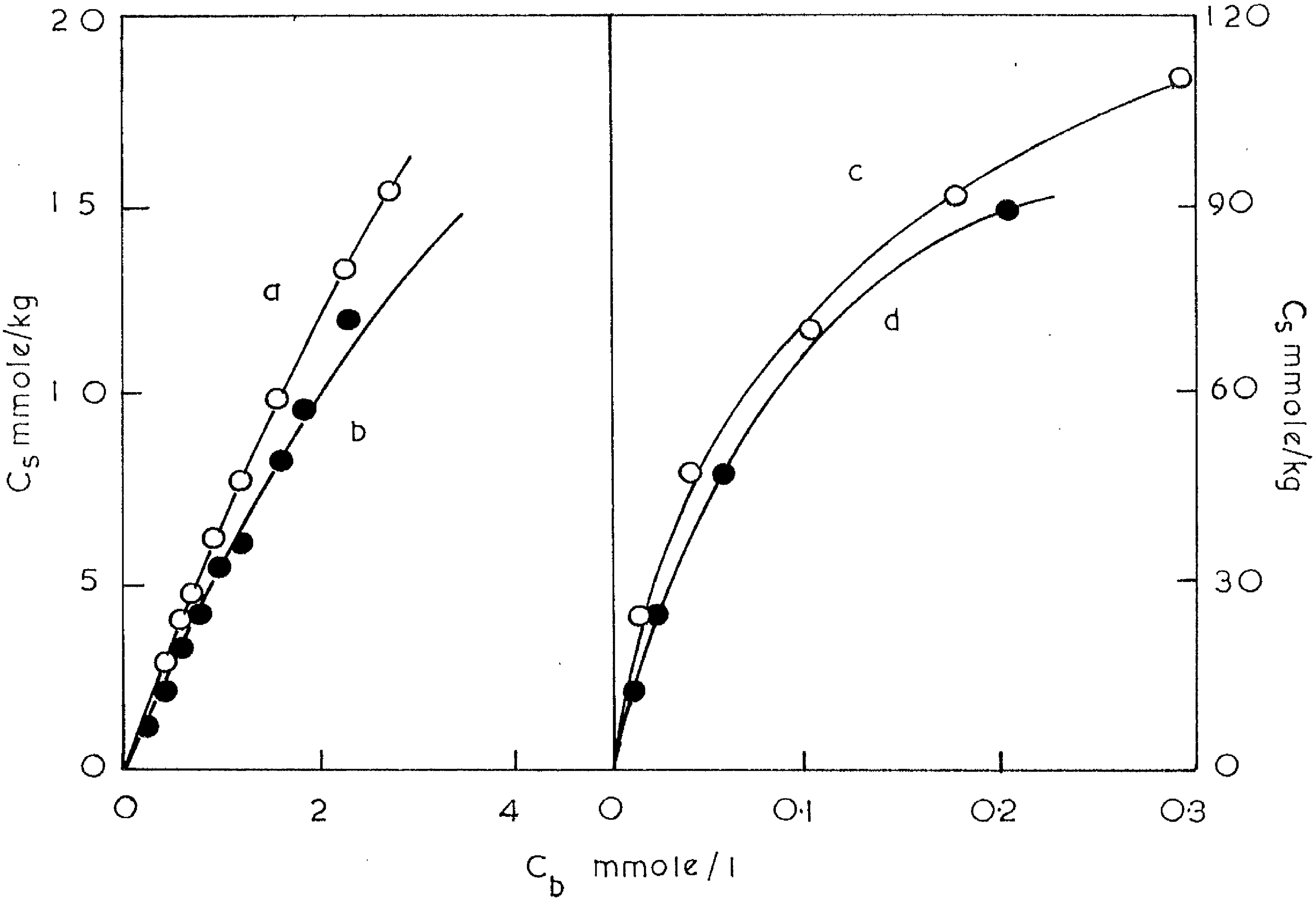


Fig. 49. Solution adsorption isotherms of Lissamine Green BN (C.I. 44,090) on chromatographic alumina (ref. 55; specific surface area 50.0 $m^2 g^{-1}$). From 50% (v/v) aqueous Solketal at (a) 60°C and (b) 38°C. From methanol at (c) 19.5°C and (d) 36.5°C.

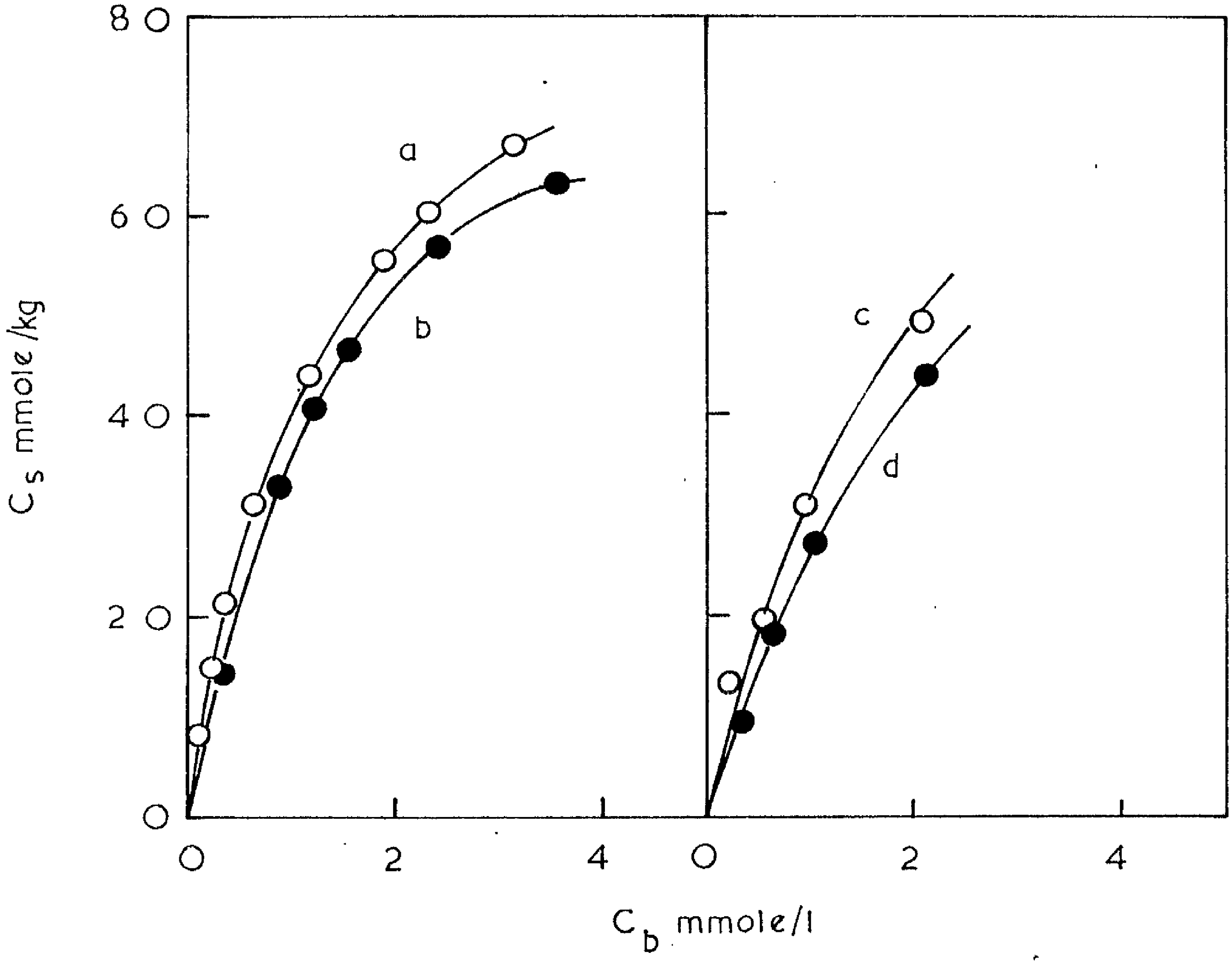


Fig. 50. Solution adsorption isotherms of Janus Red B (C.I. 26,115). From 50% (v/v) aqueous Solketal at (a) 57°C and (b) 38°C on silica (specific surface area 5.0 $m^2 g^{-1}$). From methanol at (c) 16°C and (d) 37°C on silica (specific surface area 0.62 $m^2 g^{-1}$).

