STUDIES IN MONOLAYER ABSORPTION

By

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PUBLICATIONS

The following parts of this work have appeared in print:-

PART I, Section I.

"Researches on Monolayers. Part VI. A Study of Reactions in Surface Films of Acetates and Ketones and their Relation to Adsorption by Cellulose Acetates" by A.Cameron, C.H.Giles and T.H.MacEwan. J.Chem.Soc., 1957, 4304-4311.

"The Adsorption of Dyes by Cellulose Acetates" by A.Cameron, C.H.Giles and T.H.MacEwan. J.Soc.Dyers and Colourists, 1957, 73, 511-512.

Section IIA

"Researches on Monolayers. Part VII. Reactions of Casein with Dyes and other Aromatic Solutes and their Relation to Adsorption by Protein Fibres", by A.Cameron, C.H.Giles and T.H.MacEwan. J.Chem.Soc., 1958, 1224-1230.

A paper embodying most of the work recorded in Sections IIB and IIC has, since the compilation of this thesis, been accepted for publication in the Journal of the Chemical Society under the title "Researches on Monolayers. Part VIII. Reactions of 2:1-Metal-complex Unsulphonated Dyes, with Protein and Polyamide Monolayers, and their Relation to Dyeing Mechanisms" by C.H.Giles and T.H.MacEwan (Paper No.9/693).

The work done by the author, recorded in Graph No.20 (Part I) has been shown in the following paper, Bruce, Giles and Jain, J.Chem.Soc., 1958, 1610-1613.

PART II.

Some of the work recorded in Part II of this thesis has been published as "Classification of Isotherm Types for Adsorption from Solution", by C.H.Giles and T.H.MacEwan. Proc.IInd Internat.Congr. of Surface Activity, London, 1957, 3, 457-461; a second paper on the same subject embodying the quantitative evidence given in the present thesis, is at present being prepared for submission to a journal.

The work by the author that is recorded in Graph No.10 (Part II) has been shown in the following paper, Galbraith, Giles, Halliday, Hassan, McAllister, Macaulay and Macmillan, J.Appl.Chem., 1958, 8, 416-424.

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S U M M A R Y

SUMMARY

The main aims of this work are to interpret mechanisms of adsorption of dyes, etc. by fibres, especially protein, nylon, and other hydrophobic fibres, e.g. cellulose acetate, from the results of (i) monolayer experiments with model compounds, and (ii) a systematic study and classification of the forms of adsorption isotherms.

(i) Experiments in Monolayers:

The action of aqueous tannic acid solutions on monolayers of stearyl alcohol, N-methylstearamide, cetyl acetate, cetylaniline and cellulose triacetate has been studied. A mixed film, and other techniques, have been used to study the interaction between cellulose triacetate and a non-ionic 'disperse' dye. (The dye alone was found to be capable of forming a condensed film on water). The results, in conjunction with earlier work, are used to interpret the mechanism of adsorption of solutes by cellulose acetates.

The molecular area and compressibility data of the force/area curves show that in the presence of water the ketone group has much weaker hydrogen-bonding power than the acetate group, and the films of ketones are expanded much less by all the solutes than the acetate films are. Highly ionised compounds, including sulphonated dyes, cause considerable expansion of the cellulose triacetate films, even though they

have no affinity for this material in bulk, whereas, the films appear to be unaffected by a highly substantive non-ionic 'disperse' dye. Several hypotheses are suggested to account for these facts.

Further support for these arguments is set out in an Appendix, based on the work of earlier investigators.

The effect of aromatic sulphonates, including some dyes, upon casein monolayers spread on acid or on buffer solutions near the isoelectric point has been studied. Large dye molecules with a non-ionic proton-donor group at each end have an effect on the film similar to that of tannic acid. Surface-active mono-basic dye molecules with weak hydrogen-bonding groups penetrate the film and at high pressures increase its solubility. It is suggested that the latter effect may be due to the adsorption of a layer of dimerised dye molecules below the film.

Small sulphonate molecules and disulphonates with weak hydrogen-bonding centres (e.g. anthraquinone-disulphonates) are probably adsorbed beneath the film. The results are used as a basis for the hypothesis that the affinity of mono-basic anions for protein fibres arises from their own mutual attraction, which assists them in forming a monolayer or a layer of micelles adsorbed on the fibre, rather than from specific anion-fibre attraction.

2:1-Unsulphonated azo-dye metal complexes and other solutes have been applied to monolayers of edestine and methoxymethylnylon. The dyes are highly aggregated in the cold and their effects on the films are explained as the result of adsorption in the form of aggregates. It is shown that the aggregate, if it is an ordered one, very probably has a structure with "fins" of protruding aromatic nuclei, between which chain molecules in the film engage, by non-polar, and in some cases polar, forces. A complex without pendant polar groups markedly increases film rigidity; proton-acceptor groups in a complex solubilise the films; and proton-donor groups cross-link and stabilise them.

The mechanism of dyeing of nylon and protein fibres with these complexes is considered to be adsorption (probably of micelles),

(a) in water-accessible regions by

(i) ion exchange, (ii) van der Waals forces, and

(iii) (if suitable groups are available) hydrogen bond donation by the dye to backbone -CONH- groups; and

(b) in water-inaccessible regions by hydrogen-bonding.

Process (b) ("solid solution") gives linear portions of adsorption isotherms.

(ii) Adsorption Isotherms.

Part II of this work is a study of the general factors

responsible for determining the form of isotherms for adsorption of a solute by a solid from solutions, illustrated by examples from recent experimental work. The isotherms for this type of adsorption are divided into four main classes, characterised by the initial portion being convex (S-type) or concave (L-type) to the solution-concentration axis, linear (Ln-type), or coincident with the substrate-concentration axis (HA-type). The 'L'-type curve is the most common and usually represents adsorption of a high affinity-solute; the others are encountered only in more particular systems. The 'S'-type curve may perhaps represent high affinity of the solvent for the solid substrate and low affinity of the solute, but often it appears to indicate that the adsorbed solute molecule (or ion) is oriented perpendicular to the solid surface. The 'Ln' type curve occurs when the solvent has low swelling power for the substrate; and the 'HA' type only in rare cases where the solid has very high, and the solvent very low, affinity for the solid. The present evidence suggests that this isotherm, when observed in adsorption of ionised solutes from water, probably always represents adsorption of ionic micelles.

GENERAL INTRODUCTION

No one can say when the ancients first observed, and put to their advantage, the film-forming properties of oils. Pliny the Elder (A.D.23) speaks of the mariners of his day, using oil to protect their ships from breakers. He also tells of divers discharging a mouthful of oil, which, on rising to the surface, creates a calm patch and enhances visibility at the sea bed. Benjamin Franklin experimented with oil (probably olive-oil) on the surfaces of ponds and he observed that a teaspoonful of oil was sufficient to calm the waves over an area of half an acre. More than a century later in 1891, Fraulein Pockels[1] described a method of handling insoluble oil films. The surface film was contained between glass barriers lying along the surface of a trough, which was filled to the brim with water. The films could be compressed by moving the barriers along the surface, the surface behind the barrier being left perfectly clean. She found that with a large surface area and a minute amount of oil, no lowering of the surface tension was observed until the area was reduced to a certain critical value. Fraulein Pockels' observations were confirmed a few years later by Rayleigh[2], and a fundamental contribution to the theory of surface films was made by his suggestion that the critical value was attained when the molecules form a closely packed layer, one molecule thick, in contact with each other over the entire surface. For the first time actual molecular

sizes could be determined.

No further major contributions to the study of surface films were made until Langmuir's[3] investigations in 1917.* New experimental techniques, together with new conceptions, introduced an element of exactitude into this branch of science. A trough fitted with two barriers was used for direct measurement of the outward surface pressure of a film. The film was prepared on a trough which was filled to the brim with water and was confined to the area between the two barriers, one of which incorporated a device for direct measurement of the force exerted on it, the other was capable of movement along the surface in a step-wise fashion and by this method the outward force was studied with varying surface area. Instead of 'oils' of unknown constitution, pure substances were used, and the effects of varying constitution were observed. Solid substances were spread from solution in a volatile solvent, which quickly evaporated, leaving the film. By spreading exact amounts the force-area curve could be constructed, with the areas expressed in sq.A. per molecule, for each surface pressure. Normal, saturated fatty acids and alcohols gave stable films, which were capable of withstanding considerable lateral compression, and gave a clearly marked critical area at which surface pressure first appeared. It was also shown that surface pressure was not detected until the area

* Devaux however published in this field before 1917.

occupied by each molecule was 22 sq.A., and at areas of 20.5 sq.A. the pressure increased very rapidly with decrease in area.

Langmuir found that the shape of the curve was independent of hydrocarbon chain length, provided there were more than 14 carbon atoms in the molecule, though at longer chain lengths the films are extremely rigid and do not yield readily to small lateral pressures, for this reason the finer details of the curves tend to be obliterated. This showed that the molecules must orient steeply to the surface and at the same angle in all the films. These findings added greatly to the knowledge of forces acting between molecules and allowed the simple rules concerning the spreading characteristics of a compound to be formulated.

In the normal, long chain acids and alcohols which form stable films the -COOH or -OH group is situated at the end of the molecule and in the lower homologues these groups are capable of conferring solubility on the whole molecule, thus these groups have been named hydrophilic or water-attracting. With long chain acids and alcohols the pull of the hydrophilic group is insufficient for complete solubility, owing to the resistance of the aliphatic chain to immersion, thus these compounds are capable of spreading over the surface as a monomolecular film. Long-chain paraffins do not

form surface films.

Formation of stable monomolecular surface films is possible when the molecule consists of two parts, one part being water-attracting (polar), the other part being hydrocarbon (non-polar), the former confers the necessary adhesion to, and the latter the requisite insolubility in, the aqueous substrate. The lateral adhesion between the hydrocarbon chains causes them to pack side by side and prevents the chains from being immersed in the aqueous layer. This adhesion is the main factor in keeping the molecules together as a coherent film.

Adsorbed surface films of shorter chain, slightly soluble acids were also studied by Langmuir and these were found to give 'gaseous' films, where the molecules move about separately and lie flat on the surface instead of being steeply oriented as in the case of coherent films. It was predicted that, as the chain length increased, transitional phenomena would be found between the coherent films of long chain insoluble fatty substances and the gaseous adsorbed films of soluble fatty substances, which would be analogous to the evaporation and critical phenomena of liquids and vapours in three dimensions.

Schofield and Rideal[4] in 1926 showed that as the length of the hydrocarbon chains in soluble fatty acids

increases, the lateral adhesion between the molecules in the gaseous films adsorbed at the surface increases, until with the acid with twelve carbon atoms in its molecule, the lateral adhesion is almost sufficient for formation of a coherent film. Using a sensitive instrument for measuring surface pressures, Adam and Jessop[5] in the same year, were able to trace in detail the transition between gaseous and coherent films. A close resemblance was found to exist between these transitions and the condensation of three dimensional gases to liquids. Additional complexities in the coherent type of film were found by Langmuir and were further investigated by Labrouste[6], Adam and others. The existence of a coherent 'expanded' state in insoluble surface films of fatty substances was established. Films in this state are intermediate in area between the very closely packed condensed films and gaseous films.

Types of Surface Films.

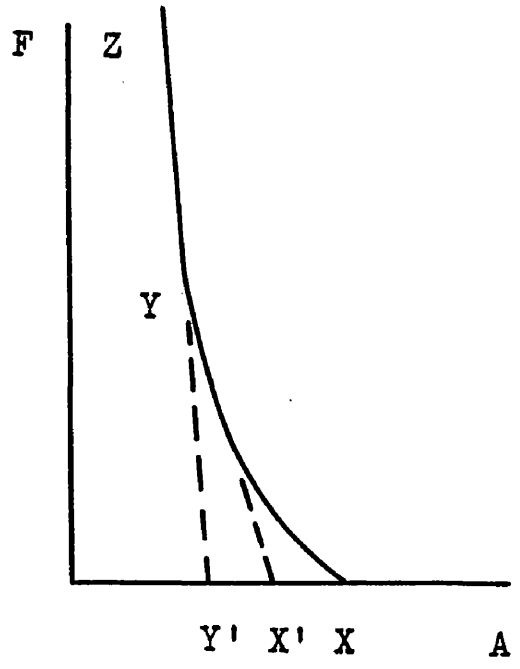
The early workers recognised from a study of force-area curves for a number of substances, that surface films could exist in various physical states, and that the state of the film depends to a great extent on the nature of the forces acting between the film molecules. These forces are determined by the size and shape of the polar and non-polar parts of the molecule. The present work was concerned mainly with condensed and liquid-expanded films.

The three main types of films are condensed, liquid-expanded, and gaseous, and each is described below.

Condensed Films.

These are the most commonly found. Molecules with large lateral adhesion form condensed films. If there is more space at the surface than can be covered by the adhering molecules, the surface becomes a two phase system consisting of isolated islands of material and clean surface, readily detected by large fluctuations of surface potential. Fig.1 represents a typical force-area curve for a condensed film.

Fig.1.



In some cases the two portions XY and YZ both occur, in others only one portion is obtained. For straight alkyl chains at zero compression the area at Y′ is always[7] 20.5 sq.A., while the area at X′ may extend over 30 sq.A. Several attempts to draw analogies between the two-dimensional condensed films and gases have been made, and it has been suggested that the regions YZ and YX correspond to the solid and liquid states respectively.

Adam[8] suggested that the two parts XY and YZ can be attributed to close-packed heads and close-packed chains respectively. Lyons and Rideal[9] considered the chains to be inclined at an angle of 26.5° or 45° to the vertical, since this tilt would allow the chains to interlock. If the cross-sectional area of the alkyl chain is taken[10] as 18.5 sq.A., the interlocking position gives areas of 20.7 sq.A. and 26.2 sq.A. for Y′ and X′ respectively. Adam[11], however, pointed out that although there may be some evidence for the first interlocking position there is none for the second.

The question is still open as to whether the area of 20.5 sq.A. for the films of close-packed chains, is due to the chains being packed exactly as in crystals at a tilt of 26.5°, or to the chains being vertical and packed less closely owing to the influence of water molecules.

It has been shown that the XY portion of the curve gives a measure of the cross-sectional area of the head groups as packed in films, and that they can be divided into two groups according to whether or not they can be rearranged on compression. Those with high compressibility, e.g. fatty acids on acid solution, belong to the first class and those with much lower compressibilities, e.g. phenols and ureas belong to the second. Schulman and Hughes[12] have criticised the concept of head compression along XY on the basis of surface potential measurements. They found that the vertical component of the apparent dipole moment remains almost constant throughout this region, and suggested that the compression along XY is due to expulsion of solvent molecules, oriented between the polar groups, into the substrate.

Dervichian[13] has drawn analogies between monolayers and three-dimensional matter, and claimed that the lattice structure and the tilt of the molecules in the different forms are the same in two and three dimensions. Alexander[14] has criticised this theory by pointing out that if it were

correct, then all substances which are solid at room temperature should also give condensed monolayers; this, however, is known to be incorrect in many cases. He supported the view[15] that in the YZ region the long chains are close-packed but not as tightly as in the crystalline state, being vertically arranged in all cases. Alexander also showed that the surface moment of condensed films of ethyl stearate requires vertically oriented chains[16]. He also maintained that the structure in the more compressible region, XY, is a composite effect depending upon both the packing of the hydrocarbon chains and on the packing of the heads. Condensed monolayers were classified according to the factors which are primarily responsible for limiting the area at X, these are:-

(a) The Size of the Head Group.

In many cases the size of the head group is responsible for the area at zero compression. Substances containing head groups which would be expected to be large, from the constitutional formula, usually give films with large areas at zero compression.

(b) Cross-hydrogen Bonding.

This is believed to be a factor in limiting the area of unsubstituted fatty acids, ureas and amides. In

certain cases where hydrogen bonding was expected, but prevented by steric factors, a bond through a water molecule was postulated[17].

(c) Packing of the Chains.

This is believed to be the deciding factor in the case of cis- and trans-unsaturated compounds, methyl ketones and others in which attractive forces between the head groups are likely.

Alexander concluded that the limiting area of compounds having chains of 14-20 carbon atoms depends upon the film taking up a configuration of minimum energy, which is determined by the orientation of the dipole moment and also by the packing of the chains.

Gaseous Films.

These are the simplest type of films and ideally consist of molecules of negligible size having no lateral adhesion but being attracted by the water surface. The theoretical behaviour of these films can readily be calculated and is closely approached in some cases. The film is considered to consist of molecules lying flat on the surface and moving at random. The surface pressure is due to continuous bombardment of the boom by the 'swimming' film molecules.

Adam[18] has shown that molecules of this type lie flat on the surface and it is sometimes possible to convert a coherent film into a gaseous one by introducing a second hydrophilic group some distance from the first, e.g.

$$C_2H_4OOC(CH_2)_{11}COOC_2H_4$$

It has also been shown that for an ideal gaseous film[19],

$$FA = kT \text{ (k is the gas constant)}$$

Several cases have been found in which insoluble films give nearly the theoretical value of k. This may be compared to the gas equation (PV = RT) and the proof follows that for the gas laws very closely.

Liquid-Expanded Films.

These films are intermediate in property between gaseous films and condensed films, and they are often found with long chain aliphatic substances.[20] Langmuir's explanation is generally accepted for the properties of these films, in particular, the fact that the limiting area does not correspond to any definite orientation of the molecules, but is intermediate between that of molecules standing upright and lying flat.

Techniques Employed in the Study of Monolayers.

Simultaneous measurement of surface pressure and potential is the most widely used technique in monolayer studies. In the present work a study of both was attempted, but with very limited success, and consequently the potential measurements were abandoned. The apparatus and methods used are described later.

Surface Potential Measurements.

The surface potential is defined as being the difference in potential of a clean surface and the film-covered surface. Measurement of potential is a valuable ancillary technique to pressure measurement, especially for the detection of unspread material, which, when the surface is explored with the air electrode, causes wide fluctuations in the potential.

The change in surface potential (ΔV) may be written thus:

$$\Delta V = 4 \pi n \mu^{18}$$

where n is the number of molecules in the film, and μ would be the vertical component of the dipole moment of one film molecule, if all the surface potential were due to the dipole moments of the film molecule in a plane and if the dielectric constant of the film could be treated as unity.

Interpretation of surface potential is much more complex than surface pressure, but, however, the following points have been established.

With compounds of similar end groups and similar constitution, a rise in the value of μ probably indicates an increasing tilt of the dipole to the surface. Further chemical changes, especially those leading to ionisation of the end group, may lead to large changes in the value of μ. When, as sometimes occurs, surface potentials are negative, this indicates that the negative end of the total dipole of the molecules in the film is uppermost. Potential measurements may thus furnish useful information regarding the changes of orientation of the film molecules. The technique has been found to be useful for following chemical reactions in films and it has been widely used for that purpose. Although it had been known for some time that surface films affect the contact potential between the liquid and air, it was not until 1924 that this was first measured[21]. These measurements were continued by Frumkin[22] and in 1931 Schulman and Rideal[23] made a detailed study of several types of insoluble films and compared surface potentials over a large range of areas. This work has been continued by Rideal, Schulman, and Hughes and also by Adam and others.

In the study of surface films of polymers, (a

considerable portion of the present work is concerned with polymers), surface potential measurements have not found as wide an application as in the study of simpler surface-active compounds. Indeed Holt[24] questions the validity of surface potential measurements in the study of the interaction of polymers with monolayers, since the potential varies widely over the surface and the value measured depends on the size of the polymer which is adsorbed immediately beneath the electrode.

Examination of Light Reflected from Surface Films.

Freundlich et al.[25], Bouhet[26], and other workers have described an apparatus for measuring the ellipticity of light reflected from surfaces covered with monolayers. The nature of the reflected light depends on the structure of the surface film, but owing to the difficulties of interpreting the results in terms of molecules and their orientation, this approach has so far not made a great contribution to the elucidation of the structure of surface films.

Ultramicroscopic Examination of Surface Films.

Zocher and Stiebel[27] introduced this method in 1930, and in a modified form it was used later by Adam[28]. A powerful dark-ground illuminator of the cardioid type,

fixed in the bottom of the trough, was focussed sharply on the water surface. A monomolecular film spread on the surface scatters no light under these conditions and appears dark; any unspread material, however, shows up as a brightly illuminated region, different in appearance to dust particles which invariable settle on the surface. Although this method yields no information as to the structure of the film, it is a valuable ancillary technique in that it reveals whether or not the film is properly spread.

Other Methods.

A recent method of investigating the structure of monolayers is by electron microscopy[29,30]. Monolayers of synthetic linear polymers (nylon, cellulose acetate and polyvinyl alcohol) have been examined by this method. At low pressures the monolayer consisted of winding microfibrils, on compression a large number of microfibrils oriented at right angles to the direction of the compression were formed. Further compression produced visible striations on the film.

Measurements of viscosity of monolayers have yielded much valuable information. Langmuir[31] used an oscillating disc method for viscosity measurements with protein monolayers. Pankhurst and co-workers[32] have described a surface viscometer (developed from that of

Chaminade, Dervichian and Joly[33]), which they used in their extensive studies on the tanning of protein monolayers. In this instrument the film is confined within a floating framework of waxed mica, which contains in a circular compartment a floating waxed ring which is connected to a rotating shaft through a torsion wire, and the viscous drag imposed by the film which covers the annular space between ring and frame is measured in terms of the angular displacement between the ring and the rotating shaft.

Lanham and Pankhurst[34] have found this instrument to be a valuable tool in elucidating the rôle played by hydrogen bonds in the tanning of protein monolayers with vegetable tanning agents. It provides a most sensitive method of following the tanning interaction in monolayers, since surface viscosity undergoes enormous changes during the process, whereas pressure and potential changes may be comparatively slight.

Recently L. de Bernard has described a new surface viscometer[35] which incorporates two concentric rings, where the torque is measured on the outer motionless ring, the inner ring being the mobile one. This instrument is claimed to be suitable for work with very fluid monolayers, and also useful for very viscous monolayers. It is also claimed to be more sensitive and have other advantages over the type described above.

EXPERIMENTAL

PREPARATION AND PURIFICATION OF COMPOUNDS

THE FILM BALANCE, ITS CONSTRUCTION AND OPERATION

Preparation and Purification of Compounds.

The long chain compounds used in Part I, Section I of this work were prepared by the following methods.

p-Cetylaniline.

Cetyl alcohol (1 mole), aniline (1 mole), aniline hydrochloride (0.3 mole) and zinc chloride (0.66 mole) were heated together at 270° for 10 hours, while the water formed was allowed to distil off, and thereafter for a further 12 hours[36]. The product, a zinc chloride double salt, was cooled, broken up and heated for 4 hours with 50% aqueous sodium hydroxide. The oil thus formed was dissolved in ether, washed with dilute hydrochloric acid, then with water and dried over calcium chloride. The ether was then distilled off and the dry oil distilled *in vacuo*. B.p.240°, 11 mm.

Cetyl acetate.

Dry hydrogen chloride was bubbled through a mixture of cetyl alcohol (0.3 mole) and glacial acetic acid (0.6 mole). The mixture was then heated for several hours on a warm water bath. The acetate was then isolated from the reaction mixture by vacuum distillation. B.p.200°, 15 mm. M.p.22°.

N-Methylstearamide.

Methylamine hydrochloride (1.1 mole) was suspended in dry chloroform and to this was added during 5 minutes stearoyl chloride (1 mole) in dry chloroform at room temperature, with stirring and cooling. N-methylmorpholin (2.3 mole) dissolved in chloroform was then added during 30 minutes. After a further hour, the solution was filtered, and washed with dilute hydrochloric acid, sodium carbonate and water successively. After drying the chloroform was distilled off and the residue recrystallised from alcohol. Colourless prisms, m.p.91°.

N-Stearylamine hydrochloride.

N-Stearamide was prepared by dropping stearoyl chloride (0.16 mole) from a dropping funnel into an ice-cold solution of (0.88 S.G.) ammonia[37]. The amide was filtered off, washed with water and dried.

The N-stearamide (0.15 mole) was reacted with thionyl chloride (0.3 mole) to yield the low melting N-stearonitrile. It was then reduced by refluxing with excess sodium in ethanol for several hours. On addition of hydrochloric acid and cooling, the amine hydrochloride crystallised out. This was distilled with quicklime, the distillate warmed with acetic anhydride a few minutes, and the product crystallised from acetic acid with the aid of charcoal.M.p.70°.

Purification of Compounds.

The dyes used were purified from commercial samples. Owing to the diverse nature of the dyes used, no one general method of purification could be adopted, and it was usually necessary to work out a separate method for each individual dye. The most general method used was to salt out the dye from a hot concentrated solution, and after being allowed to cool, the dye was filtered and washed many times with ice-cold water. This method produced electrolyte-free dyes, but in certain cases it gave a low yield, especially with dye of small molecular weight or with dyes which contain a large number of solubilising groups. The dye was then recrystallised several times from a suitable solvent (usually water) and analysed.

4N-Ethyl sodium ethyl sulphate 4'-nitroazobenzene.

The commercial sample of this Solacet (ICI) dye was extracted with acetone in a Soxhlet extractor and was recrystallised several times from acetone.

4N-Ethylhydroxyethyl-4'-nitro-2'-chloroazobenzene.

The commercial sample of this disperse dye was extracted with benzene in a Soxhlet extractor. It was then recrystallised several times from benzene.

Haematoxylin.

The commercial product (100 g.) was dissolved in 500 c.c. of boiling water containing a little sulphur dioxide; the solution was clarified with charcoal, filtered, and cooled. The long thin colourless needles which separated were washed with water containing a little sulphur dioxide and dried in a desiccator.

Haematein.

Pure commercial haematoxylin (100 g.) was dissolved in 1250 c.c. of hot water, 125 c.c. of ethanol was added, and the solution cooled; 140 c.c. of sodium hydroxide (400 g./litre) was then added, with stirring and cooling to below 25°, followed by gradual addition of 37 c.c. of aqueous hydrogen peroxide (100 vol.) diluted to 50 c.c. After 5 minutes the solution was neutralised with dilute hydrochloric acid and acidified with dilute acetic acid. An amorphous brown precipitate of haematein settled out, which was filtered, washed with water, and then gently warmed on a water-bath in 700 c.c. of water, whereby it was changed into the crystalline form. The crystals were filtered off, washed with methanol and dried.

All other substances used were either Analar reagents or were purified by normal methods.

Analysis of Dyes[38].

The dyes were all purified to 91-98% from commercial samples and were estimated by titanous chloride reduction. The dye was determined by one of the following methods:-

(a) If the dye was soluble in water and not precipitated by hydrochloric acid then a 1% dye solution was prepared and a known volume was transferred to a conical flask containing 10 c.c. concentrated hydrochloric acid. The solution was titrated at the boiling point in a stream of carbon dioxide, until it was colourless. The purity of the dye was calculated from the volume of titanous chloride required.

(b) If the dye was soluble in water but was precipitated by hydrochloric acid, then sodium tartrate was used in place of hydrochloric acid, the procedure being the same as in (a).

(c) If the dye was not soluble in water then it was dissolved in glacial acetic acid and the analysis was carried out as in (a), but without the addition of hydrochloric acid.

The anthraquinone dyes were also analysed with titanous chloride, using a back titration method, but this was not always wholly successful, owing to the difficulty of

determining the end-point. Indications of the purity of one of these dyes (Alizarin Cyanine WRS) were given by comparing a solution spectrophotometrically with a solution made from a small amount of pure dye. With another two anthraquinone dyes (Solway Blue BN and Solway Blue RN) purity was indicated when successive recrystallisations produced no further increase in the optical density of dilute solutions, when they were examined with a Unicam Photoelectric Spectrophotometer S.P.600.

Preparation of Solutions.

(a) Substrate Solutions. Aqueous solutions were used in all cases and were prepared by dissolving the requisite amount of material in water which was twice distilled. When dilute acid or buffer solutions were used the ionic strength was kept constant throughout that section of the work. In all cases control experiments were made on blank control solutions in order that any variation in film characteristics could be attributed to the presence of the dye or related compound in the sub-solution.

(b) Solutions of Surface-active Materials. The surface-active materials were all spread from solution. The monomeric films (Section I) were prepared from solutions containing 10-20 mgm. of material per 25 c.c. of solvent. Protein films (Section II) were prepared from

alkaline solutions, which were freshly made every few days. N-methoxymethyl nylon (Nylon Soluble Polymer Type CA, ICI) films were prepared from methanol solution, made fresh daily.

Material	Solvent
Cetylaniline	Benzene *
Cetyl acetate	Benzene
N-methylstearamide	Methanol/, benzene
Stearyl alcohol	Benzene
Stearamine Hydrochloride	Water, methanol and benzene (volume ratio 1:2:2)
Dispersol dye I	Benzene
Cellulose triacetate	Chloroform/
Casein	0.15% solution with 0.025 M sodium hydroxide
Edestine	(0.01% solution with 2 M sodium chloride (0.10% solution with 0.5 M sodium hydroxide
N-methoxymethyl nylon	0.01% solution with methanol.

Surface Pressure Measurements.

The main approaches to a study of surface films are given by measurement of pressure, potential, and viscosity of the film at various areas. Modified forms of the original film balance, as designed by Langmuir, are generally used for

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* Benzene - 'Pure for Molecular Weight Determination' grade
/ Methanol, Chloroform - Analar grade.

studying the force-area characteristics of surface films. The balance used in the present work incorporates several innovations and is described below. (Diagram I).

The balance is similar to one described by Allan and Alexander[39] which was used for low surface pressure measurements, in so far as a balancing system is used instead of the torsion wire technique. In this case a heavier balance head is used to cover the required pressure range.

The Balancing System.

The balance head is shown in Diagram 2; it consists of a brass block into which two agate knife-edges (C) are clamped by a brass plate (B). A mirror (D) is also fitted into the block. The calibration and counterpoise arms (F and A) are attached by inserting a thin brass rod through the block, the former having a notch 5 cm. from the knife-edges and the latter carrying a brass counterpoise which can be screwed along the arm. A small brass block, carrying a brass rod, bent as shown, is fitted to the centre of the underside of the block and to the ends of this rod are brazed two heavy platinum wires. These wires pass through holes drilled in the boom (E) which is made of Teflon (poly-tetrafluoroethylene). The assembly of the balance head with the rest of the balance is shown in Diagram I.

The advantages of this method of measuring surface

pressure over the torsion wire method are: ease of removal of balance head, which facilitates the cleaning process, constancy of instrument sensitivity throughout an experiment, ease of alteration of sensitivity, when required, by addition of weights below the level of the knife-edges. The system is also robust and parts do not need renewing.

The Trough.

The use of plastics in film balance construction is now common practice and both Perspex and Teflon[40] have been used. In the present work Polythene has been used and has been found to be satisfactory. Owing to its water-repellent properties it does not need to be heavily waxed and also, since it is inert, the risk of contamination is reduced and it is easy to clean.

The trough was milled out from a block of Polythene (24 cms. x 14 cms. x 1 cm.) to give the following internal dimensions: 20.5 cms. x 10 cms. x 0.6 cms. It was screwed to a flat stainless steel plate.

The movable barrier consists of a strip of Polythene (14 cms. x 1.6 cms. x 0.3 cms.) bolted to a brass strip (23 cms. x 1.6 cms..x 0.6 cms.). The bolt heads are counter-sunk, and are heavily coated with paraffin wax. This barrier is operated by a screw mechanism from outside the aluminium

case which encloses the film balance.

The boom is of Teflon (8.3 cms. x 1.3 cms. x 0.1 cms.) and has good water-repellent properties and, being quite rigid, requires no reinforcement. Two holes 3 cms. apart were drilled in the boom to accommodate the platinum wires from the balance head.

Several materials were tested, for sealing the boom to the sides of the trough, the most successful being Polythene monofilament (0.005 in. - Courlene X3, Courtaulds Ltd.).

The Optical Lever.

The pressure exerted by the film on the boom is measured by means of an optical lever as shown in Diagram 3, consisting of a light source (L), two biconvex lenses, and two mirrors, one of which is fitted into the balance head. By means of the two biconvex lenses placed 4 cms. apart, the image of the light source is focussed on the mirror in the balance head, it is then reflected to mirror (M) and then to a centimetre wall scale placed one metre distant from the balance head. This magnifies on the wall scale any small movements of the balance head and enables pressures of 0.1 dyne/cm. of boom length to be detected.

Calibration Weights.

Phosphor-bronze wire was used for making rings of 0.1 gm., 0.075 gm. and 0.05 gm. weight, which were used for calibrating the boom-balance head assembly. Periodically the rings were checked against standard weights.

Operation of the Instrument.

The following procedure was adopted for each experiment:-

(1) Preparation of the Balance.

The trough, boom, and barrier were cleaned with benzene between experiments and then, after checking that all bolt heads on the barrier were well coated with paraffin wax, were thoroughly washed with distilled water. Periodically the bolt heads were rewaxed, but any other waxing was unnecessary.

The threads connecting boom to trough were sealed with paraffin wax as shown in Diagram 4. Renewal of the threads between experiments was found to be unnecessary.

(2) Cleaning the Surface.

The movable barrier was adjusted to within a distance of 1 cm. from the boom, before the sub-solution was introduced behind the movable barrier until the trough was filled. The threads were carefully inspected to ensure that

they lay flat on the surface and that there were no gaps through which leakage could occur.

The surfaces on both sides of the boom were then cleaned with a suction pump, the solution level being maintained by additions behind the movable barrier. The movable barrier was then drawn back, sweeping any surface contamination before it and exposing a clean surface between boom and barrier.

The surface was assumed to be clean, if a pressure of no more than 0.1 dyes/cm. was developed when the area was reduced by three-quarters.

(3) Calibration of the Instrument.

After establishing that the surface was clean, the barrier was retracted, the calibration weights were placed on the hook of the balance head and the corresponding deflections on the wall scale were noted. This enables deflections on the wall scale to be interpreted in terms of dynes/cm. of boom length.

(4) Spreading of the Film.

A known weight of the film-forming material was introduced to the surface from a solution which was ejected from an Agla Micrometer Syringe (Burroughs Wellcome and Co.). This instrument is widely used for accurate measurement of

small volumes of solution and is graduated to deliver any volume of solution up to 0.5 c.c., and is accurate to 0.0002 c.c.

The time allowed to elapse, to allow the material to spread, before compression of the film is dependent on the natures of the surface-active material and the sub-solution. This time varied from about one hour with certain protein experiments to about a few minutes with the monomeric surface-active materials.

(5) Compression of the Film.

The film was compressed by moving the barrier in stages towards the boom and the reading on the wall scale was noted at each compression stage. The time allowed to elapse between subsequent compressions was again dependent on the material and the nature of the sub-solution.

This gives sufficient information for a plot of the force-area characteristics of the surface-active material to be constructed.

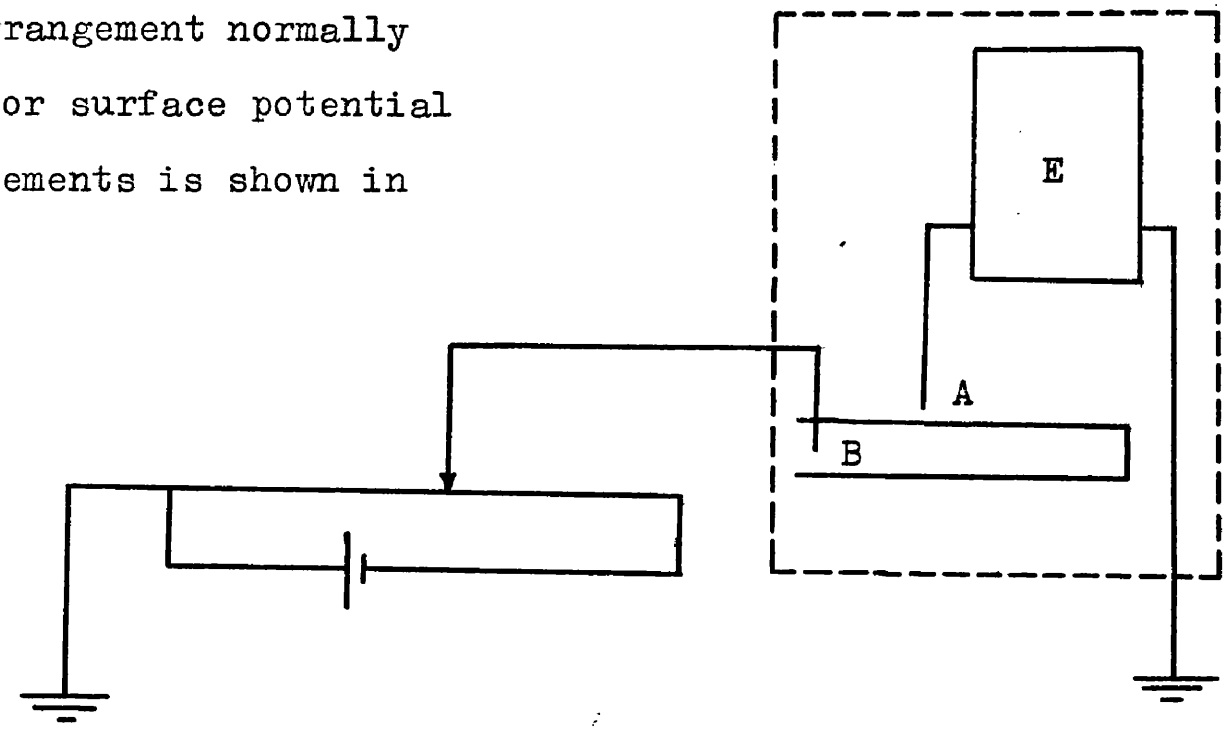
(6) Detection of Leakage.

Film leakage at the threads, boom, or barrier is made apparent by a rapid fall in pressure. The source of leakage is readily detected by dusting fine talc on to the surface and noting the movement of the particles on further compression.

Surface Potential Measurements

It is often desirable in surface chemical studies to make simultaneous measurements of surface potential along with measurements of surface pressure. Hence Cameron, working in this laboratory, constructed an apparatus incorporating a triode valve. This he found to be unsatisfactory, as the circuit was unstable. Construction of a unit with the triode valve replaced by a balanced double tetrode valve was commenced. The present writer completed this construction, but the apparatus was not wholly successful and only some exploratory tests were completed.

The arrangement normally used for surface potential measurements is shown in Fig.2.



A (the air electrode) is an insulated metal wire which is held just above the surface of the liquid in the trough and is connected to the electrometer unit E. B(the reversible electrode) is a calomel half-cell dipping into the solution in the trough.

The major difficulty in the measurement of air-liquid potentials is that air is normally non-conducting. This difficulty is overcome by ionising the air-gap by coating the tip of the air electrode with radioactive material, such as polonium; even so the air-gap still has a high resistance and thus the measurement of e.m.f. requires the use of an electrometer unit.

The arrangement thus constitutes a complex electrolytic cell with two electrolytes, the liquid in the

trough and the ionised air, and three surfaces, namely the reversible electrode in the liquid, the air-liquid surface and the surface of the air electrode. The potential difference of the air-liquid surface is the only one which can be altered by the presence of an insoluble surface film and hence by measuring the e.m.f. of the cell before and after spreading the film, the surface potential of the film can be measured.

Construction of the Apparatus.

The method used was based on the circuit designed by Few and Pethica[41]. The valve (Ferranti BDM 20) used in the circuit has an indirectly heated cathode, the advantages of which have been summarised by Little[42]. The circuit is shown in Diagram 6. The electrometer assembly is screened in an earthed aluminium box with a separate screened box for the Langmuir trough and the air electrode is connected to the operating grid of the valve by a screened cable.

The air electrode (0.93 mm. diameter) is a platinum wire coated with polonium (1.6 m.c.) (supplied by the Radiochemical Centre, Amersham) and is fitted into a brass holder. The screened cable connecting the air electrode to the operating grid of the valve passes through a block of Tufnol to a brass screw device, into which the brass holder containing the ionising tip is attached. This enables the tip to be

raised or lowered to the required height above the film surface.

The Tufnol block is held above the surface by means of a vertical brass bar, to which are connected two horizontal brass rails. The block is moved along these rails by means of a metal rod attachment (controlled from outside the screened box) and by this means the ionising tip can be made to cover any point across the trough. The tip is moved along the trough by a slide mechanism attached to the vertical brass bar. Thus the entire trough area can be examined by the tip with the box closed, the two controls being on the outside.

Operation of the Instrument.

With the trough set in position and filled level with solution, the surface was carefully cleaned, the ionising tip was set 2-3 mm. above the surface and the calomel half-cell was then dipped into the solution.

The filament current was adjusted to 125 ma. and the valve passed 250 /ua plate current in each half, with the screen and cathode potentials as shown in Diagram 6. The potentiometer was then calibrated with a standard cell and with the air electrode out of circuit, R3 and R4 were adjusted to give zero deflection on the galvanometer.

The air electrode was then switched into circuit

by means of the earthing switch S (this is a mercury change-over switch and the contacts are well insulated by paraffin wax) and the deflection in G was balanced out by applying a potential from P. This gave the potential at the clean water surface. A traverse of the surface was then made with the ionising tip and the potential at the various points was noted.

A film was then spread and the potential over the surface was measured by adjusting P. The film was then compressed and the potential over the surface was determined at each compression stage.

Galvanometer Circuit.

The galvanometer used in the electrometer circuit was also used to calibrate the potentiometer and a method allowing a rapid change-over from one to the other was essential. The circuit is as shown in Diagram 5, C and D in this circuit being connected to corresponding points in the electrometer circuit. When the galvanometer was being used to standardise the potentiometer the electrometer terminals were left in open circuit. After calibration of the potentiometer the galvanometer was then switched over for use in the electrometer circuit. The galvanometer then had a 470 ohm shunt in parallel and the galvanometer terminals on the potentiometer were then connected to complete the circuit.

Results of Surface Potential Measurements.

The results obtained are shown in Graphs No.11 and 12 in Section II of this work.

Several difficulties were met with in making these determinations and they may be briefly summarised.