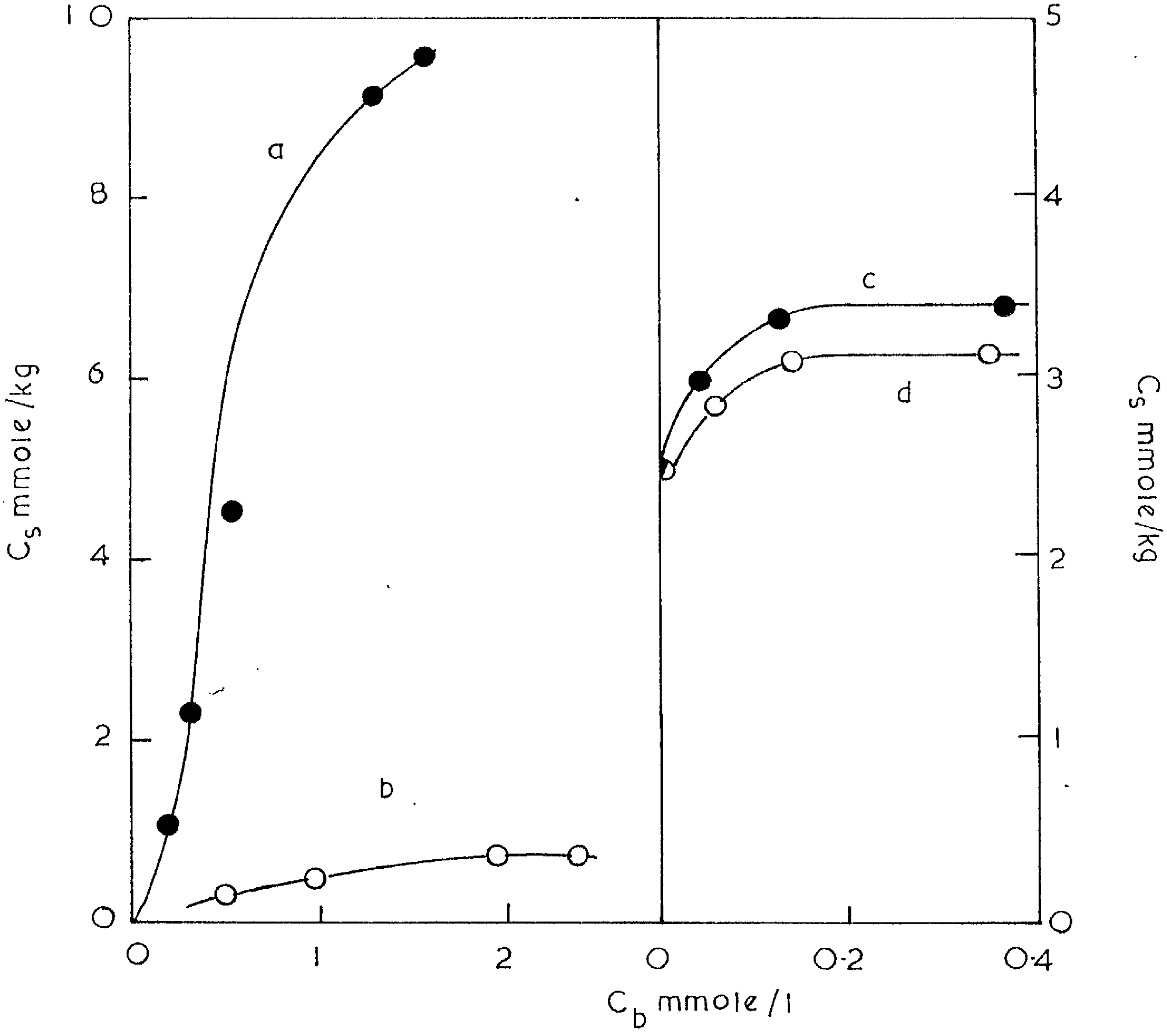


Fig.51. Solution adsorption isotherms of Orange I (C.I. 14,600). From 2.5% aqueous phenol solution on silica (MSC brand) at (a) 71°C and (b) 21.7°C. From 50% (v/v) aqueous glycerine on graphite at (c) 35°C and (d) 60°C.

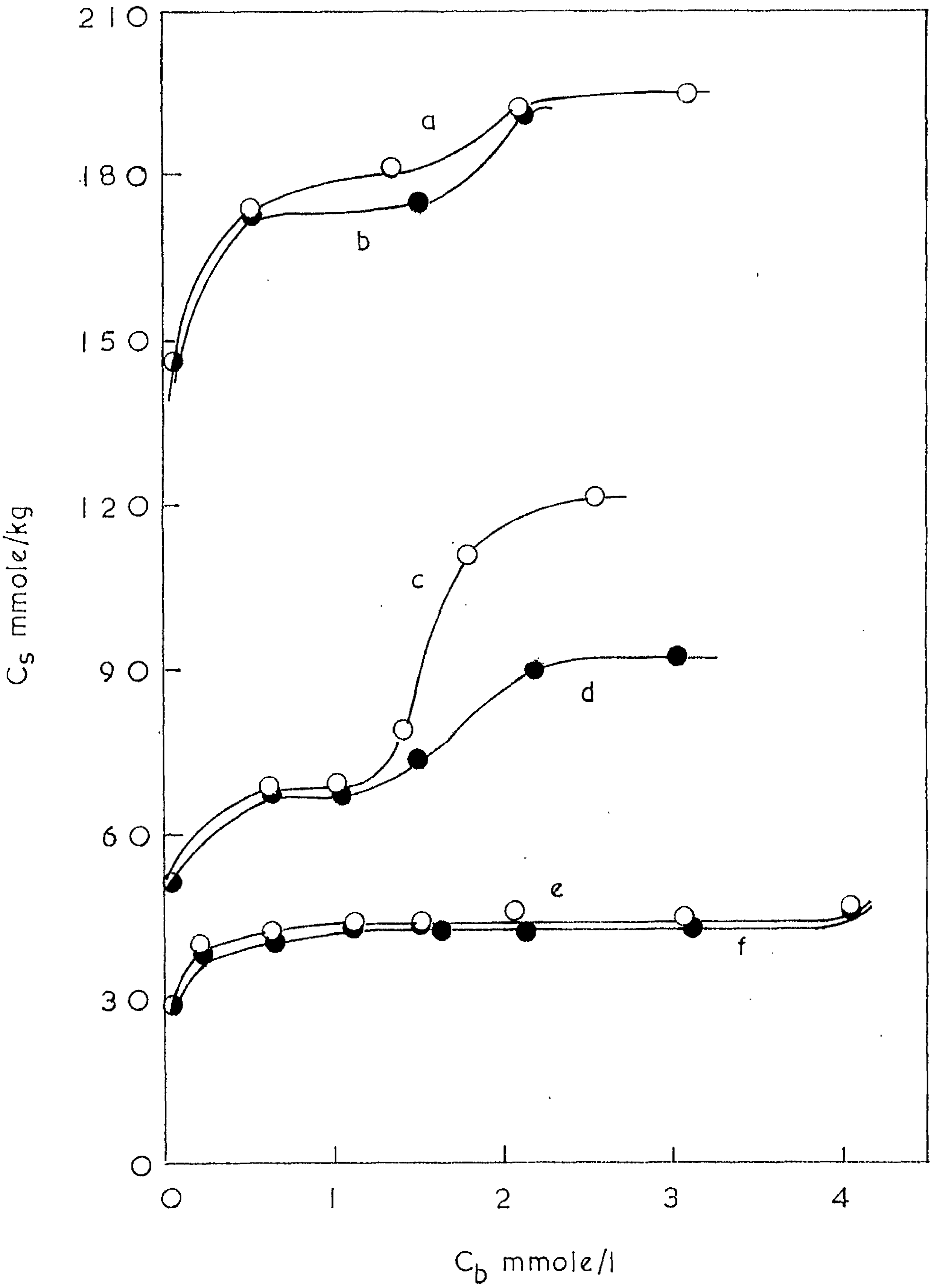


Fig.52. Solution adsorption isotherms of Naphthalene Scarlet 4R (C.I.16,255). On wool at (a) 50°C and (b) 70°C. On acid-treated alumina at (c) 40°C and (d) 60°C. On silk at (e) 40°C and (f) 60°C.

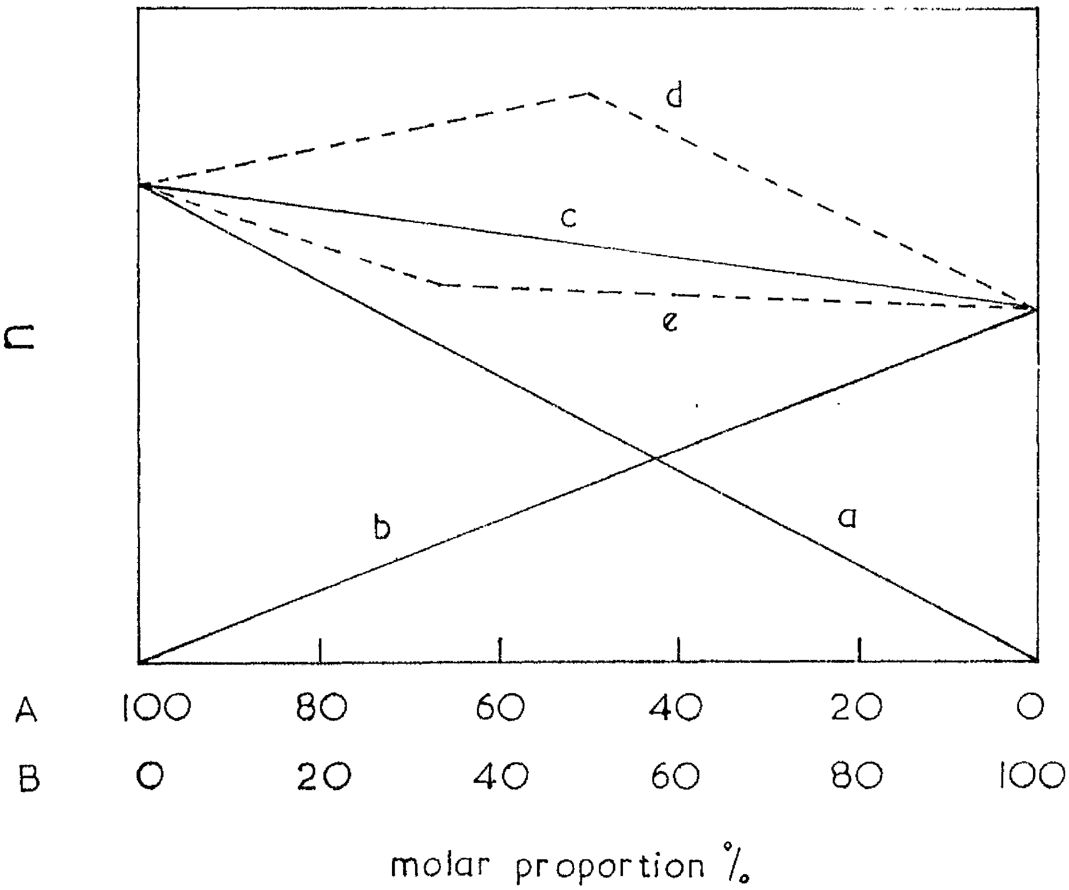


Fig. 53. Theoretical curves showing relation between refractive index (n) and component ratio in solutions of two solutes, A and B.

(a) Solutions of A alone.
(b) Solutions of B alone.
(c) Binary solutions of A and B if no complex is formed.
(d) Binary solutions of A and B if a complex AB^* is formed.
(e) Binary solutions of A and B if a complex A_2B^* is formed.

* The inflections in curves (d) and (e) may be either maxima or minima according to circumstances.

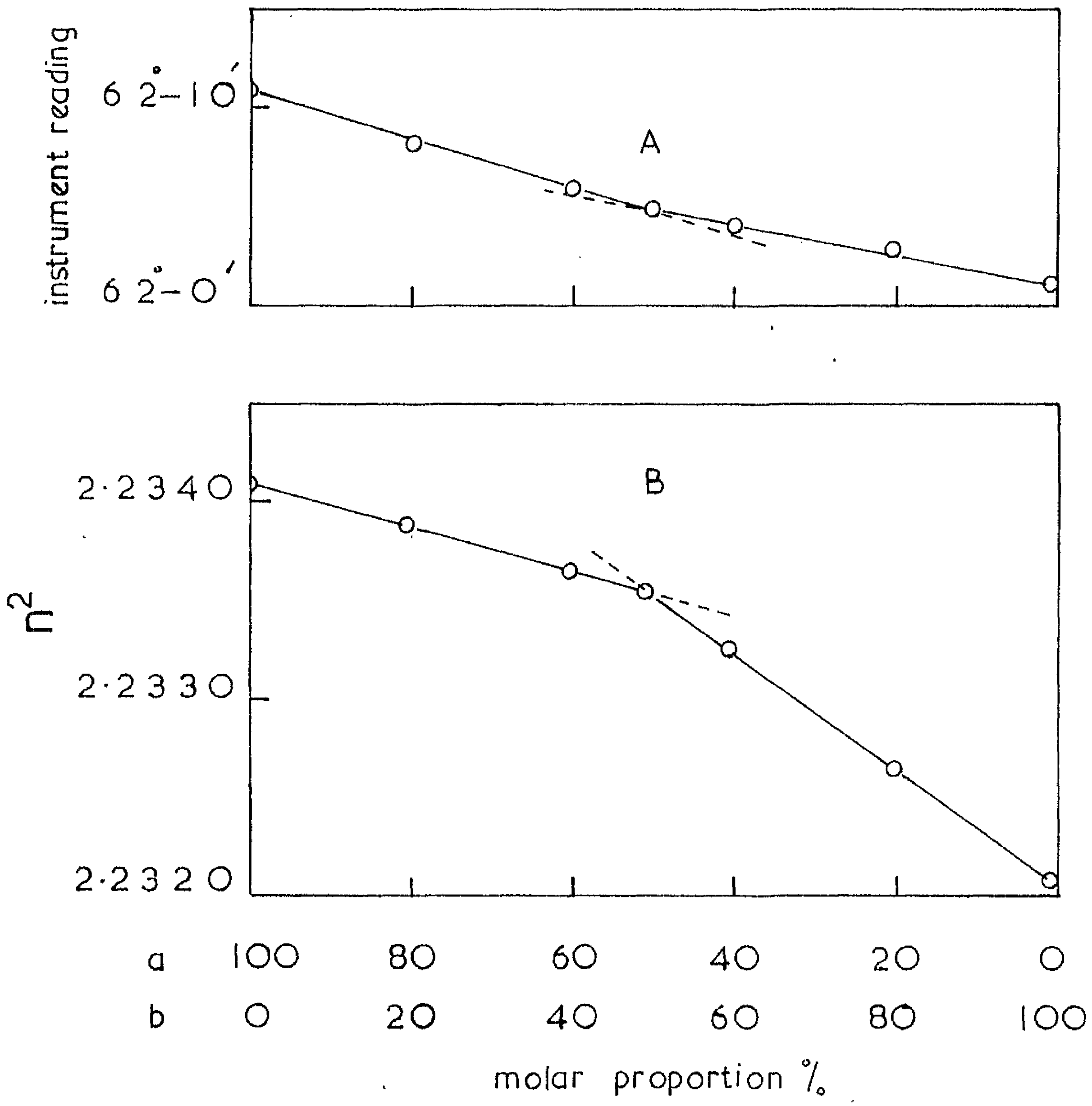


Fig.54. Relation between the instrument reading or the square of the refractive index and the component ratio in solutions of binary mixtures of solutes.
A: a, chlorobenzene; b, phenyl acetate; solvent: 50% (v/v) aqueous ethanol; temperature: 14°C.
B: a and b, as A, solvent: benzene; temperature: 21°C