The electrometer circuit was only stable for limited periods of time. Stability was greatest during the first 15-30 minutes after switching on. This is rather surprising, since a balanced double tetrode is considered to be relatively insensitive to variation in supply voltages and ambient temperature. Stability was slightly improved when the NiFe cells were replaced by a series of lead-acid accumulators.

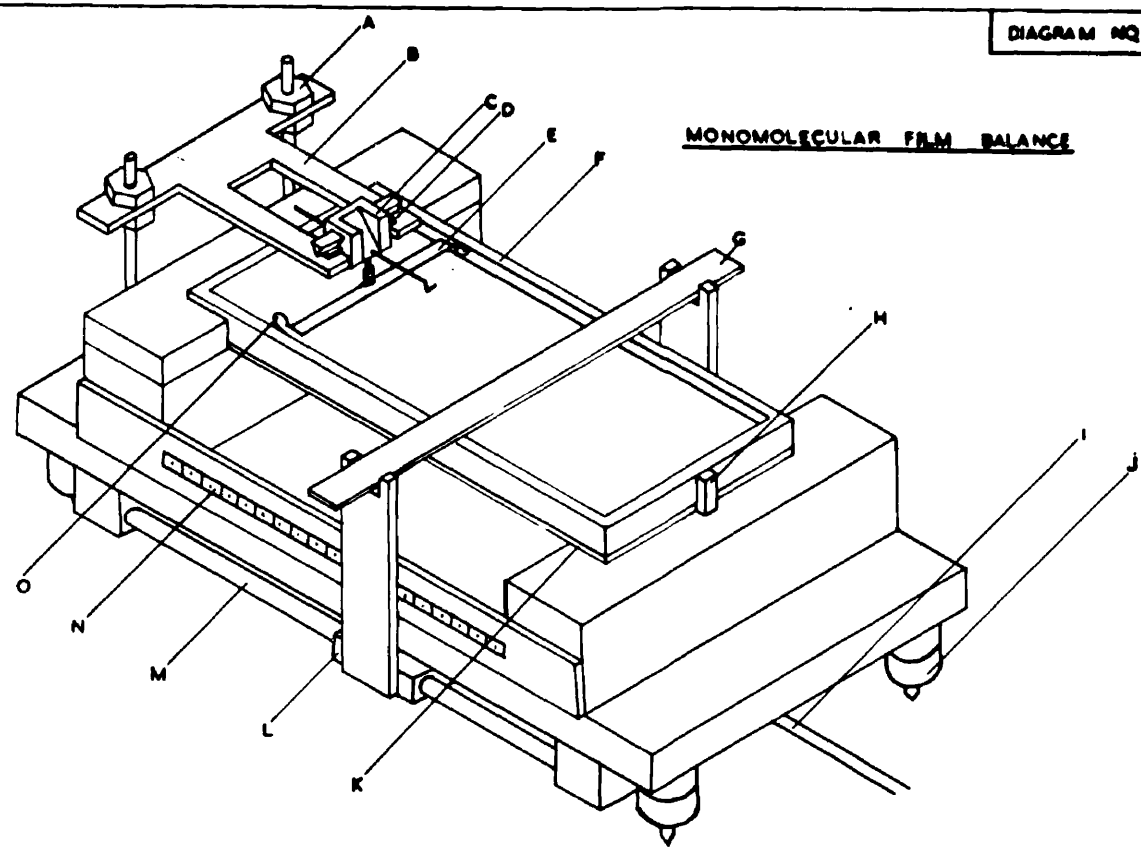
Pick-up of stray voltages caused further difficulties in making these determinations. The switching on or off of apparatus in the vicinity was sufficient to cause wide fluctuations (of the order of 100 mv.) in the potential measurements. The screening of the boxes and earth connections were carefully checked, but no improvement was made.

For these reasons satisfactory reproducibility was almost unobtainable. Duplicate determinations gave $\Delta V - A$ plots which varied from a smooth curve (see Graphs No.11,12 in Section II) to a random scatter of points. In consequence the plotted data are to be accepted with some reserve.

D I A G R A M S

DIAGRAM NO 1.

MONOMOLECULAR FILM BALANCE



A – SCREW FOR ADJUSTING LEVEL OF B.

B – BRASS PLATE TO CARRY BALANCE HEAD.

C – BALANCE HEAD.

D – AGATE PLANE.

E – TEFLON BARRIER.

F – POLYTHENE TROUGH.

G – MOVABLE BARRIER.

H – PIN TO KEEP TROUGH IN POSITION.

I – SCREW MECHANISM FOR BARRIER G.

J – LEVELLING SCREW.

K – BRASS BASE FOR TROUGH.

L – ATTACHMENT TO SCREW MECHANISM.

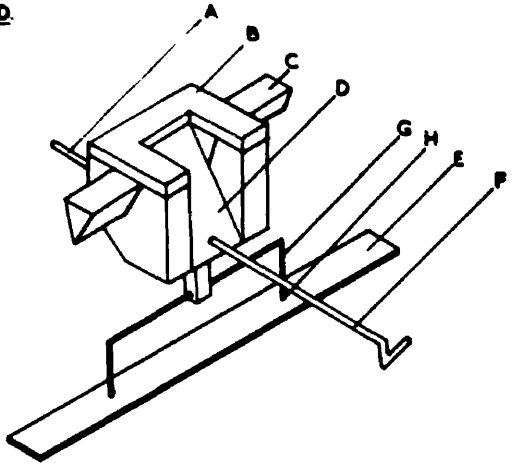
M – SLIDE FOR L.

N – CENTIMETRE SCALE.

O – POLYTHENE THREADS.

DIAGRAM NO. 2

BALANCE HEAD.



A — COUNTERPOISE ARM.

B — BRASS PLATE TO CLAMP C.

C — AGATE KNIFE-EDGE.

D — MIRROR.

E — TEFLON BARRIER.

F — CALIBRATION ARM.

G — BRASS ROD

H — HEAVY PLATINUM WIRE

DIAGRAM NO. 3

OPTICAL SYSTEM

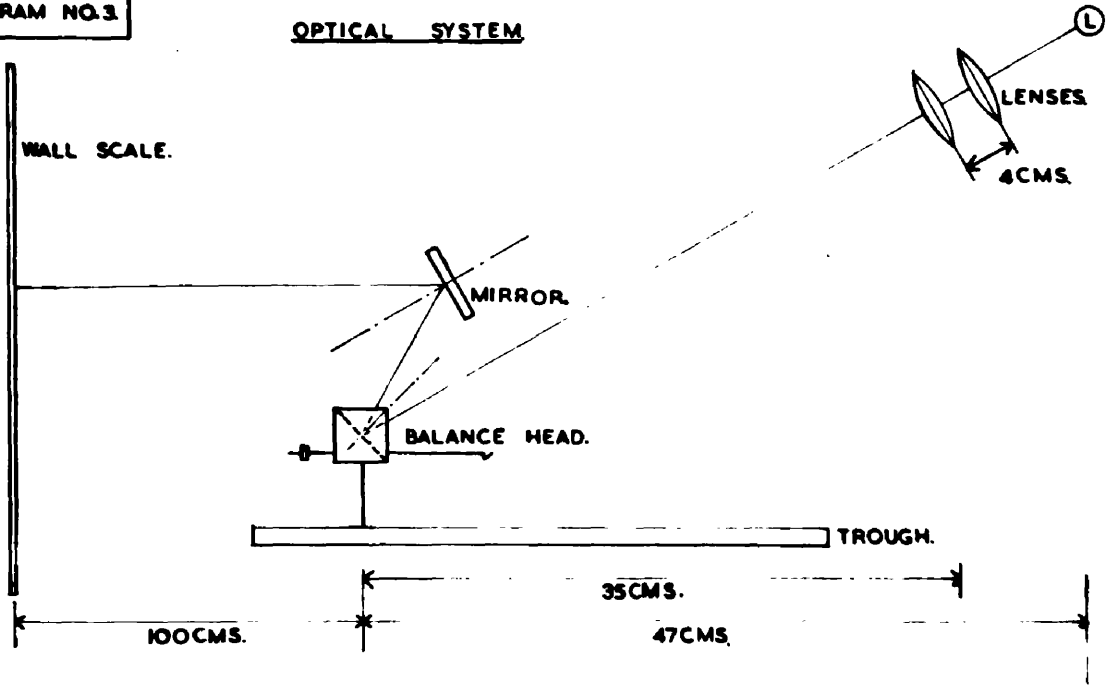
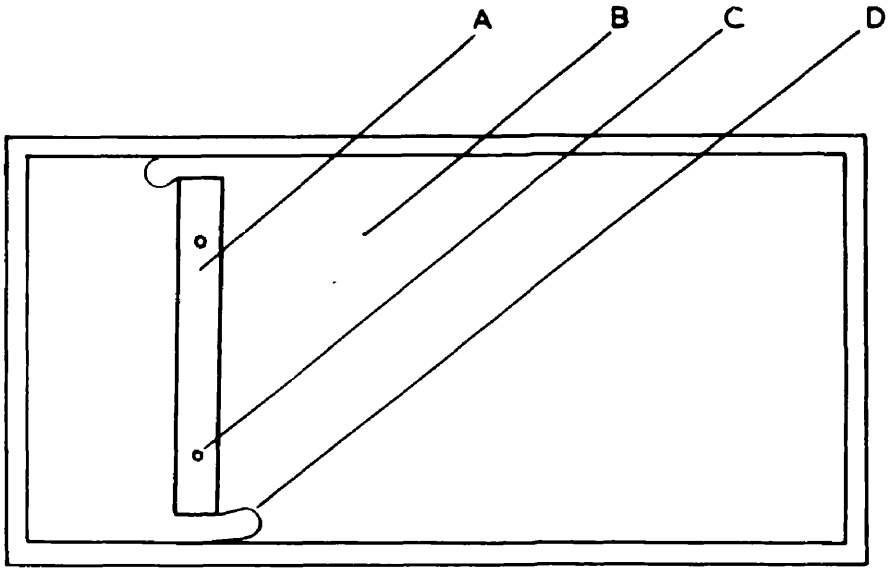


DIAGRAM No.4

ATTACHMENT OF FLOATING BARRIER TO THE TROUGH.



A — TEFLON BARRIER.
B — TROUGH.
C — HOLE IN BARRIER FOR FITTING BALANCE HEAD.
D — POLYTHENE THREAD.

DOUBLE TETRODE ELECTROMETER.

KEY TO VALVE CIRCUIT. (DIAGRAM NO. 6)

R1 and R2	25 K w.w. 5w.
R3	5 K w.w. Berko potentiometer
R4	250 w.w. Berko potentiometer
R5	3 K w.w. Berko potentiometer
M1	0 - 1 Milliammeter
M2	0 - 200 Milliammeter
E1	29v. NiFe Battery (later lead accumulators).
E2	10v Lead accumulators
T	Balanced double tetrode (Ferranti BDM 20 with internal and external guard rings earthed).
R6	470
R7	0 - 20 w.w. Berko potentiometer
G	Galvanometer
S	Earthing switch
X	Connection for calomel half-cell
Y	Connection for air electrode
P	Accurate 2v. potentiometer.

DIAGRAM No. 5.

POTENTIOMETER CONNECTIONS.

SWITCHES SET FOR SURFACE POTENTIAL MEASUREMENT.

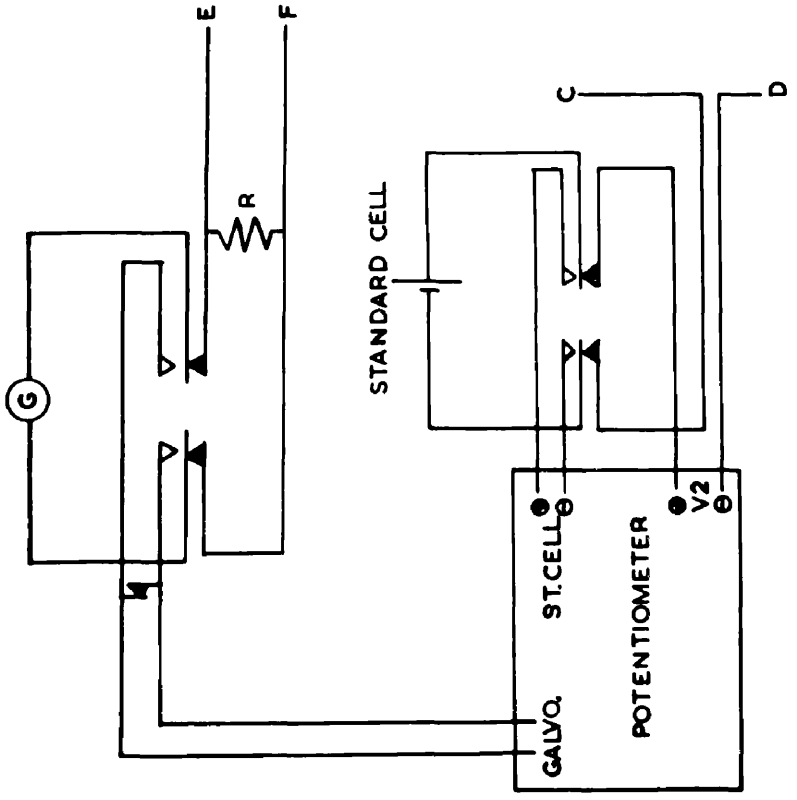
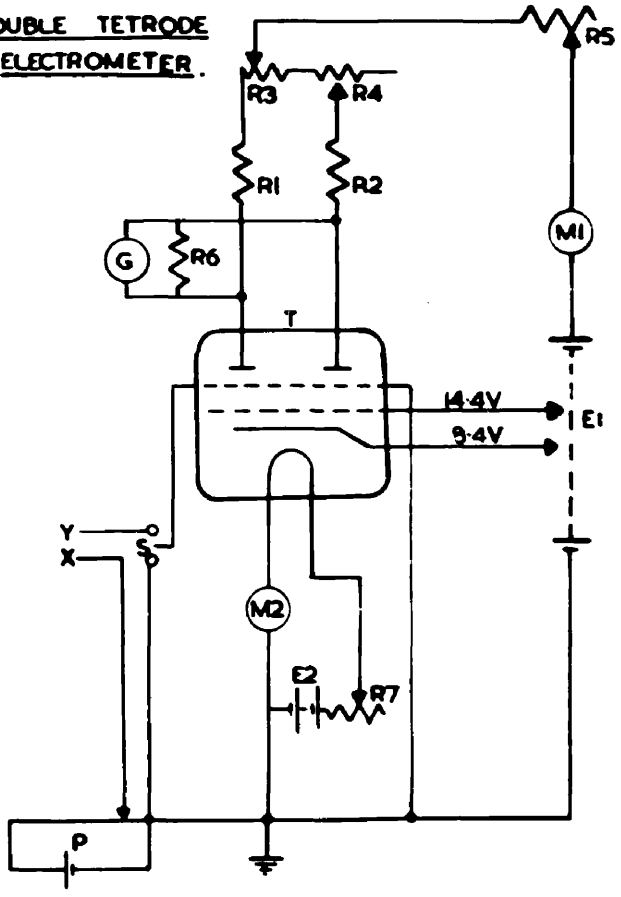


DIAGRAM NO.6.

DOUBLE TETRODE ELECTROMETER.



SECTION I

REACTIONS IN SURFACE FILMS OF ACETATES, KETONES AND CELLULOSE TRIACETATE, AND THEIR RELATION TO ADSORPTION BY CELLULOSE ACETATE.

Introduction

Although a number of ether and ester derivatives of cellulose are known and some are produced commercially, the acetate is the only derivative which finds wide application as a textile fibre. The nitrate has been produced in fibre form, but it has the disadvantage of being extremely inflammable. Two acetyl derivatives of cellulose are produced, cellulose triacetate and cellulose "diacetate"; the former being produced by treating cellulose, in the form of cotton linters, with a mixture of glacial acetic acid, acetic anhydride, and sulphuric acid, the latter by controlled partial hydrolysis of the triacetate. Fibres are produced by spinning a concentrated solution of "diacetate" in acetone, into a current of warm air. The two derivatives exhibit considerable differences in properties from the parent cellulose, for example in their dyeing characteristics.

The Structure of Cellulose Triacetate.

Cellulose is made up of long chains of glucose residues linked together in an alternating manner. Thus any particular group is in the same position in every second unit, corresponding to a spacing of 10.3 A. Each glucose residue has three hydroxyl groups available for acetylation and the commercial triacetate corresponds to the almost

completely acetylated material. In the "diacetate" material esterification is fairly uniform, each glucose residue containing at least two acetyl groups.

Astbury[43] has shown by X-ray examination that the commercial "diacetate" has a low degree of orientation, yielding an ill-defined and probably composite photograph, but it was also shown that for more highly oriented specimens the molecular period along the fibre axis is practically the same as that of cellulose itself, illustrating that the process of acetylation merely altered the side dimensions of the chain molecules.

Adsorption by Cellulose Acetate.

Acetyl celluloses are completely different in dyeing behaviour from the parent cellulose, this is considered to be due to the changes in the surface characteristics of the fibre on acetylation. Cellulose is hydrophilic and is considerably swollen in aqueous solutions, but the acetyl derivatives, are hydrophobic and are consequently little swollen in aqueous solutions. This is illustrated by a consideration of the water absorption of the two fibres; 8% at saturation for cellulose "diacetate" compared with 40% at saturation for viscose rayon (cellulose). Thus, in aqueous media the intermicellar canals are narrow and the entry of large dyé molecules, and their subsequent diffusion into the

fibre is severely restricted. Acetylation also alters the negative surface potential exhibited by cellulose in water, the acetyl derivatives having much higher negative potentials, which assist the repulsion of dye anions. For these reasons direct cotton dyes and most acid dyes leave the fibre uncoloured, but because of the high negative potential at the surface, the fibre adsorbs cationic basic dyes. Cross section examination of the fibre showed that the basic dye was confined to the outer skin and that no penetration had occurred[44].

It has been considered that cellulose "diacetate" in an aqueous dyebath contains no pores large enough to admit dye molecules, therefore, dyes which do colour the fibre must pass through the substance of the fibre itself, so that the process of dyeing may be considered as being analogous to the formation of a solid solution of dye in the fibre. A dyeing process of this nature is quite different from that of other fibres. This hypothesis has been supported by Kartaschoff[45], who observed that the fibre is dyed when it is shaken with dry dye powder. Furthermore, Knoevenagel[46] has found that with increasing concentration a constant partition ratio is observed for the distribution of aniline and phenol between the fibre phase and the solution in the same manner as the distribution of a solute between two immiscible solvents. Cellulose acetate has thus been considered to act as a solid

solvent, because if not, the amount of solute taken up should bear a logarithmic relation to that in solution (Freundlich isotherm). If, however, the Langmuir isotherm is applicable and if the number of adsorption sites is large then this isotherm also will be expected to give a constant partition coefficient at low concentration. Therefore the discrimination between adsorption and solution is not possible on the basis of these results alone.

Marsden and Urquhart[47] made a detailed study of the adsorption of phenol on cellulose acetate sheet material, each sheet being of different acetyl content. The increase in volume of the sheets and the amounts of phenol and water adsorbed were determined. In contrast to the work of Knoevenagel they did not find a constant partition of phenol between the two phases. They postulated a hydrogen bond mechanism of adsorption, the bond being between the undissociated phenol molecule and the carbonyl oxygen of the acetate group. (They did not consider any ionic theory of swelling to be applicable, since phenol is capable of producing a large swelling from solution in petrol ether, which has no swelling action itself and is a solvent in which phenol is undissociated.) The heat of reaction values, however, are lower than those usually associated with hydrogen bonding. The phenol molecules are adsorbed on the intermicellary canals existing in the fibre but are too bulky to penetrate

the micelles until the swelling pressure disrupts the fibre. It is therefore unlikely that bulky dye molecules of even larger size than phenol will be able to diffuse through the unswollen fibre substance, thus this work tends to disprove the solid solution theory.

The hydrogen bond theory of Marsden and Urquhart has been extended by Vickerstaff[48] to cover the dyeing of cellulose acetate fibre with the commonly employed 'disperse' dyes. These are anthraquinone or azo-derivatives devoid of powerful water-solubilizing groups, and are applied as dispersions in water. It is considered that they penetrate the fibre by virtue of their extremely slight water-solubility[49]. Most of these dyes contain potential proton-donating groups, usually -OH and $-NH_2$, which might well combine in the manner suggested for phenol. There is, however, other evidence which tends to cast doubt upon the exact characterisation of the hydrogen-bonding mechanism in this substrate. For example:

(i) certain dyes which have affinity for cellulose acetate, e.g. nitroazobenzene derivatives (for formulae, see Knight[50]), have no hydrogen atom in their molecule available for bonding;

(ii) proton-acceptors, e.g. azobenzene or benzoquinone are capable of forming complexes with aliphatic acetates, presumably through a hydrogen atom of the methyl

residue in the acetyl group, which is activated by the adjacent carbonyl oxygen atom[51]. Thus, the methyl group acts as a proton donor, and the C - H . . . O bond formed would be expected to be weak.

Furthermore, recent investigations on hydrogen bond complex formation[52] support this theory and it has been found that there is no conclusive evidence of a carbonyl oxygen atom forming a hydrogen bond in water. Campbell and Cathcart[53] have shown that a bond of the form -O - H . . . O can exist in water, and they have suggested that proton-donors bond with cellulose acetate at the ether oxygen atom of the acetyl group. The -C - H . . . bond, which is probably a weaker one, is therefore likely to be formed with proton-acceptors.

Majury[54] has studied the dyeing of cellulose acetate with non-ionic dyes and has postulated, from their absolute heats of association, that the bond energies are chiefly ascribable to interactions between the permanent dipoles of the carbonyl groups in the acetate and permanent or induced dipoles in the dye molecule. Majury has also shown that the apparent diffusion coefficients of dyes have a twofold activation energy; one part attributable to the free energy of dyeing and the other to mechanical obstruction of the diffusing dye by the body of the substrate[55]. From

these results it has been suggested that a dye molecule penetrating cellulose acetate undergoes alternate adsorption and solution by the water.

A dyeing mechanism in terms of non-polar bonding between the hydrophobic surfaces of the dye and the fibre has been suggested[56]. This theory has been extended to explain the dyeing mechanism of other fibres, and helps to account for the increase of fibre affinity for dyes containing long saturated alkyl chains which cannot be interpreted in terms of polar forces. It has, however, also been pointed out that dye affinity is not as closely related to molecular weight as it would be if only non-polar forces were operating[57].

Results and Discussion.

Previous Work.

Although the monolayer film-forming properties of carbohydrates and derivatives have been the subject of considerable study, few reports have been made on dye interaction with these monolayers. Carbohydrate derivatives have been spread from organic solvents by Katz and Samwel[58], and Adam and Harding[59].

Cellulose yields only a surface precipitate from cuprammonium hydroxide solution, because the internal cohesion is large and is considered to be due to the existence of inter-chain hydrogen bonding between hydroxyl groups along the molecular chains. With removal of hydroxyl groups by substitution of ester or ether groups, such bonding is decreased and spreading is facilitated. Although the results of the early work show reasonable agreement, Adam has expressed doubt whether these compounds all give uniformly spread films, since in some, such as cellulose triacetate, unspread patches may be seen under dark-field illumination. Katz, however, claims that identical specific areas were found with various samples of cellulose acetate, although in some cases the films were optically clear, while in others heterogeneous patches were visible. Hence, the amount of unspread material seems to be insignificant.

Adam and Harding[59] spread cellulose acetate on solutions of methyl violet and malachite green, to see whether the dye had any influence on the nature of the film, but the surfaces of these solutions became dirty so rapidly that no accurate experiments could be made, except on methyl violet of 0.004%. On this solution the films were indistinguishable from those on water. On solutions of picric acid, however, the surface potential was markedly lowered with trimethyl and triacetyl cellulose; the amount of lowering increased with increasing concentration of the picric acid. The surface pressure was not perceptibly affected by picric acid. They explain the effect of the picric acid in diminishing the surface potential as an adsorption of the acid or its anion below the film, the film exercising an orienting effect on the molecules or ions of picric acid. There did not appear to be a stoichiometric chemical combination between the picric acid and the film, but the Freundlich isotherm could be applied with fair accuracy.

Previous workers in this laboratory have shown that certain dye molecules dissolved in the sub-solution are capable of penetrating films of cetyl acetate[51]. This substance was used as a model compound to represent cellulose triacetate and from the results obtained a dyeing mechanism has been suggested. These initial investigations have been extended by Cameron[60], and the present author, working in

conjunction with Cameron has continued these studies.

Cameron prepared films of cetyl acetate and stearyl ketones on solutions of various solutes and he observed the changes in the force-area curves, from which he gained information on the interactions at the keto- and acetyl groups. As these two substances must have almost identical non-polar attraction for solutes in the aqueous phase, he considered that any difference between their films in penetrability or expansion by the solute must be attributable to differences in polar attraction of the keto- and acetyl groups. Polar attraction by the keto-group is in fact likely to be very low, because ketones do not appear to form hydrogen-bond complexes with other solutes in water[52], whereas acetates do[61].

Schulman and Rideal[62] have shown that for penetration of a monolayer there must be present in the penetrant molecule both polar and non-polar attraction for the film molecules. Thus the penetration of monolayers is specific, and Cameron expected that substances with both polar and non-polar attraction would expand films of cetyl acetate, but not films of the stearyl ketones.

As the work of the present author is a continuation of Cameron's work, it is deemed necessary at this stage to summarise his findings (see Graphs No.1-5). The solutes he

used are conveniently classified according to the size of the hydrophobic residue in their molecules.

Solutes with small molecules.

There can be little non-polar attraction of these molecules for the monolayers and their expansion effects must be almost entirely due to hydrogen-bond cross-linking. The ketone films are almost unaffected by them, but the cellulose triacetate and the cetyl acetate films are expanded, so that the prediction of higher polar attraction in water by the acetate group than by the keto-group is confirmed. The solutes he used were ethylene glycol and mesaconic acid.

Solutes with medium-sized molecules.

Phenol and quinol have considerable effect on acetate films, presumably by hydrogen bonding with the head groups therein; quinol no doubt acts as a cross-linking agent, as it does for some films of azo-compounds[63]. Benzene-sulphonic acid, benzoquinone, pyridine and sucrose produce small effects and their hydrogen-bonding power is considered weak. Methylethyl ketone, which is regarded as non-hydrogen bonding in water, produces a very small effect on the cellulose triacetate film, this illustrates that the triacetate has little ability to adsorb water-soluble solutes by other than hydrogen-bond forces.

Solutes with large molecules.

Cameron also used, in the sub-solution, basic dyes and some acid dyes with several potential hydrogen-bonding groups. He found that ionic compounds expand the ketone films, presumably by non-polar association between their hydrophobic residues and the alkyl chains of the ketone. Cetyl acetate, however, is affected considerably more than the ketones, clearly by a combination of polar and non-polar forces. The triacetate film is less expanded by the solutes with large molecules than is the cetyl acetate film, because of its smaller proportion of hydrophobic residue, and a comparison of effects produced by these solutes upon the several films shows that non-polar association probably plays little part in adsorption at the triacetate film.

Present Work.

Action of Tannic Acid.

The hydrogen-bonding properties of tannic acid with surface films at the air-water interface have been the subject of considerable study by other authors by various means (see, e.g., Section II and [64]). Protein films are made less compressible by tannic acid, which is adsorbed beneath the film and condenses together a number of protein chain molecules in a horizontal raft-like structure. The author investigated the action of tannic acid on films of cellulose triacetate to

see if a similar condensation effect was exercised by proton donation from the many hydroxyl groups of the acid to acceptor groups in the cellulose triacetate. In this case a somewhat different effect is demonstrated. The force-area curve of the cellulose triacetate was not perceptibly altered by the tannic acid (Graph No.6). Several experiments were made with different concentrations of tannic acid and with different time allowance for interaction, but no significant changes in the film could be detected.

It is well established that on water cellulose triacetate polymer chains are incompletely separated and do not form a true monolayer; e.g., the apparent area per glucosidic residue, 43.5 A^2 (the author's value for material with acetic acid value 62%, which corresponds to fully acetylated material) is only about half the theoretical value[65]. The chains are probably present as micellar bundles, but these are disaggregated by powerful hydrogen-bonding agents, e.g., urea. Cellulose triacetate films on 4 M. urea were next prepared and it was found that the area per glucosidic residue was increased from 43.5 A^2 to 101 A^2, this is in agreement with the results of Borgin and Johnston[65]. When tannic acid is present under these conditions (Graph No.7) there is slight expansion of the film, which is slightly more compressible, indicating possible bonding between the tannic acid and film. It is considered

that this effect is measurable only in the presente of urea, when the triacetate is completely spread, otherwise the tannic acid molecules are attached entirely beneath the triacetate micelles and, being much smaller than the latter, do not interfere with their compression or orientation.

Further studies of the interaction between tannic acid and monolayers were made, but limited information was gained. The force-area characteristics of the following long chain compounds were determined on water and with tannic acid dissolved in the aqueous phase: cetyl acetate (Graph No.8), N-methylstearamide (Graph No.9), stearyl alcohol (Graph No.10), and cetylaniline (Graph No.10). The films of the long chain monomers are slightly expanded at high pressures by tannic acid, and very considerably expanded at low pressures they are madd considerably more compressible in all cases except cetylaniline (cf. Table I). It is suggested that at low pressures gaseous films of the hydrogen-bond complex of tannic acid with film monomer are formed, but with increasing pressure the film molecules tend to condense into the orientation normally taken up on water alone, with the tannic acid molecules bonded beneath the film. Thus the upper part of the force-area curves for films on water or tannic acid solution tend to coincide, showing that the acid has then become entirely forced out from the film into the underlying solution. The film of cetylaniline (Graph No.10) is made less

Table I

Substrate	Cellulose Triacetate				Cetylaniline				Cetyl Acetate				N-Methyl-stearamide				Stearyl Alcohol			
	a*			b/	a			b	a			b	a			b	a			b
Water	45	61	42	0.5	25	32	25	0.6	23	40	21	0.4	27	38	24	0.3	22	23	20	0.01
Tannic Acid	45	60	42	0.5	29	(37)	26	0.3	28	(100)	24	0.7	31	65	24	0.4	26	31	25	0.4
Concentration of tannic acid (mg./l.)	15				44				44				46				46			

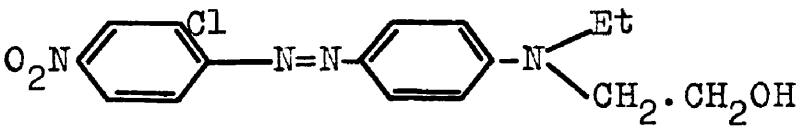
x The three figures under a show, in order: Molecular area (A^2) at zero compression, at commencement of development of measurable surface pressure, and at lowest point of upper linear part of force-area curve.

/ Film compressibility, b, is expressed as slope of upper section of force-area curve (units A^2/dynes/cm.)

compressible by tannic acid. The cause is obscure; perhaps film and solute aromatic nuclei association or especially strong $-NH_2....OH$ bonds.

Interaction of Dispersol fast crimson B.

By several different techniques the interaction between Dispersol fast crimson B and cellulose triacetate films was studied. The dye



has low water solubility and is applied to cellulose acetate from a dispersion. Films were prepared on solutions containing 6 mg./l. of this dye dissolved in water containing 2% ethanol to ensure solubilisation. On this solution the films were indistinguishable from those on water. To test for penetration, films were held at large areas for several hours on this solution, but pressure increment amounted to less than 0.5 dynes, and interpretation of alterations of film characteristics is then rendered difficult owing to contamination of the surface. Injecting various amounts of the dye under the film at different pressures produced no perceptible alteration in the film. Finally, the dye was mixed with cellulose triacetate (in ratio of two glucosidic residues to one molecule of dye) and spread on water; the F/A curve was then

the same as that of the triacetate alone on water (Graph No.11). The dye is very substantive to cellulose acetate, and it should therefore be bonded to the film. These results are somewhat surprising at first consideration, especially since the dye alone is surface-active and is capable of forming a condensed film (Graph No.12). The extrapolated area of 34 A^2 agrees closely with the value (32 A^2) estimated from models, for orientation on the hydroxyl group. Pressure steadily falls owing to the slow dissolution of the dye in the water.

If it is assumed that bonding between dye and acetate takes place (this is most certainly likely to be true from dyeing considerations), then it appears that the film exercises a powerful orienting effect on the molecules of the dye, causing them to lie flat, fitting exactly under the glucosidic residues, with no possibility of penetration.

Since completion of this work, support has been added to the above hypothesis with the recent findings of Tilak and Rao[66]. They found that certain non-planar dyes were not substantive to cellulose acetate, whereas, on the other hand, closely related planar dyes were quite substantive (see later).

Action of Non-ionic and Ionic Dyes upon Monolayers.

The above results show that a solute with a planar molecule and multiple points of attachment for hydrogen bonds around its periphery, as tannic acid has, does not necessarily cause much change in the area or compressibility of films of aliphatic compounds, including acetates, even though it is capable of forming bonds with the film molecules. Therefore, the fact that no change is observed in cellulose triacetate films when the highly substantive disperse dye is added is not inconsistent with a dye-acetate hydrogen-bond attachment. Cameron found that ionic groups in the dye (sulphate ester or sulphonate) prevent this "raft" type of attachment of dye beneath cellulose acetate, and considerable expansion occurs. This is considered to be due to the effect of solvated water around the ionic groups, which prevents the necessary close approach of the two reacting molecules over their whole areas. Instead, the solute molecules penetrate the film between the individual chains in such a manner that individual acetate groups can become attached to hydrogen-bonding centres in the solute molecule and the ionic groups remain in the water below.

From these findings of Cameron and the writer certain tentative conclusions may be drawn, and certain hypotheses are suggested to explain some of the phenomena of

dye adsorption by cellulose acetates.

Conclusions.

It is long established that the suitability of a dye for cellulose acetate fibres is closely connected with low ionising power. Thus the disperse dyes, which have polar, but not ionic, groups, dye all forms of cellulose acetate, whereas dyes having an ionisable group do not dye cellulose triacetate satisfactorily. They dye the normal secondary acetate well if they have only a weakly ionisable group (e.g. sulphate, $-O.SO_3Na$) in their molecules, but not if the strongly ionisable sulphonate group ($-SO_3Na$) is present. This fall in effectiveness of dyes with increasing ionisation has usually been attributed to their inability to bond to cellulose acetate because they are too firmly held in the water.

From the above results, it is found that strongly ionised dyes, which are not adsorbed by cellulose triacetate as a fibre, are readily adsorbed by it when it is present as a monolayer on water. The monolayer expands in presence of a dissolved ionic dye, but it is apparently unaffected by a highly substantive disperse dye. The following hypotheses are suggested to account for these facts -

(a) The ionised dyes are adsorbed by penetration between

the acetate groups in the film, the ionic groups remaining dissolved in the water below.

(b) The disperse dye is adsorbed flat against the underside of the acetylated glucosidic residues in the film, so that the latter is undisturbed in area. The ionised dyes are unable to take up this orientation on account of the interference of the solvated water they carry.

(c) The proportion of water-accessible non-crystalline regions in cellulose triacetate fibre is so low that if a dye can penetrate only those regions it is of no practical value. To produce an adequate colouration the dye must also penetrate some of the more crystalline regions, which it can do only by swelling the structure through breakage of inter-chain polar (e.g. hydrogen) bonds. For this to occur there must be high affinity arising from "multiple-point" dye-to-polymer attachment by several bonds per dye molecule. If an ionised group is present its accompanying solvated water prevents the necessary close approach of dye and triacetate chain, and 'dyeing' is confined to the amorphous regions.

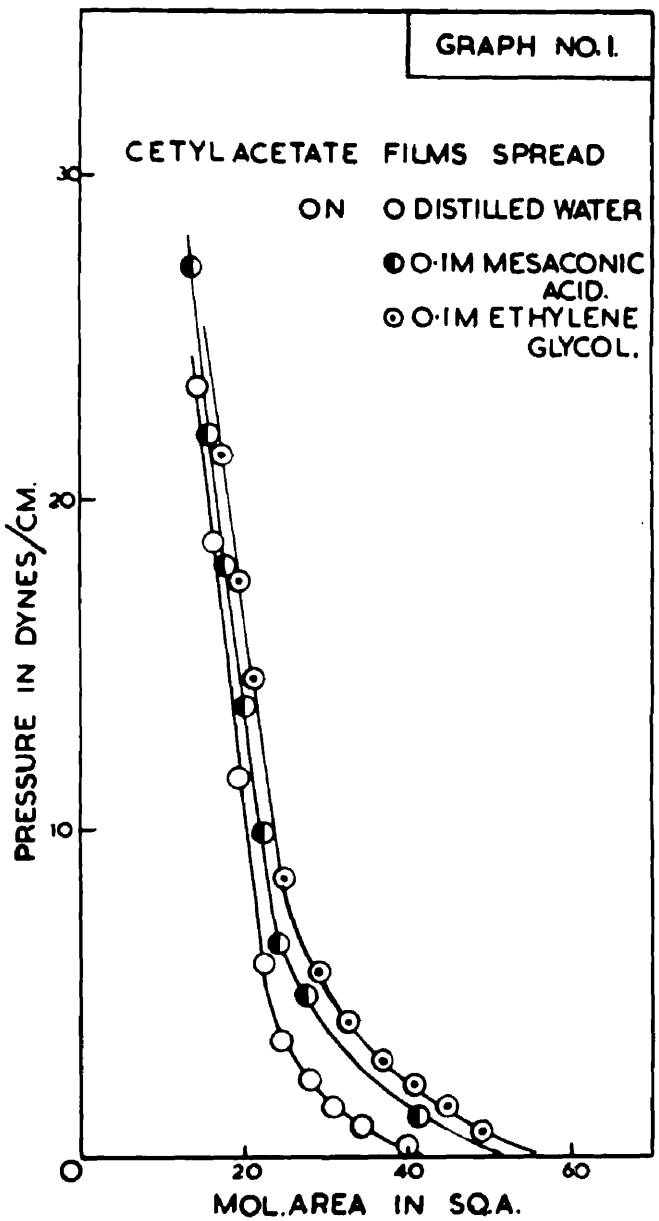
Results of measurements of the difference in expansive effects of dyes with films of cellulose triacetate and cetyl acetate, and of long chain ketones, are consistent with high polar and low non-polar attraction between dyes and cellulose acetates.

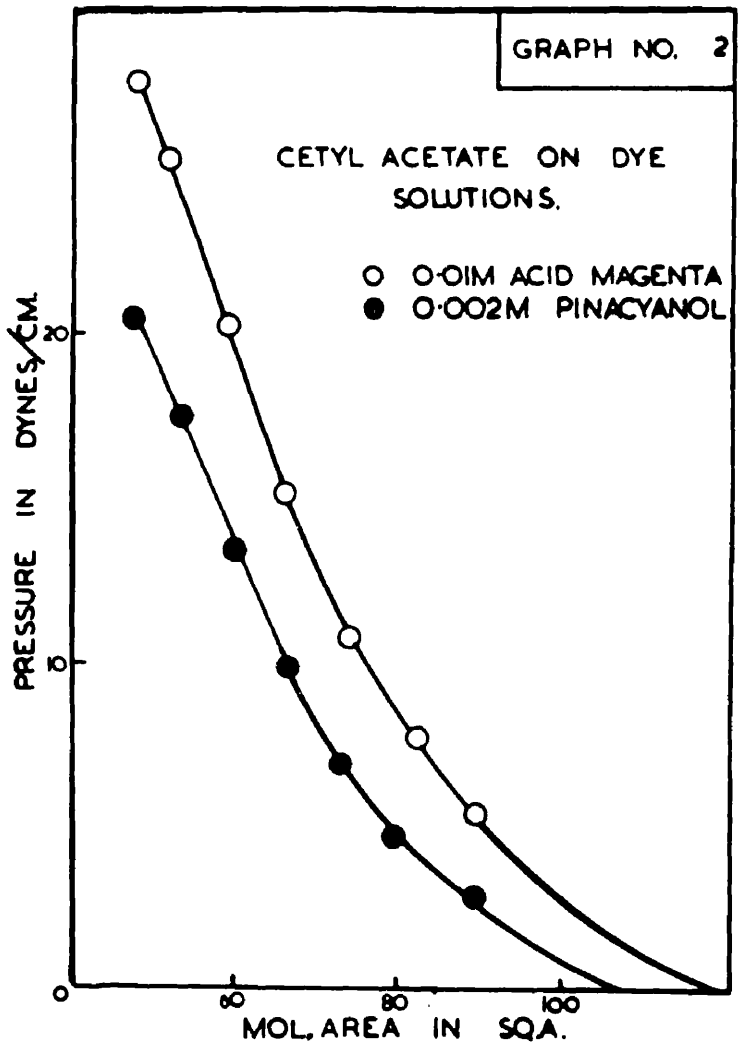
As previously mentioned, more recent work has given support to these suggestions. Tilak and Rao[66] have reported certain properties of non-planar quinonoid dyes having a phenylene nucleus oriented perpendicular to the longest axis of the molecule, in comparison with those of closely related planar dyes. They observe that the planar dyes are substantive to cellulose when used as vat dyes and to cellulose acetate when used as disperse dyes, but the non-planar ones are not substantive to either material.