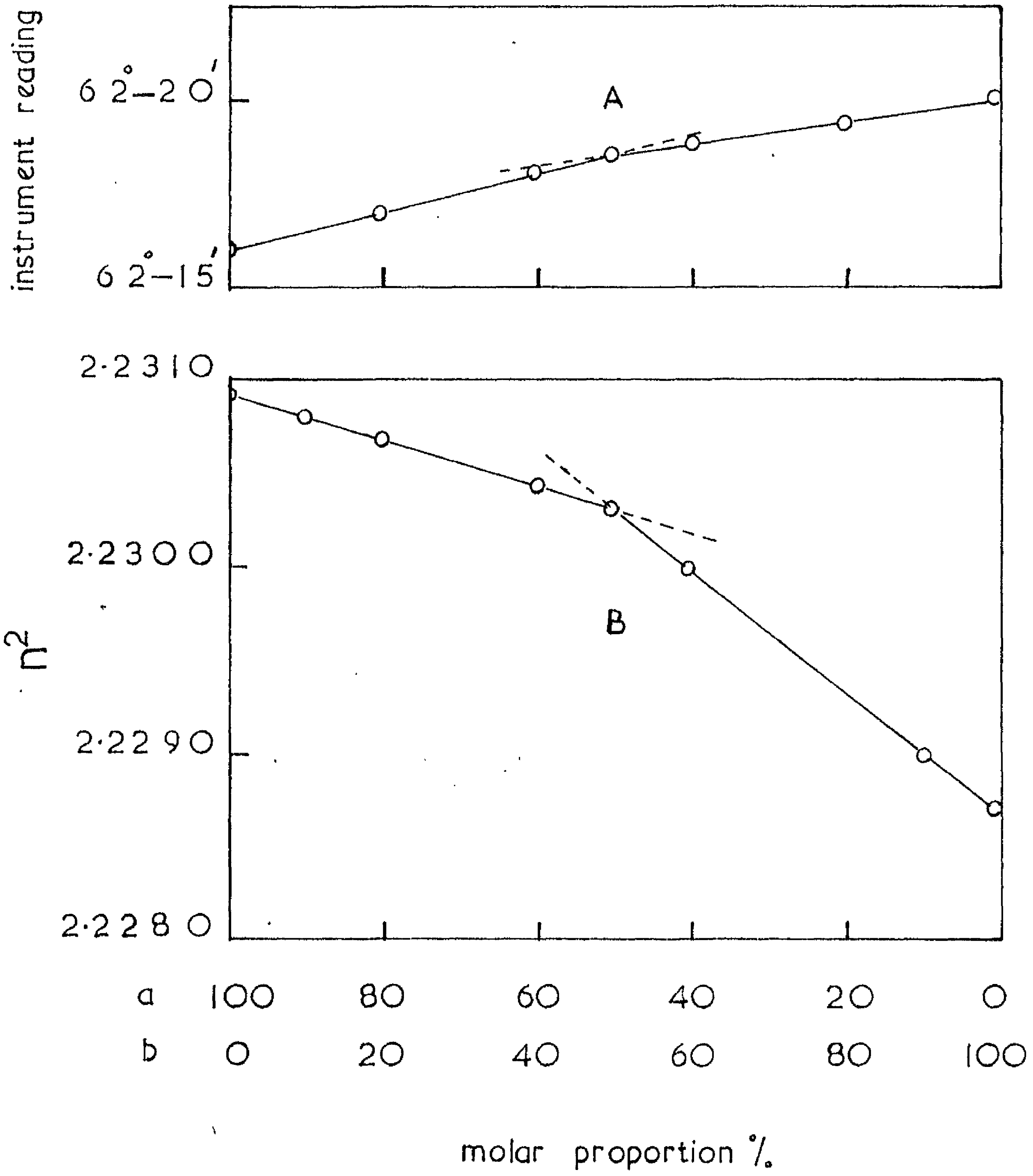


Fig.55. Relation between the instrument reading or the square of the refractive index and the component ratio in solutions of binary mixtures of solutes, A: a, nitrobenzene; b, phenyl acetate; solvent 50% (v/v) aqueous ethanol, temperature: 13°C. B: a and b, as A, solvent: benzene; temperature 24°C.