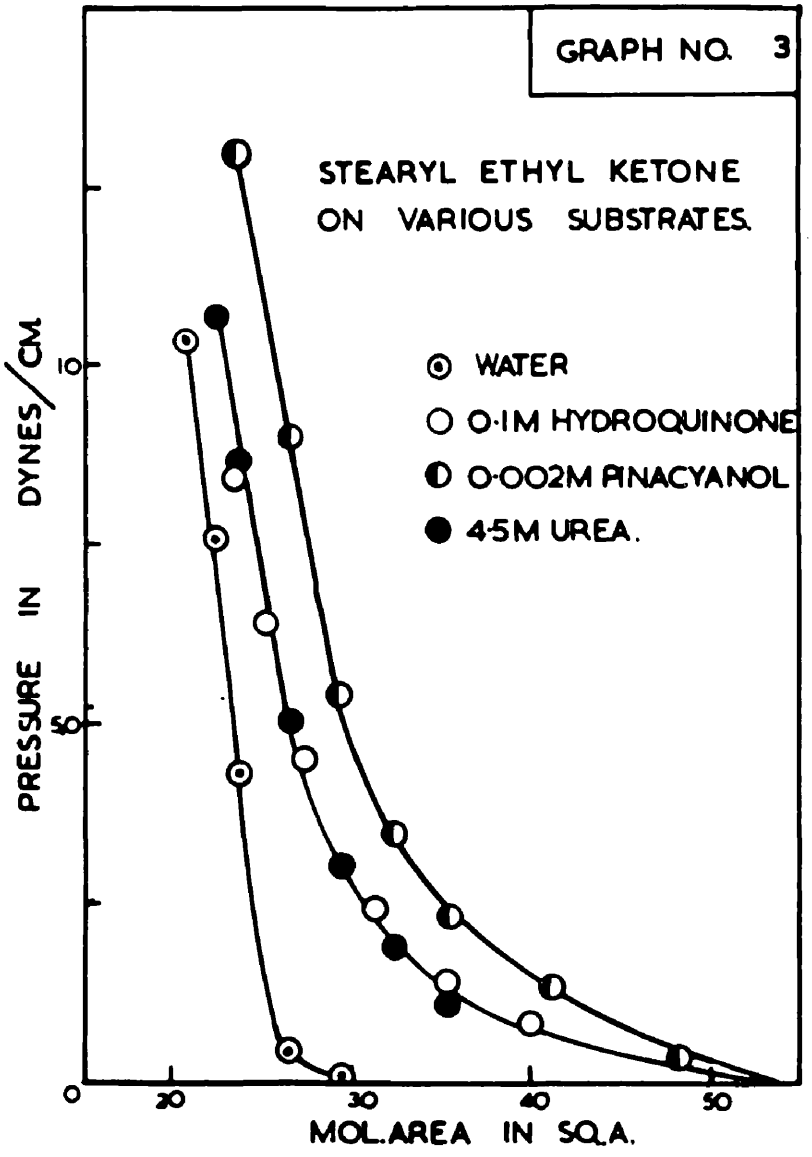
The behaviour of these compounds with cellulose acetate appears to be in accordance with the above hypothesis of a 'multipoint' dye-fibre association, the absence of substantivity of the non-planar compounds being due to the steric effect suggested to account for the non-substantivity of ionised dyes.

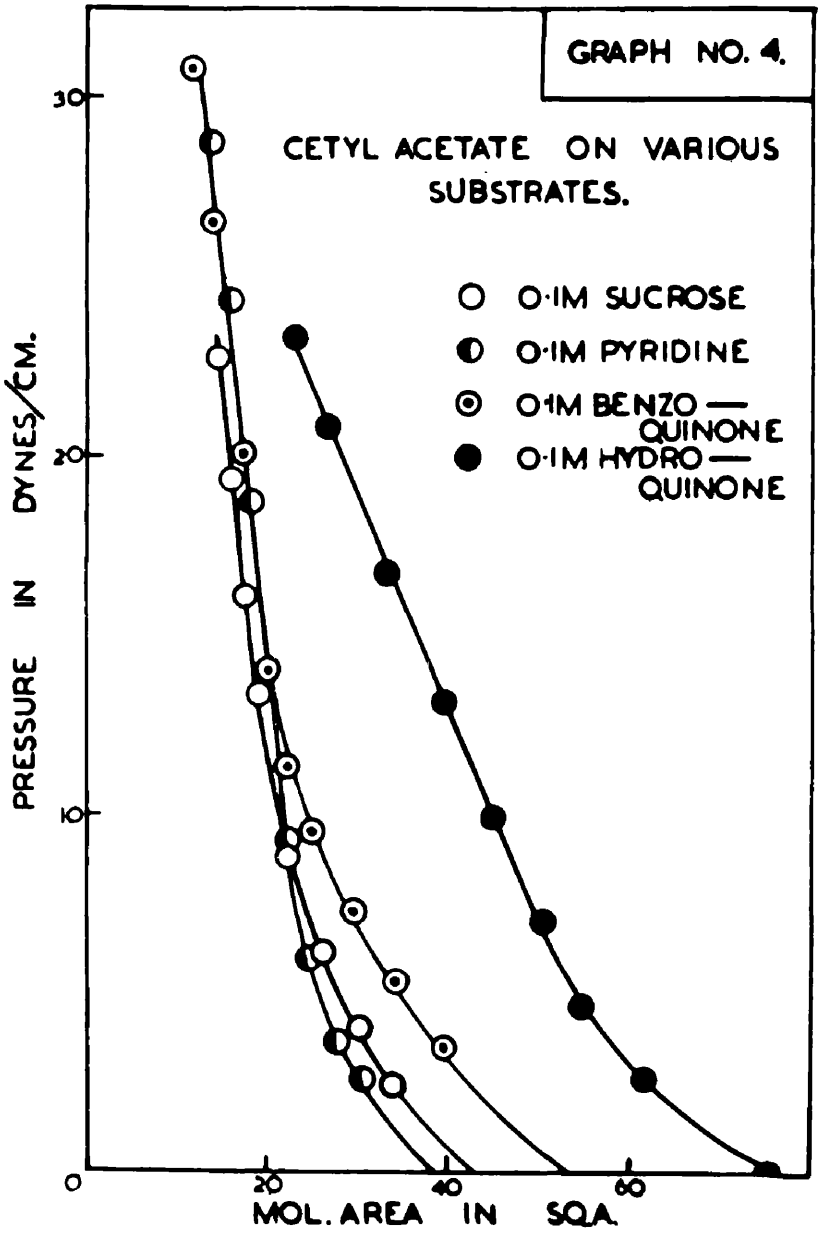
The dichroism observed with dyed oriented cellulose acetate fibres[48,67] is consistent with this form of association.

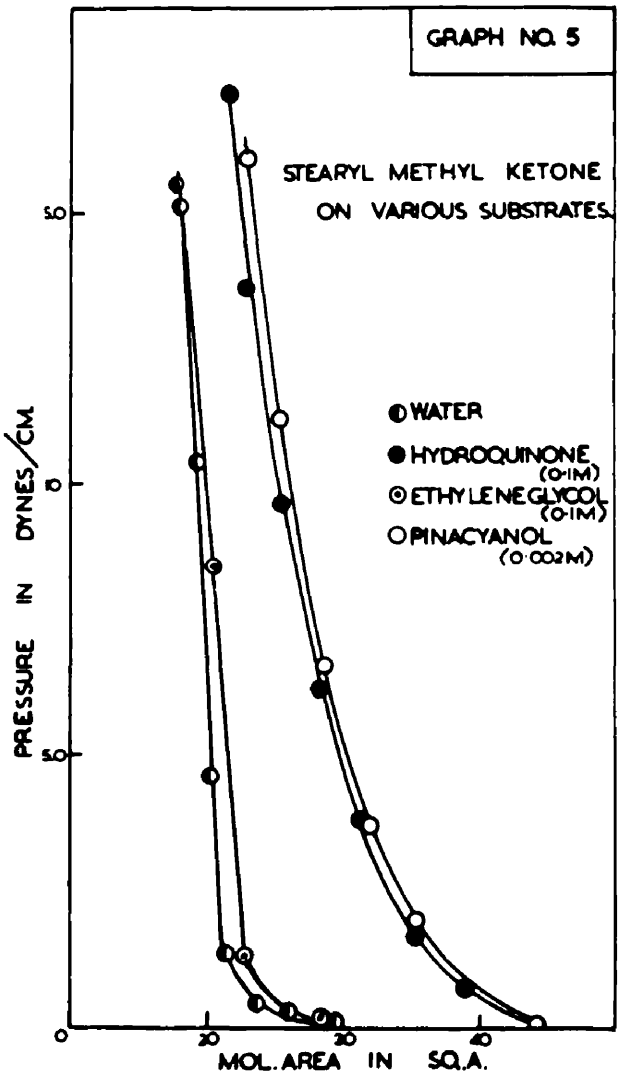
EXPERIMENTAL RESULTS

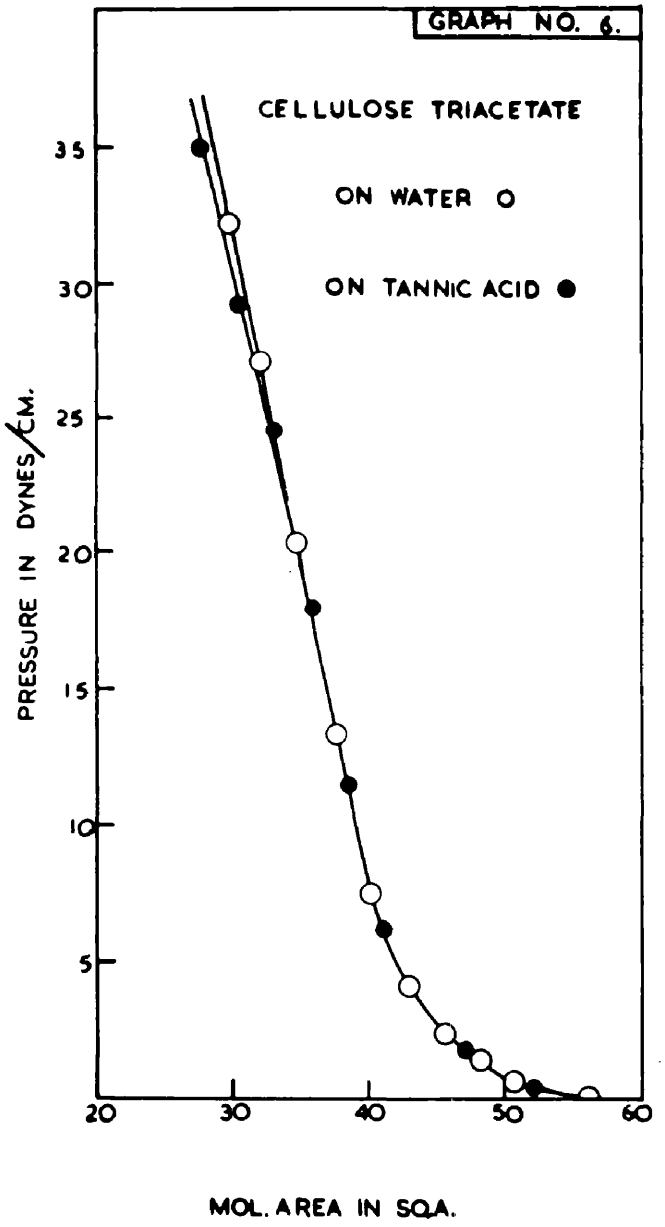

GRAPH NO. 1.
CETYL ACETATE FILMS SPREAD
ON O DISTILLED WATER
◐ O·1M MESACONIC ACID.
⊙ O·1M ETHYLENE GLYCOL.
PRESSURE IN DYNES/CM.
30
20
10
0
20
40
60
MOL. AREA IN SQ.A.

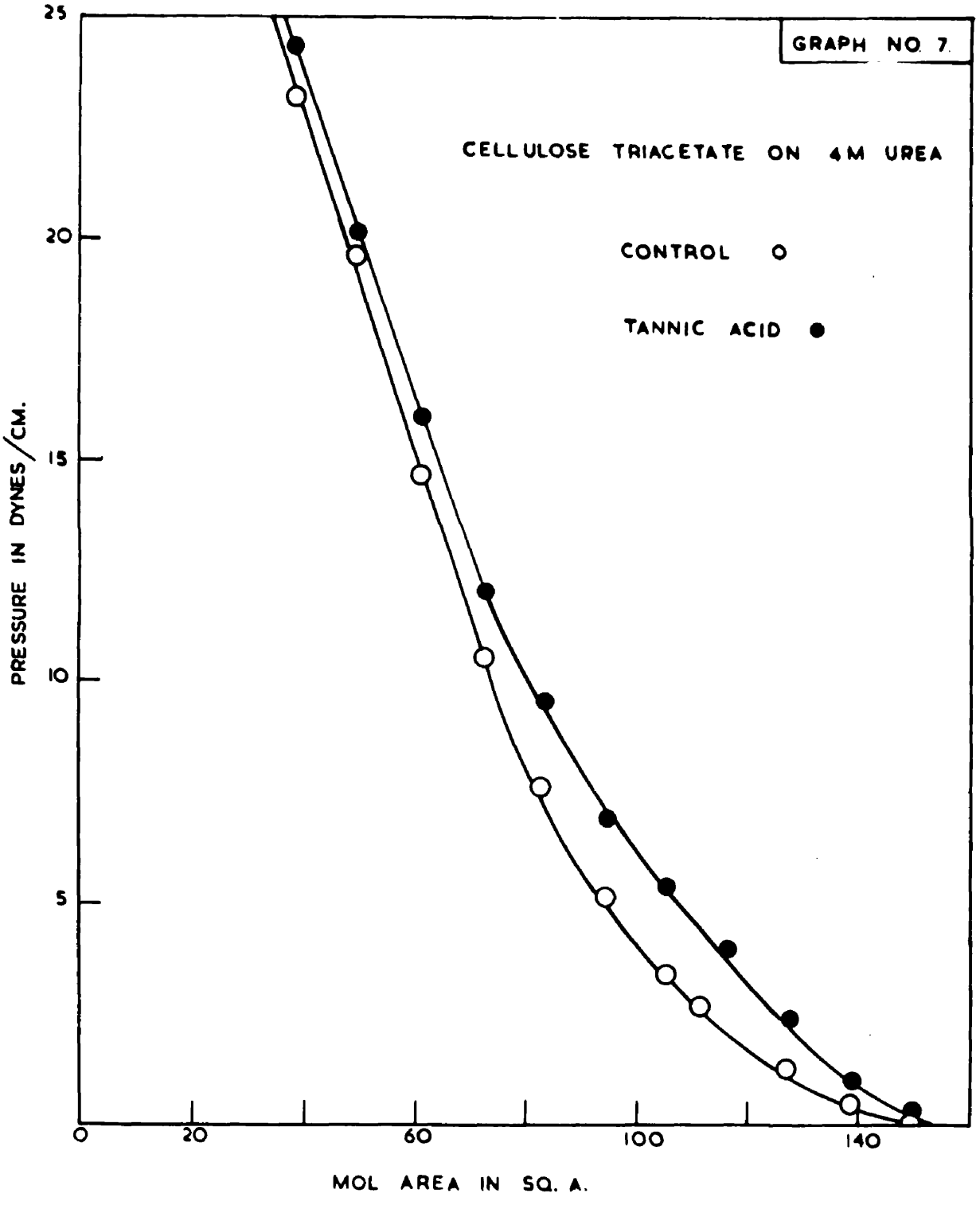

GRAPH NO. 2
CETYL ACETATE ON DYE SOLUTIONS.
O O·01M ACID MAGENTA
● O·002M PINACYANOL
PRESSURE IN DYNES/CM.
20
10
0
60
80
100
MOL. AREA IN SQ.A.

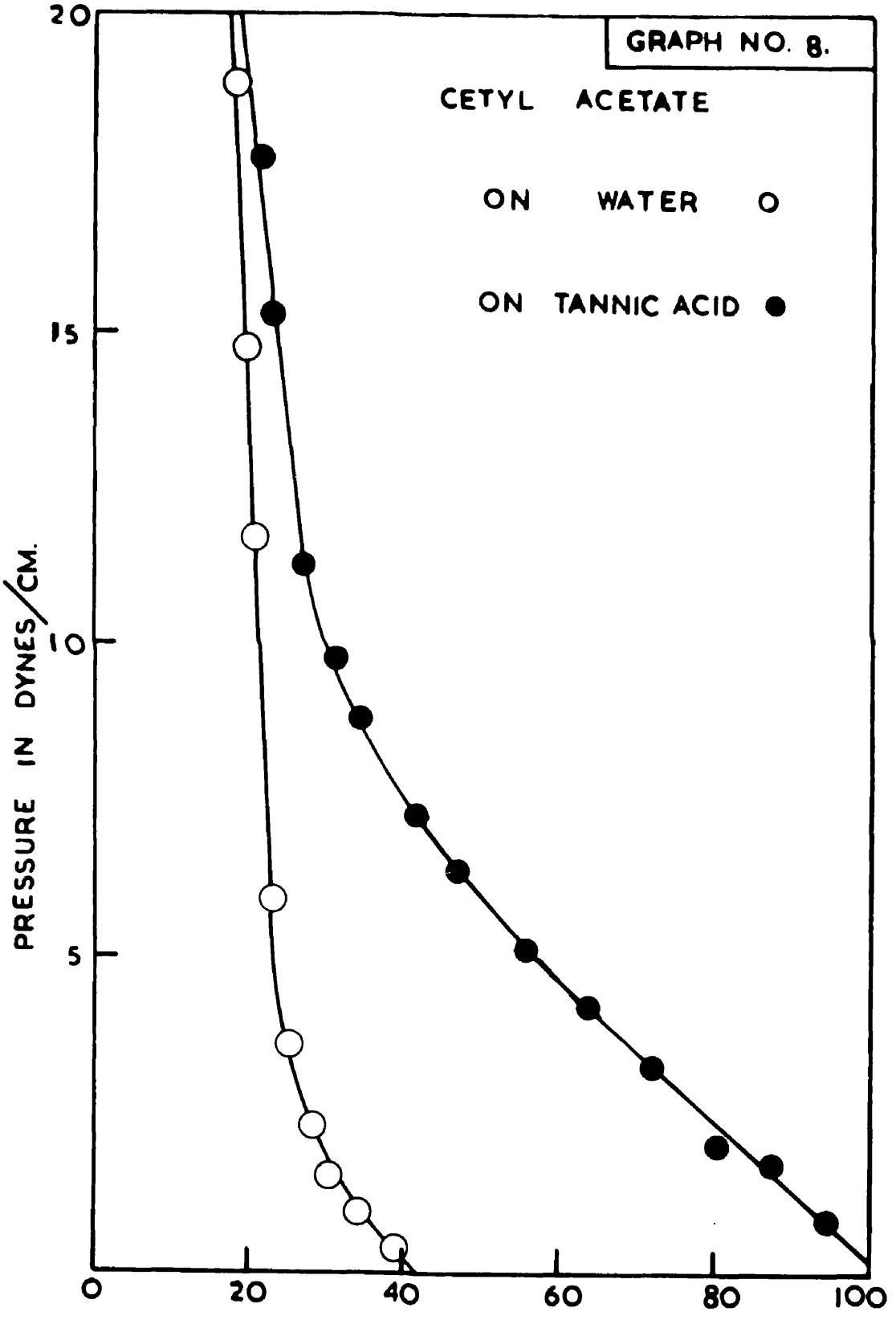

GRAPH NO. 3
STEARYL ETHYL KETONE
ON VARIOUS SUBSTRATES.
WATER
0·1M HYDROQUINONE
0·002M PINACYANOL
4·5M UREA.
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.
0
10
20
30
40
50

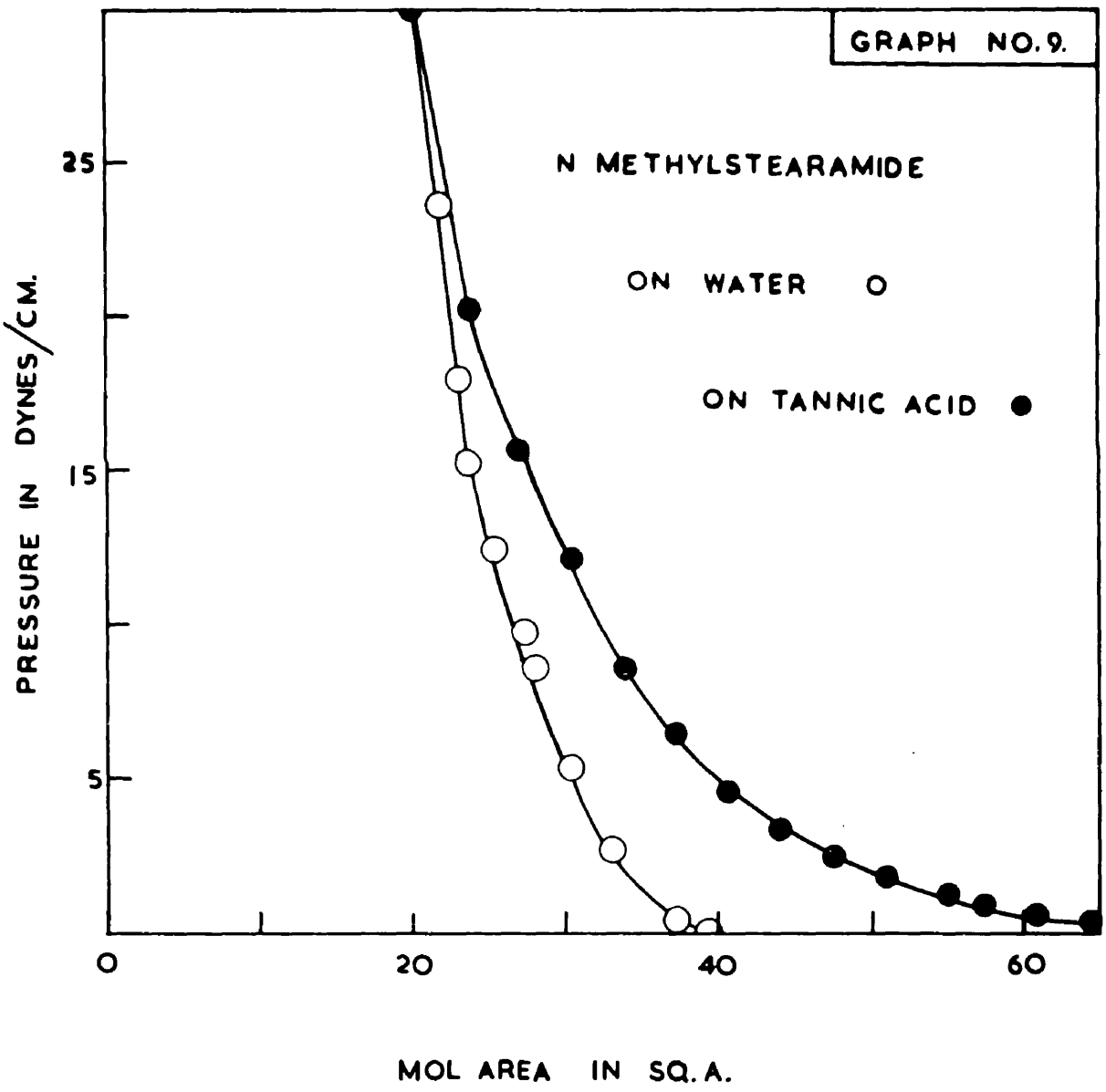

GRAPH NO. 4.
CETYL ACETATE ON VARIOUS
SUBSTRATES.
0·1M SUCROSE
0·1M PYRIDINE
0·1M BENZO — QUINONE
0·1M HYDRO — QUINONE
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.
0
10
20
30
40
60


GRAPH NO. 5
STEARYL METHYL KETONE
ON VARIOUS SUBSTRATES.
WATER
HYDROQUINONE (0·1M)
ETHYLENE GLYCOL (0·1M)
PINACYANOL (0·002M)
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.


GRAPH NO. 6.
CELLULOSE TRIACETATE
ON WATER O
ON TANNIC ACID ●
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.


GRAPH NO. 7.
CELLULOSE TRIACETATE ON 4M UREA
CONTROL O
TANNIC ACID ●
PRESSURE IN DYNES/CM.
25
20
15
10
5
0
20
60
100
140
MOL AREA IN SQ. A.

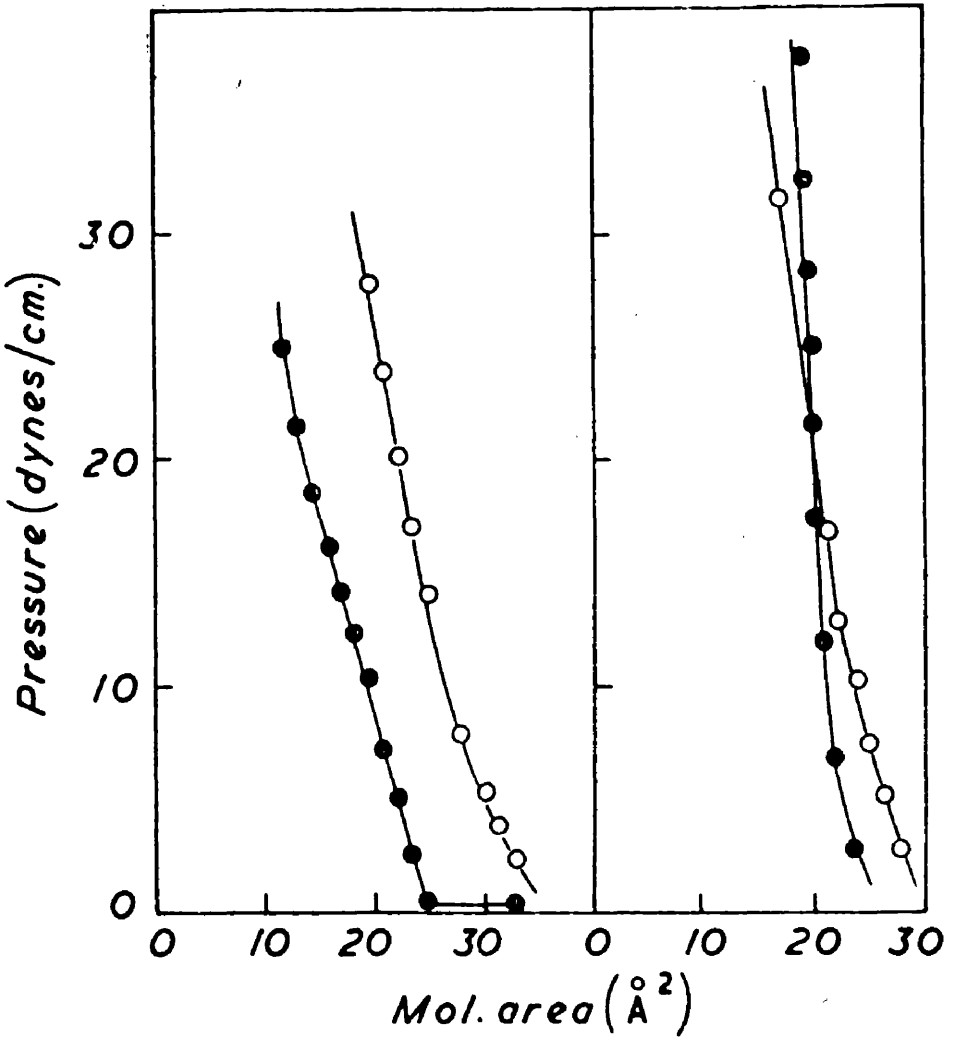

GRAPH NO. 8.
CETYL ACETATE
ON WATER O
ON TANNIC ACID ●
PRESSURE IN DYNES/CM.
20
15
10
5
0
20
40
60
80
100
MOL AREA IN SQ. A.

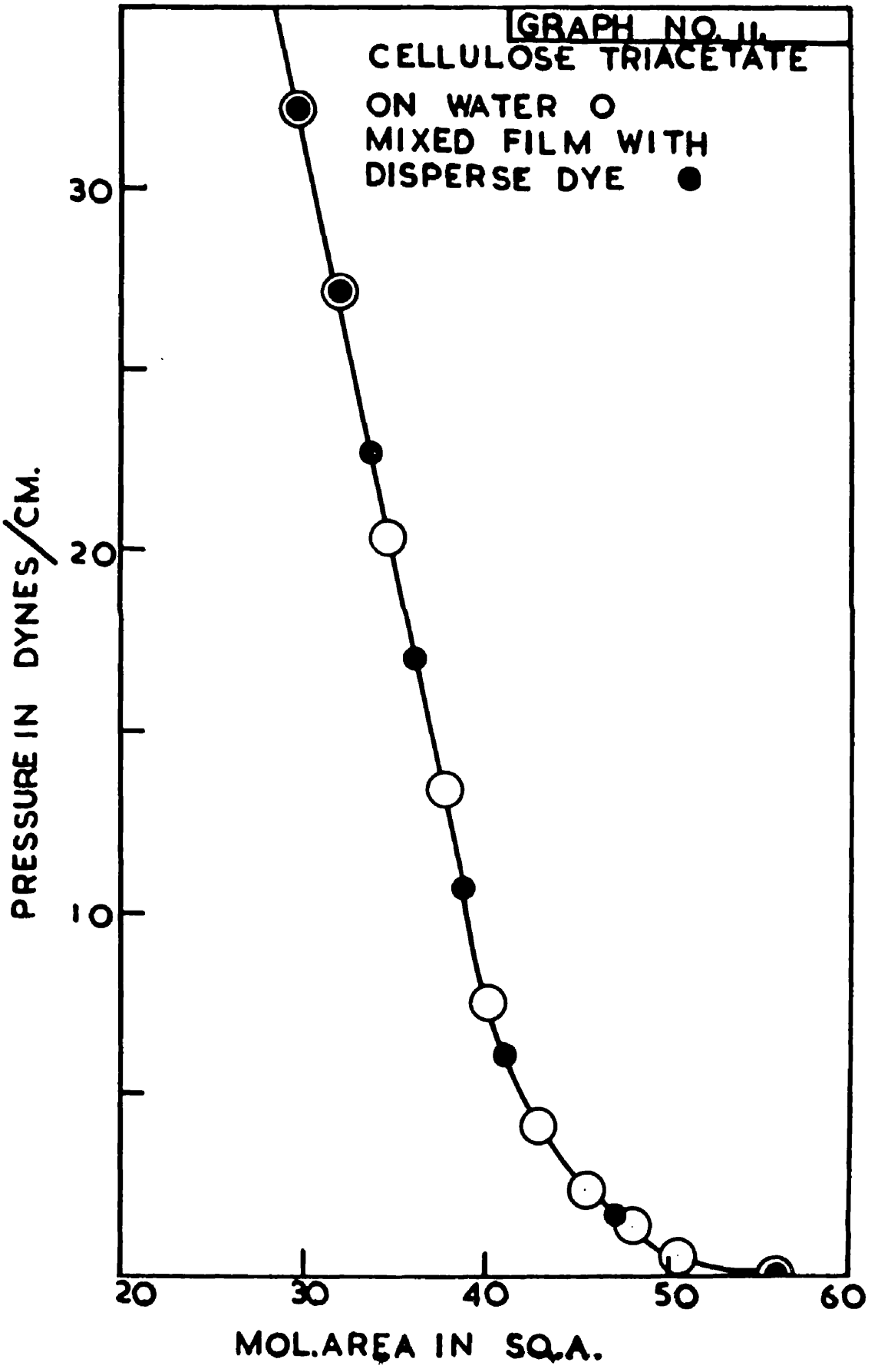

GRAPH NO. 9.
N METHYLSTEARAMIDE
ON WATER O
ON TANNIC ACID ●
PRESSURE IN DYNES/CM.
25
15
5
0
20
40
60
MOL AREA IN SQ. A.

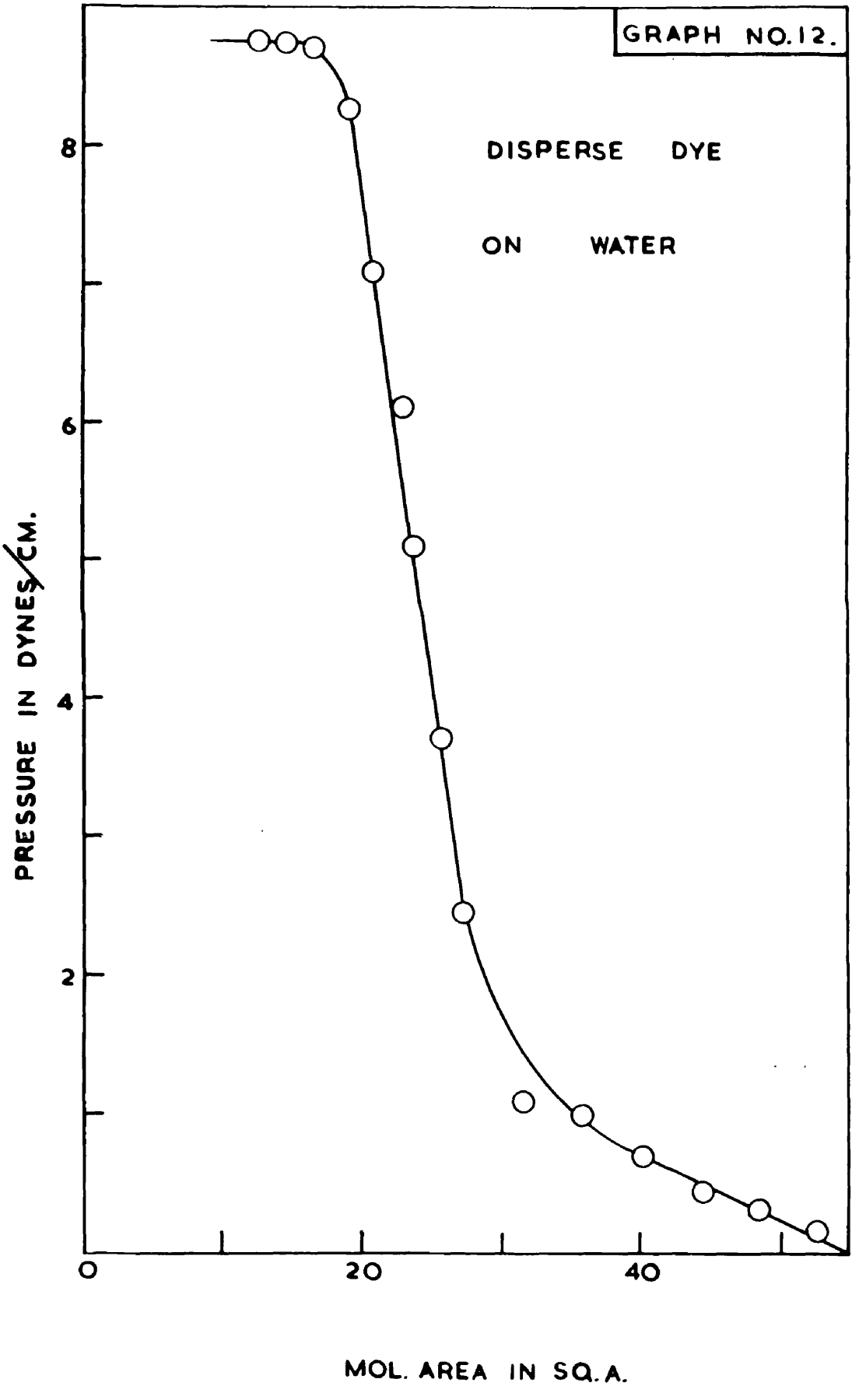
GRAPH NO.10.

(Left) *Cetylaniline films on*: ●, Water; ○, tannic acid (44 mg./l.).

(Right) *Stearyl* (n-*octadecyl*) *alcohol films on*: ●, Water; ○, tannic acid (44 mg./l.)




GRAPH NO. II.
CELLULOSE TRIACETATE
ON WATER O
MIXED FILM WITH
DISPERSE DYE ●
30
20
10
PRESSURE IN DYNES/CM.
20
30
40
50
60
MOL.AREA IN SQ.A.


GRAPH NO. 12.
DISPERSE DYE
ON WATER
PRESSURE IN DYNES/CM.
8
6
4
2
0
20
40
MOL. AREA IN SQ. A.

APPENDIX TO SECTION I

Appendix to Acetate Section.*

The suggested mechanism for adsorption of disperse dyes by cellulose acetate has recently been criticised by Daruwalla and Limaye[68], who carried out a detailed investigation into the transfer of disperse dyes from thickened paste to (secondary) cellulose acetate film by steaming. They consider that their data give no evidence of a relation between dye constitution and saturation adsorption, and indeed that the nature of the dye-cellulose attraction cannot be clearly defined. An examination of their data however gives much more interesting and positive information than they claim. Further relevant information can be obtained from earlier work on adsorption of disperse dyes on cellulose acetate by Bird and Harris[69], and by Majury[54]. In nearly all cases there exists a direct relation between hydrogen-bonding power and maximum adsorption. Dye-fibre bonding appears to occur by hydrogen-donation by the dye or by acceptance of -CH.... bonds from the acetyl groups. Adsorption rises usually in almost direct proportion with the number of hydrogen-donating or accepting groups, but in special cases where adsorption at an azo-group is promoted by an electron-releasing substituent, electron-attracting substituents progressively reduce adsorption. Non-polar forces appear to be much less important than hydrogen-bonds.

* The author acknowledges the help of Dr.C.H.Giles in drawing his attention to the subject matter of this Appendix.

Data in Tables IA - IVA show that in comparable cases adsorption is always much higher when free hydrogen atoms are present than when not, and Figs.IA and 2A show that in general it rises with the number of free hydrogen atoms.

Table IA

Maximum Adsorption Data for Miscellaneous Solutes on Cellulose Triacetate (CTA) and Secondary Cellulose Acetate (CA).

Solute		Mol.Area (A^2) *	Max.Adsorption (mmole/Kg.)
Aniline, phenol, m- or p-chloro-, methyl- or nitro-substituted phenols[47]	(from water) 25°C	40-50	>6500 (CA)
Methanol	(from benzene) 59°C[70]		ca1300 (CTA)
Methanol	(from benzene) 24°C[70]		ca6000 (CTA)
Quinol	(from water) 60°C[70]		>1500 (CTA)
p-Nitroaniline	(from water) 80°C[54]	50	945 (CTA)
p-Aminoazobenzene	(from water) 80°C[54]	100	675 (CTA)
Azobenzene	(from water) 80°C[54]	90	269 (CTA)
NN-Dimethyl-p-nitro-aniline	(from water) 80°C[54]	60	117 (CTA)
NN-Dimethyl-p-amino-azobenzene	(from water) 80°C	110	108 (CTA)

* Molecular area (flat); approx. value for smallest enclosing rectangle.

Table IIA

Relation between Constitution of Azo (etc.) Disperse Dyes and their Adsorption by Secondary Cellulose Acetate.

AZO DYES

Substituents								Mol.Area (approx) (A^2)	Max. Adsorption (mmole./Kg
2′	3′	4′	6′	2	3	4	5		
Benzeneazobenzene Compounds.									
Data of Daruwalla and Limaye[68]									
		NO_2				NMe		100	4.8
		NO_2				$N(C_2H_4OH)_2$		150	34
		NO_2				$N/Et.C_2H_4OH$		130	58
		NO_2				NH_2		90	82
Data recalculated from Bird and Harris[69]									
		NO_2				$N/Et.C_2H_4OH$		130	56
Cl		NO_2				$N/Et.C_2H_4OH$		130	61.5
Cl		NO_2	Cl			$N/Et.C_2H_4OH$		130	71
NO_2		NO_2				$N/Et.C_2H_4OH$		160	95
		NO_2				$N(C_2H_4OH)_2$		150	41
		NO_2			Cl	$N(C_2H_4OH)_2$		150	93
NO_2		NO_2				$N(C_2H_4OH)_2$		150	119
		NO_2	OMe			$N(C_2H_4OH)_2$		150	268
		NO_2		Me		$N(C_2H_4OH)_2$		150	124
		NO_2	Cl	Me		$N(C_2H_4OH)_2$		150	57
Cl		NO_2	Cl	Me		$N(C_2H_4OH)_2$		150	94
NO_2		NO_2		Me		$N(C_2H_4OH)_2$		150	85
NO_2		NO_2	Cl	Me		$N(C_2H_4OH)_2$		150	55
		NO_2				NEt_2		130	ca 8
NO_2						NH_2		130	36
		NO_2				NH_2		90	66
		NHAc		OH			Me	130	104
		NH_2				NH_2		90	250

Table III A.

Relation between Constitution of Anthraquinone (etc.) Disperse Dyes and their Adsorption by Secondary Cellulose Acetate.

ANTHRAQUINONE DYES								
Substituents					H-bonding Property		Mol. Area (A^2)	Max.Adsorption (mmole./Kg.)
1	2	4	5	8	acc*	dnr*		
Data of Daruwalla and Limaye[68]								
NHMe		NHMe			2	0	130	13
NH_2					3	7	90	48
NH_2		NH_2	NH_2	NH_2	0	4	90	51
NH_2	Me				3	1	100	52
NH_2	OMe	NH_2			3	2	130	67
NH_2		OH			2	1	90	71
NH_2		NH_2			2	2	90	71
NHMe					3	0	110	84
Data recalculated from Bird and Harris[69]								
NHMe		NHMe			2	0	130	ca 17.3
NHC_2H_4OH		NHC_2H_4OH			4	2	175	20.2
NHMe					4	0	110	35.9
NH_2	Me				3	1	100	42.2
NH_2		OH			2	1	90	46.1
NH_2		NH_2			2	2	90	50.8
NH_2	OMe	NH_2			2	2	130	67.5
NHMe		$NHCH_2OH$			3	1	140	74.5
NHC_2H_4OH					4	1	130	93.7

* acc. = probable number of atoms accepting a -CH--- bond, per dye molecule, (assuming each quinone oxygen atom can accept two bonds).

* dnr. = probable number of -OH--- or -NH--- bonds donated per dye molecule

Table IVa.

Relation between Structural Characteristics of Solute Molecules and Saturation Adsorption by Cellulose Acetate.

Structural Characteristics		Hydrogen-bonding Properties			
Number (per mol.) of		Acceptor		Donor	
Polar Groups	Aromatic Nuclei	Sat.Ads. (mmole/Kg.)	M.W.	Sat.Ads. (mmole/Kg.)	M.W.
1	1	270	182	>6500*	95
2	1	120	166	>6000*	78.5-139
	2	110	226	680	197
	3			35	237
				17	266
>2	2	8	298	40-270	242-434
	3			94	267
				20	326

Temp., 80°C; * 25°C.

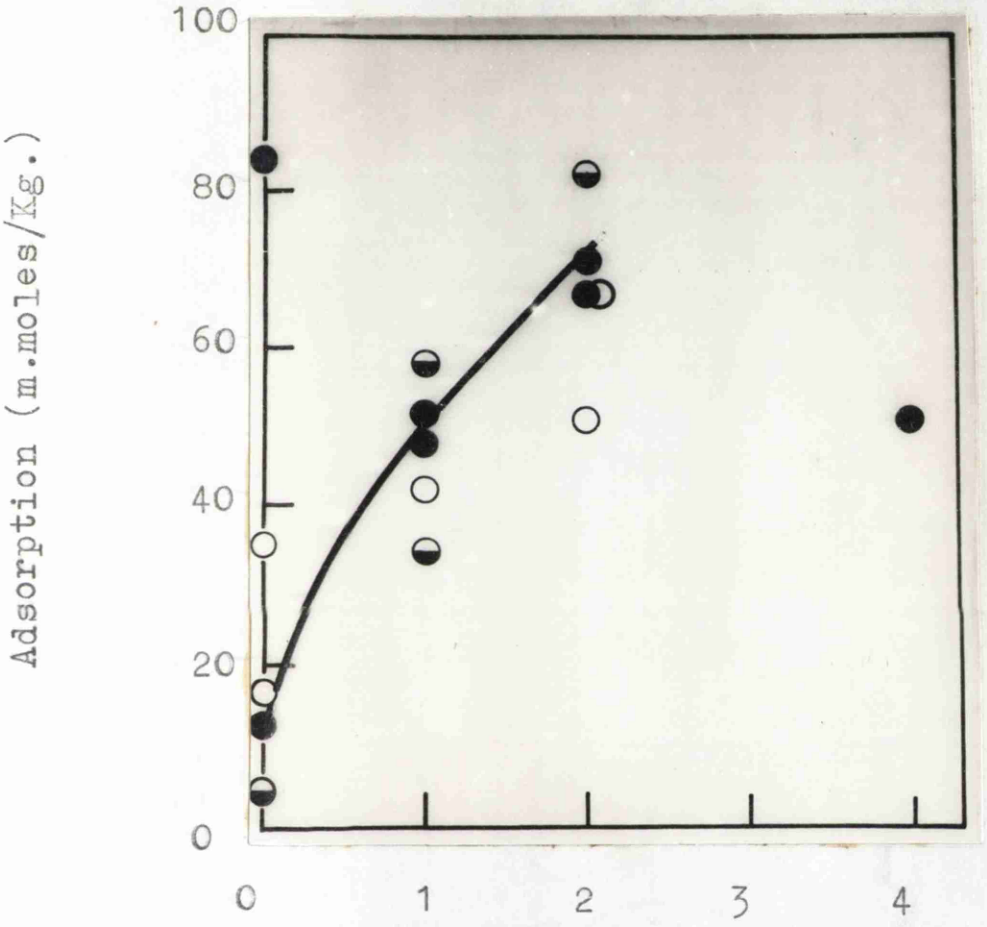


Fig.1A Relation between Number of Available Hydrogen Atoms in all Non-hydroxylic Anthraquinone Dyes and in some Azo Dyes, and their Maximum Adsorption by Cellulose Diacetate.

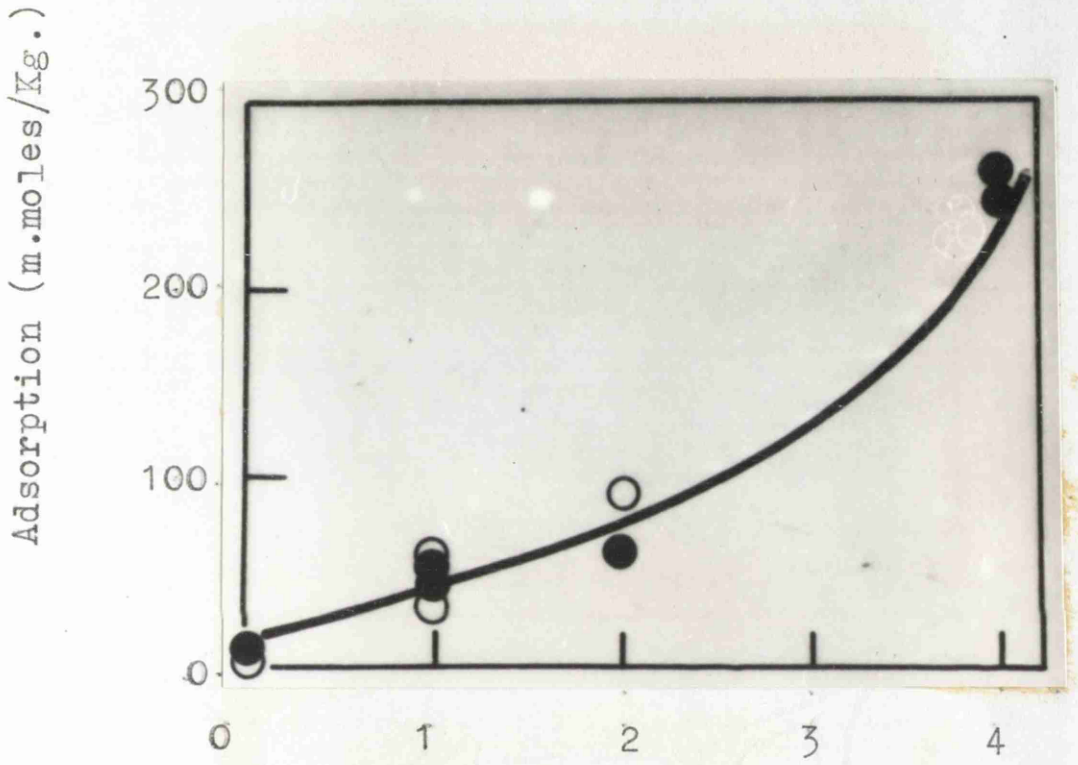
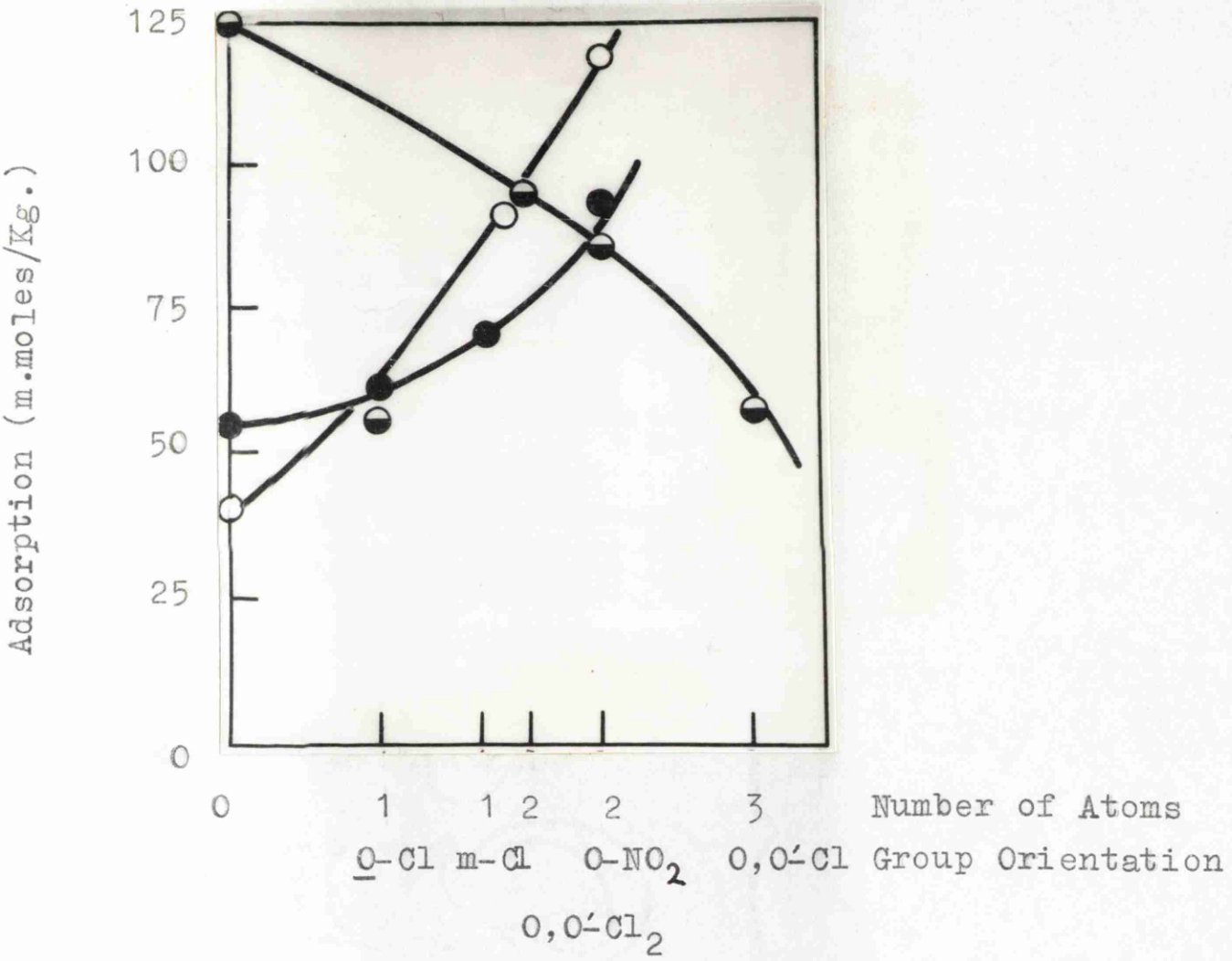


Fig.2A Relation between Number of Available Hydrogen Atoms in Multifunctional Azobenzene Dyes (2- or 2′ Substituents) and their Maximum Adsorption by Cellulose Diacetate.



Number of Hydrogen-accepting atoms and Group Orientation relative to the Azo Group.

● N-Ethyl-N-ß-hydroxyethylaminoazobenzene derivatives

O NN-Bis-ß-hydroxyethylaminoazobenzene derivatives

◒ NN-Bis-ß-hydroxyethyl-m-toluidine derivatives

Fig.3A Relation between Number of Hydrogen-acceptor Atoms in ß-Hydroxyethylaminoazobenzene Dyes and their Maximum Adsorption by Cellulose Diacetate. (On x-axis the groups are approximately in the position expected from their Hammett σ - values)[71]

SECTION II

INTERACTIONS IN SURFACE FILMS OF PROTEINS WITH DYES AND OTHER AROMATIC SOLUTES AND THEIR RELATION TO ADSORPTION BY PROTEIN FIBRES.

Structure of Proteins.

Fibrous proteins are polypeptide chain molecules formed by the linear condensation of α-amino acids.

$$- NH - \underset{\underset{R^1}{|}}{CH} - CO.NH - \underset{\underset{R^2}{|}}{CH} - CO -$$

The nature of the protein depends on the nature of the side groups R pendant to the polypeptide chain. These side groups find convenient classification into the following types:-

(a) Side Chains of Low Reactivity. Some of these groups are mere hydrocarbon residues, but some contain polar groups, e.g. -OH. These groups are usually less reactive than members of the following classes.

(b) Acidic Side Chains. All terminate in a carboxyl group which plays an important part in bonding the peptide chains and also in attaching dyes to the fibre.

(c) Basic Side Chains. These basic groups all terminate with strongly basic groupings, e.g. guanidine, iminazole and amine groups.

(d) Cross-linking Groups. Cystine is the only member of this class, and it is capable of linking two polypeptide

chains. Cystine, which is found abundantly in wool and in other animal fibres, plays an important part in determining their properties as compared with other proteins, e.g. cystine confers high internal cohesion, which renders the scleroproteins insoluble, otherwise hair, hooves, etc., would rapidly disappear with repeated wetting.

Detailed investigations by Speakman[72] and Astbury[73] have elucidated the structure of the wool fibre, and Pauling[74] and others have modified to some extent the views held regarding the three-dimensional structure of proteins in general. wool may be regarded as being built up of micelles lying parallel to the axis of the fibre and consisting of long folded or coiled peptide chains linked together by cystine and salt linkages which keep the molecule more or less in one plane. These planes are themselves held together by hydrogen bonds or weak Van der Waals forces. The micelles are regarded as lamellar in shape, about 200 A thick and 2,000 A long.

The intermicellar space has pores of the order of 6 A in the dry unswollen state and about 40 A when swollen in water and even more in acid solution. It is through these pores that the dye molecules penetrate into the interior of the fibre.

Dyeing of Proteins.

Considerable study has been given to the dyeing of proteins and a brief review of the theories which emerged from this study is given.

Knecht[75] has proposed a chemical theory for the dyeing of wool by acid dyes; this has been extended by **Fort.** It is assumed that on immersion in the dyebath the wool first combines with the colourless acid to form a protein salt, and the next stage is the formation of a protein-dye salt. The overall reaction may be represented by the following equations -

$$NH_3^+ : \bar{O}OC + HCl \longrightarrow NH_3^+ \bar{Cl} + HOOC$$

$$NH_3^+\bar{Cl} + NaD \longrightarrow NH_3^+ D^- + NaCl$$

(where D represents the dye anion).

Elöd[76] gives further support to this view by quantitative measurements of the replacement of chloride ions in the wool fibre by dye anions. Speakman and Stott[77] have established that wool has a maximum combining capacity of 0.82 equivalents of monobasic acid per kilogram at pH 1.00, this approximates closely to the number of amino groups in the wool. If this chemical theory of wool dyeing is correct then dyed wool would have a smaller combining capacity for acids

than undyed wool, this has been shown to be true[76]. The work of Speakman and Stott[77] gives further support to this theory by showing that de-aminated wool has a considerably reduced acid combining capacity, and that whatever adsorption by it takes place is probably due to the imino groups in the peptide chain.

It has been shown that the affinity of dyes for wool increases with the size of the dye anion, i.e. the larger the anion, the lower the degree of acidity required to induce maximum adsorption. This rise in affinity appears to have no relation to the dissociation constant of the acid and must be due to non-ionic forces between the substrate and the anion, but their exact nature has hitherto been in doubt. Vickerstaff[57] and Meggy[78] have pointed out the importance of Van der Waals forces in this connection. There exists a linear relationship between the affinity for wool, and either the length of an attached alkyl chain or the total molecular weight, of certain azo dyes, which suggests the operation of physical forces between the dye and the fibre. Steinhardt, Fugitt and Harris[79] have found that wool adsorbs weak organic acids to a greater extent than hydrochloric acid, and since the hydrophobic portions of these molecules are too small to exhibit sufficient Van der Waals attraction it appears that a hydrogen-bonding mechanism must be responsible for their attachment to the fibre. The adsorption on wool of

aliphatic and aromatic non-ionic compounds from various solvents has been studied by Chipalkatti et al.[80], and they found that hydroxy-compounds appear to be adsorbed from non-aqueous solutions by the formation of hydrogen bonds, perhaps with the enolic forms of the amide or peptide groups in the fibres.

A thermodynamic treatment of wool dyeing has been given by Gilbert and Rideal[81]. This theory requires the anions and the cations to be adsorbed on specific sites in the substrate, and the fibre to contain an equal number of positive and negative sites having the same properties. According to this theory the adsorbed ions are free to occupy any site irrespective of whether or not the adjacent sites are occupied.

Another theory has been put forward by Peters and Speakman[82] who suggest that only the cations are adsorbed by the fibre and that the anions do not combine, but are dissolved in the internal aqueous solution without restraint.

With certain limitations both theories agree with experimental findings, but they do not enable an unequivocal picture of the mechanism of dye adsorption by wool to be obtained.

Protein Monolayers.

Protein monolayers have been the subject of considerable study by many different workers using widely varying techniques with different purposes in view. Such studies were initiated with Devaux's observation (1903) that when a very small amount of the white of an egg is applied to the surface of clean water a coherent elastically compressible film spread over the surface. He concluded that the protein formed a single layer of molecules and estimated the thickness of the film to be 10 to 20 A. Gorter and Grendel[83] made a systematic study of monolayers of various proteins. Very considerable additions to the study of protein monolayers were made by Langmuir (see, e.g.[31]), Schaefer[84], Blodgett[85], and Schulman and Rideal[62].

More recently Sher and Sobotka[86] have pointed out that spread protein molecules are an interesting laboratory artefact but their properties and reactivities are not so closely related to those of the native proteins as is often tacitly assumed. In the study of dyeing mechanisms the limitations raised by Sher and Sobotka are of little consequence, indeed, several advantages are to be gained by using spread protein molecules for interaction with dyes dissolved in the sub-solution. Furthermore, Pankhurst[64] et al. have used this technique in their extensive studies on the tanning

of collagen, and it has enabled them to give a rational explanation of the tanning process.

Interpretation of the interaction between dyes and protein fibres such as wool in an attempt to formulate the sites and types of bonding which occur in the dye-fibre complex is made difficult because of the fibre's complex histological structure and heterogeneous chemical composition. Peters and Lister[87] pointed out the difficulties which are encountered in attempting to estimate the affinity of dye anions for solid proteins because of the dominating effect of the hydrogen ion, and Gilbert[88] has suggested that more direct information may be obtained from studies on dissolved proteins. It is considered that when the protein is spread as a monolayer film and its reaction with dyes at the air/water interface is studied, the problems of accessibility of potential bonding sites to the dye resulting from steric factors which may occur in the coiled polypeptide chain in solution is minimized. For these reasons this technique involving spread protein molecules has been found to be of value in the study of dyeing mechanisms, and as previously mentioned its usefulness has also been demonstrated in studies of tanning[64].

Previous Work on Dye-Protein Monolayer Interactions.

Very few authors have examined reactions between protein monolayers and dyes dissolved in the aqueous sub-solution. Wunderby[89] removed protein monolayers from the surface of solutions of several azo-dyes by lifting them on a glass slide, then redissolved the dye-protein combinations in alkali and examined the solutions spectrophotometrically. He considered that the extent of reaction depended on the colloidal nature of the dye. While the present work was in progress, Harrap[90] reported experiments on spreading a monolayer of a soluble wool keratin derivative on buffered solutions of Orange II. He observed effects indicating interaction between the protein derivative monolayer and the dye, beyond simple additive penetration. Interaction due to ionic binding occurs below pH 4. At high dye concentrations in the aqueous solution (0.1 - 0.5 M) increased interaction takes place, apparently owing to the ability of the dye to aggregate and orient at the surface, and to its penetration being facilitated by the increased screening of negatively charged protein side-chains when the ionic concentration rises.

Previous Work on Tannin-Protein Interactions.

Although few reports have been published on the dyeing of protein monolayers, considerable attention has been paid to related tanning studies on protein monolayers. Thus Schulman and Rideal[62], and Cockbain and Schulman[91] studied the interaction of tannic acid and gliadin monolayers by injecting an aqueous solution of tannic acid under a monolayer of gliadin. Gorter and Blokker[92] studied this reaction by preparing a gliadin film on the surface of a dilute solution of tannic acid. These workers observed that the tanning of the film is characterised by a reduction of the surface potential by ca. 100 mV, and the production of a less compressible and considerably more rigid film. Pankhurst[64,34] and his collaborators have studied the tanning of collagen and N methoxymethyl nylon monolayers. They find that tanning is characterised by the development of a highly viscous film along with changes in pressure and potential. The fact that surface potential is not invariably altered is used to postulate a hypothesis that tanning can take place between non-ionic reactants, i.e. that hydrogen bonds are formed, probably between hydroxyl groups of the phenolic tannin and the carbonyl groups of the keto-imide groups in the backbones of the protein. It is also suggested that ionic reactions play a subsidiary rôle. These changes are explained in terms of a multipoint association between

vegetable tannin and protein. Pankhurst points out that certain size requirements are to be met with for these conditions to hold, thus the tannin must have at least more than one reactive group, and these groups must be so spaced that they are able to combine inter-molecularly with the protein. The fact that mono-, di- and even tri-hydric phenols are not capable of tanning collagen monolayers lends support to his theory.

While the present work was in progress, Holt[24,93] and his collaborators reported some very interesting results on the interaction of silicic acid with collagen, gelatin, insulin, albumin and polyamide monolayers. They find that a polyamide monolayer interacts with polysilicic acid over a wide pH range (2 to 9), and is tanned between pH 4.5 and 6.5, and conclude that this interaction must be due to the formation of hydrogen bonds. On that basis, they postulate that the interaction of insulin and albumin with polysilicic acid is also probably due mainly to the formation of hydrogen bonds between the keto-imino groups of the proteins and the hydroxyl groups of the silicic acid. They find that silicic acid alters the force/area curves of insulin, albumin and polyamides only if it is polymerised. Furthermore, films of the fibrous proteins collagen and gelatin are scarcely altered with unpolymerised silicic acid in the subsolution. This agrees with the size requirements for tanning

of collagen monolayers that were pointed out by Pankhurst[64].

Penetration and Complex Formation in Monolayers by Organic Molecules.

As the cross-linking of a protein film at the air/water interface with a polyfunctional molecule dissolved in the water below is only a specific example of complex formation in monolayers, and as other types of interaction between dyes and protein films are to be described in this work, it is considered necessary at this stage to review briefly penetration and complex formation in monolayers in general.

Adam[94] observed that large molecules are capable of exerting a condensing effect on smaller molecules when both are present in a mixed monolayer film. It has been shown that cholesterol condenses myristic acid films; this is considered to be the result of reduction of the vibratory movements of the hydrocarbon chain by the presence of large inert molecules and not to complex formation. Leathes[95] observed that cholesterol condenses an expanded film of lecithin and it was shown by Hughes[96], by surface potential measurements, that this condensation is not accompanied by any significant change in the dipole moments of the two components. Schulman and Hughes[97], studying various types

of mixed films, showed that the condensing effect was but one of several distinct phenomena which are observable when a capillary active substance is introduced beneath a pre-existent film of another substance. If the film and the capillary active substance are represented by A and B respectively then the following may occur:-

(1) Film of A can be completely replaced by monolayer of B.

(2) B can penetrate film A and produce a stable mixed film of A and B.

(3) Neither replacement nor penetration takes place.

They suggested a tentative explanation for (2) by assuming that the molecules in the film A are in equilibrium with a definite, though small, bulk concentration of its molecules. The equilibrium $A_{film} \rightleftharpoons A_{dissolved}$ will be disturbed on the introduction of a second molecule B which alone would set up its own equilibrium $B_{film} \rightleftharpoons B_{dissolved}$. When a molecule of A leaves the surface either A or B may return and an interchange of A and B will be effected, dependent upon the relative adhesional forces of A to A, A to B and B to B. If the attractive forces between A and B are greater than the cohesional forces between A and A or B and B a mixed film of an AB complex will result.

Harkins and Myers[98] spread a mixed film of Nujol (a liquid hydrocarbon of low volatility) and a saturated fatty acid. In the expanded region the Nujol affected the force/area curve markedly, but at higher pressures the Nujol was forced to the top of the film where it no longer exerted any influence.

The injection of substances under a monolayer of oriented molecules has been investigated[99,62]. When the injected molecules are similar in structure to the film molecules (i.e. having a polar head group and a hydrophobic tail) then the following can occur:-

(a) If association takes place between polar groups only then adsorption occurs below the monolayer with a consequent change in the surface potential. When the injected molecules are polyfunctional rigid films are obtained owing to cross-linking.

(b) Penetration of the monolayer resulting in the formation of equimolar complexes was observed when there was association between both the polar and non-polar parts of the two molecules.

(c) No change in the surface potential or film characteristics was observed when there was no polar interaction.

Thus the necessity of having present both Van der Waals attraction between the non-polar portions and polar attraction between the head groups imparts a high degree of specificity to interactions resulting in penetration.

Adam, Askew and Pankhurst[100] have shown that substances such as butyric acid or phenol are capable of disrupting the cohesion of an insoluble film, converting it usually into a vapour-expanded film at low pressures; on increase of pressure the penetrant is displaced from the surface. By increasing the chain length of the penetrant molecule the penetration becomes more powerful and displacement becomes increasingly difficult[101]. Similar effects have been observed by Cockbain and Schulman[102].

Attention has been given by several authors to the interaction between detergents and proteins. Injection of detergent molecules under a protein film causes penetration and displacement of the film[103,104], but interpretation has been found difficult. Doty and Schulman[105] injected proteins under monolayers of detergents and they recognised three distinct processes; adsorption, penetration, and solution. If the film was held at constant area adsorption took place, whereas if the pressure was kept constant, solution or penetration occurred characterised by the rate of the expansion.

Matuura[106] showed that dyes expand stearic acid

films and that different forces operate depending on the type of dye used. With acid dyes under acidic conditions, where both the film and the penetrant are present as anions, he observed expansions which decreased with the size of dye molecule, this he considered to be due to Van der Waals forces. He considered that basic dyes expand the film by adsorption of the dye by ionic forces. Giles et al.[51] found that dyes expand films of long chain compounds containing groups which are present in fibres.

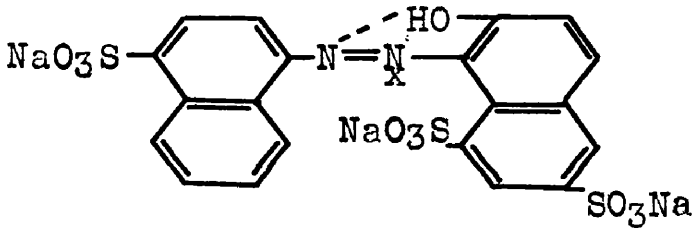
Results and Discussion

Section II A. Casein Monolayers

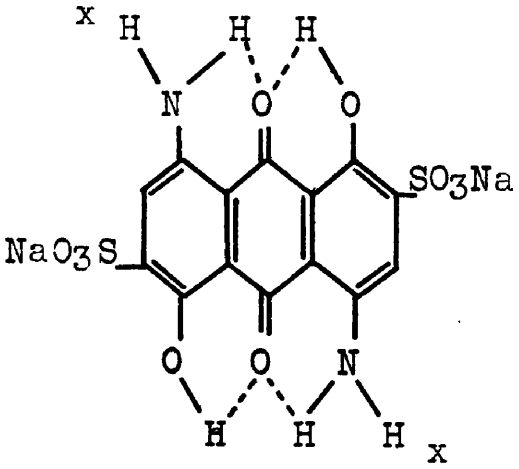
The present work was undertaken to define more clearly the source of affinity of organic ions for protein fibres and to resolve some of the apparently conflicting evidence regarding the rôle of polar and non-polar forces in adsorption of dyes by proteins. Casein monolayers were spread upon water and aqueous solutions of a variety of solutes, including polar non-ionic compounds and a number of aromatic ionic compounds of various molecular sizes and containing different numbers and types of potential hydrogen-bonding groups. Non-ionic solutes used were: tannic acid, glucose and m-inositol (this compound is an isomer of glucose with a ring structure and steric arrangements of hydroxyl groups similar to glucose but with the exception that it is homo-cyclic and has no reducing group) and anionic solutes were either (A) of small molecular area or with hydrogen-bonding groups or (B) monobasic, having a large hydrophobic residue (i.e. weakly surface-active).

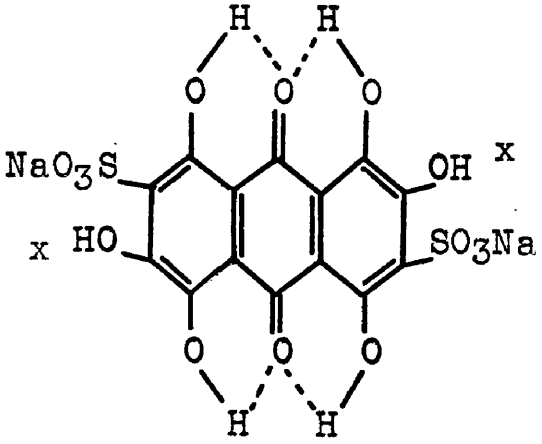
(A)-type solutes used.

Sodium benzenesulphonate,
Sodium naphthalene-2-sulphonate,
Sodium 2-hydroxynaphthalene-7-sulphonate,
Sodium anthraquinone-2-sulphonate,
Sodium anthraquinone-1:5-disulphonate,
Sodium anthraquinone-2:7-disulphonate,
Naphthalene Scarlet 4R (C.I.16255)[107],
Solway Blue BN (C.I.63010)
Alizarin Cyanine WR (C.I.58610)



Naphthalene Scarlet 4R





Solway Blue BN

Alizarin Cyanine WR

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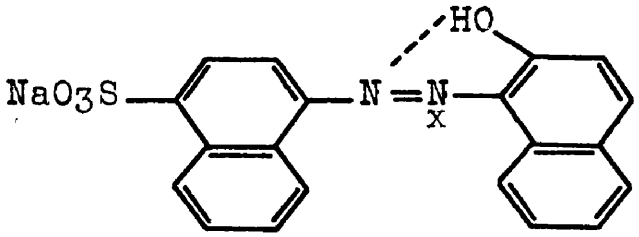
* indicates the probable hydrogen-bonding centres, based on direct determination of complex-ratios with phenol in aqueous solution.

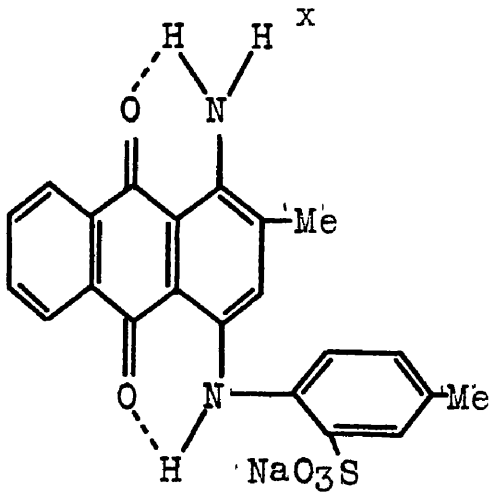
(B) - type solutes used:

Naphthalene Red J (C.I.15620),

Solway Blue RN (C.I.62085).



Naphthalene Red J.



Solway Blue RN

Casein was spread from a 0.15% solution in 0.025 M. aqueous sodium hydroxide. Preliminary tests showed that the time required for complete spreading was dependent on substrate pH. Graph No.1 illustrates the development of pressure with time when casein is spread on distilled water. On acid buffers this slow rate of spreading was not observed, in this case maximum spreading was almost immediately obtained. Other tests showed that in most cases equilibrium between film and substrate was attained in about 15 minutes, but in each case after spreading 30 minutes were allowed before the film was compressed. Subsequent stages of compression were measured after intervals of 3 minutes, which was normally sufficient to allow the film to regain equilibrium. During this time the pressure decreases slightly, possibly owing to reorientation of side-chains with weakly hydrophobic groups being forced into the water.

Effect of Non-ionic Compounds.

Tannic acid (43 mg./l.) has a similar effect upon casein (Graph No.10) as it has on collagen monolayers[64]; it condenses the film, making it more rigid, i.e., less compressible. The hydroxy-groups in the tannic acid molecule form hydrogen bonds with specific groups in a number of protein chains, the whole complex forming a raft-like structure in which the tannic acid molecules lie horizontally in the water

below the film. This type of complex can form only with large polyfunctional solute molecules[64] and not with the small molecules of glucose and inositol (see later). These compounds (both 0.01 M, pH 4.34) have no apparent effect on the casein film (Graph No.7).

Effect of Anionic Solutes in Acid Solution.

Hydrochloric acid alone, 1.0 M has little effect on the film, Graph No.2 (this gives the two control curves). When an aromatic anionic solute is present in the sub-solution considerable expansion occurs, with in most cases some change in compressibility (Graphs No.3-6). Ellis and Pankhurst[64] found that basic chromium sulphate expands a gelatin monolayer without causing any noticeable change in compressibility and attributed the effect to the action of coulombic forces between the solute ions and oppositely charged side-chains of the protein. The expansion of the casein films is attributable also to coulombic attraction, but the compressibility changes are probably due to forces acting between the protein and the organic residues of the solute ions in the water below the film, see Fig.1. The expansion may then be the result of the interposition of the solvated water atmospheres around the individual ionic centres. The compressibility of the films varies with the nature of the solute anion, and the variations suggest differences in the location of the attached anions.

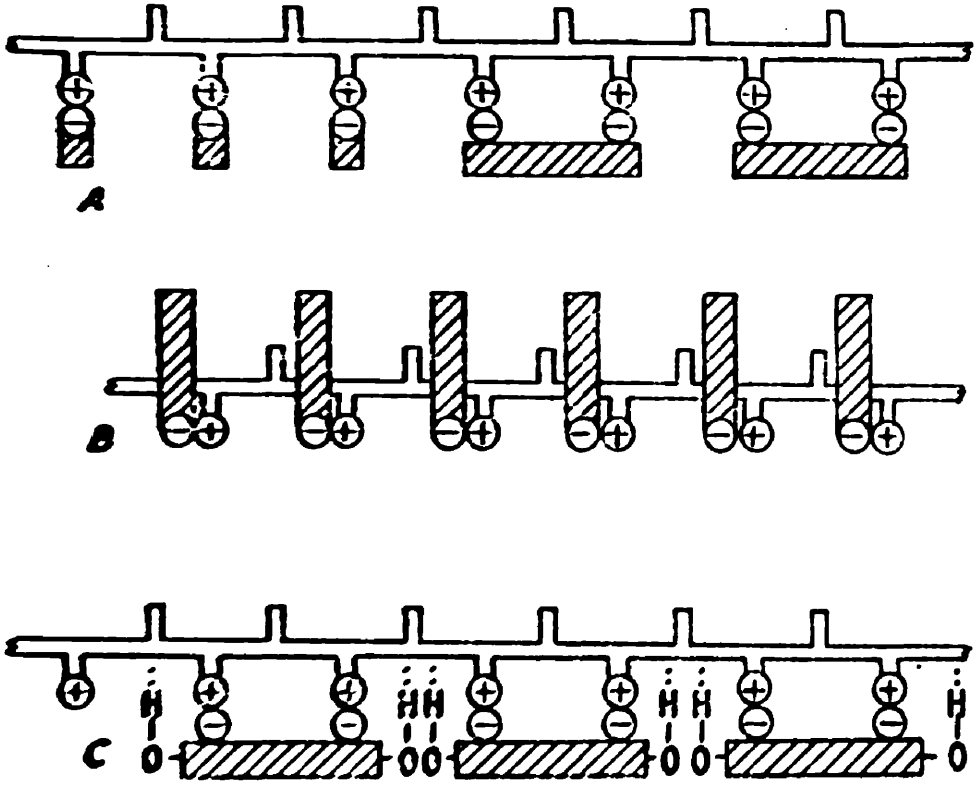
There are three distinct effects.

(i) Slight increase in compressibility. This occurs with the small monobasic anion, i.e., sodium benzene-sulphonate (Graph No.3) and with the di- or tri-basic anions which have no strongly hydrogen-bonding centres and no very large unsulphonated residue, i.e., the anthraquinone-sulphonates (the force/area curves for casein spread on the three anthraquinonesulphonates, all 10^{-3} M., are coincident) (Graph No.3). The azo-dye Naphthalene Scarlet 4R (Graph No.5) also causes a slight increase in compressibility. These compounds have neither surface activity nor groups capable of cross-linking the protein chains, so they must be located in the water just below the film (Fig.1A).

(ii) Great increase in compressibility. The two mono-basic dyes Naphthalene Red J and Solway Blue RN cause consid-erable increase in film area and compressibility (Graphs No.5 and 4). The liquid-expanded type of film obtained resembles those observed when one monomeric surface-active compound penetrates a film of another[101,108]. There is clearly ion-ion association between the charged cationic groups of the protein and the dye sulphonate groups. In the greatly expanded state the dye molecules must be lying flat on the surface, their large area causing the protein chains to be widely separated.

It was also found that injection of solutions

FIG. 1. *Schematic diagram of suggested mechanism of casein–dye attachment under acid conditions.*



Ion–ion bond with small uni- or bi-valent anions.

Ion–ion bond and film penetration with large univalent anions at moderate pressure.

Ion–ion and hydrogen bonds with bivalent anions containing at least two bonding groups.

(final concentration in the trough 4 x 10^{-5} M.) of the dye Naphthalene Red J below casein films on pH 4.34 buffer previously compressed to 5 and 8 dynes/cm., caused the pressure to increase and eventually to reach that pressure which is obtained when the film is initially spread on dye solution (cf. Graph No.8). This evidence of penetration of a film of one compound A under pressure by another compound B injected below it implies that a stable complex is formed between A and B[97]. The complex appears to be stable over the whole pressure range examined, for the curve for the mixed film intersects that for casein alone at high pressures (Graph No.5). This implies that the film does not return to its normal state under high pressure but remains actually more soluble than it is in the absence of dye, and that therefore sulphonate groups in the complex must be in contact with the water.

The mechanism of association at the higher pressures may well resemble that postulated by Pankhurst[109] for gelatin-sodium alkyl sulphate detergent complexes formed in solution. Under acid conditions the ion-ion attraction causes a mono-layer of detergent molecules to be built up on the protein, with the polar groups oriented towards the protein and the hydrocarbon groups directed outwards, giving the complexes oil-solubility. Further detergent anions are adsorbed in the reverse manner, being attached to the first layer by

Van der Waals forces between the hydrocarbon chains. A reverse-adsorbed layer of this nature, beneath the casein film, would give the latter a closely-packed surface of sulphonate groups, which would account for its high solubility. The two dyes Naphthalene Red J and Solway Blue RN, which cause increase of film solubility, each have a structure which would favour dimerisation by Van der Waals attraction, giving a complex with a sulphonate group at each end. A similar dye (Orange II, sulphanilic acid ⟶ 2-naphthol) has been shown by Derbyshire[110] to exist in dilute aqueous solution largely in such a form.

At an intermediate stage between the liquid-expanded film and the final state, the aromatic portions of the dye molecules may be forced out of the film to stand vertically upwards (Fig.1B). If this does occur, then with increasing compression the orientation of the adsorbed dye molecules may be envisaged as passing through three stages with possible buckling of the film in each.

(iii) No change, or decrease in compressibility. The dye Alizarin Cyanine WR produces a marked decrease in compressibility (Graph No.6), doubtless a tanning effect caused by hydrogen-bond cross-linking of protein chains with active phenolic groups at opposite ends of the dye molecule (cf. Fig.1C). Qualitative tests with powdered talc on the surface

illustrate the marked increase in rigidity of the film, indeed, vigorous blowing or rapid agitation were insufficient to move the powder along the surface. In view of the very similar 'tanning' effect shown by some of the 2:1-metal complex dyes, discussed below, which is attributed to adsorption of micelles, the possibility arises that Alizarine Cyanine WR may be present as micelles (it is, e.g. of low water solubility). Further investigation would be required to settle this matter.

The other anthraquinone dye, Solway Blue BN, with two hydrogen-bonding centres produces no change in compressibility (Graph No.4). Its effect is thus intermediate between the anthraquinone sulphonates (Graph No.3) or Naphthalene Scarlet 4R (Graph No.5) and Alizarin Cyanine WR (Graph No.6), and it is probably causing a small degree of hydrogen-bond cross-linking, the affinity of its bonding centres under acid conditions being low, and only slightly greater than that of the quinone groups.

Effect of Anionic Compounds near the Isoelectric Point.

The isoelectric point of casein is at pH 4.6, and on buffer solutions in this region the ion-ion attraction is low and any changes in the films must be due to non-ionic and some ion-dipole forces. The compressibility changes are similar to those observed with acid solutions, but the

expansions are less (see Graph No.7).

The form of the curves obtained with the two monobasic dyes Naphthalene Red J and Solway Blue RN (Graphs No.9 and 8) is very similar to that obtained with these dyes on acid solutions, and a sequence of orientation changes can be suggested to occur here similar to those on acid solutions. Pankhurst[109] observed that the sequence of changes in the properties of detergent-gelatin complexes is much the same above as below pH 2, but in the latter conditions the detergent : protein ratio required to give maximum hydrophobic properties is higher, and some inorganic salt must also be in the solution; the anions are probably first adsorbed at the ketoimide groups in the backbone of the protein, rather than on side chains. In the present case the buffer gives the required salt effect.

Nature of Non-ionic Dye-Protein Interactions.

The present results help to elucidate the non-ionic reactions of dyes and other ionised solutes with protein fibres and help to reconcile some of the apparently conflicting evidence obtained by earlier investigators. It appears first that non-ionic polar groups in sulphonate anions can form hydrogen bonds with casein in water over quite a wide pH range. In anions with weak hydrogen-bonding power, however, bonding effects with the casein monolayer are masked

by other effects produced either by surface-activity in "unsymmetrically" sulphonated dyes (e.g., Naphthalene Red J and Solway Blue RN) or by high water-solubility in "symmetrically" sulphonated compounds (e.g., anthraquinone disulphonates and Naphthalene Scarlet 4R). If it is assumed that suitable polar groups are accessible in wool as in casein it follows that there can be hydrogen-bond adsorption by that fibre of anions with active polar groups.

From a consideration of the present results and those, for example, of Pankhurst's work on gelatin complexes[109] the known phenomena of anion affinity for wool can be accounted for by the following tentative hypothesis.

The affinity for a protein fibre P of surface active anions $R.SO_3'$, i.e., those having their ionic group or groups at one end of the molecule, and having only weak hydrogen-bonding power, arises from the mutual forces between the anions themselves, i.e., the forces (largely of Van der Waals nature) between R and R, rather than between R and P. These mutual forces assist the adsorbed anions to form either a condensed monolayer or micelles. Evidence in favour of this suggestion is:

(i) The rise in affinity for wool of monobasic aromatic anions with increase in their molecular size[48,57] (the affinity of some dyes rises linearly with increase in length of an attached alkyl chain). If the affinity were

due to R-P attraction it would be unlikely to rise regularly with size of R, because the protein molecule would become more and more inaccessible to the anions as they increased in size (cf. ref.[111]).