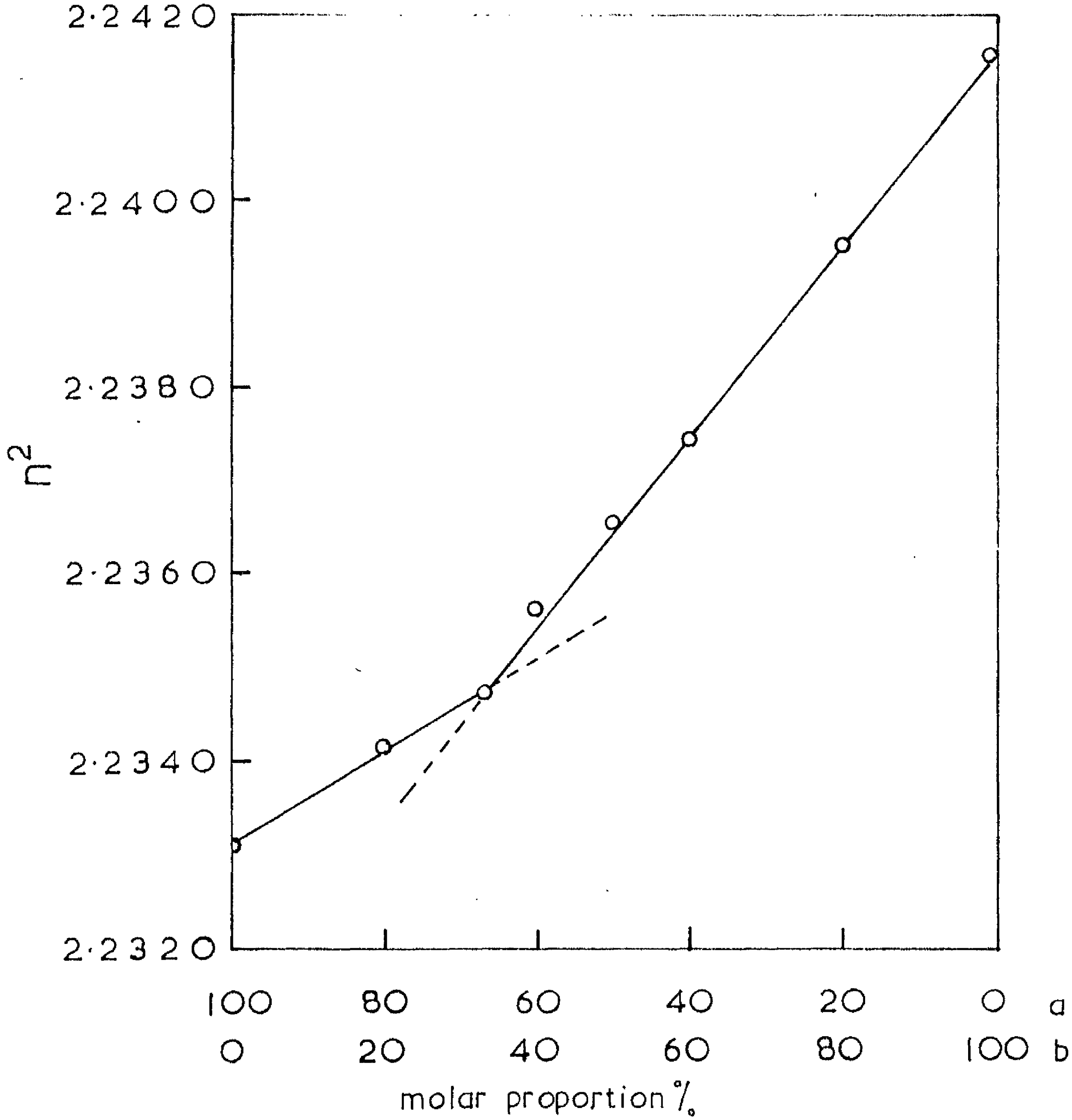


Fig.56. Relation between the square of the refractive index and the component ratio in solutions of binary mixtures of solutes. a; chlorobenzene; b: ethylene glycol dibenzoate; solvent: benzene; temperature: 21°C.

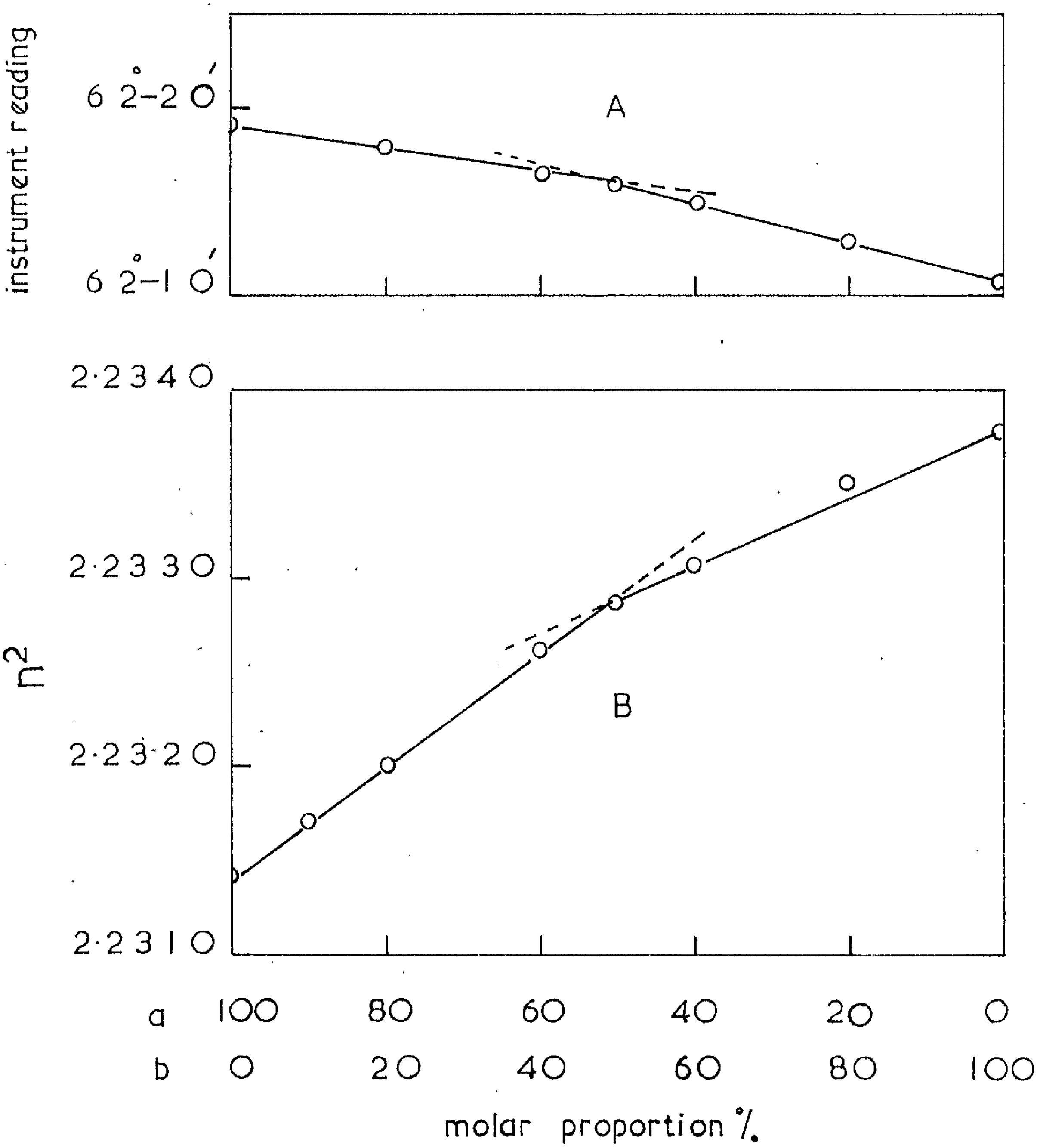


Fig.57. Relation between the instrument reading or the square of the refractive index and the component ratio in solutions of binary mixtures of solutes. A: a, ethyl acetate; b, chlorobenzene; solvent: 50% (v/v) aqueous ethanol; temperature: 14°C. B: a, nitrobenzene; b, ethylene glycol dibenzoate; solvent: benzene; temperature 23.5°C.

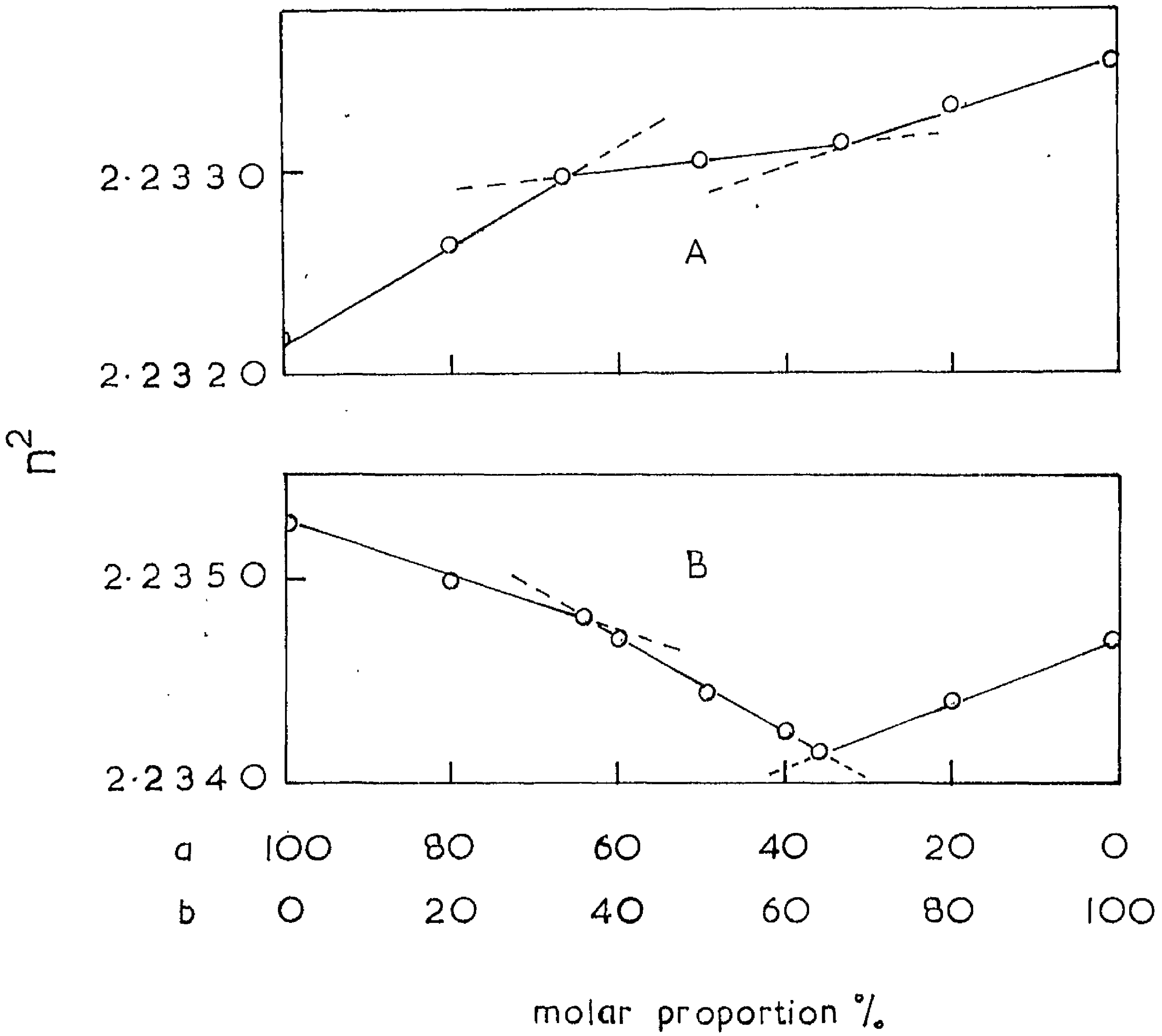


Fig. 58. Relation between the square of the refractive index and the component ratio in solutions of binary mixtures of solutes.

A: a, ethyl acetate; b, phenoxypropionic acid; solvent: dioxan; temperature: 22°C.

B: a, ethyl acetate; b, phenoxyisobutyric acid; solvent: dioxan; temperature: 22°C.

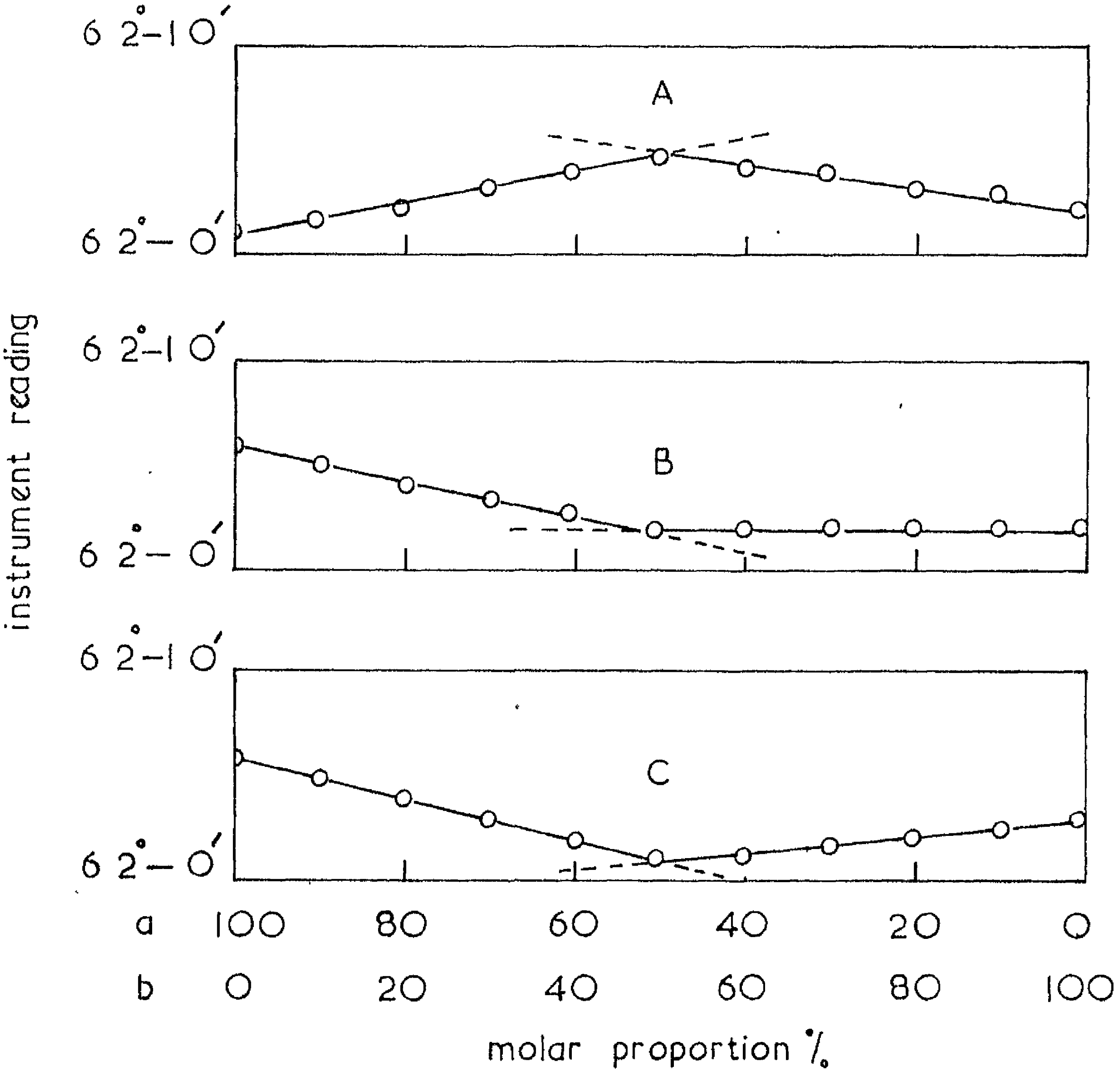


Fig. 59. Relation between the instrument reading and the component ratio in 50% (v/v) aqueous ethanol solutions of binary mixtures of solutes.

A: a, 2,4,6-trichlorophenoxyacetic acid; b, chlorobenzene; temperature, 12°C.

B: a, 2,4,6-trichlorophenoxypropionic acid; b, chlorobenzene; temperature: 12°C.

C: a, α-2-Methyl-4,6-dichloropropionic acid; b, chlorobenzene; temperature: 13°C.