(ii) The similarity in heat of reaction in water of the dye Orange II (as the free acid) with wool (-9.27 kcal./mole) and (as the sodium salt) with itself (-10.48 kcal./mole)[110]. If the reaction were between the dye anion and hydrophobic parts of the protein molecule the "heat of dyeing" would be expected to differ from the heat of dimerisation, e.g the heat of reaction of the dye anion with several amino-acids even including tyrosine, whose side-chain, being aromatic, is nearest in type to the dye itself, is only about -1 kcal./mole[112].

(iii) The behaviour of a monolayer of long-chain alkyl sulphate ($C_{22}H_{45}SO_4Na$) when a protein (haemoglobin) is injected beneath it. No penetration occurs at the isoelectric point of the protein, but it does occur under acid conditions, where ion-ion attraction between sulphate and protein is powerful enough to expand the film[113]. This suggests that the attraction of one alkyl chain for another in the condensed monolayer is greater than its attraction for the protein.

(iv) The character of the surface of wool dyed with

surface-active sulphonated dyes containing paraffin chains. A brief report by Preston[114] is that when dyed under acid conditions the fibre surface is hydrophobic and when dyed neutral it is hydrophilic. In acid solution sulphonate groups of the dye are attached to the charged groups in the fibre and the alkyl chains are directed outwards; in neutral solution the sulphonate groups are not attracted by the uncharged fibre, but are directed towards the water. These observations suggest that the dye anions on the fibre surface, in both sets of conditions, are present either in a condensed monolayer oriented perpendicular to the surface, or in micelles. The mutual attraction between the hydrophobic portions of the anions themselves must therefore be greater than their attraction for the hydrophobic parts of the wool fibre.

Section IIB

Edestine Monolayers

By using the same technique as before, interactions between films of the protein edestine were studied with variou solutes in the sub-solution, including six unsulphonated 2:1-metal complex dyes. This programme was undertaken to extend the work recorded in the previous section, and to attempt to formulate a mechanism of dyeing with unsulphonated 2:1-metal complex dyes, which has hitherto received little attention. These dyes are now of considerable technical importance on account of their low dyeing rate and high fastness properties.

According to Fosbinder and Lessig[115] edestine exhibits no tendency to spread on substrates of pH between 5.0 and 11.0, but spreading was observed on solutions which were either more acid or alkaline than the pH stability range. They state that for an isodisperse protein having a particle mass greater than 34,500, spontaneous spreading to form a homogeneous film does not occur if the pH of the substrate is within the pH stability range of the protein. In this work edestine films were examined in the pH range 2.3 - 4.7. In all cases the spreading was spontaneous and the films were quite stable (Graph No.11). Most of the films were prepared from a 0.1% solution in 0.5 M. sodium hydroxide, although some preliminary tests were made with a 0.01% solution in

2 M.-sodium chloride (see Graph No.11).

The surface potential measurements are recorded in Graphs Nos.11 and 12, but for the reasons previously given these are of doubtful significance.

Solutes.

The solutes used can conveniently be divided into three groups. Groups A and B were used as models in studying the effect of certain solute constitutional characteristics upon the films.

Group A. Hydroxylic Compounds:

D-Glucose;

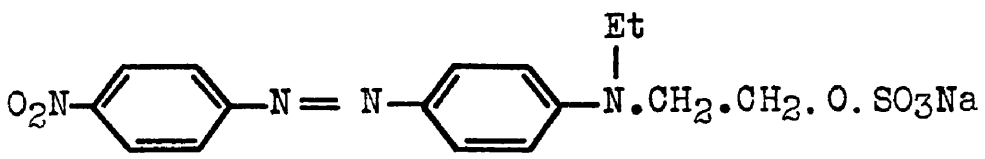
m-Inositol;

Alizarin Cyanine WR (see formula on p.79 above).

Group B. Sulphate Esters and Monosulphonated Dyes:

Tetradecyl sodium sulphate;

Solacet Fast Scarlet B -

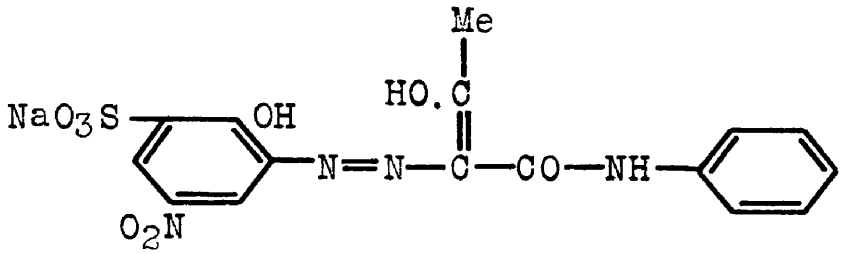


Solacet Fast Scarlet B

Naphthalene Red J, (C.I.15620) and two sulphonated 1:1-metal complex dyes, viz.

Ultralan Yellow R (C.I.13900) -

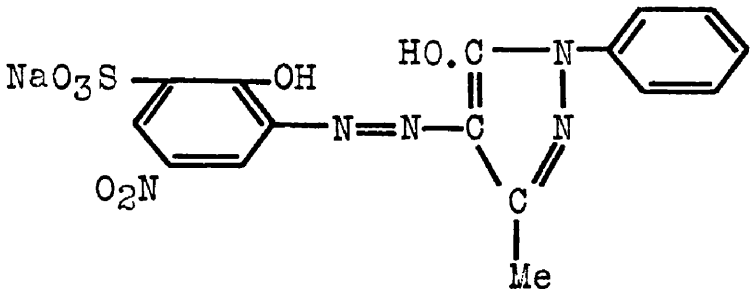
1:1-Cr complex of:-



Ultralan Yellow R.

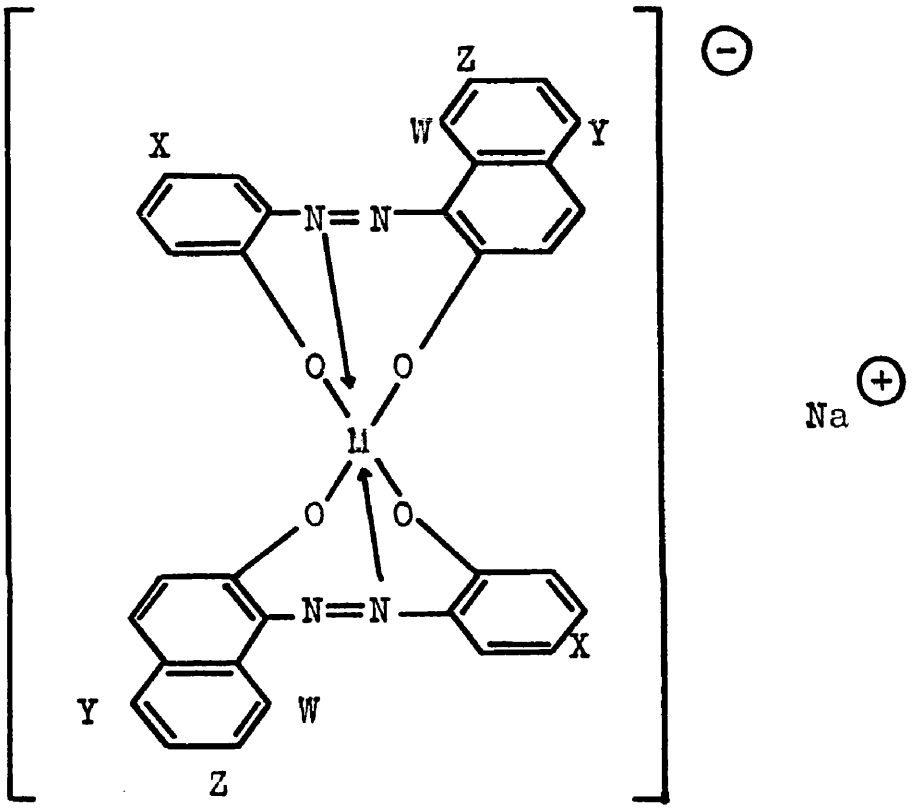
Ultralan Orange G (C.I.18745) -

1:1-Cr complex of:-



Ultralan Orange G.

Group C. 2:1-metal Complex Dyes.



Proton-accepting polar complexes

No.I M=Cr; X=SO_2Me; W, Y, Z = H

No.II M=Co; X=SO_2Me; W, Y, Z = H

Non-polar complex

No.III M=Cr; W, X, Y, Z = H

Proton-donating polar complexes.

No.IV M=Cr; W=NHCoMe; X=SO_2Me; Y, Z = H

No.V M=Cr; X=SO_2Me; Y=NHCoMe; W, Z = H

No.VI M=Cr; W, X, Y = H; Z = OH.

Effects produced by Hydroxylic Solutes.

With casein, glucose and inositol do not appear to form complexes with the film (Graph No.7); similar observations have been made in refractometric tests[116]. With edestine, glucose has no significant effect on the film, but inositol appears to have a slightly greater effect, which may be due to inositol having a tendency to cross-link the film (see Graph No.12). Evidence of hydrogen-bond formation between inositol and edestine was given by refractometric measurements in 1.0 M.-sodium hydroxide. There is no evidence of bond formation between glucose and edestine (see Graph No.20). The difference between glucose and inositol in their ability to form hydrogen bonds has been attributed to differences in their mutual attraction for water, reflected in their solubilities[116]. The fact that inositol does not cause any significant increase in the rigidity of the edestine film is consistent with earlier observations on the effects of hydroxylic molecules. Ellis and Pankhurst[64] observed that collagen films did not condense with monomeric mono-, di-, and trihydric phenols, but only with polyhydric phenols of molecular weight greater than the catechin monomer; Clark, Holt, and Went[24] found that protein films are condensed by silicic acid only after the latter has been polymerised.

In both these cases the condensation takes place through film-solute hydrogen bonding. Alizarin Cyanine expands the film and makes it more rigid by cross-linking (see Graph No.12).

Effects produced by Sulphate Esters and Monosulphonated Dyes.

Work with casein films showed that monosulphonated dyes exhibit surface-active properties, penetrate the film and at higher surface pressures increase its solubility. With edestine similar effects are observed, only in this case the film-dye complex seems to be much more soluble (see Graph No.13). The three solutes, sodium tetradecyl sulphate, Solacet Fast Scarlet B, and Naphthalene Red J are surface-active. They are adsorbed at the air/water interface, this was made apparent when the surface was being swept (to remove contamination before spreading the protein), by the appearance of small pressures, which usually disappeared rapidly as the weakly hydrophobic parts were forced into the aqueous phase. When the edestine was spread on these solutions there was a spontaneous development of pressure to about 1-2 dynes; this pressure decayed after a few minutes. Pressure was developed with compression, but at each compression stage there was first a rapid fall of pressure (taking 1-3 minutes), followed by a slow fall, which lasted a considerable time. This slow fall of pressure was not observed to the same

extent with casein films. In Graph No.13 the pressures of the "first compression" curves are the pressures between the end of the rapid fall and the start of the slow fall, thus these "first compressions" are not equilibrium force/area curves. The films were held at the top pressures for 30 minutes. Slow expansions followed with a 30-minute time allowance between each expansion stage. At each stage the pressure fell, then rose slowly until an equilibrium value was attained. The second compression was then completed. With adequate time allowances between each stage, during expansion and second compression these two curves are coincident or nearly so. Graph No.13 shows that some of the film is forced irreversibly into solution. The second compression curves are shown in Graph No.14.

Sodium tetradecyl sulphate has a greater solubilising effect than the sulphate ester dye (Solacet Fast Scarlet B). This is probably due to its hydrophobic residues being smaller in cross-section and being able to pack more closely; thus the external surface of the protein-solute complex must have a greater concentration of ester groups for a given area than that of the dye.

The two 1:1-metal complex dyes examined, Ultralan Yellow R and Ultralan Orange G, also solubilise the film, but to a much lesser extent. Ultralan Yellow R has a greater solubilising effect than the other complex, a similar

reason for this to the one given above may apply here also, since Ultralan Yellow R has a smaller cross-section, and therefore a greater charge/area ratio.

An explanation of the increased solubilisation of the protein film by surface-active dyes has already been given (see Fig.1B and pages 83-85). An alternative explanation to that of adsorption of a duplex film or micelle could however be given, thus. The surface-active dye forms a film, but this is both penetrated into, and supported by, the protein film. If more anionic dye molecules are present in the film than are required to combine with the cationic groups of the protein, the excess ionic groups will increase the solubility of the film.

2:1-metal Complex Dyes.

The 2:1-metal complex dyes, first introduced in 1949, are as already stated, of much technical importance. They are used for colouring wool and synthetic fibres. They are anionic, being salts of strong acids, but they differ from the 1:1-metal complex wool dyes in being unsulphonated and having their water-solubility conferred by non-ionic polar groups. They are distinguished by slow dyeing rate and very high fastness to wet treatments and to light, even in pale depths. Schetty[117] has given a full account of the chemistry and development of these dyes.

Little is known of the mechanism of dyeing of this type of dye, and the following work was undertaken to help define the source of affinity of these dyes for protein fibres. The mechanism of dyeing must differ from that of most other wool dyes, which usually contain strongly ionic groups (generally $-SO_3Na$). Schetty[117] considers that the dyeing process is similar to that of cellulose acetate with the non-ionic disperse dyes; the metal atom does not take part in the dye-fibre linkage, which he considers is primarily a Van der Waals attraction. Zollinger[118] has obtained isotherms for two 2:1-metal complex dyes on several fibres and has interpreted them as evidence of a "solid solution" mechanism, i.e. one similar to cellulose acetate dyeing. The following work supports and extends the views of both these authors.

Effects produced by 2:1-Metal Complex Dyes.

The force/area curves obtained with these dyes dissolved in the sub-solution are shown on Graph No.15, and are interpreted on the following basis: a fall in curve slope shows that the film solubility increases; a rise in slope shows that cross-linkage has occurred and the film has become more rigid.

These dyes produce most unexpected effects on the films. Thus complex No. III, which has no available polar

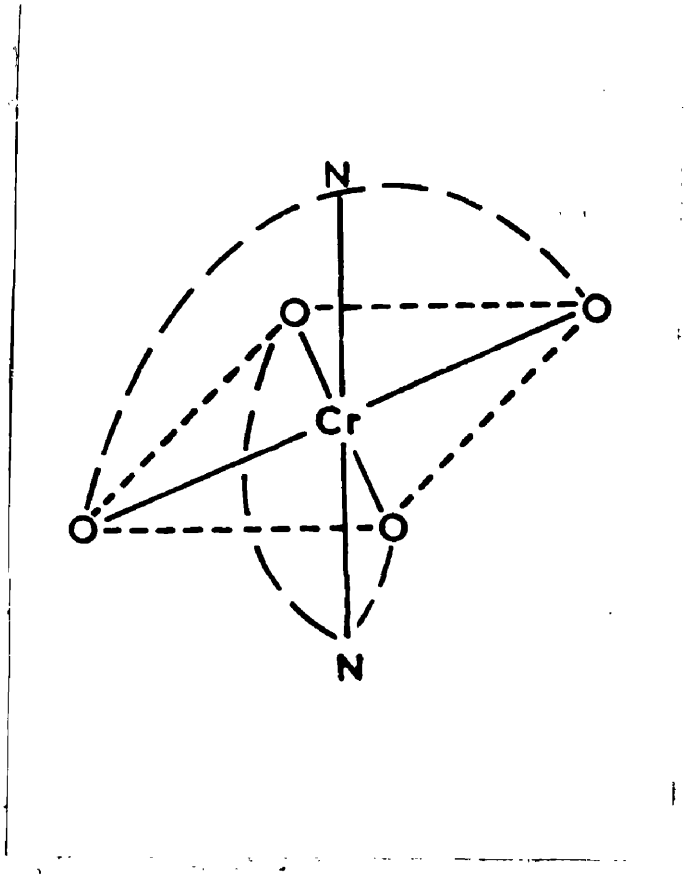
groups causes an increase in film rigidity, of a magnitude previously only observed with large, polymeric, powerfully proton-donating solutes; and the addition of such groups, as in complexes IV, V and VI, slightly reduces rigidity. Further, complexes I and II, which are not surface-active*, behave like normal surface-active dyes (e.g. Solacet Fast Scarlet B and Naphthalene Red J) in making the films extremely compressible. The most reasonable interpretation of these phenomena, consistent with other known properties of the dyes, is that the adsorbed species is in all cases a dye micelle. This is best considered with reference first to the geometry of the individual dye molecules.

Nature of the 2:1-Metal Complex Dye Micelle.

Models show that the four oxygen atoms of the o-hydroxy-groups in the complex lie in one plane, with the respective co-ordinated nitrogen atoms of the two azo-groups arranged perpendicularly to this plane and equidistant from all the oxygen atoms. The two parts of the complex molecule, which are planar, are at right angles to each other (cf. [119]) (see Fig.2A).

* None of these 2:1-complexes gave any evidence of being surface-active, certainly not to the same extent the other surface-active dyes did, i.e. no pressure was developed when the surface was being swept clean.

Fig.2. Structure of 2:1 dye-metal complex molecule and micelle.



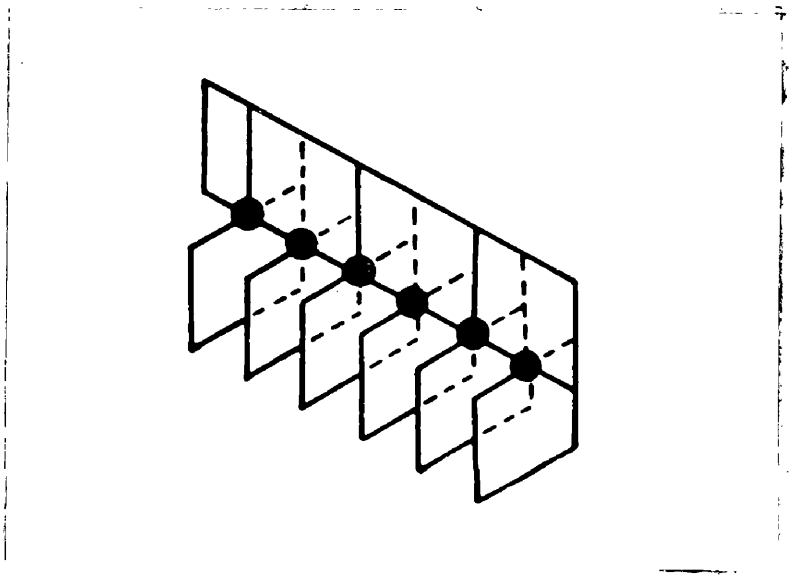
A Arrangement of co-ordinating atoms (schematic). The four oxygen atoms are in one plane. The curved broken lines show the three chelating atoms respective azo-dye molecules.

These dyes are generally of low water solubility and are highly aggregated in the cold[117] (some of the present examples flocculated on standing and III had particularly low solubility - ca. 10^{-5} M. in acid solutions). The principal aggregating force must arise in planar contact of adjacent azo-dye units. The models show that apparently the only way in which this association can operate to build up an aggregate is in the form similar to that represented in Fig.2 B,C. This is the most closely-packed possible arrangement. This structure can clearly be elaborated in three dimensions. The gegenions (sodium) may be accommodated partly in the gaps inside the structure and partly in the surrounding solution.

Nature of Micelle-film Bonds.

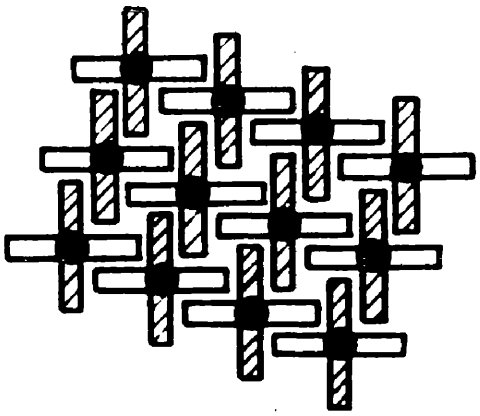
A study of the suggested micellar structure (Fig. 2, B.C.) shows that (i) its external surface consists of planar dye units protruding as a series of "fins" and that (ii) protein or other linear polymer chains can stretch across the surface, held in the channels between the "fins" whether these have small pendant polar groups or not (Fig.3A). There are narrow, parallel straight channels across the surface of the micelle of complex III, but wider channels could be followed by the film chains if they are bent or helical. In the absence of polar groups on the dye units non-polar forces must hold the protein backbone in these channels, the whole

Fig. 2B



Isometric projection of one line of associated complex molecules in suggested micelle. (Azo-dye units are shown as plain rectangles for clarity. Central metal atom represented by ●).

Fig.2C



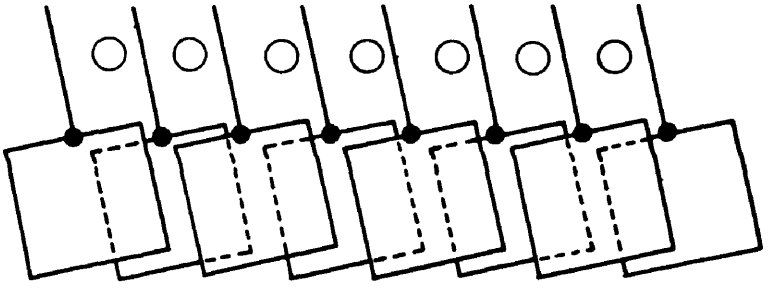
Plan of one part of a layer of suggested micelle, showing interlocking of azo-dye units by planar association. Hatched rectangles show units below, and white rectangles show units above the line of metal atoms.

forming a rigid network. Thus this structure can account for the observed rigidity produced by complex III, which has no available polar groups and if molecularly dispersed would not be expected to have any such effect. In the structure actually shown in Fig.2C, adsorbed protein backbones would be nearly twice as far apart as when close-packed alone on the surface. The actual increase observed with III is about 80%. The micelle structure also accounts for the effects of the other 2:1-complexes as follows.

(i) The micelles formed from complexes I and II have an exterior surface exposing strongly polar, water-attracting proton-accepting groups ($-SO_2Me$) (Fig.3B). Models show that the micelle can tilt to give an upper hydrophobic and a lower hydrophilic surface. The under-surface of the film-dye assemblage is thus water-soluble and the whole film shows the force/area curve characteristic of normal surface-active dye-protein films, with very high compressibility.

(ii) The films with complexes IV and V also have strongly water-attracting under surfaces. Their effect in increasing the film solubility is however masked by the competitive action of the polar groups in the upper surfaces of the micelles. These groups are strongly proton-donating and appear to form stable hydrogen-bond crosslinks with the protein chains. The net result is that these complexes do

Fig.3. Schematic representation of possible mode of film-dye micelle association. Film chain molecules (O) oriented perpendicular to the paper. For clarity dye units shown as rectangles (face-on) and lines (edge-on), and tilted.



A Adsorption of non-polar Complex No.III

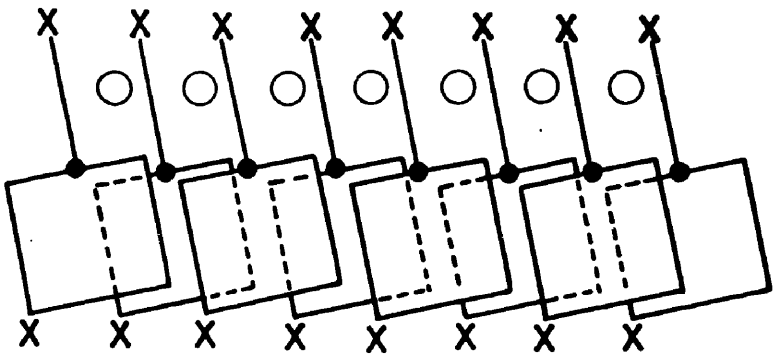


Fig.3B Adsorption of Complexes No.I and II at high film pressures. Proton-acceptor groups X beneath the micelle confer high solubility.

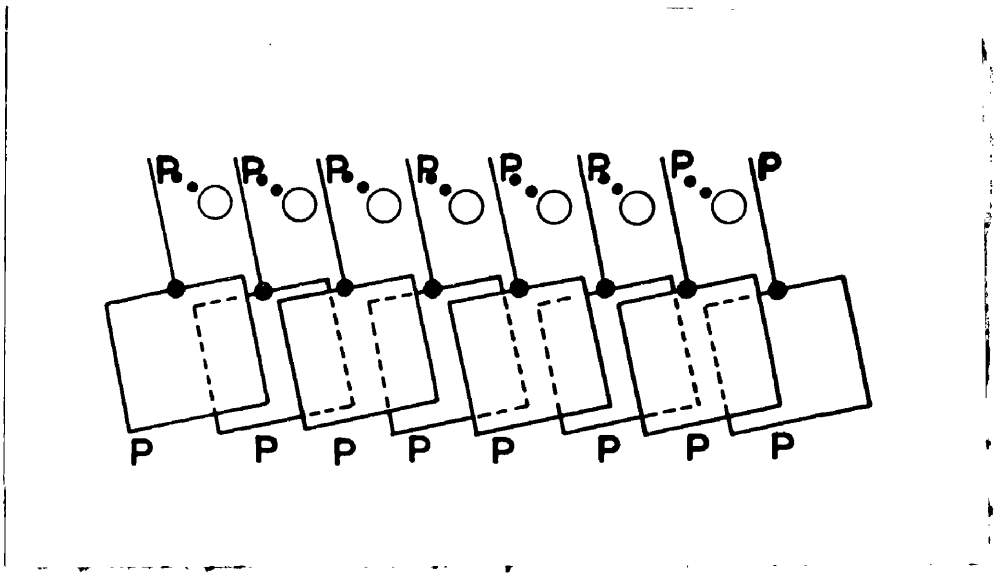


Fig.3C. Adsorption of Complexes No.IV - No.VI. Proton-donor groups P bond with film chains above micelle, and with water below.

increase the rigidity of the film considerably, but a little less so than does the non-polar complex III, and they increase the film area less than III does, probably because of their stronger cross-linking action.

Change in pH from 3.3. to 4.7 has no effect on the percentage increase in edestine film area produced by the proton-donating complex VI, but it slightly reduces (by ca. 5%) the increase given by the non-polar complex III (see Graph No.16).

Effect of Chelation.

The acetylamino-group in complex IV is chelated with the azo-group[117]. The complex is thus not a proton-donor. This explains its marked expansive and solubilising effect on edestine films at pressures less than 10 dynes/cm. (see Graph No.15). The net result of chelation is to produce, in effect, another aromatic ring which makes complex IV closely resemble complexes I and II, as indeed it does in the lower pressure regions. At pressures greater than 10 dynes/cm. the complex does behave as a proton-donor (cf. V, VI, Graph No.15); when the complex molecules are forced close to the protein the chelate ring presumably breaks and a complex-protein hydrogen bond forms preferentially. This is consistent with the known weakness of a second hydrogen-bond to an azo group.

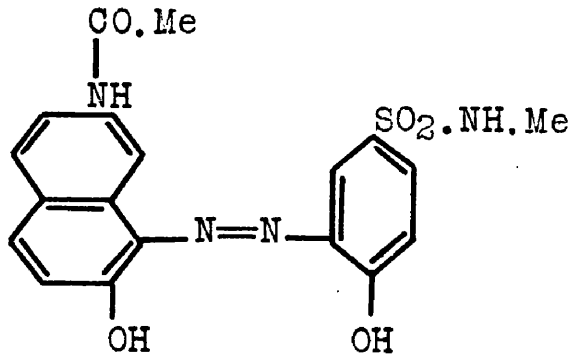
Nature of Film-dye Hydrogen Bonds.

The dye Alizarin Cyanine WR, which is capable of proton-donation, has much less effect on N-methoxymethyl nylon films than on edestine (see Graphs No.12 and No.18, also pages (111,112) below; the hydrogen-bond acceptor centres in the films are therefore probably the backbone -CONH- groups. In contrast, the non-polar complex III has a similar effect on both films (see Graphs No.15 and No.19), confirming that there is no hydrogen-bond adsorption with this complex. Earlier adsorption tests[80,120] showed that some proton-donors are much more strongly adsorbed than proton-acceptors by protein or nylon fibres, from solutions, or as vapours. The solutes used now and previously show a similar phenomenon. In ability to bond with proteins or nylon, groups fall roughly , in this sequence: ArOH > ArNHCOMe > $ArNH_2$ > ArNHR > Alk-OH > proton-acceptor groups.

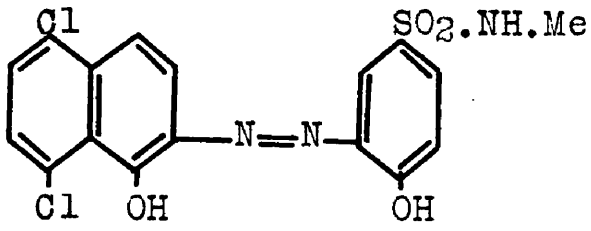
Isotherms for Adsorption by Fibres.

Zollinger[118] postulated salt-formation by the sodium salt of the dye together with solid solution of its free acid to account for the isotherms he obtained, shown in Graph No. 22 for the 2:1-chromium complexes of:-

Compound A, 2:1-Cr complex of:-



Compound B, 2:1-Cr complex of:-



This interpretation is now confirmed, and may be extended in the light of the present and other work. The normal ('L' type - see Part II) curves for silk (c) and wool (f), represent mainly ion-exchange adsorption in water-accessible regions of the fibres. Linear portions of curves, for acetylated wool* (a), acetylated nylon* (b, very low slope), and stretched nylon (d) represent mainly hydrogen-bond adsorption in water-inaccessible regions. All the curves for nylon (b, d, e, g, h), unlike those for silk and wool, have ('HA', i.e. high affinity, see Part II) character, i.e. initially they coincide with the y-axis. There is therefore a source of high affinity in nylon which is not present in the protein; this source must be Van der Waals attraction by the hydrocarbon portions of the nylon chains. Very possibly this high affinity arises from the engagement of the chains with the dye micelle (see Fig.3A and the strong adsorption of complex III to the films). Other work done in this laboratory shows that HA curves are almost always due to micellar adsorption (Part II).

In unstretched nylon all the regions of the fibre accessible to dye are accessible to water - the isotherm has no linear portion. In the stretched fibre there are regions accessible to dye but not to water - the isotherm has a linear

---

* Acetylation removes the ion-exchange centres ($-NH_3^+$ groups) in the fibre.

portion.

B has higher non-polar attraction than A has for nylon; this follows from these considerations: (i) the adsorption of B is higher on both forms of nylon (Graph No.22 h, d); (ii) a lower proportion of the total adsorption of B than that of A is due to ion exchange, since acetylation reduces adsorption of B much less than A (Graph No.22 h, g; d, b); (iii) the non-linear isotherms indicate adsorption in water-accessible regions, in which B, not being a proton-donor, has low hydrogen-bond affinity. Therefore, the main affinity of B must be non-polar, probably Van der Waals attraction between the planar dye molecules and the hydrocarbon portions of the nylon molecular chain.

Models give evidence of a possible reason for the affinity difference between A and B. Thus: (a) the longest molecular axis parallel with the micelle surface (i.e. length of "fin") is longer in B (ca. 14.5 A) than in A (ca. 12 A); (b) the -NHCOMe substituent in A may interfere sterically with penetration of the nylon chain between "fins". Both effects (a) and (b) will tend to reduce the area of direct contact of dye and fibre molecule, and thus will reduce their mutual Van der Waals attraction.

Micellar Adsorption.

The properties of these dyes in fibres are consistent with their presence as large micelles of fairly uniform size. Dyeing is normally carried out at the boiling point, and under these conditions the dyes have low degrees of aggregation[117]. Dye molecules entering the fibre may therefore be nearly mono-disperse. Aggregates must then build up on the internal fibre surfaces, probably during dyeing, but possibly during subsequent cooling or drying.

Light Fastness of 2:1-Metal Complex Dyes.

Schetty[117] reports that a noticeable difference between the (Irgalan) 2:1-metal complex dyes and ordinary acid wool dyes "is that the former show within narrow limits constant light fastness when applied to the most diverse substances, such as silk, wool, nylon, Perlon, acetate rayon, and lacquers." Large aggregates of dye fade much more slowly than monodisperse dye molecules[121]. The micellar structure of these dyes postulated here would be expected to persist in all media - aqueous or non-aqueous - because of the high mutual attraction of the planar aromatic nuclei - and if it does, the consistently high light resistance of these substances is explained.

Earlier experimental work[121] in this laboratory has shown that dyes in monodisperse form fade approximately at a

first-order rate, i.e. exponentially, but when they are entirely in aggregated particles, e.g. as insoluble pigments, they fade at a steady rate (zero order) indicative of fading of particles at the outer surface only. Most normal soluble dyes in transparent substrates, e.g. gelatin, at first fade exponentially, and then, after a small proportion, of the order of 10% has been destroyed, the rate becomes steady[121]. This behaviour indicates the presence of a little monodisperse dye, which fades first, and some associated dye, which fades more slowly. Thus a fading rate test can give useful information on the physical state of the adsorbed dye. Fading tests were therefore made in this investigation as a check on the hypothesis that the 2:1-complex dyes are adsorbed mainly as micelles. These tests were made with formaldehyde-hardened gelatin films dyed with complexes No.I, III and IV (Graph No.21). These films were exposed on a radius of 8 in. from a (400 w.) mercury-vapour lamp, for periods up to 78 hours. There was no evidence of an initial rapid loss in optical density (see Graph 21; indeed, no significant loss of optical density occurred at all). This behaviour is characteristic of dyes which are present largely in aggregated form, thus it appears that the 2:1-metal complex dyes tested may well exist entirely as micellar aggregated particles in the gelatin. This lends further support to the postulated micellar structure of these dyes and enables a mechanism of dyeing to be suggested.

Mechanism of Dyeing.

Conclusions:- All the facts available suggest the following tentative picture of the dyeing mechanism on nylon and protein fibres. The dye builds up in the fibre during dyeing (probably) or subsequently, as "network" micelles (Fig.2 B,C). The adsorption forces are:

(a) in water-accessible regions of the fibres: (i) ion-exchange of the dye sodium salt with cationic amino-groups in both types of fibre, (ii) Van der Waals attraction between the hydrocarbon parts of the nylon chain and (probably) the aromatic residues at the surface of the dye micelles, (iii) hydrogen-bond donation by the dye (if suitable groups are present) with backbone -CONH- groups in the fibre;

(b) in water-inaccessible regions, the free acid may be adsorbed preferentially, by both methanism (ii) and (iii) and also by, (iv), hydrogen-bond acceptance by the dye.

Section II C.

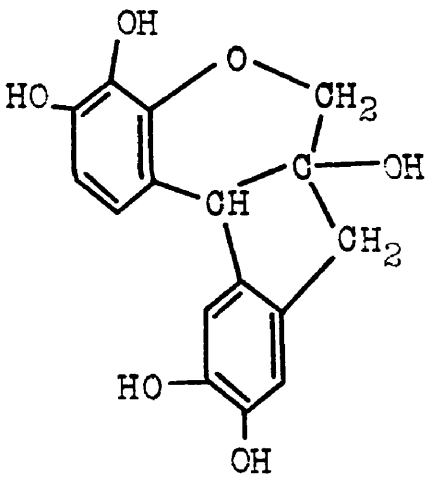
N-Methoxymethyl Nylon Monolayers.

Other investigators have recently studied interactions with polyamide monolayers, see e.g.[34,24]. In this work a few tests were made with N-methoxymethyl ('MM') nylon (I.C.I., 33% methoxymethyl substitution in the amide group of 6, 6 nylon), which was spread from a 0.01% solution in methanol. The results are shown in Graphs No.18 and 19. These results help to indicate that the source of hydrogen-bond acceptance in the protein films is probably the -CONH- group of the protein backbone.

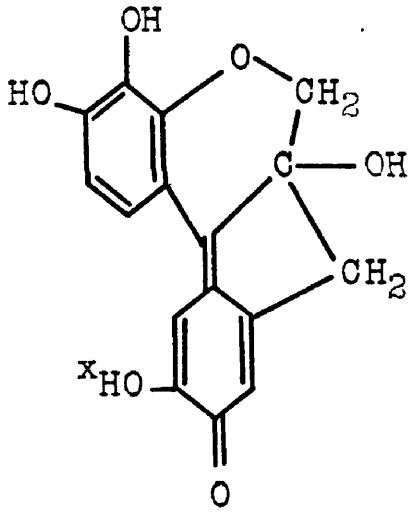
The dye Alizarin Cyanine has a much greater effect on casein and edestine films than on those of MM nylon (the compressibility is not increased by such a large factor). This points to the conclusion that with the protein films the carbonyl portions of the keto-imide backbone groups are predominantly involved in the proton-acceptance.

The non-polar 2:1-metal complex dye (III) has similar effects on edestine and MM nylon films, indicating that the suggested non-hydrogen-bond adsorption mechanism is more plausible than the alternative, which would involve proton-donation to the dye, and from earlier observations this is known to be unlikely.

Films of MM nylon were also prepared on solutions of the two polyhydric phenols, haematoxylin and haematein, and two different effects were observed (see Graphs No.18 and 19).



Haematoxylin

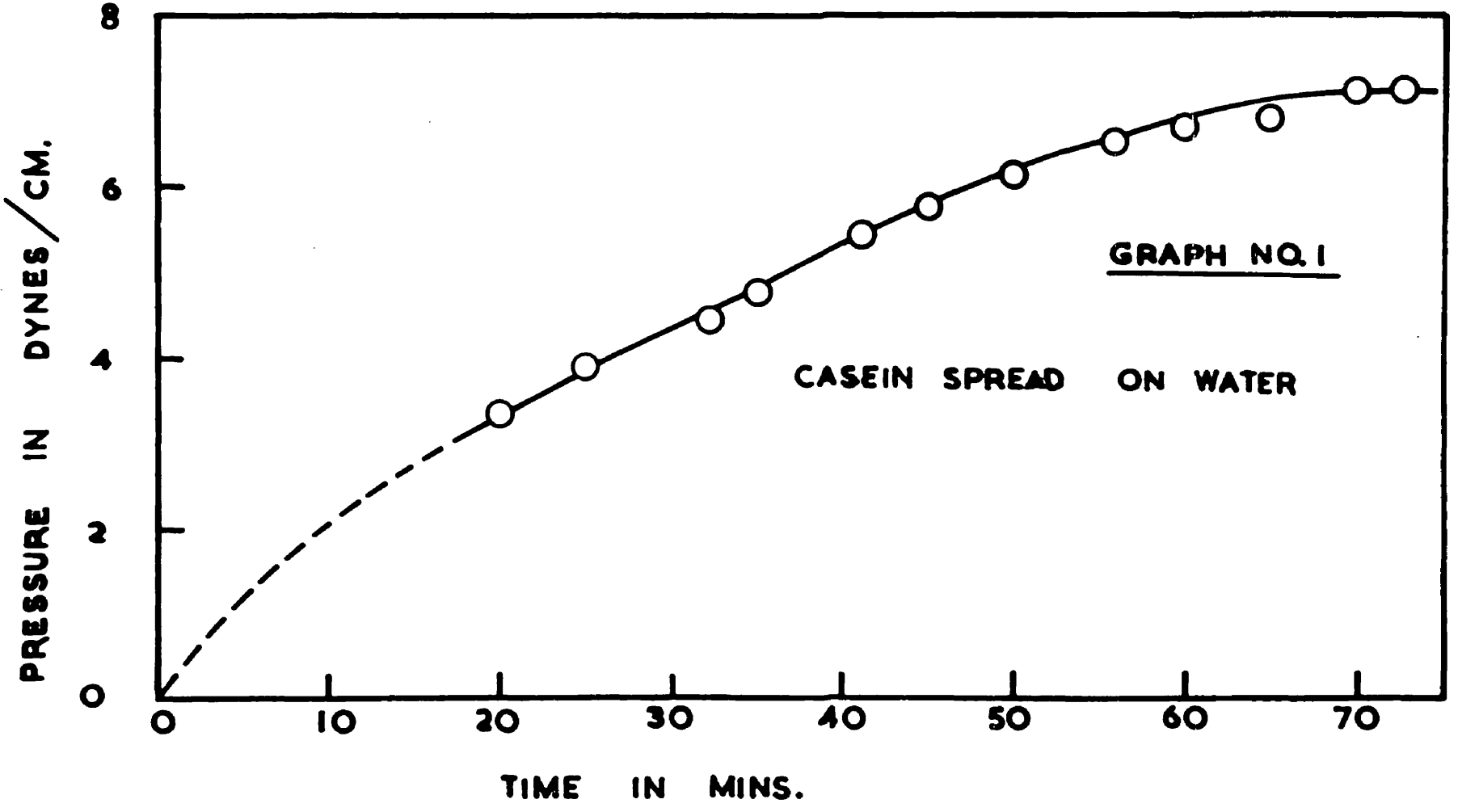


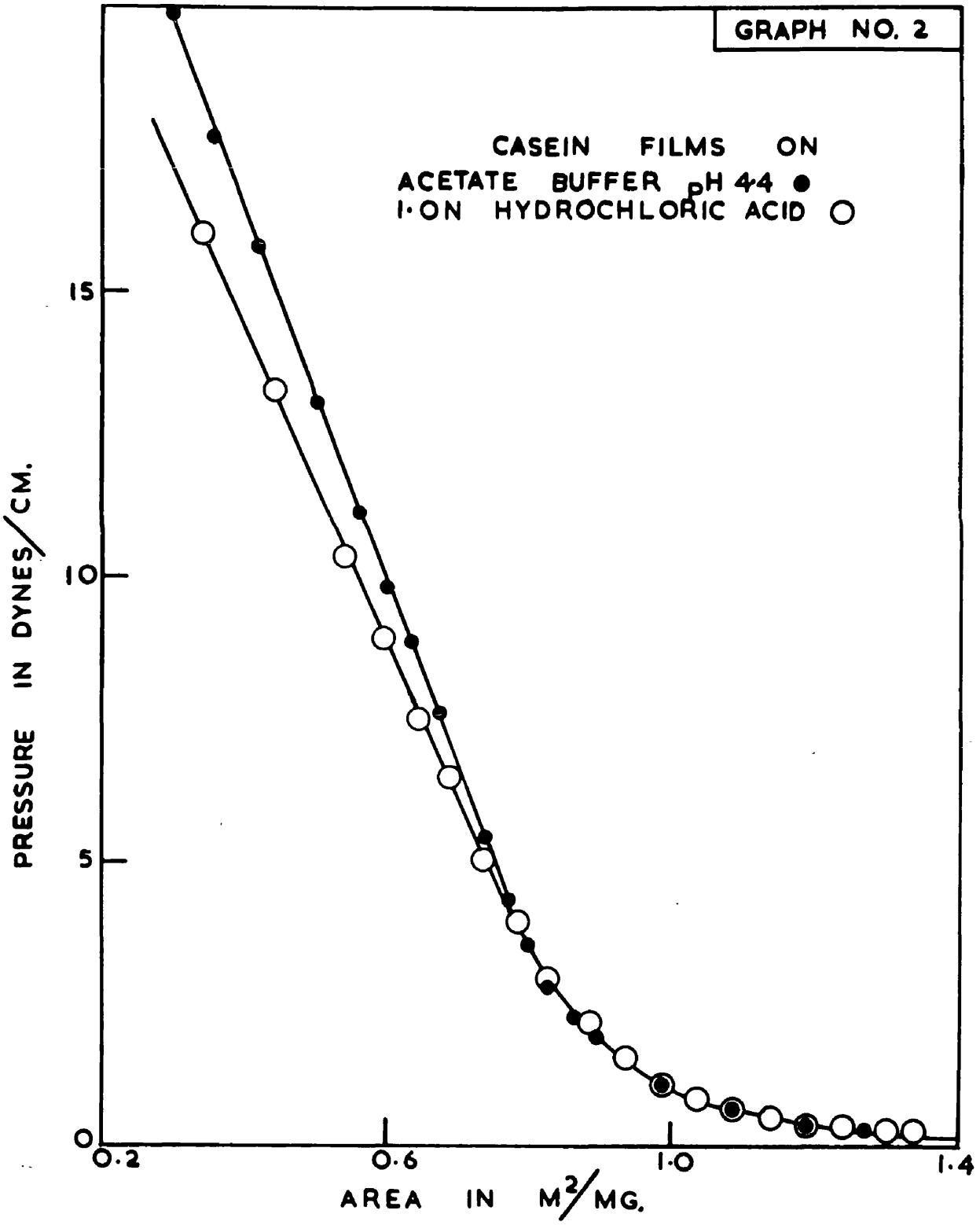
Haematein

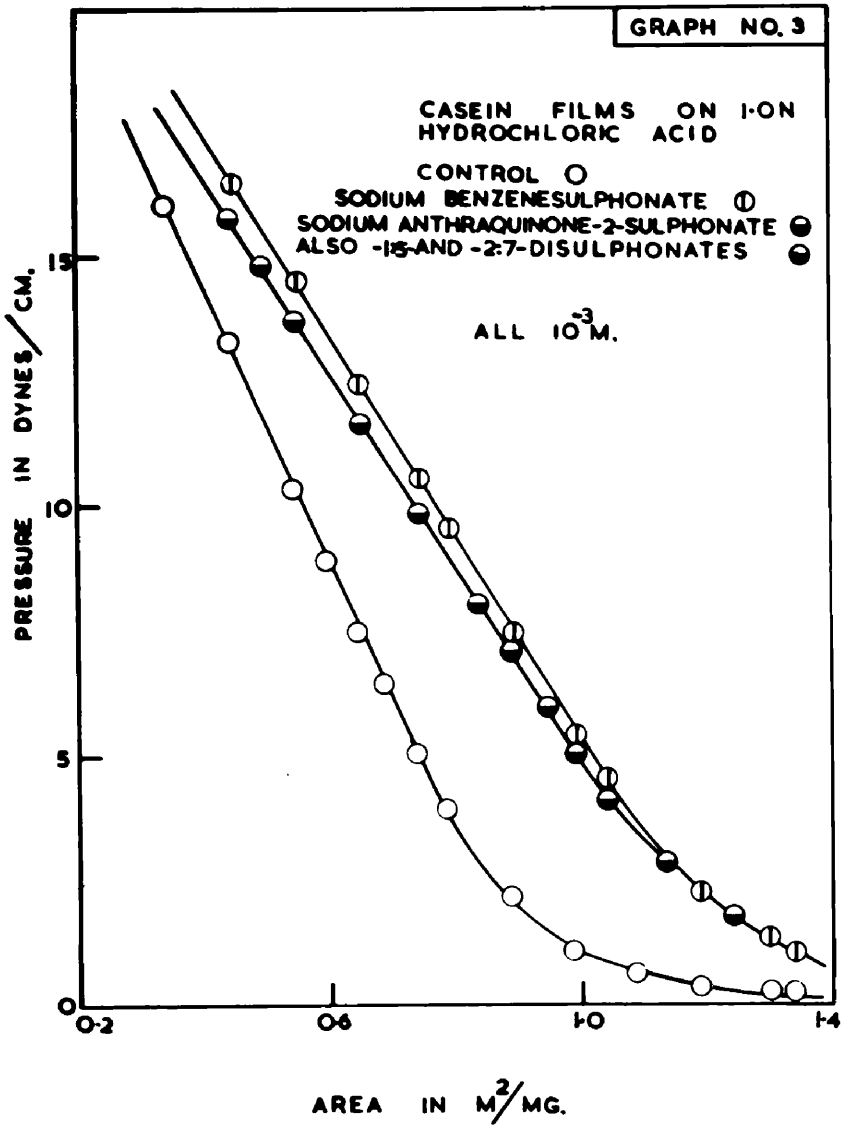
Haematoxylin condensed the film, making it more rigid; but haematein made the film slightly more compressible. Haematoxylin acts as a polyfunctional hydrogen-bonding agent and is capable of cross-linking the polyamide chains. Haematein exhibits surface-active properties* no doubt due to

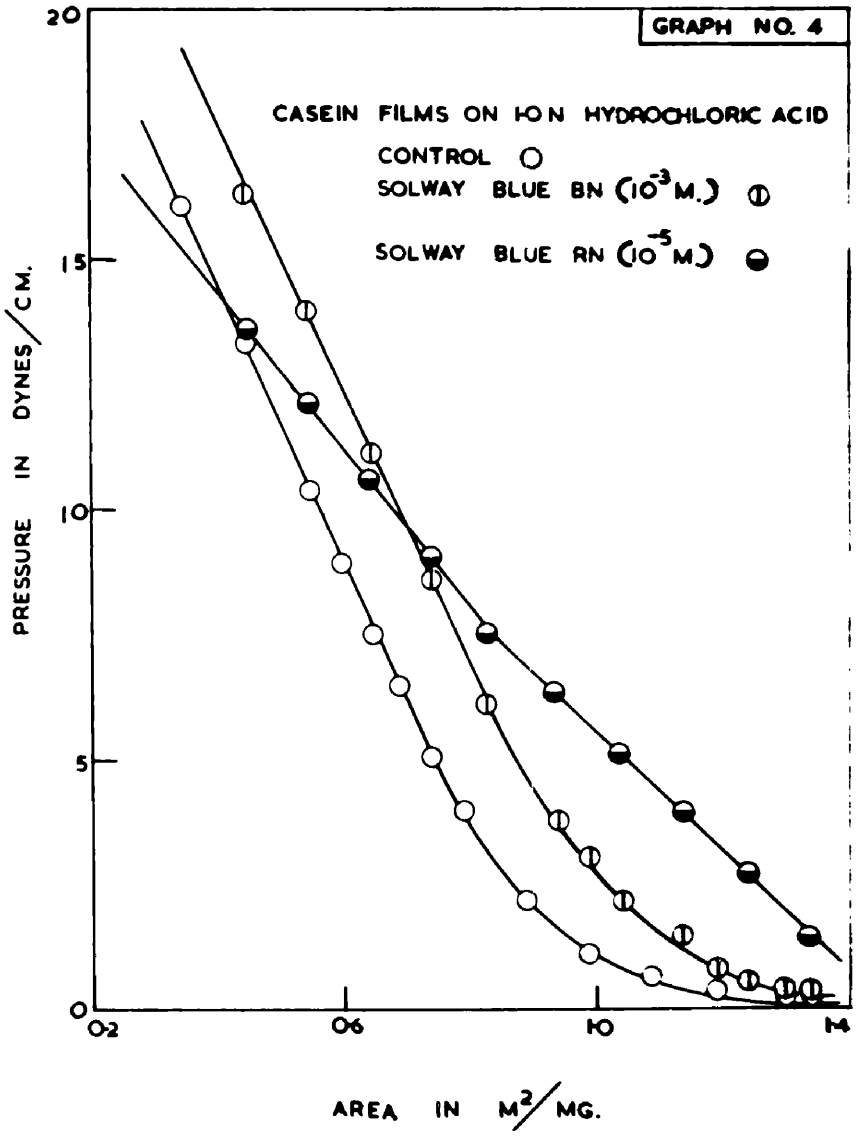
* Haematein alone forms a monolayer film on 2N-hydrochloric acid, with a molecular area of ca.48 A^2, which is in reasonable agreement with the value (54 A^2), estimated from models, for orientation on the activated phenolic group. The estimated area for the molecule lying flat is ca. 66 A^2. Haematoxylin does not form a film.

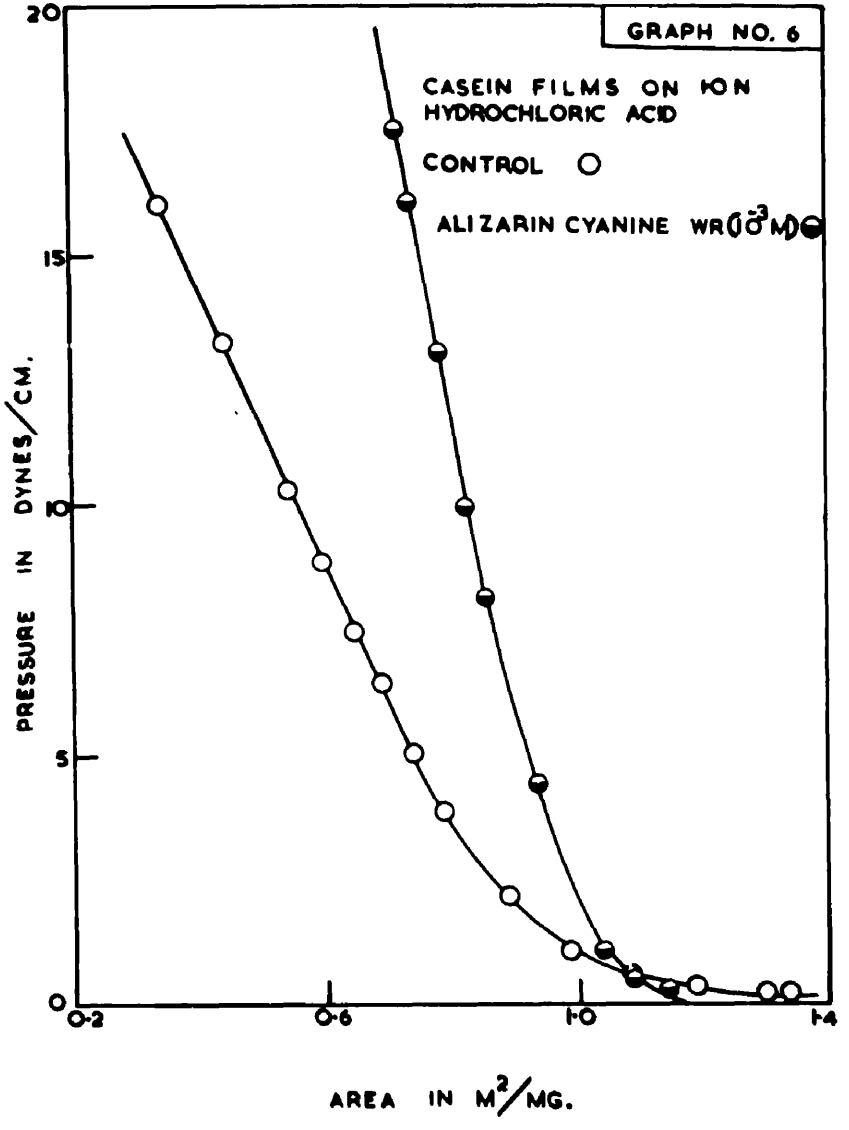
the activation of the adjacent phenolic group (*) by the quinone group, which give it a lack of symmetry. This prevents the haematein molecule lying flat, and cross-linking the film. (This point will be dealt with more fully in Part II of this thesis).

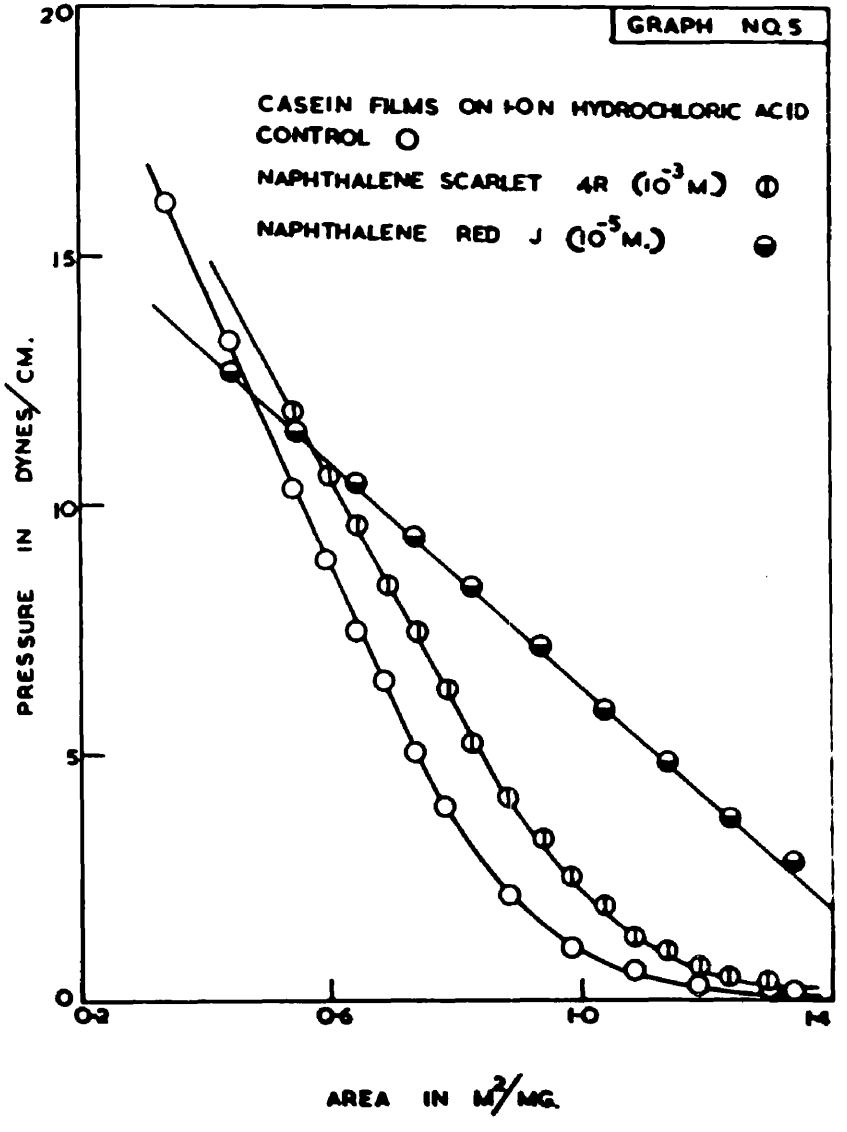

PRESSURE IN DYNES/CM.
8
6
4
2
0
0
10
20
30
40
50
60
70
TIME IN MINS.
GRAPH NO. 1
CASEIN SPREAD ON WATER

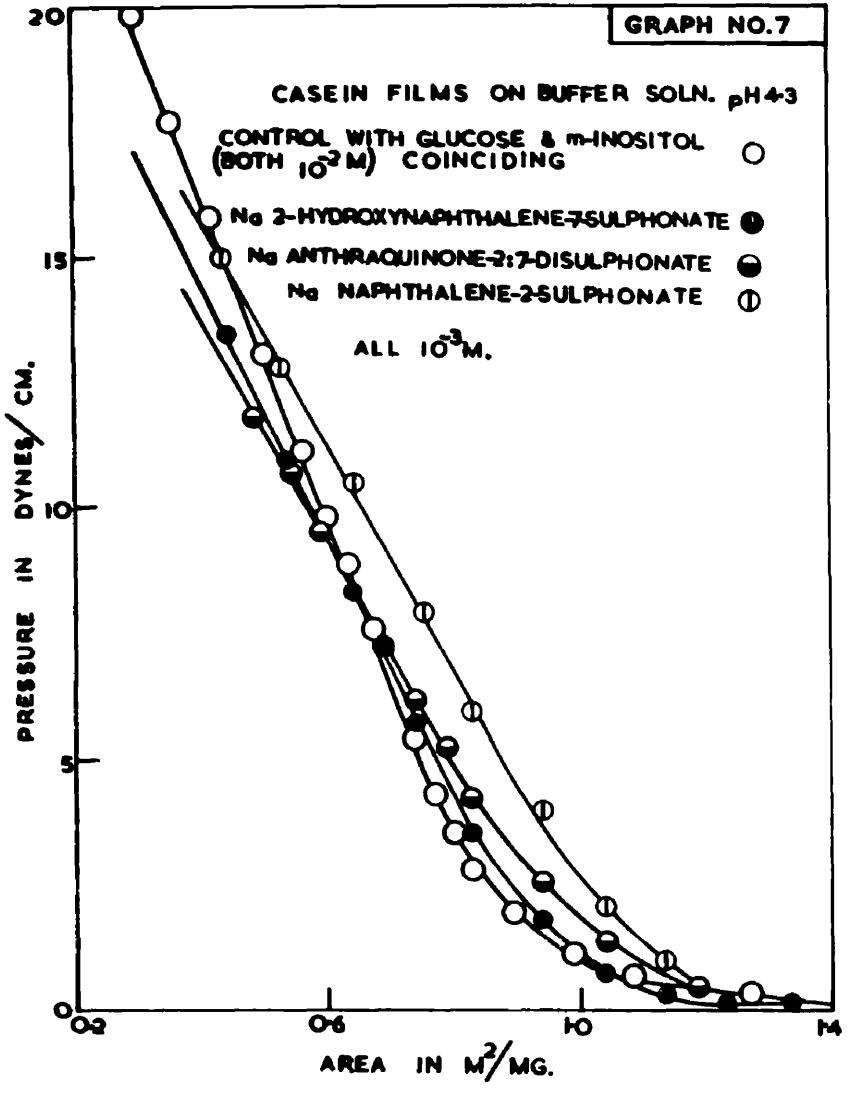

GRAPH NO. 2
CASEIN FILMS ON
ACETATE BUFFER pH 4·4 ●
1·0N HYDROCHLORIC ACID ○
PRESSURE IN DYNES/CM.
15
10
5
0
0·2
0·6
1·0
1·4
AREA IN M²/MG.

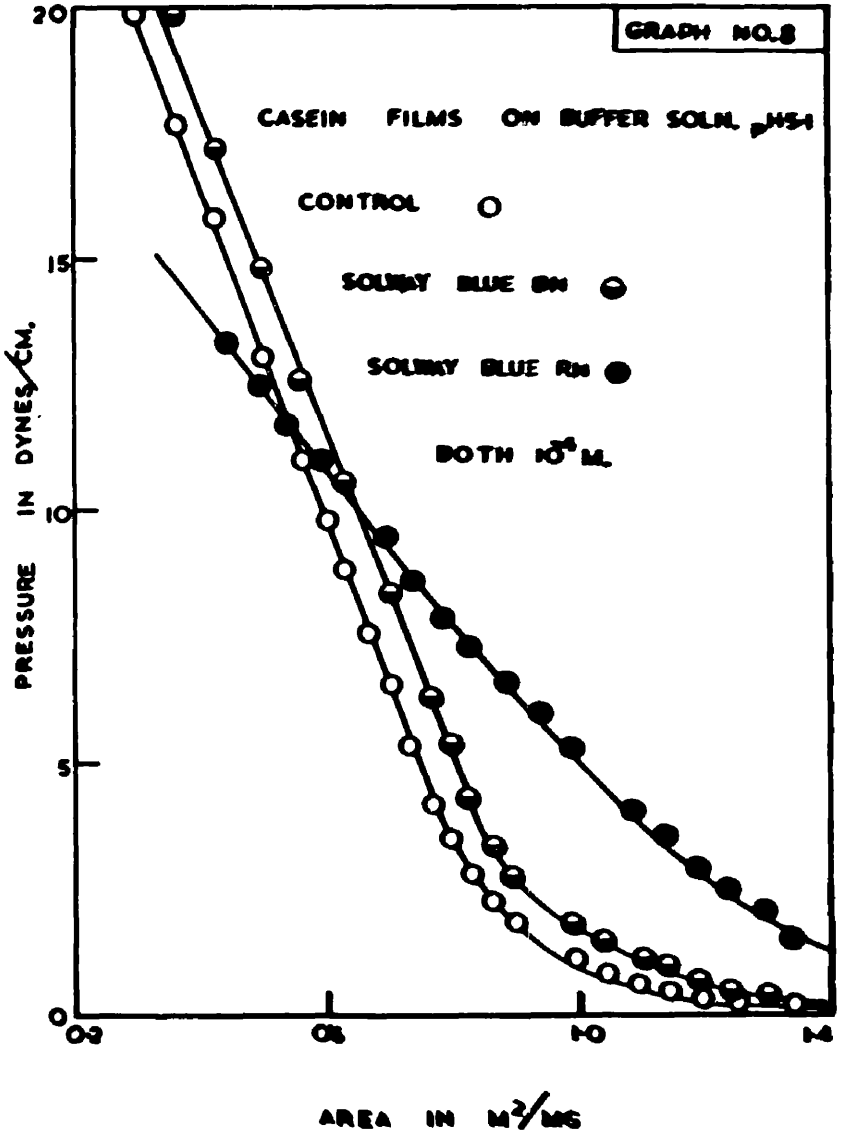

GRAPH NO. 3
CASEIN FILMS ON 1·0N HYDROCHLORIC ACID
CONTROL O
SODIUM BENZENESULPHONATE ◐
SODIUM ANTHRAQUINONE-2-SULPHONATE ◒
ALSO -1:5-AND -2:7-DISULPHONATES ◒
ALL 10^{-3}M.
PRESSURE IN DYNES/CM.
0
5
10
15
0·2
0·6
1·0
1·4
AREA IN $M^2/MG.$

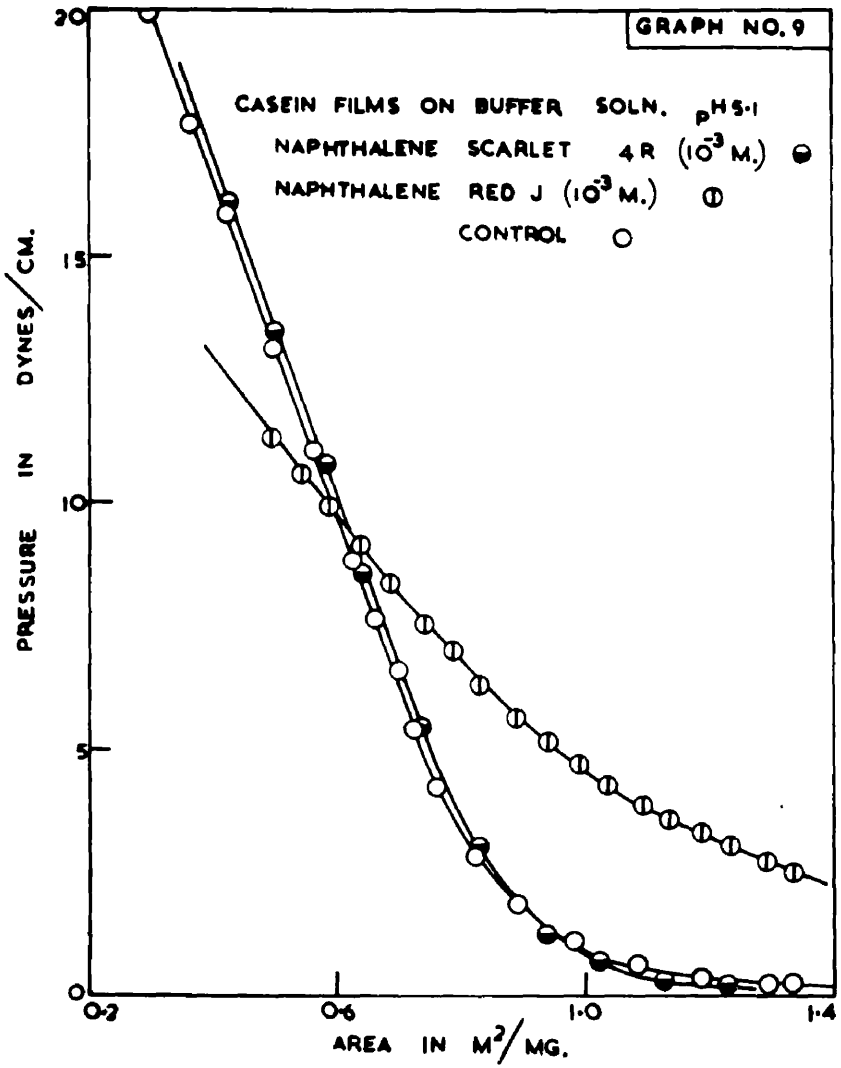

GRAPH NO. 4
CASEIN FILMS ON 1·0N HYDROCHLORIC ACID
CONTROL O
SOLWAY BLUE BN (10^{-3}M.) ◐
SOLWAY BLUE RN (10^{-5}M.) ◒
PRESSURE IN DYNES/CM.
0
5
10
15
20
0·2
0·6
1·0
1·4
AREA IN $M^2/MG.$

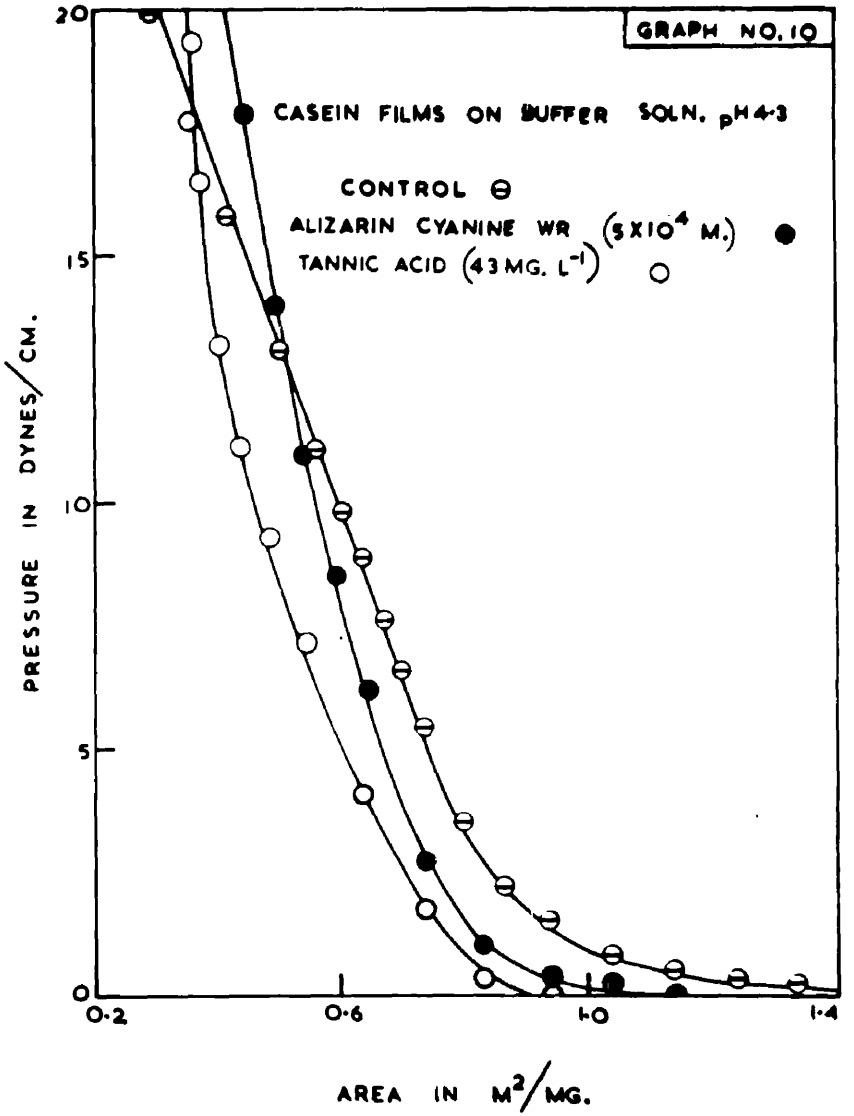

GRAPH NO. 6
CASEIN FILMS ON 1ON HYDROCHLORIC ACID
CONTROL O
ALIZARIN CYANINE WR(10⁻³M)
PRESSURE IN DYNES/CM.
AREA IN M²/MG.
0
5
10
15
20
0·2
0·6
1·0
1·4

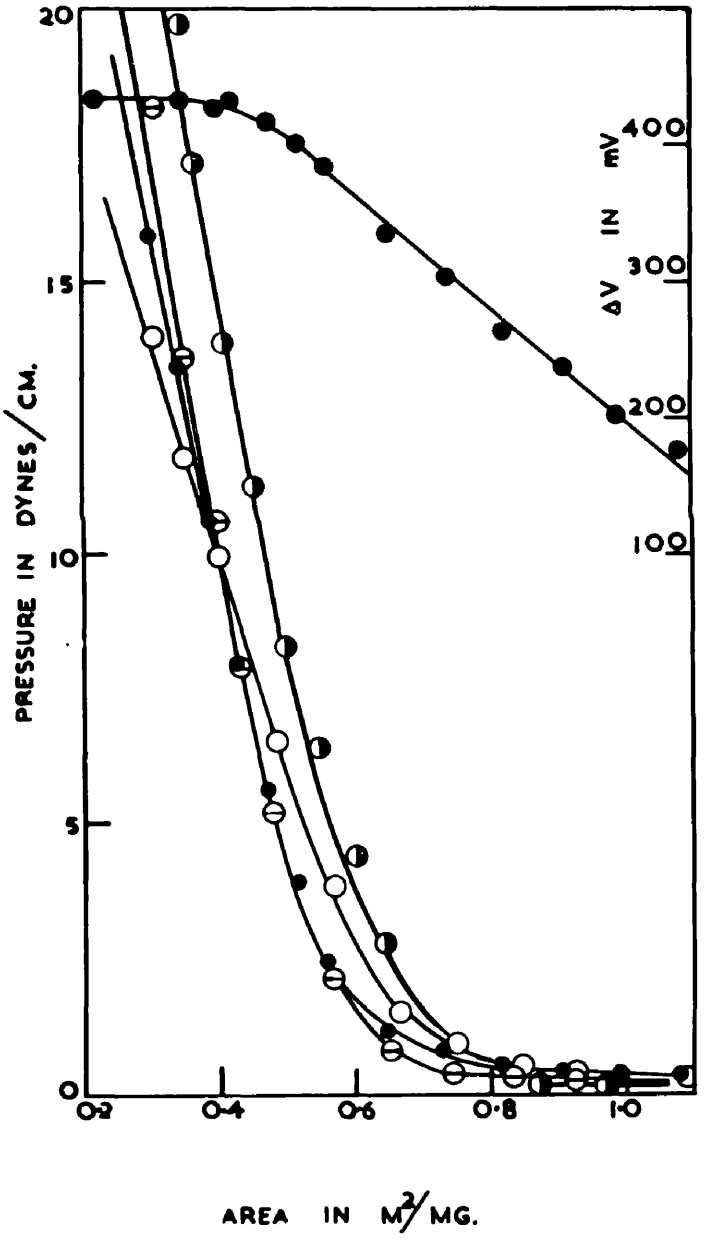

GRAPH NO.5
CASEIN FILMS ON 1ON HYDROCHLORIC ACID
CONTROL O
NAPHTHALENE SCARLET 4R (10⁻³M)
NAPHTHALENE RED J (10⁻⁵M.)
PRESSURE IN DYNES/CM.
AREA IN M²/MG.
0
5
10
15
20
0·2
0·6
1·0
1·4


GRAPH NO.7
CASEIN FILMS ON BUFFER SOLN. pH 4·3
CONTROL WITH GLUCOSE & m-INOSITOL (BOTH 10^{-2} M) COINCIDING
Na 2-HYDROXYNAPHTHALENE-7-SULPHONATE
Na ANTHRAQUINONE-2:7-DISULPHONATE
Na NAPHTHALENE-2-SULPHONATE
ALL 10^{-3} M.
PRESSURE IN DYNES/CM.
AREA IN M²/MG.
0
5
10
15
20
0·2
0·6
1·0
1·4


GRAPH NO.8
CASEIN FILMS ON BUFFER SOLN. pH 5·1
CONTROL
SOLWAY BLUE BN
SOLWAY BLUE RN
BOTH 10^{-6} M.
PRESSURE IN DYNES/CM.
AREA IN M²/MG
0
5
10
15
20
0·2
0·6
1·0
1·4


GRAPH NO. 9
CASEIN FILMS ON BUFFER SOLN. pH 5·1
NAPHTHALENE SCARLET 4R (10^{-3} M.)
NAPHTHALENE RED J (10^{-3} M.)
CONTROL
PRESSURE IN DYNES/CM.
AREA IN M^2/MG.
0
5
10
15
20
0·2
0·6
1·0
1·4


GRAPH NO. 10
CASEIN FILMS ON BUFFER SOLN. pH 4·3
CONTROL
ALIZARIN CYANINE WR (5×10^{-4} M.)
TANNIC ACID (43 MG. L^{-1})
PRESSURE IN DYNES/CM.
AREA IN M^2/MG.
0
5
10
15
20
0·2
0·6
1·0
1·4



GRAPH NO.11

EDESTINE FILMS ON BUFFER SOLNS.

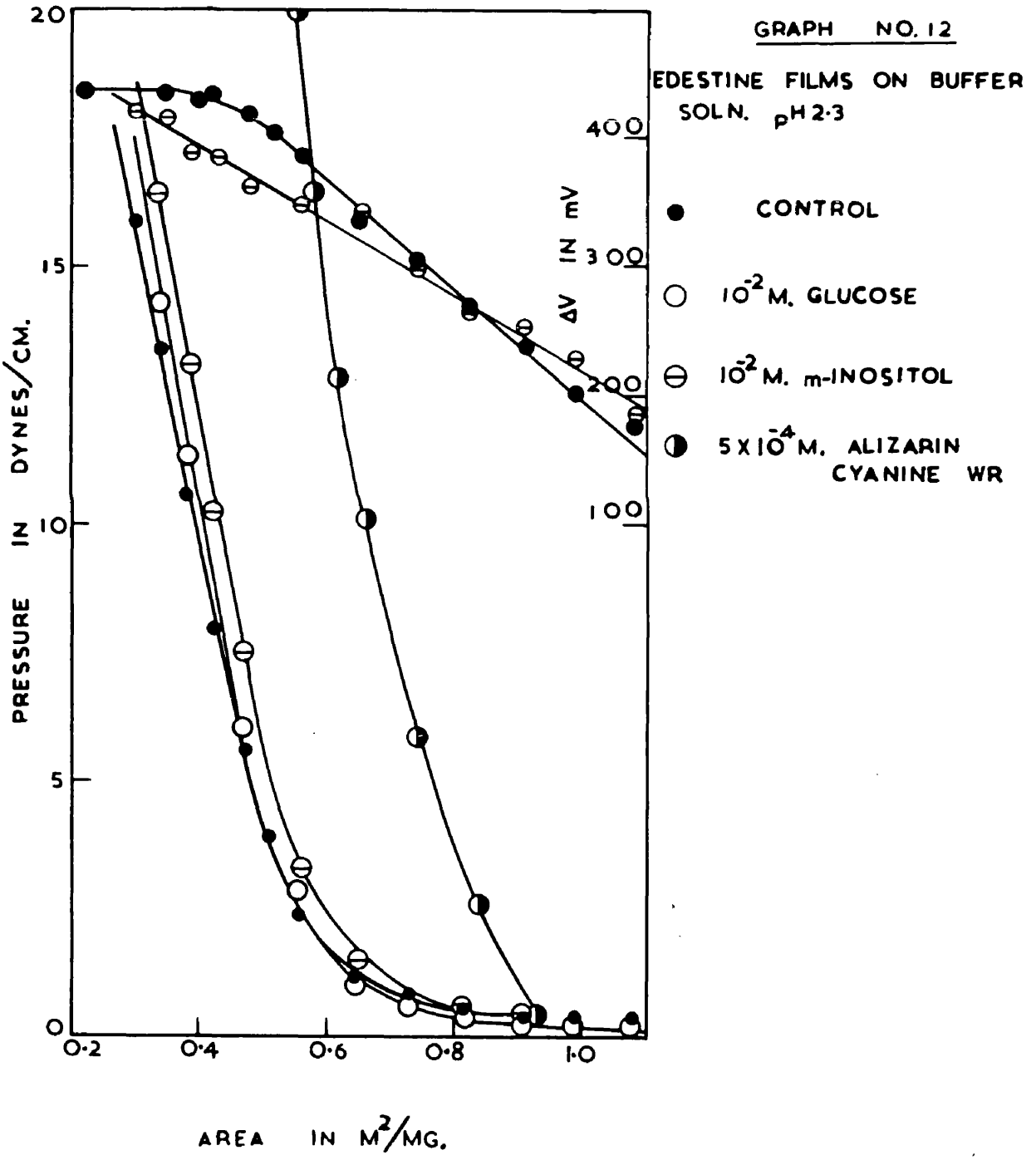
○ ON pH 2·3 SPREAD FROM 0·1 % w/v 0·5 M. NaOH

● ON pH 2·3 SPREAD FROM 0·01% w/v 2·0 M. NaCl

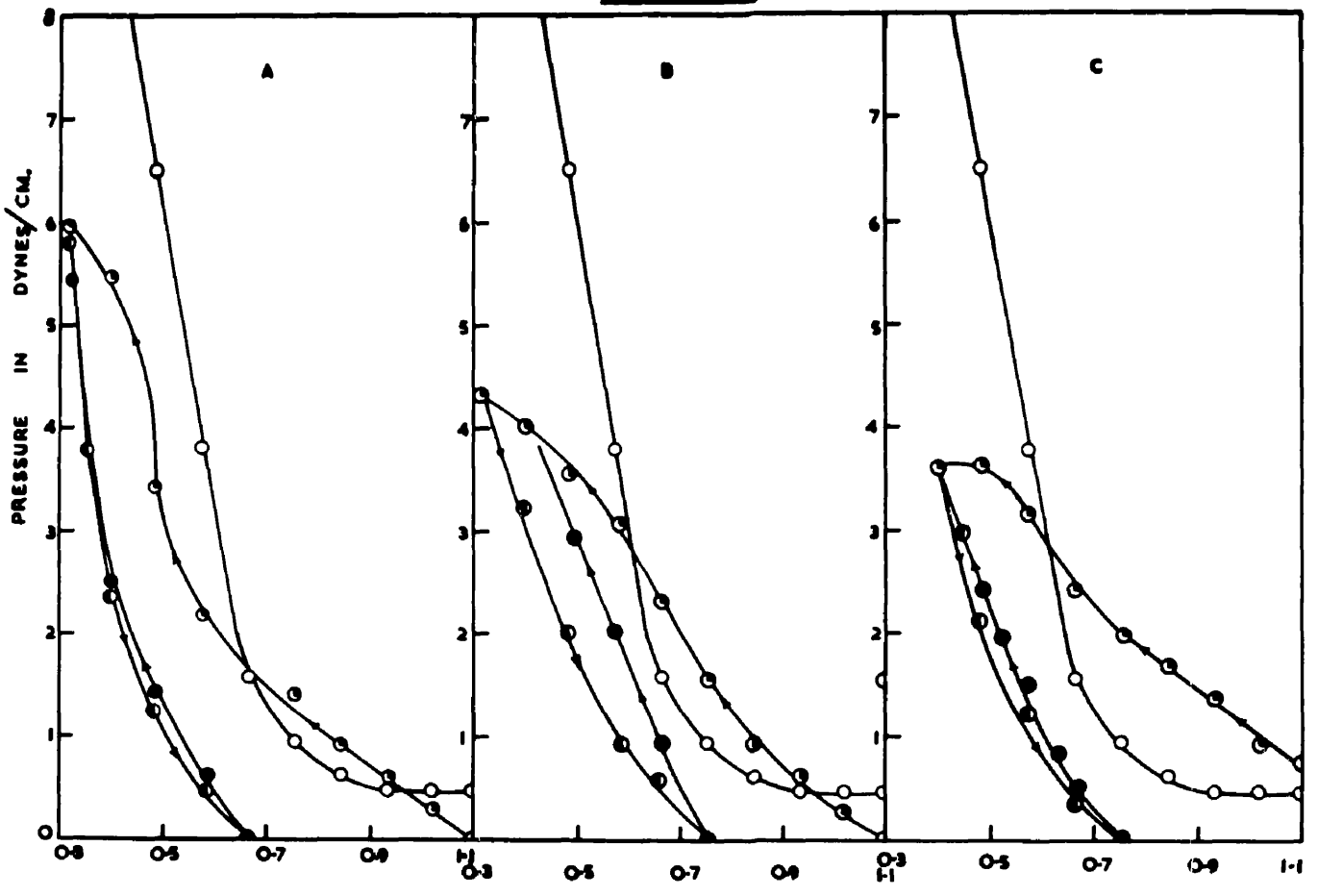
⊖ pH 3·3

BOTH FROM 0·5 M. NaOH

◑ pH 4·7

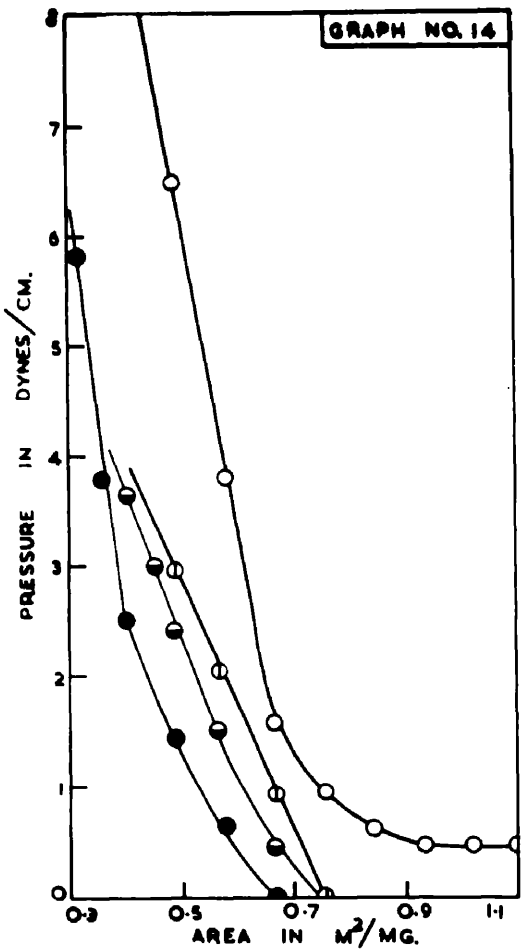

GRAPH NO. 12
EDESTINE FILMS ON BUFFER SOLN. pH 2·3
CONTROL
10⁻² M. GLUCOSE
10⁻² M. m-INOSITOL
5 X 10⁻⁴ M. ALIZARIN CYANINE WR
PRESSURE IN DYNES/CM.
ΔV IN mV
AREA IN M²/MG.
0
5
10
15
20
100
200
300
400
0·2
0·4
0·6
0·8
1·0

GRAPH NO. 13



EDESTINE FILMS ON BUFFER SOLUTION pH 2·3. ○ CONTROL, ● 1st. COMPRESSION, ◐ EXPANSION, ◑ 2nd COMPRESSION.