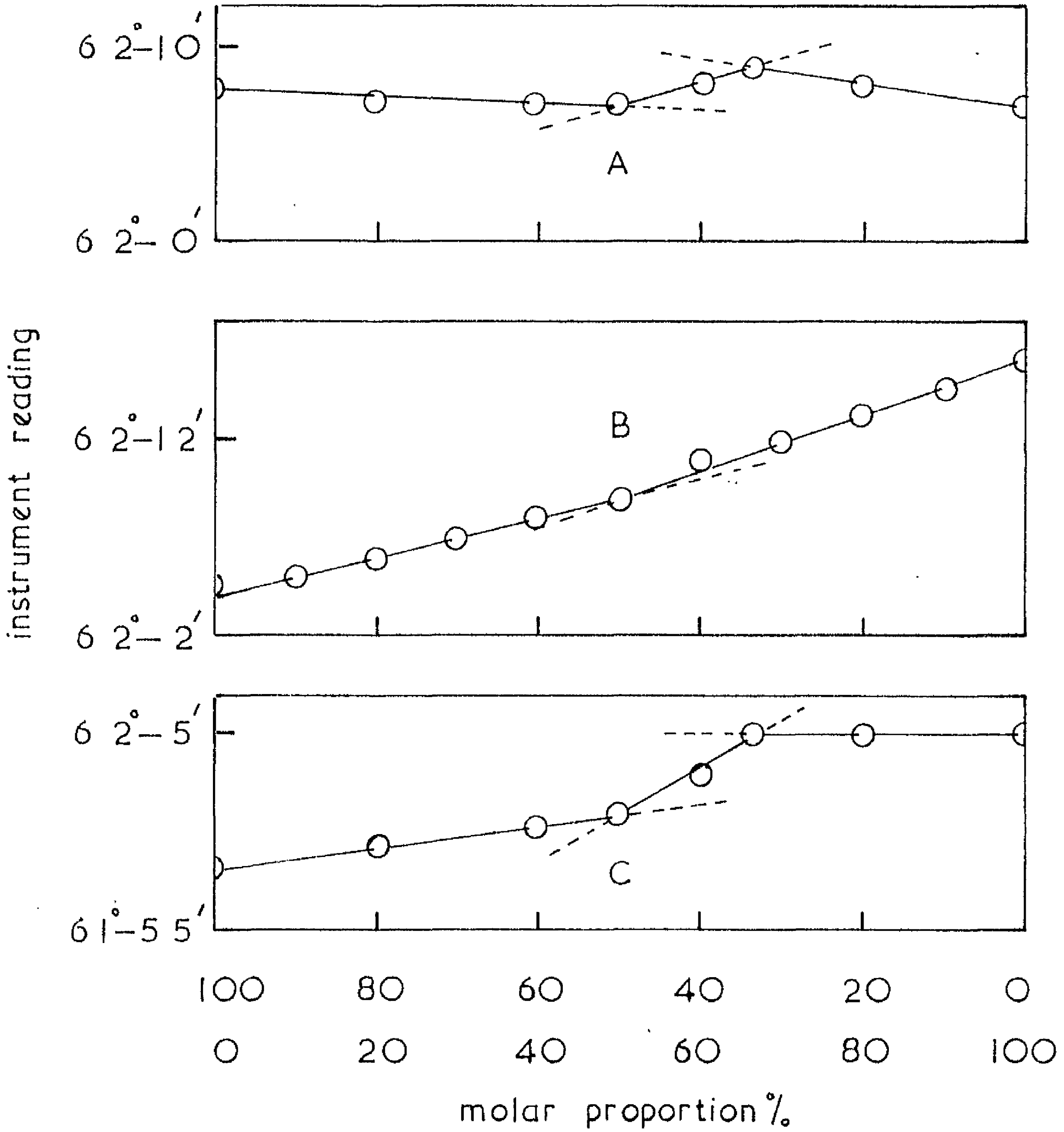


Fig. 60. Relation between the instrument reading and the component ratio in 50% (v/v) aqueous ethanol solutions of binary mixtures of solutes.

A: a, 4-chlorophenoxyacetic acid; b, chlorobenzene; temperature: 10°C.

B: a, $\underline{\alpha}$-4-chlorophenoxypropionic acid; b, chlorobenzene; temperature: 13.5°C.

C: a, $\underline{\alpha}$-4-chlorophenoxy-$\underline{n}$-butyric acid; b, chlorobenzene; temperature: 10°C.

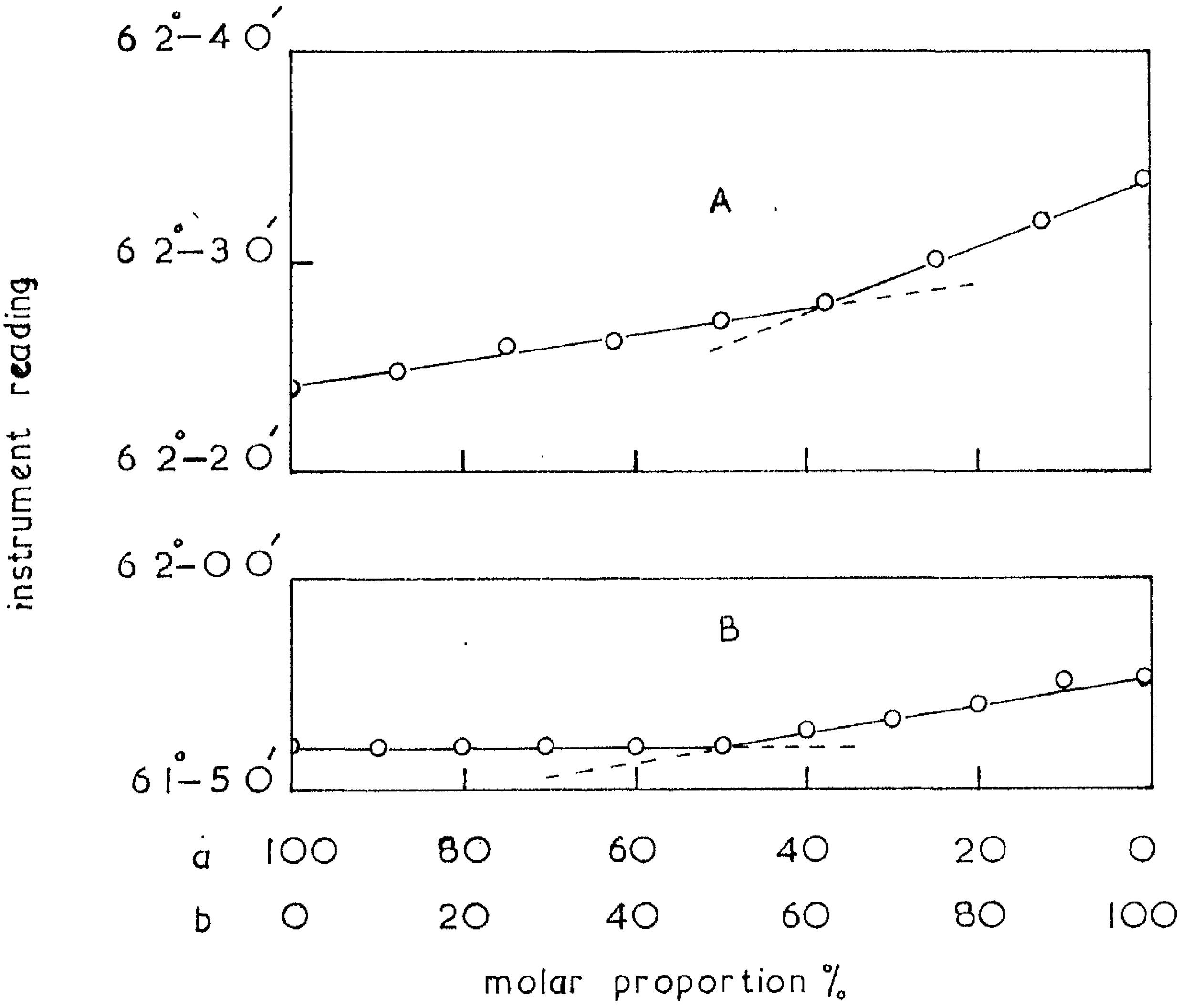


Fig. 61. Relation between the instrument reading and the component ratio in 50% (v/v) aqueous ethanol solutions of binary mixtures of solutes.

A: a, 2,4,5-trichlorophenoxyacetic acid; b, chlorobenzene; temperature: 10°C.

B: a, α-2,4,5-trichlorophenoxypropionic acid; b, chlorobenzene; temperature: 11.8°C.