A 5×10^{-5} M. Na TETRADECYL SULPHATE. B 10^{-4} M. SOLACET FAST SCARLET B. C 10^{-4} M. NAPHTHALENE RED J.



EDESTINE FILMS ON BUFFER SOLN. pH2·3.

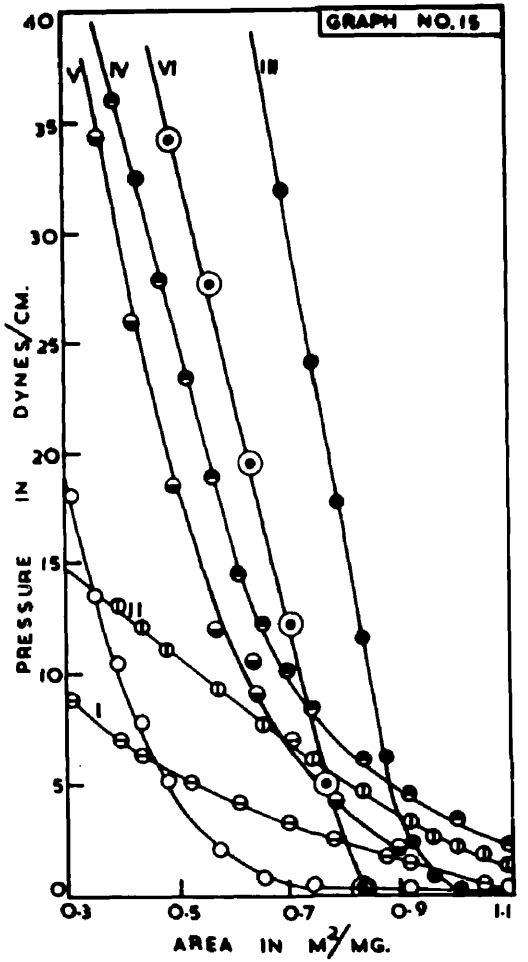
○ CONTROL.

① 10^{-4}M. SOLACET FAST SCARLET B.

◒ 10^{-4}M. NAPHTHALENE RED J.

● 5×10^{-5}M. Na TETRADECYL SULPHATE.

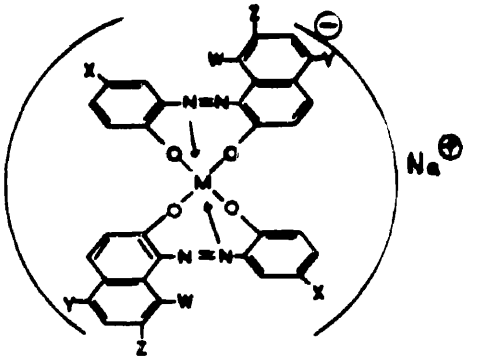
ALL ARE 2nd COMPRESSIONS.



EDESTINE FILMS ON BUFFER SOLN. pH3·3.

WITH VARIOUS 2:1 METAL COMPLEX DYES.

ALL 10^{-5}M.



COMPLEX NO. I. M=Cr, X=SO_2CH_3, W,Y & Z=H

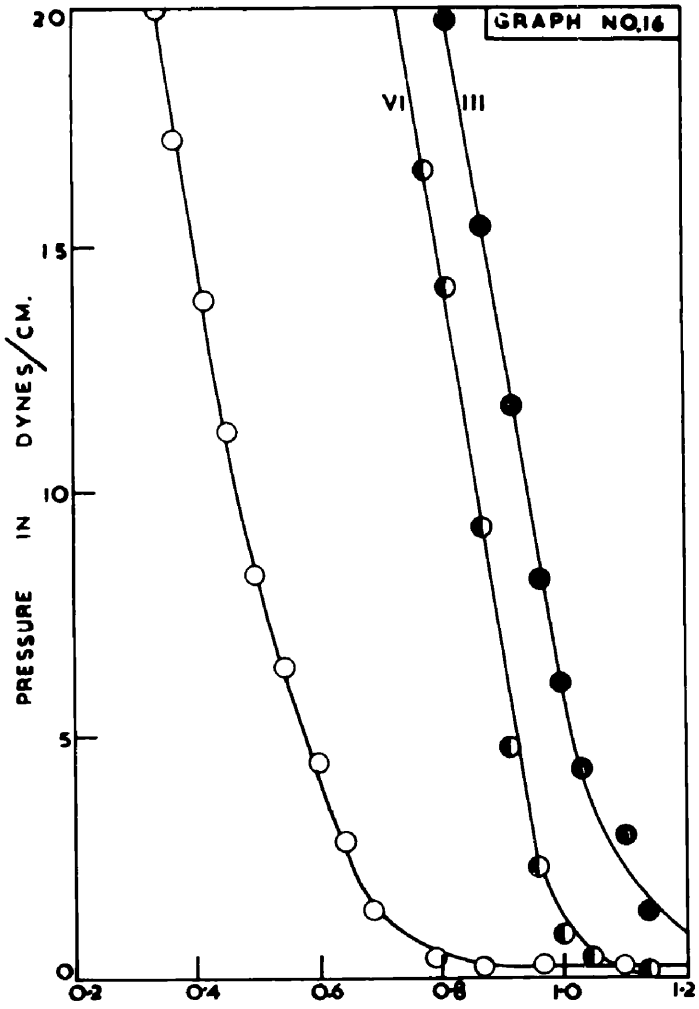
NO. II. M=Co, X=SO_2CH_3, W,Y & Z=H.

NO. III. M=Cr, W,X,Y & Z=H.

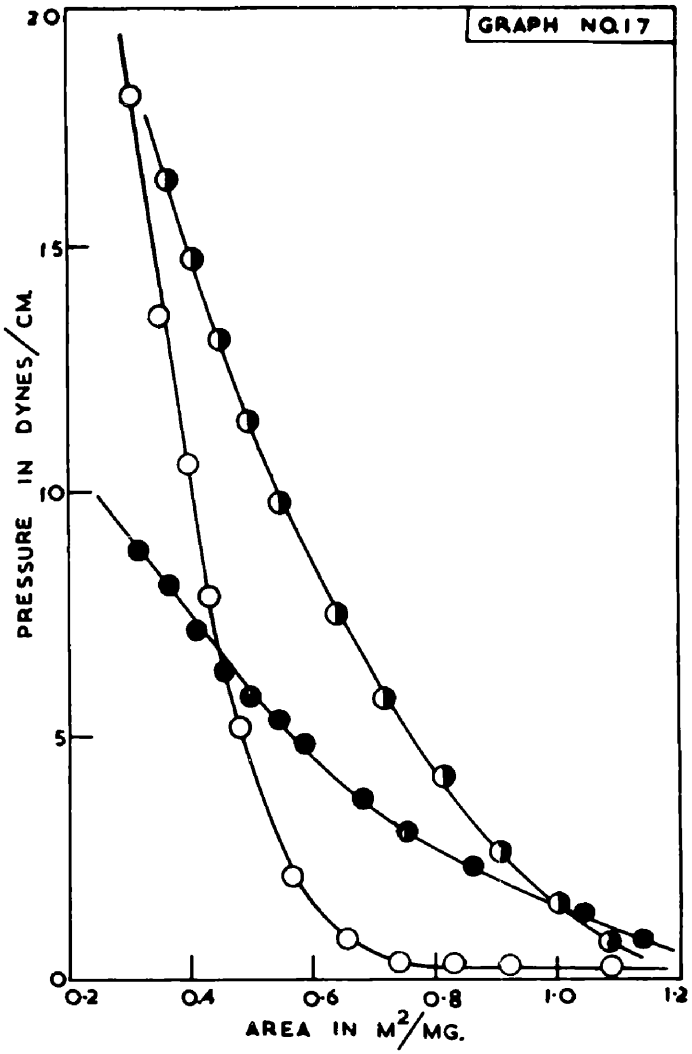
NO. IV. M=Cr, W=$NHCOCH_3$, X=SO_2CH_3, Y & Z=H.

NO. V. M=Cr, X=SO_2CH_3, W=$NHCOCH_3$, W & Z=H.

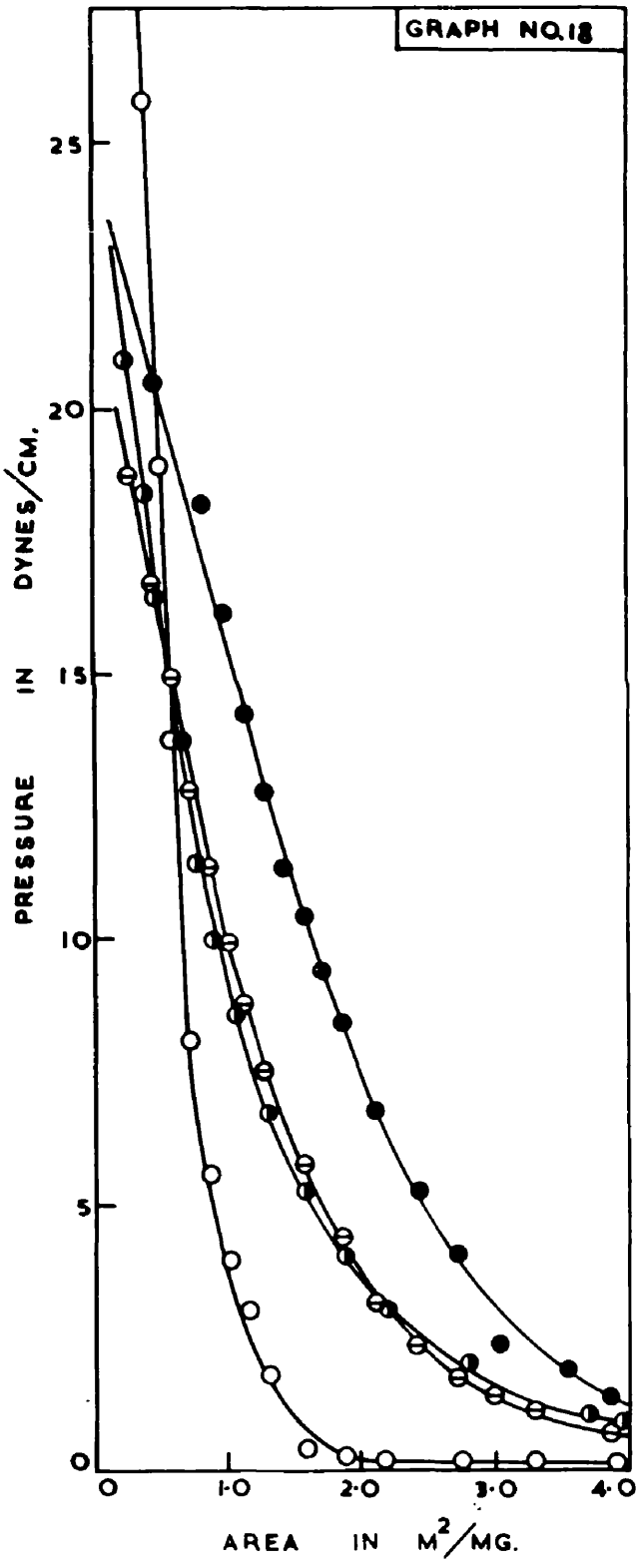
NO. VI. M=Cr, Z=OH, W,X & Y=H.



EDESTINE FILMS ON BUFFER SOLN. pH 4·7.
WITH 2:1 METAL COMPLEX DYES NOS. III & VI.
BOTH 10^{-5} M.



EDESTINE FILMS ON BUFFER SOLN. pH 3·3.
WITH 1:1 METAL COMPLEX DYES.
○ CONTROL ● ULTRALAN YELLOW R.
◑ ULTRALAN ORANGE G.
BOTH 10^{-4} M.



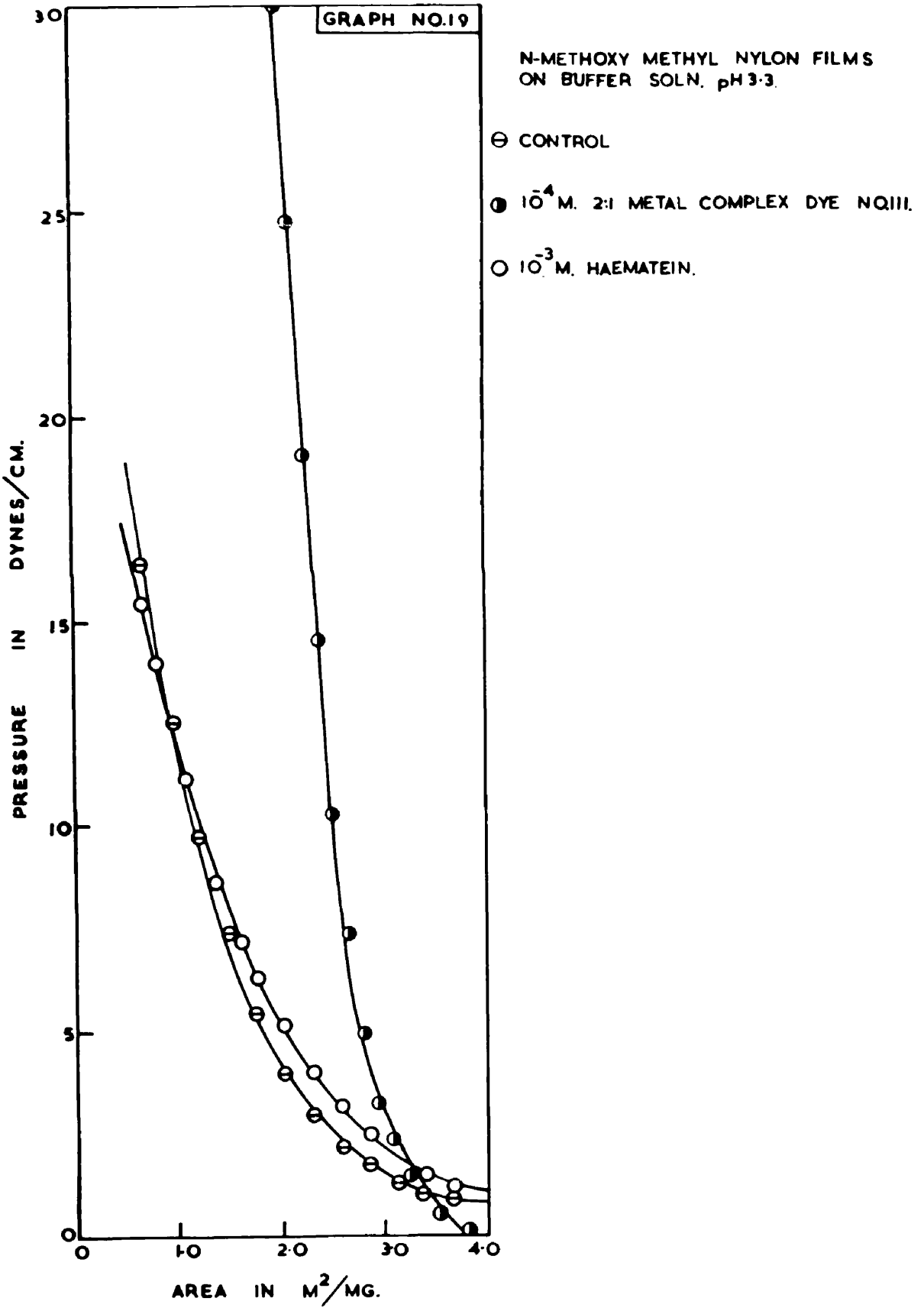
N-METHOXY METHYL NYLON FILMS ON BUFFER SOLN. pH1·6.

● CONTROL

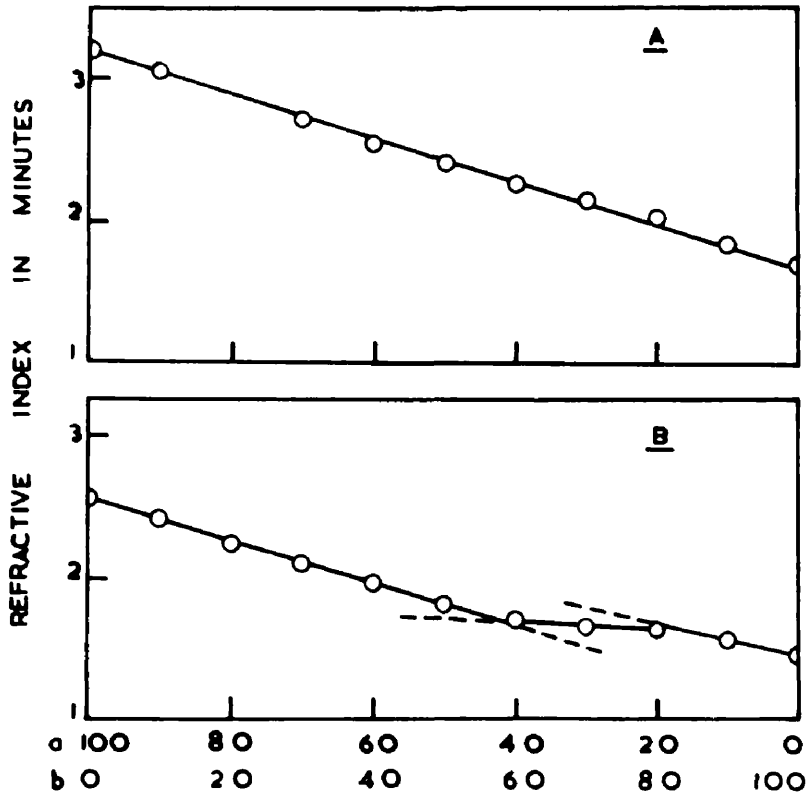
⊖ 5×10^{-4}M. ALIZARIN CYANINE WR.

◑ 10^{-3}M. HAEMATOXYLIN.

○ 40 MG.L^{-1}. TANNIC ACID.


GRAPH NO.19
N-METHOXY METHYL NYLON FILMS ON BUFFER SOLN. pH 3·3.
⊖ CONTROL
◑ 10^{-4} M. 2:1 METAL COMPLEX DYE NO.III.
○ 10^{-3} M. HAEMATEIN.
PRESSURE IN DYNES/CM.
AREA IN $M^2/MG.$
0
5
10
15
20
25
30
0
1·0
2·0
3·0
4·0

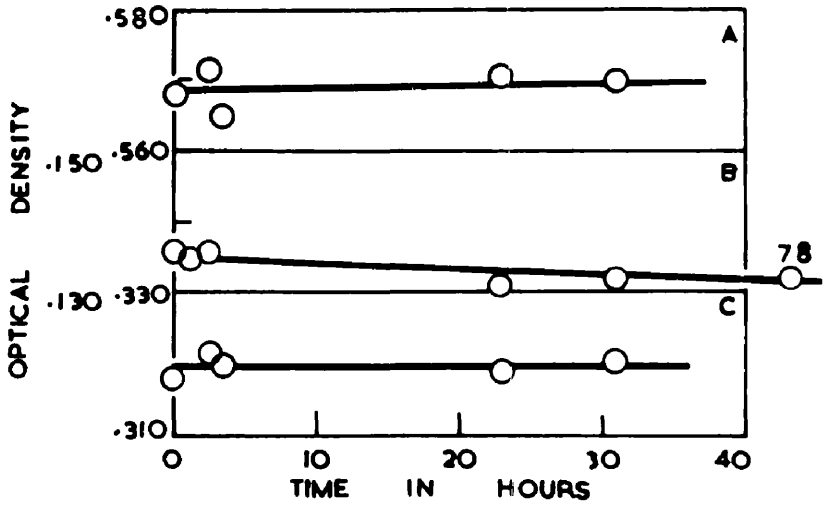
GRAPH NO. 20



A: a, D-GLUCOSE ; b, EDESTINE.

B: a, m-INOSITOL ; b, EDESTINE.

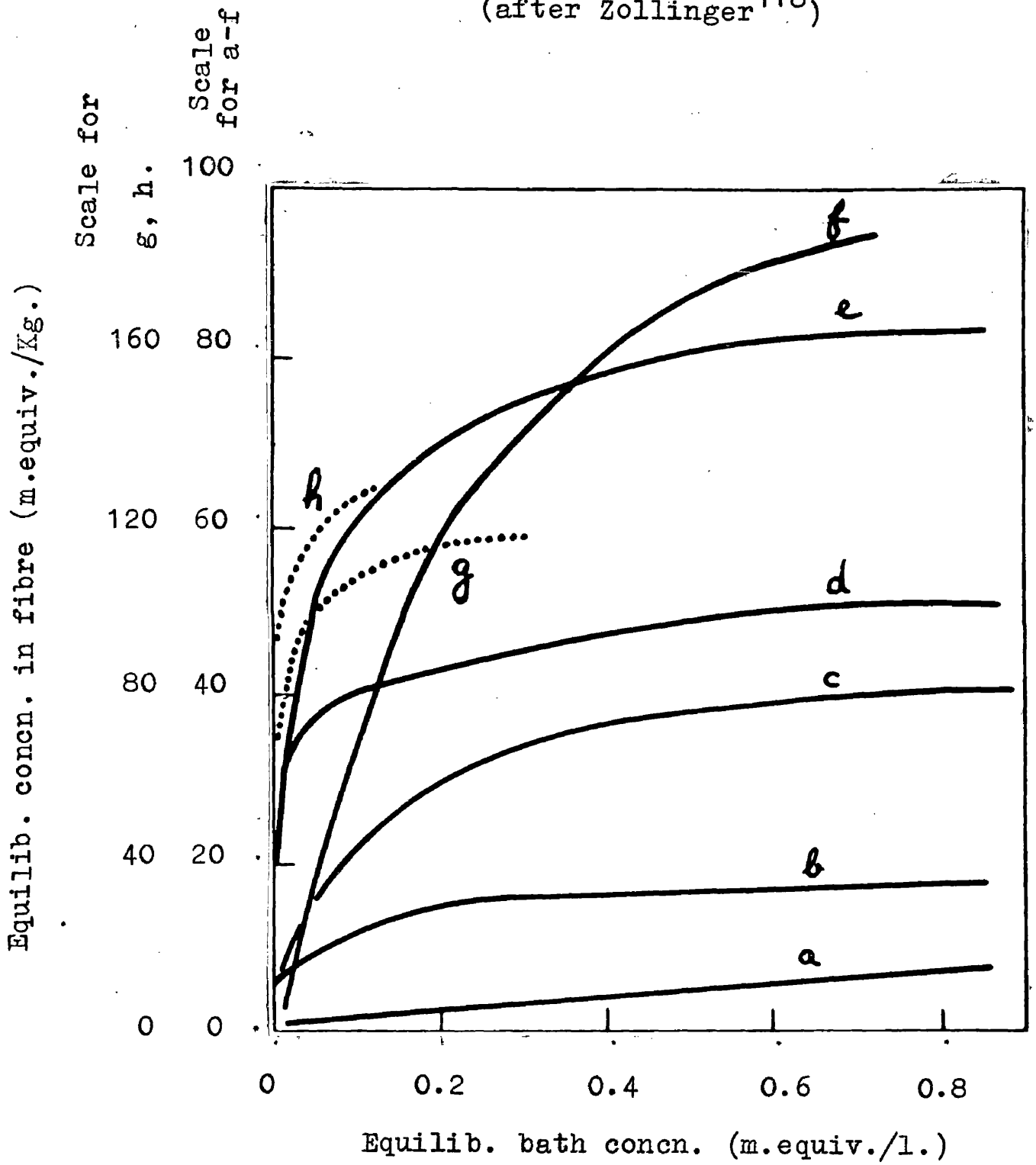
GRAPH NO. 21



FADING RATE CURVES ON GELATIN.
2:1 - METAL COMPLEX DYES

A - COMPLEX NO.I
B " NO.III
C " NO.IV

Graph No.22. Adsorption isotherms of 2:1-metal complex dyes (after Zollinger[118])



Dye A: a, Acetylated wool; b, acetylated nylon 66; c, silk; d, stretched nylon 66; e, unstretched nylon 66; f, wool.

Dye B: g, Acetylated nylon 66; h, nylon 66.

PART II

CLASSIFICATION OF ISOTHERM TYPES

FOR ADSORPTION FROM SOLUTION

Introduction.

The work recorded here is a preliminary study of the general factors responsible for determining the form of isotherms for adsorption of a solute by a solid from solution. 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 results of the present writer's experimental investigations. The net result is a qualitative analysis of the factors responsible for isotherm forms. A quantitative analysis of these factors has not been attempted, and is not considered to be possible until the general principles governing (a) the inter-relation between the adsorption process and the shape of the isotherm and (b) the physical state of the adsorbed solute, have been firmly established.

Numerous technical and laboratory adsorption processes take place from solution. The form of the isotherm of vapour phase physical adsorption by solids has been the subject of considerable qualitative and quantitative study, but isotherms of physical and chemical adsorption from solutions have received much less attention, and the detailed factors which determine their form have apparently not been hitherto discussed. The isotherm for adsorption from solution is readily determined and often yields valuable

information, seldom easily gained by other techniques. The shape of the isotherm can e.g. help (a) in the diagnosis of the mechanism of adsorption, (b) in revealing some facts regarding the physical state of both the solute and the substrate, and (c) in measuring specific surface areas. (c) has been its main use hitherto, though this application has been severely restricted by lack of knowledge of the state of the adsorbed solute.

Brunauer[122] has divided vapour-phase adsorption isotherms into five classes, according to shape; it is found that adsorption isotherms from solutions may be classified into four main types, which are shown in Fig.I.

System of Classification.

In this work the isotherms are considered as being plotted on an arithmetical scale, with y-axis representing equilibrium concentration in substrate, and x-axis representing equilibrium concentration in external solution.

The four types are conveniently named the S , the Ln (i.e. 'linear'), the L (since it is the form associated with the well-established Langmuir treatment), and the HA (i.e. 'high affinity') isotherms. The S and L forms are identical with V and I respectively in Brunauer's five types of vapour-phase adsorption isotherm[122].

The isotherms are characterised by the initial portion being convex (S type) or concave (L) to the solution concentration axis, linear (Ln), or coincident with the substrate-concentration axis (HA), i.e. the HA isotherm starts at a positive value on the y (concentration in substrate) axis. Every isotherm must, of course, have a point of origin and at least one maximum, though in practice even a first maximum is not always reached; the form of the initial portion can in theory change from S , through L to HA with progressive changes in the system, and many borderline cases are naturally encountered. The variations within the four main classes are illustrated in the lower portion of Fig.1 and in the discussion the classification is extended to considerations of multilayer or aggregate formation or of the opening up of an additional range of reaction sites which 'take' the isotherm beyond the first plateau, and sometimes to a second plateau. This extension enables the shape of almost any isotherm to be classified. The species actually adsorbed from solution may be either an unionised molecule, a solvated ion, or a micelle or aggregate; the general principles apply to all three, but for simplicity in the argument the term molecule is used in most cases.

Samuelson[123] has described briefly how the initial portion of an isotherm for ion-exchange on resins may be concave or convex to the x-axis, or linear, according to the

The isotherms are characterised by the initial portion being convex (S type) or concave (L) to the solution concentration axis, linear (Ln), or coincident with the substrate-concentration axis (HA), i.e. the HA isotherm starts at a positive value on the y (concentration in substrate) axis. Every isotherm must, of course, have a point of origin and at least one maximum, though in practice even a first maximum is not always reached; the form of the initial portion can in theory change from S , through L to HA with progressive changes in the system, and many borderline cases are naturally encountered. The variations within the four main classes are illustrated in the lower portion of Fig.1 and in the discussion the classification is extended to considerations of multilayer or aggregate formation or of the opening up of an additional range of reaction sites which 'take' the isotherm beyond the first plateau, and sometimes to a second plateau. This extension enables the shape of almost any isotherm to be classified. The species actually adsorbed from solution may be either an unionised molecule, a solvated ion, or a micelle or aggregate; the general principles apply to all three, but for simplicity in the argument the term molecule is used in most cases.

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Experimental.

Graph No.1 shows some of the isotherms considered in this survey and a list of some isotherms classified under the present rules is given in Table 1. The results of the present writer's investigations are shown in Graphs No.2-11. These results were obtained by adherence to the following experimental procedure.

Preparation of the Substrate.

Wool:- Root ends of a Lincoln fleece were scoured in a dilute solution of Lissapol N (ICI) at 60°C. for 5 minutes, then rinsed first in hot and then in cold distilled water, dried at 95°C., and extracted with methylene chloride in a Soxhlet apparatus for 24 hours. The wool was then oven-dried at 100-110°C., then allowed to condition in air at room temperature for 24 hours, and stored in a stoppered bottle.

Cellulose Triacetate:- This was the same as was used in Part I, Section I of this work. It was ground into the form of a finely-divided powder.

Stearyl Alcohol:- Pure B.D.H. material was used in the form of a fine powder.

Graphite:- Commercially pure graphite (ca.99.5%) was used, in the form of microscopic, very thin flakes.

The specific surface area of the flakes was determined by a colleague of the author, Dr.A.S.A.Hassan. He measured the average superficial area of the particles by the optical microscope with a Fairs graticule, and their average thickness by the electron microscope, after shadow casting with gold.

Preparation of the Solutes

The solutes were purified by the methods described in the earlier part of this work.

Adsorption Procedure

In most of the adsorption tests 5 or 10 ml. of the solution of the compound to be investigated was placed in a soda glass test tube along with a weighed amount of the substrate. The amount of substrate used in each test was dependent on several different factors (e.g. bulk of substrate, concentration and volume of solution, solubility of solute). An amount which was sufficient to produce an accurately measurable concentration difference in the solution was used, - normally 0.1 gm. was adequate. In doubtful cases preliminary tests were used to determine the optimum amounts of substrate, solute and solvent for measurable concentration differences. The tube was then sealed in a Bunsen flame and immersed in a thermostat tank at the required experimental temperature. Constant agitation of the contents of the tube

was effected by attaching it to an electrically driven horizontal shaft, revolving at 35 r.p.m., under the water in the tank. This apparatus and technique is described elsewhere[124].

To ensure sufficient time allowance for equilibrium to be established in the system during the adsorption tests, it was necessary to measure the rate of adsorption, which was effected by placing several sealed tubes with substrate and solution, of one concentration (representative of the concentration range to be examined) in the thermostat and the tubes were removed at various time intervals (measured from the time of immersion) and substrate and solution were immediately separated; the latter was then analysed. Thus the state of the solution/substrate system could be specified after the adsorption process had continued for different periods of time. Analysis of solutions removed after a period of immersion, which varied with substrate, solute and experimental temperature, from ca.30 minutes to ca.24 hours, showed constant distribution of the solute between substrate and solvent, which indicated the establishment of equilibrium in the system.

Adsorption isotherms were plotted from results obtained by immersing a number of sealed tubes in the thermostat, each containing one of a range of concentrations of solute. The tubes were left in the thermostat until

sufficient time had elapsed for the attainment of equilibrium.

Analytical Techniques.

The amount of solute adsorbed was calculated from the difference in initial and final concentrations of the solution measured using a Unicam S.P.500 photoelectric spectrophotometer. 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. Investigation of light absorption spectra before and after the adsorption test proved to be useful in detecting decomposition of the solute.

Phenol in isooctane was estimated spectrophotometrically, but the method of Redman, Weith and Broch[124A] (using brominating solution, potassium iodide and estimating the free iodine with thiosulphate) was found to be more accurate for the estimation of phenol in aqueous solution.

The spreading tests with haematein and haematoxylin were made from solutions with a water, ethanol, benzene solvent mixture (ratio 1:2:2). The interaction tests with these two solutes dissolved in buffer solution under films of MM nylon are described in the previous section (Part I, Section IIC).

RESULTS AND DISCUSSION

Results and Discussion.

Significance of Initial Slope. An approach to an understanding of the meaning of the isotherm is to consider the significance of the slope of the initial portion, starting from the origin. The best known isotherm, associated with the name of Langmuir, is concave to the x-axis. This means that with successive equal increments of solute concentration in the equilibrium external solution the successive amounts of solute adsorbed steadily decrease and reach zero at the plateau. As the available sites get filled up it becomes more and more difficult for a bombarding solute molecule to find a vacant site. In contrast, an initially convex curve shows that as more solute is adsorbed, further adsorption becomes easier. In adsorption from solution, unlike adsorption from the vapour-phase (normally carried out in vacuo), the distribution of solute between solution and solid surface at equilibrium is the result of a competition between solvent and solute molecules for the surface, and therefore their relative affinity for the surface exerts an influence on the shape of the curve.

The results are most conveniently discussed under sub-divisions based on the four types of isotherms.

The S-curve. Examples of S-curves are given in Graphs No. 1-5 and in Table I.

This is comparatively rare in cases of adsorption from solution and few occurrences have previously been recorded. It appears in the three following systems.

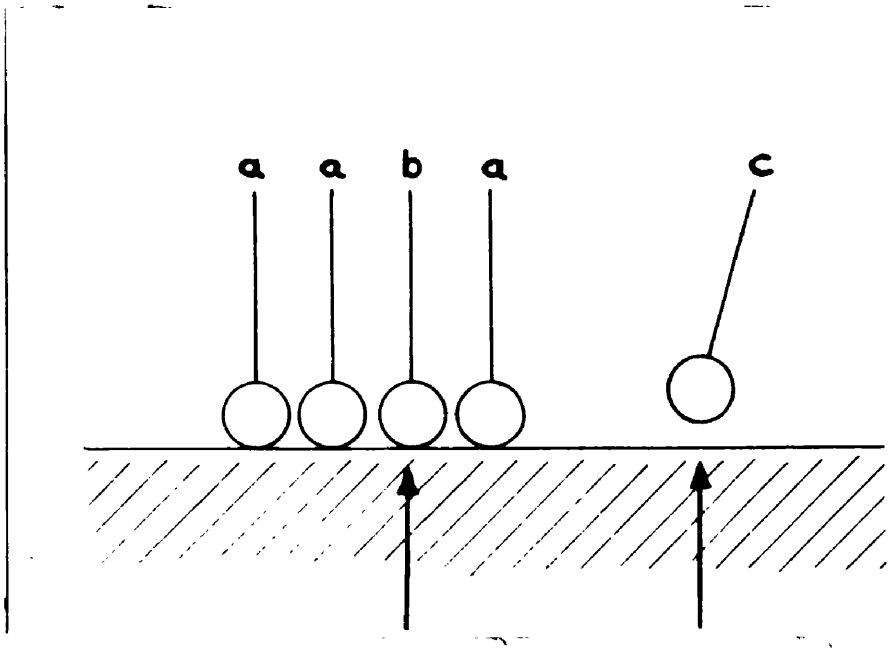
(a) Low affinity solutes, i.e. those having small aromatic molecules, in water, on cellulose substrates and chitin.

(b) Monofunctional phenolic compounds on many substrates.

(c) Low affinity solutes adsorbed by ion exchange on inorganic substrates.

On the basis of this and further evidence the following comprehensive generalisation may be drawn; the S-curve indicates adsorption in solvent-accessible regions with vertical orientation of the solute at the solid/liquid interface.

The shape of the initial pprtion shows that the adsorbed layer becomes more stable with increase in concentration, i.e. that the adsorbed molecules interact and assist binding to the surface. This suggests a layer of vertically oriented molecules, attached at one end to the surface and held side-by-side by their mutual intermolecular attraction. The simple illustration shown here may help to clarify this point.

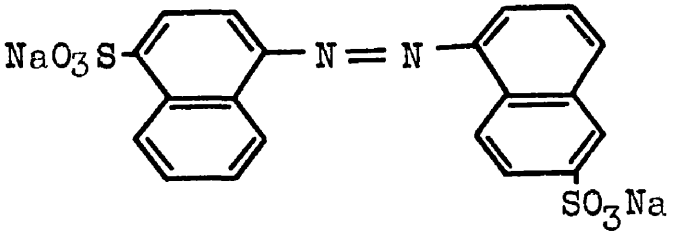


Consider a surface on which some vertically-oriented molecules (aa) are already adsorbed; a bombarding solute molecule arriving at this surface will be retained more readily in a position (b) between those already there, than in an isolated position (c).

The S-curve is always given by 'monofunctional' solutes adsorbed as single molecules or ions, 'monofunctional' meaning that the attraction for the surface resides mainly in a single centre in the molecule. A vertical orientation seems to be the most appropriate for the other cases under (b) above. Thus a monolayer of the aromatic sulphonic acids (e.g. naphthalene 2-sulphonic acid, anthracene 2-sulphonic acid) on cellulose or chitin will tend to form in such a way

that the maximum surface of ionic groups is presented to both the water and the substrate, since the carbohydrate hydroxy-groups in the cellulose and chitin chains remain firmly surrounded by a layer of water[51,52,125]. The most probable arrangement is then likely to consist of a vertically oriented sandwich of solute molecules, with the ionic groups alternatively arranged towards the substrate and towards the water.

On graphite the acid dye Naphthalene Red EA, (C.I.16045)



gives the S-isotherm from water[126]. It is then probably forming a monolayer with the ionic groups as far away from the hydrophobic graphite surface as possible. This is possible with an edge-on orientation.

There is a tendency for adsorption curves for planar

azo-dyes from water on cellulose and chitin to take this form when they have a high ratio of sulphonate groups to aromatic nuclei. Possibly they may be oriented edge-on.

Three S-isotherms have been discovered for monofunctional highly surface-active solutes adsorbed from water (Table I). These must almost certainly be adsorbed partly as micelles. Thus it appears that the S-isotherm for non-surface-active solutes is an indication that the first layer is a condensed one of close-packed vertically oriented molecules or ions. In almost all cases the adsorbed species is monofunctional, i.e. it has one predominantly active centre. Not all monofunctional solutes give S-isotherms however. When they do not it may indicate one of two conditions: (a) there are other, weaker, active centres in the solute molecule which enable it to remain stable when adsorbed flat from dilute solutions; or (b) some or all of the solute is adsorbed as micelles.

The Ln Curve. Examples are given in Graphs No.1 and 6, also in Table I.

The best known systems giving the linear isotherm are those of the non-ionic ('disperse') dyes on cellulose acetate and other hydrophobic fibres, in water. The isotherm resembles that for the partition of a solute between two

immiscible solvents and many investigators have termed the dye adsorption a "solid solution", though it is doubtful if the term should be applied to such systems. Fundamentally the linearity shows that the number of sites for adsorption remains constant with increase in solution concentration, thus as more solute is adsorbed more sites must be created. Such a situation would arise where the solute has a higher attraction for the substrate molecules than the solvent itself has. Thus the solute can break inter-substrate bonds and if its molecular dimensions are suitable it can penetrate readily into the structure of the substrate in regions not already penetrated by the solvent. A simple analogy compares this action to the opening of a zipp fastener, the fastening representing the inter-molecular bonds of the substrate, and the slider the first molecule to penetrate. The action stops abruptly when more crystalline regions of the substrate are reached, and the isotherm usually abruptly changes direction to the horizontal plateau.

Thus a linear isotherm indicates that the solute is penetrating solvent-inaccessible regions. As mentioned, this isotherm is best known for non-ionic dyes on cellulose esters and on polyethylene terephthalate (Terylene). It has however now been discovefed to apply to several other systems (see Graph No.1, Table I), including some in which the solute is liquid. In all these cases it is obvious that

the solute has much higher affinity (by hydrogen bonds) with the substrate than the solvent has.

The L-Curve. This is much the commonest type and is observed in many different systems, a few of these being:

(a) Sulphonated dyes adsorbed from water by alumina, graphite, nylon or proteins.

(b) Cationic dyes adsorbed by silica or graphite.

(c) Polyfunctional phenolic compounds, e.g. haematoxylin or resorcinol, adsorbed from water by diverse substrates.

(d) Polar solutes adsorbed by polar substrates, e.g. alumina or wool, from non-polar solvents which have low affinity for the substrate.