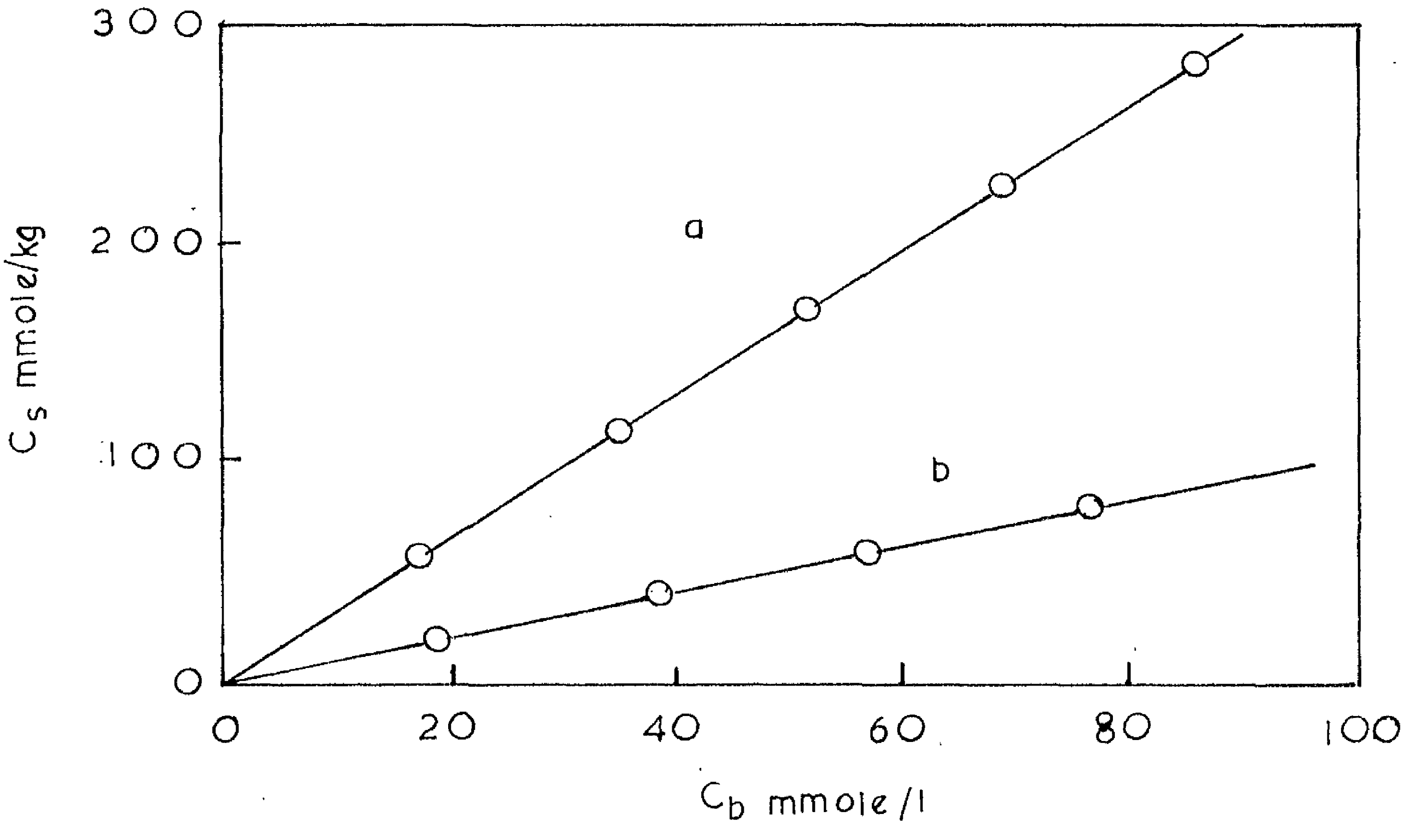


Fig. 62. Adsorption isotherms of (a) chlorobenzene and (b) phenol on cellulose triacetate powder, in 50% (v/v) aqueous ethanol at 53°C.

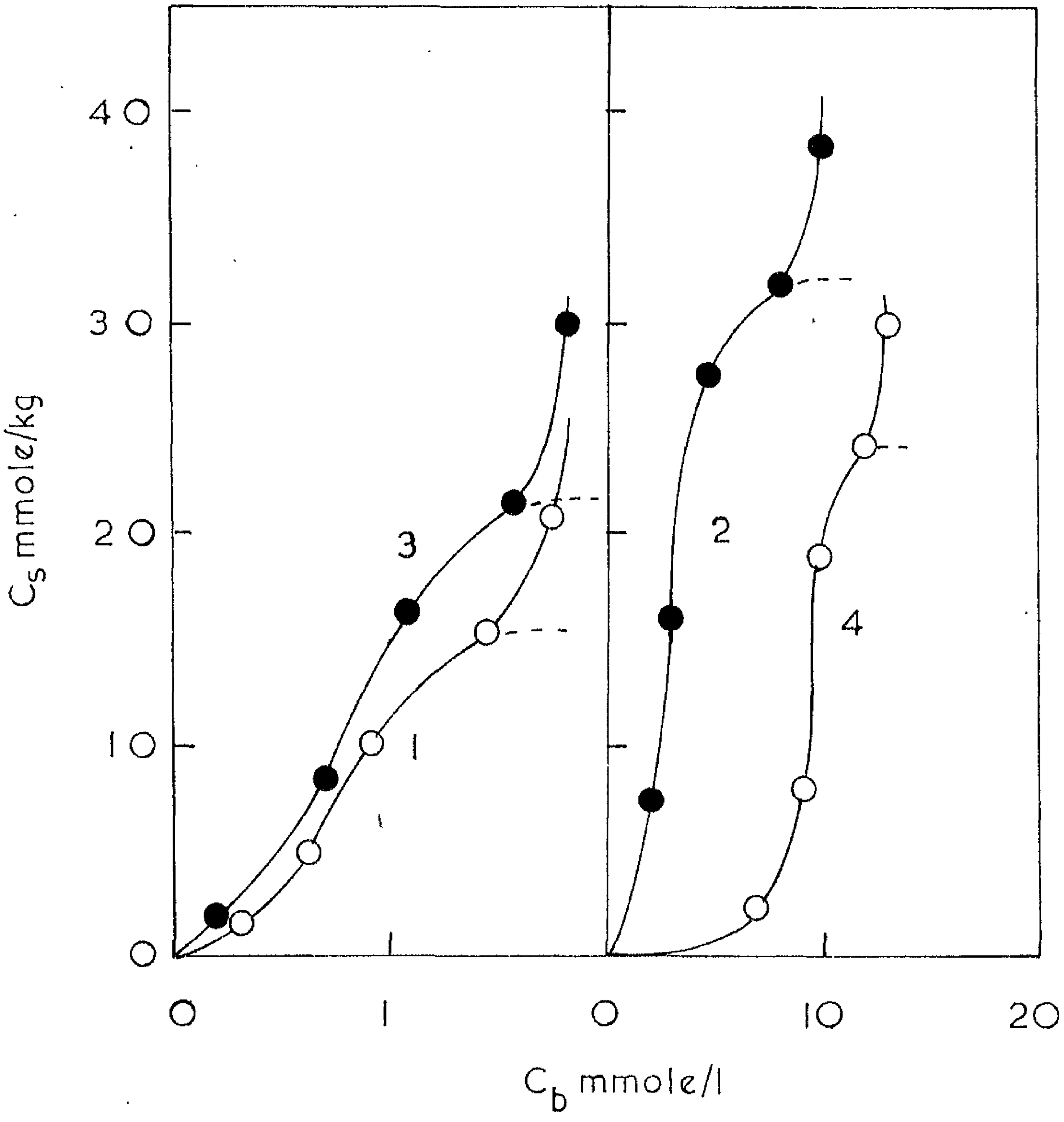


Fig.63. Adsorption isotherms of acid wool dye (C.I.62,055) from water on types of TiO_2 at 17°C. (1) Type 1; (2) type 2; (3) type 3; and (4) type 4.

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