(e) Highly surface-active compounds on several substrates.

Examples are shown in the Graphs and in Table I.

This curve has the familiar form of the Langmuir vapour-phase isotherm, for a similar reason, viz., that the adsorption sites are at first readily available to all the entering adsorbate molecules, but as the sites become filled the chance of a bombarding adsorbate molecule finding one vacant steadily decreases. Thus the rate of increase of external concentration must be steadily raised to maintain a

given rate of increase of solute adsorbed. In the Langmuir treatment the adsorption sites are unoccupied before the adsorbing vapour molecules enter. In adsorption from solution they are probably occupied already by solvent molecules, but the solute molecule must be able to displace this readily. It is therefore evident that the L isotherm is characteristic of a system in which two conditions hold. These are: (a) The whole surface at which adsorption can ultimately occur is available to the entering solute molecules even in the most dilute solution; this applies when the substrate is a rigid non-swelling solid, or an organic polymer which is fully swollen by the solvent alone. (b) The solute has high affinity and can readily displace solvent at the substrate surface.

In confirmation of this picture of the adsorption process, the substrates which give L isotherms in adsorption from water are in fact either hydrophilic fibres, e.g. wool, silk, and cellulose fibres, or inorganic materials, e.g. charcoal, graphite, silica, and the solutes are those of high affinity, e.g. the more highly conjugated planar aromatic compounds (on cellulose), acid dyes (on alumina, protein fibres, and nylon) and basic dyes on silica. Solutes containing long alkyl chains seem also to favour this form of isotherm in adsorption from water, presumably because they are highly surface-active and readily form a stable monolayer

at the solid/liquid interface. There is also the strong likelihood of these compounds being adsorbed as micelles, which would favour the formation of the L-isotherm.

The L-isotherm is frequently used for surface area determinations, especially in gas adsorption. It has also found similar application for liquid phase work, on the assumption that the plateau (or the intercept for the reciprocal plot) represents a true monodisperse monolayer. It will be shown below, however, that in many cases this assumption is not correct.

The HA Curve. This is a special case of the L-isotherm in which the initial adsorption from dilute solutions is so high that no solute is left in solution, and the curve is at first coincident with the y-axis. It occurs with several adsorptions from water, viz., (a) some ion-exchange adsorptions at inorganic surfaces and (b) Van der Waals adsorption of unsulphonated 2:1-metal dye complexes on nylon fibres, (where there is attraction of the dye's aromatic nuclei for the hydrocarbon part of the fibre's molecular chain). In both cases the adsorbed species apparently has considerably higher affinity for the surface than the water (or hydrated ions in (a) that is displaced. On present evidence this isotherm, when observed in adsorptions from water probably always represents adsorption of ionic micelles. In inorganic systems

it represents chemisorption by a strong irreversible bond.

Comparison of Conditions Producing S-, Ln and L-isotherms.

The cause of the difference between these isotherms can most simply be demonstrated by considering certain phenolic substances. Thus phenol itself can give all three types (Graph No.1). On a hydrophilic fibre (wool) it acts as a monofunctional hydrogen-bonding agent, giving an isotherm of the S-type (see Graph No.2). On cellulose acetate, from a poorly-penetrating solvent (isooctane) it penetrates solvent-inaccessible regions and the curve is Ln (linear) (see Graph No.6). Phenol does not form a hydrogen bond with graphite, but is adsorbed thereon flat (in the initial stage), by reason of the Van der Waals attraction between its aromatic nucleus and the planar graphite crystal lattice. Thus the L-isotherm is obtained (see Graph No.10).

The two polyhydric phenols, haematein and haematoxylin (formulae given on page 112) were used in similar tests to the above. Haematoxylin gives an L curve for adsorption on hydrogen-bonding fibres (for adsorption on wool see Graph No.12) and is obviously bifunctional or polyfunctional; haematein gives S-curves, which suggests that it is behaving as a monofunctional phenol (see Graph No.12). In haematein the active centres at the two ends of the molecule have different affinities for the fibre (the o-hydroxyquinone

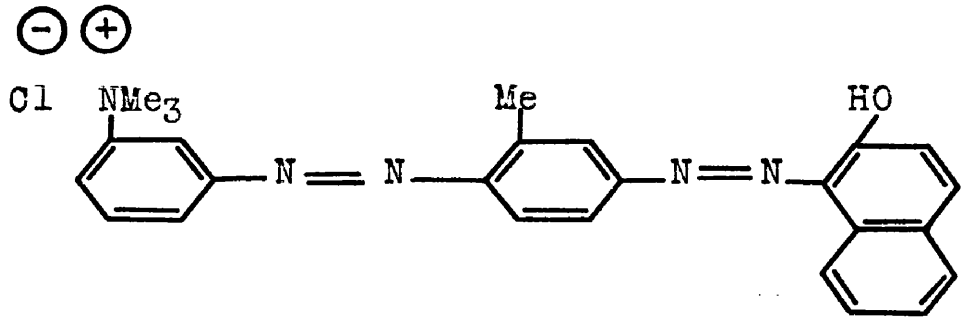
centre is probably the most active one).

The interactions of these two compounds with spread MM nylon films when dissolved in the sub-solution lend further weight to this argument. Haematoxylin condenses the film, making it more rigid, an action which is typical of a large polyhydric phenolic compound. Haematein, however, makes the film slightly more compressible, an action which is typical of monofunctional dyes when dissolved in the sub-solution under a protein film (Part I, Section IIA, IIB, IIC (See Graphs No. 18 and 19 in Part I, Section IIC)). This suggests that haematein is not oriented flat in the film, but possesses a degree of surface activity. Confirmation of this was given by spreading tests on 2M.-hydrochloric acid. As stated above, haematoxylin did not form a film, whereas haematein formed a fairly stable film (see Graph No.11) with an extrapolated area of 48 A^2, which is in reasonable agreement with the value (54 A^2) estimated from models for vertical orientation on the activated phenolic group.

Micellar Adsorption.

Long alkyl chain sulphates and many basic dyes (which have a large aromatic nucleus and a cationic substituent group) often given L- or HA curves when adsorbed on rigid surfaces (alumina, silica, graphite). Calculations of apparent specific surface area from the isotherms and other

tests show that the isotherm plateaux represent the completion of a monolayer of adsorbed ionic micelles, rather than of single ions or molecules. Thus, e.g. Janus Red B (C.I.26115)



has an HA isotherm on silica (see Graph No.1, J, a) in which the adsorption at the plateau level (at 30) is over 18 times as high as required by a monolayer of end-on oriented single molecules. This dye gives very colloidal solutions and is clearly adsorbing as cationic micelles.

Thus in general it may be stated that when a monofunctional solute gives an L- or HA isotherm on a polar substrate micellar adsorption is occurring.

The present evidence indicates that if an adsorption from solution follows the normal Langmuir isotherm or the linear reciprocal plot (i.e. 1/concentration in substrate vs 1/concentration in solution) it does not necessarily mean that the adsorbed solute forms a true monolayer. Hence for measuring specific surface areas Langmuir isotherms may well

yield spurious information. In fact "Langmuir" adsorptions of monovalent ions from water may give values from 2 to 10 times too great or more.

This survey points to the S-type isotherm as being more suitable for use in determining specific surface area, because with this type the first plateau or inflection (Point B) represents a true condensed monolayer.

Variations in Basic Shapes.

As can be seen from the experimental results the isotherms may vary greatly after the initial portions already classified. The variations may be attributed to the following causes:-

Second rise with or without second plateau or inflection, (a) reorientation of adsorbed solute; or (b) build-up of a second layer of adsorbed solute, or (c) irruption of solute into new regions of the substrate.

Phenol on graphite (see Graph No.10) gives a good example of a "stepped" curve. The specific surface area data agree closely with a flat orientation at the first inflection and a vertical one at the second, respectively 1.3 and 1.2 times the calculated monolayer capacities for the two orientations.

Successive monolayers are sometimes encountered,

though seldom more than two. Thus a cyanine dye on silver halide gives an example of two layers[127]. On graphite the azo-dye (C.I.16045) referred to above gives a two-stepped curve[126] in which the successive steps correspond closely with calculations for one and two monolayers of edge-on oriented dye molecules. In this orientation the ionic groups are in the water and as far as possible from the hydrophobic graphite surface. The orientation of the second layer might be the same as the first, or reversed, with a layer of water molecules between the adjacent ionic groups of the two layers, as in the well-known "J-band" aggregates of cyanine dyes[127]. (The phenol-graphite isotherm discussed above could also be interpreted as a two layer one, but the calculated areas agree closer with the re-orientation hypothesis).

Irruption into new areas occurs with sulphonated dyes on anodic alumina film prepared in acid solutions. The evidence is in favour of a dye-film bond of a covalent nature (Al - O_3SR), and it is possible that in forming this, some of the bonds in the oxide crystal structure are broken, leading to a gradual breakdown of the film. Certainly the curves, after the first (monolayer) inflection rise without showing subsequent inflections, and under some conditions the heavily-dyed film becomes friable and readily detached from the metal base.

The two-stage curve also appears to be given by many solutes on wool fibres (e.g., see Graph No.3), but the evidence at this stage is not sufficient to assign a cause. Here the possibility of the solute gaining access to a new range of sites must be considered.

Inflection without Plateau. If there is a second rise, the first plateau is sometimes obscured. In this case calculations made from the Brunauer "Point B" (i.e. the beginning of the linear portion beyond the inflection) appear to correspond well with monolayer capacities, as they do in vapour-phase adsorption, and it can be assumed that this point represents the capacity of the first monolayer.

A number of curves are found which have a linear portion of low slope after the first inflection. Several causes can be assigned to this, e.g. (i) slow accumulation of aggregates, as with highly colloidal dye on graphite[126]; (ii) slow penetration of solute and solvent into new regions of the crystal structure; (iii) penetration of solute itself into solvent-inaccessible regions of a fibre (as with normal linear isotherms).

Occasionally a fall in slope occurs after the first inflection, i.e. the isotherm has a maximum. 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.

It is made apparent that no general rule can be formulated for all curves having these variations. The causes must be judged on a knowledge of the other properties of the whole adsorption system.

Estimation of Specific Surface Area.

Many methods are used for estimating the specific surface areas of powders and porous solids, several of them requiring the use of complex equipment. One of the most reliable methods is gas (usually nitrogen) adsorption at low temperatures. The specific surface area may be readily calculated from the isotherms. Liquid-phase adsorption of solutes is a much simpler and often a more rapid procedure, which has sometimes been used for the purpose, but the results have been subject to uncertainty because of lack of knowledge of the state of coverage of the surface, so that other methods have been preferred. Thus the adsorption of basic dyes, especially methylene blue (C.I.52015), has been used, because the solutions are readily analysed. From this study it now appears that basic dyes are probably unreliable for this purpose, because of the ease with which they are adsorbed as micelles, and so give fictitiously large surface area values. The use of any substances having large aromatic molecules is probably undesirable unless the exact mode of attachment to the surface is known, or can be inferred with confidence.

Naturally, the results of specific surface area measurements on any given solid may vary with the method used because of variations in accessibility of the surface. Thus a static measurement by nitrogen adsorption may give higher

values than a dynamic one by air permeability because nitrogen penetrates small fissures in the surface which do not affect the air flow. Measurements by adsorption from solution will indicate probably only the area accessible to the solvent molecules, but this may be the most useful information in any case. Thus in all cases where the material is to be used in contact with water, measurements by adsorption from water could give the "true" specific surface area. The general considerations outlined in this work may help to establish more reliable methods using adsorptions from solution.

Adsorption tests from solution can be made very simply, and need not require complex equipment. From the considerations given in this work it is seen that the requirements are for a solute whose molecule has the following characteristics:

(a) Reasonable solubility, in common solvents, especially water.

(b) Small size with no surface-activity (so that micelle formation is unlikely).

(c) Planar shape, for ease of estimation of its surface coverage, when close-packed.

(d) Ease of analysis (coloured if possible).

This work indicates that a simple phenol (e.g. p-nitrophenol) would probably best meet all these requirements,

furthermore, this solute appears to be adsorbed by many substrates of widely diverse characteristics. The nature of the substrate would, of course, need to be considered in some detail in interpreting the results.

EXPERIMENTAL RESULTS

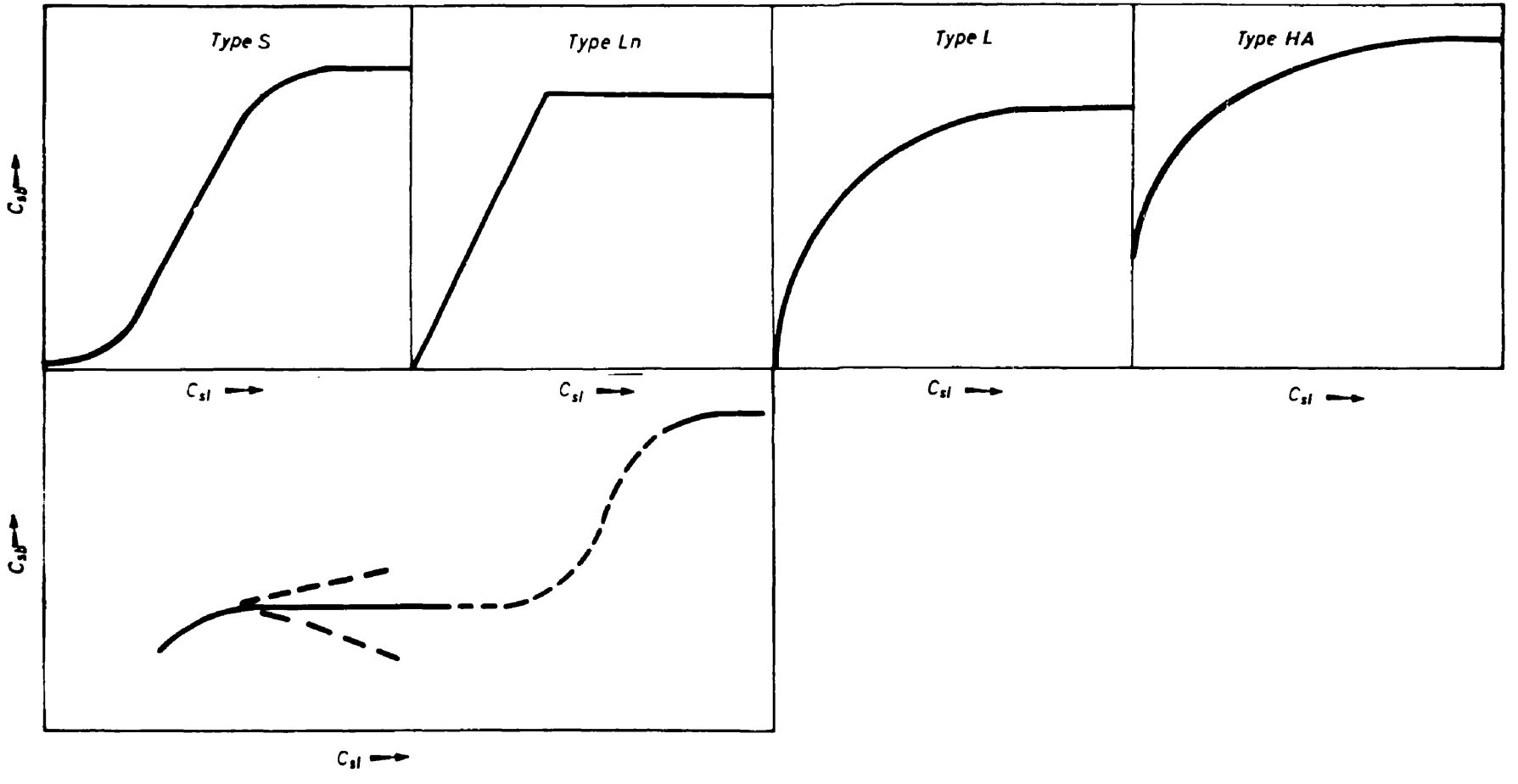
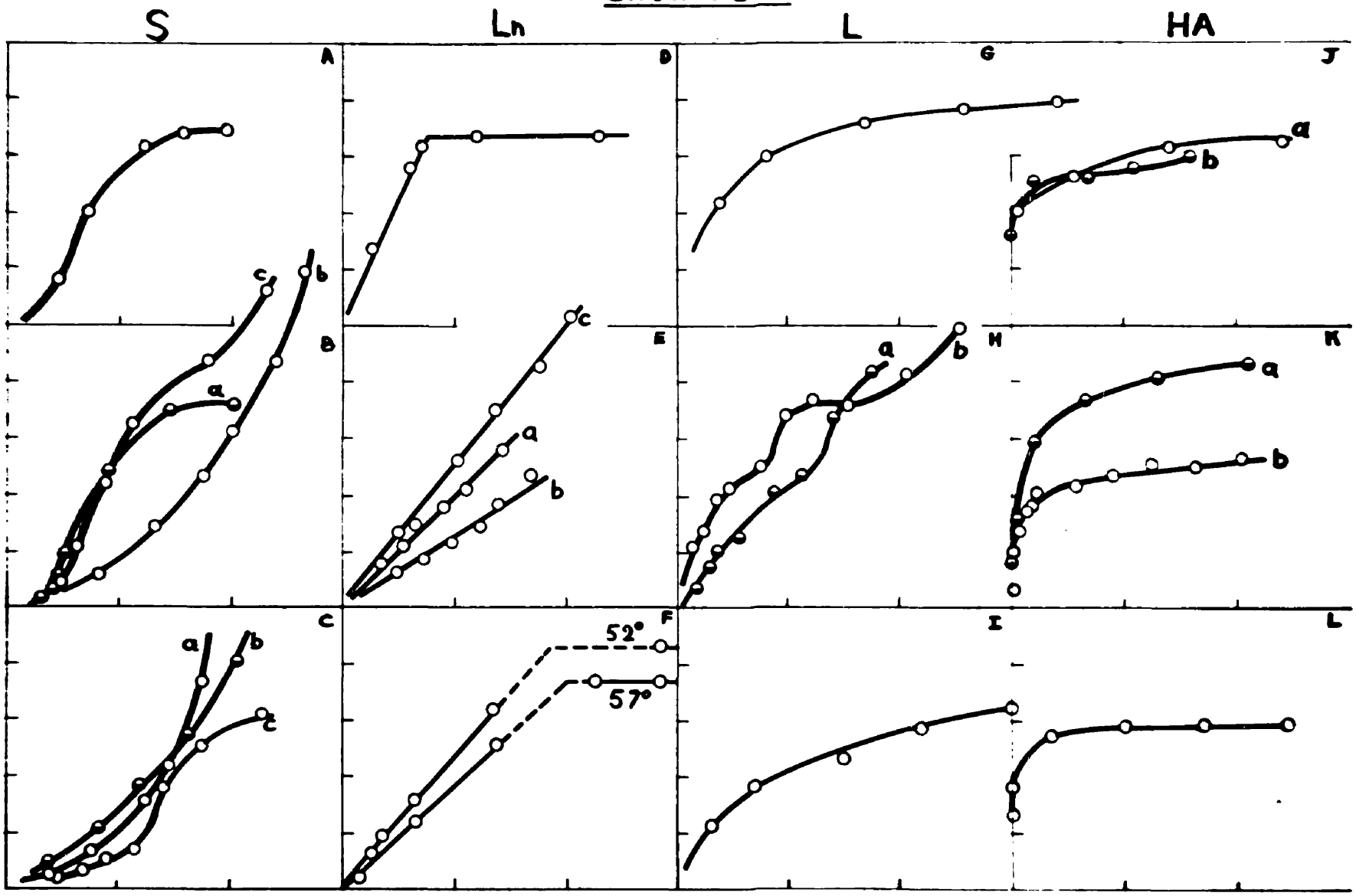


Figure 1. Fundamental types of isotherm for adsorption from dilute solution. C_{sb} — equilibrium concentration of adsorbed solute in substrate; C_{sl} equilibrium concentration of solute in external solution

GRAPH NO. 1



Examples of the four Isotherm Types (C_{sl} in mm./l. and C_{sb} in mm./Kg. - unless otherwise stated).

(Key to) GRAPH No. 1

S		Ln	
Naphthalene Red J (C.I.15620) on Alumina Film[128] Scale: C_{sl} in mm./l; 0,2,6 C_{sb} in mm./Kg;0,200 ---400	A	Dispersol Fast Scarlet B on cellulose diacetate[68] C_{sl} in mg/g; 0,5,10,15,20 C_{sb} in mg/g; 0,0.5,1.0,1.5	D
(a) Phenol on alumina powder[128] (b) Phenol on wool** (c) 2:4-dinitrophenol on wool** C_{sl} for a; 0,40,80,120 C_{sl} for b; 0,5,10,15 C_{sl} for c; 0,0.1,0.2,0.3 C_{sb} for a; 0,100,200,300,400 C_{sb} for b and c; 0,20,40,60,80	B	(a) Phenol from isooctane on cellulose triacetate at 29°** (b) As above at 59° ** (c) Methanol from benzene[130] on cellulose triacetate C_{sl} for a and b; 0,2,4,6 C_{sl} for c; 0,200,400,600 C_{sb} for a and b; 0,100,200,300 C_{sb} for c; 0, $2x10^3$--- $8x10^3$	E
(a) Phenol on stearyl alcohol from 10% Ag.Na_2SO_4 ** (b) Phenol on stearyl alcohol from water** (c) Naphthalene sulphonic acid on cellulose [129] C_{sl} for a and b; 0,100,200,300 C_{sl} for c; 0,20,40,60 C_{sb} for a; 0,10^3, $2x10^3$,--- $8x10^3$ C_{sb} for b; 0,500,1000, --- 2000 C_{sb} for c; 0,10,20,30,40	C	Water on wool from n-butanol at 52° and 57° [130] C_{sl} in gms/l; 0,20,40,60 S_{sb} in m.mols/gm; 0,2,4,6,8	F

~~S_{sl}~~ ———

** Denotes work done by the present author

(Key to) GRAPH No. 1. (cont'd)

L		HA	
Resorcinol on alumina powder[128] C_{sl}, 0,20,40,60 C_{sb}, 0,25,50,75,100	G	(a) Janus Red (C.I.26115) on silica[131] (b) Methyl Violet (C.I.42535) on graphite[131] C_{sl} for a; 0,0.2,0.4,0.6 C_{sl} for b; 0,0.1,0.2,0.3 C_{sb} for a; 0,25,50,75,100 C_{sb} for b; 0,2.5,5,7.5,10	J
(a) Hydroquinone on wool[**] (b) Phenol on graphite[**] C_{sl} for a; 0,10,20,30 C_{sl} for b; 0,20,40,60 C_{sb} for a; 0,20,40,60,80 C_{sb} for b; 0,5,10,15,20	H	(a) 2:1 metal complex dye on unstretched nylon[118] (b) As above on stretched nylon[118] C_{sl} for a and b; 0,40,80,120 C_{sb} for a and b; 0,20,40,60,80	K
Anthracene-1-sulphonic acid on graphite[129] C_{sl}, 0,5,10,15 C_{sb}, 0,2.5,5,7.5,10	I	Sulphanilic acid → R acid on alumina powder[128] C_{sl}, 0,10,20,30 C_{sb}, 0,20,40,60,80	L

Table I

List of some Isotherms classified under the present rules*

S-type

Substrate	Solvent	Solute	Reference
Cellulose	Water	Naphthalene-2-sulphonic acid	134
Alumina (anodic film)	Water	Monosulphonated dyes	128
		Azo-dye monosulphonated ester	135
Wool	Ethanol	Phenol	80
Wool	Benzene	Azobenzene	80
Wool	Benzene	Stilbene	80
Nylon	Benzene	Stilbene	80
Wool	Benzene	p-Aminoazobenzene	80
Stearyl alcohol	Water	Phenol	**
Cellulose	Methanol	Benzene	134
Cellulose	Water	Naphthalene-2-sulphonic acid	134
		and	
		2-Naphthol-6-sulphonic acid	134
Chitin	isoOctane	Phenol	134
"	Benzene	Methanol	134
Nylon	Water /	Phenol	80
Nylon,wool	Benzene	Azobenzene	80
Wool	Water	Phenol	**
Wool	Water	2:4-Dinitrophenol	**
Wool	Water	p-Nitrophenol	**
Wool	Water	Haematein	132
Alumina (HCl treated powder)	Water	Phenol	128
"	Benzene	Nitrobenzene	128
"	Water	Cellobiose	128
Silica	Water	Orange II	131
Graphite	Water	Many sulphonates and sulphonic acids with 2-4 benzene nuclei and more than one sulphonic acid group	126

* Temperatures mainly 30°-80°C.; for details see references. Temperature change does not appear to alter isotherm shape.

** Denotes work done by the present author.

/ In the paper the curve is (probably wrongly) shown as L-shaped but the points would fit an S-curve better.

Table I (cont'd)

Ln-type

Substrate	Solvent	Solute	Reference
Cellulose Acetate	Water	Non-ionic ('disperse') dyes.	69,68
Polyethylene terephthalate (Terylene)	Water	Non-ionic ('disperse') dyes.	136
Wool	n-Butanol	Water	130
Cellulose Acetate	Benzene	Phenol	70
Cellulose Acetate	Benzene	Methanol	70
Alkali-treated wool	Benzene	Azobenzene	130
Cellulose Acetate	isoOctane	Phenol	**

L-type

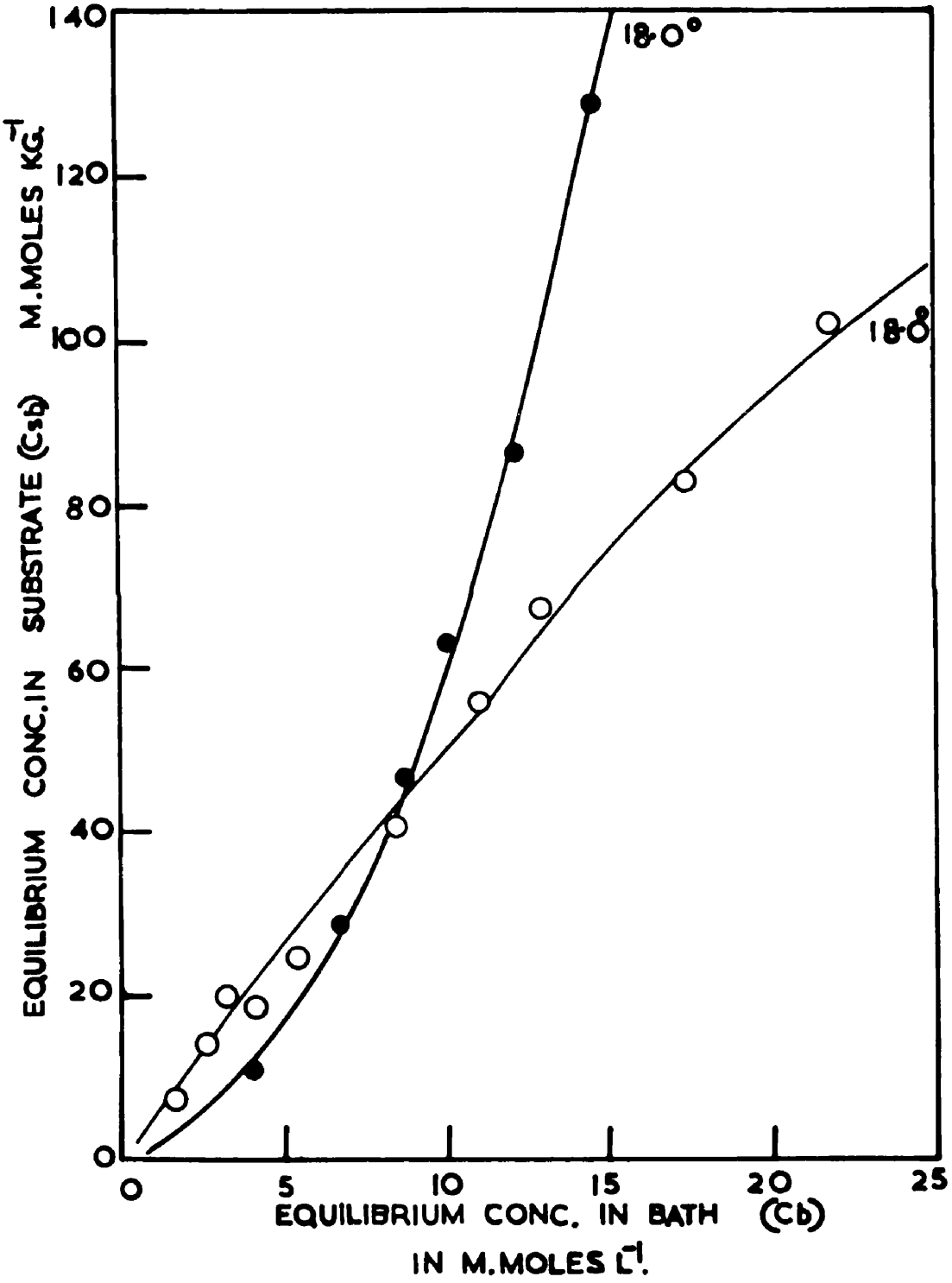
Orlon	Water	Sulphonated dyes	137
Wool	Water	Sulphanilic acid ⟶ R-acid	**
Wool	Water	Hydroquinone	**
Wool	Water	Solway Blue BN (C.I.63010)	**
Wool	Water	Orange II	**
Graphite	Water	Phenol	**
Graphite	Water	p-Nitrophenol	**
Wool	Water	Many mono-, di- and trisulphonated azo dyes.	48
Protein	Water	Alkyl sulphonate	138
Calcium carbonate	Water	Stearic acid	139
Cellulose Chitin	Water	Flavanthrone leuco sulphuric ester	134
Cellulose Chitin	Water	Sulphonated alizarin planar azo dyes e.g. Benzeneazonaphthalene dyes and benzidine bisazo dyes.	134

Table I (Cont'd)

HA-type

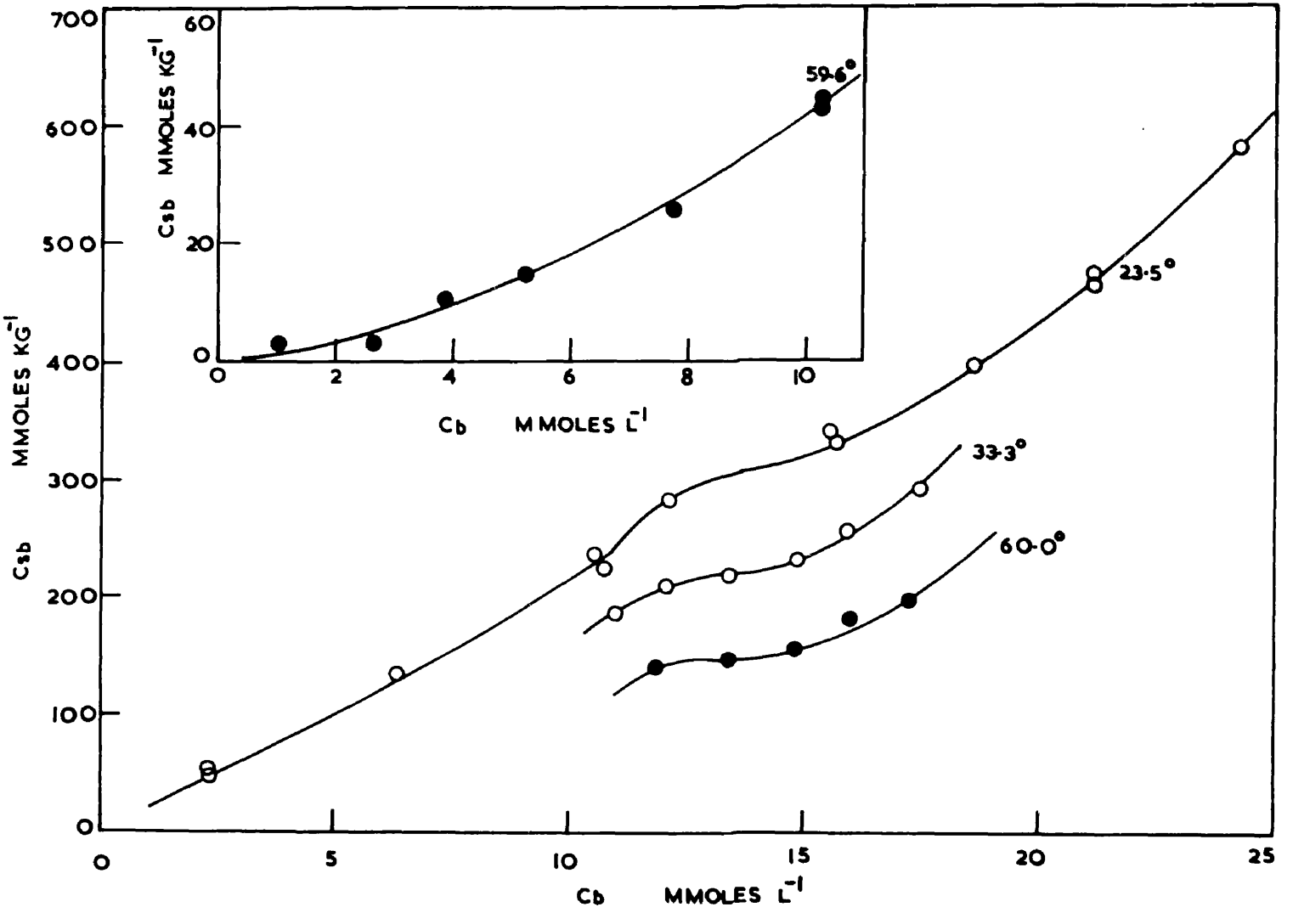
Substrate	Solvent	Solute	Reference
Alumina (HCl treated powder)	Water	Many sulphonated dyes	128
Alumina (acid anodic film)	Water	Sulphonated dyes with more than one sulphonic acid group.	128
Graphite	Water	Glucose and Sucrose	126
Alumina (anodic film)	Water	Sodium oleyl- and tetradecyl sulphate	135
Graphite	Water	Methyl Violet (C.I.42535)	126
Silica	Water	Orange I (C.I.14600)	131
Silica	Water	Janus Red (C.I.26115)	131

GRAPH NO.2



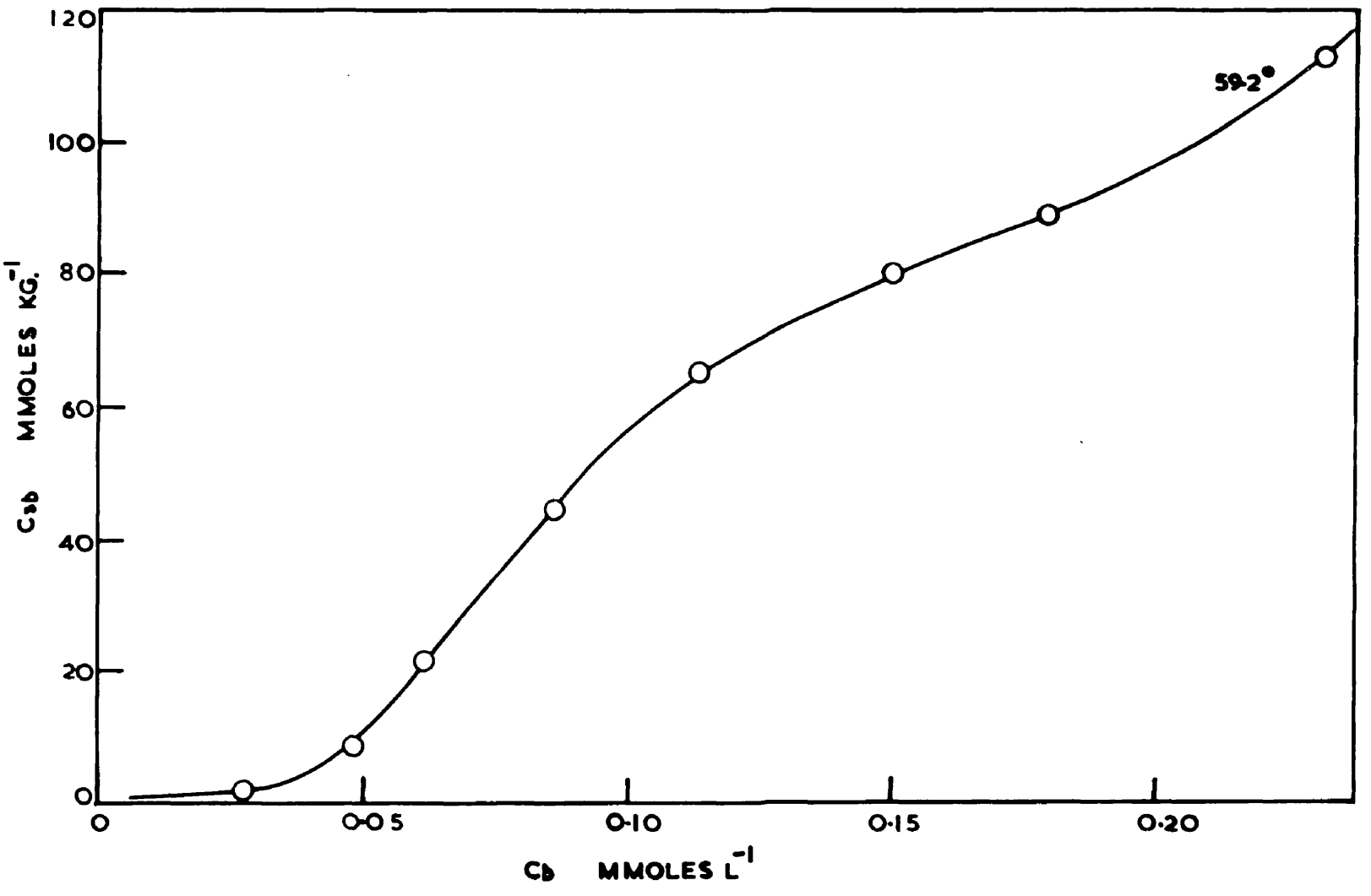
ADSORPTION ISOTHERMS OF ● PHENOL, O QUINOL ON WOOL FROM WATER

GRAPH NO3



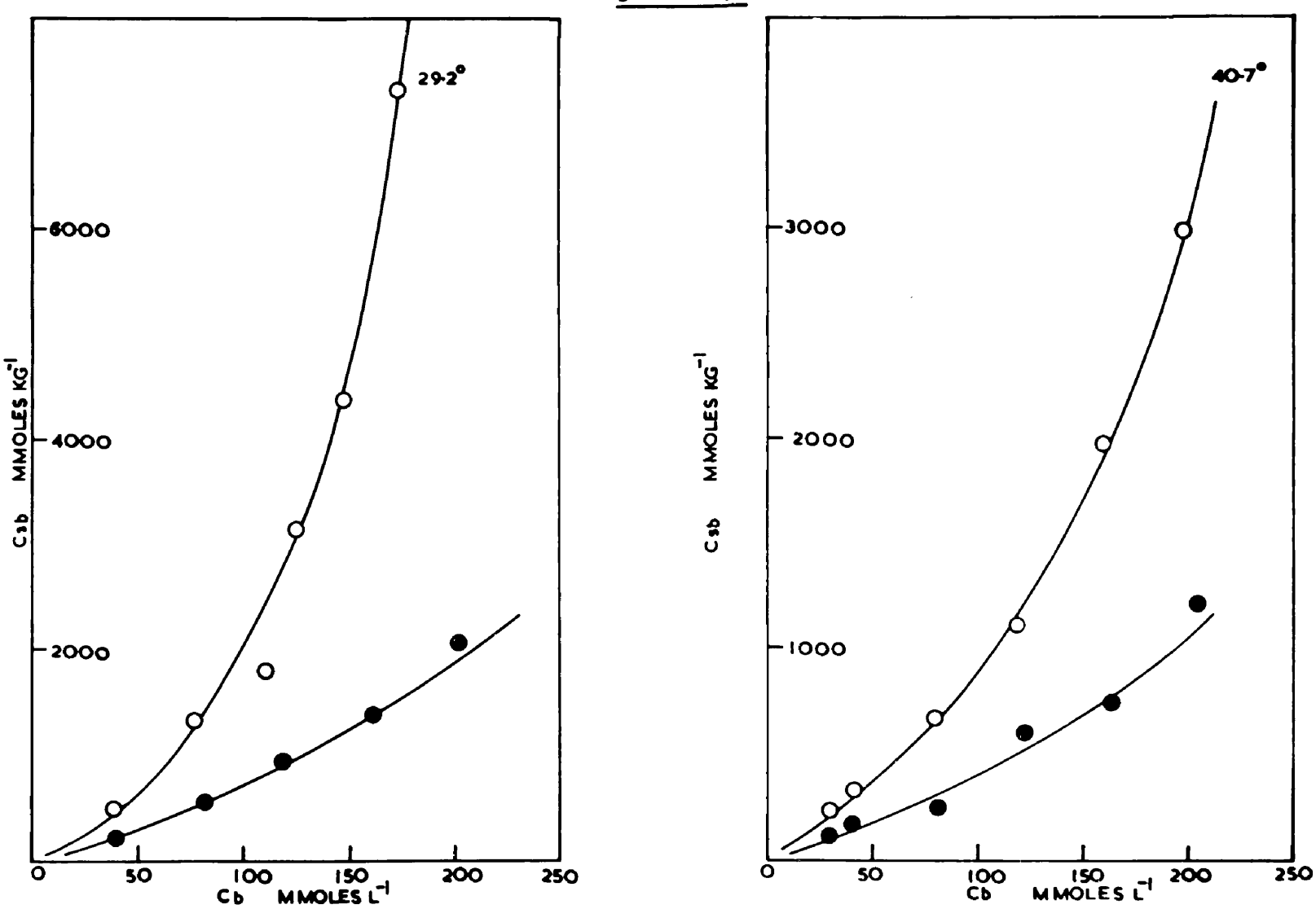
ADSORPTION OF p-NITRO-PHENOL ON WOOL FROM WATER

GRAPH NO. 4



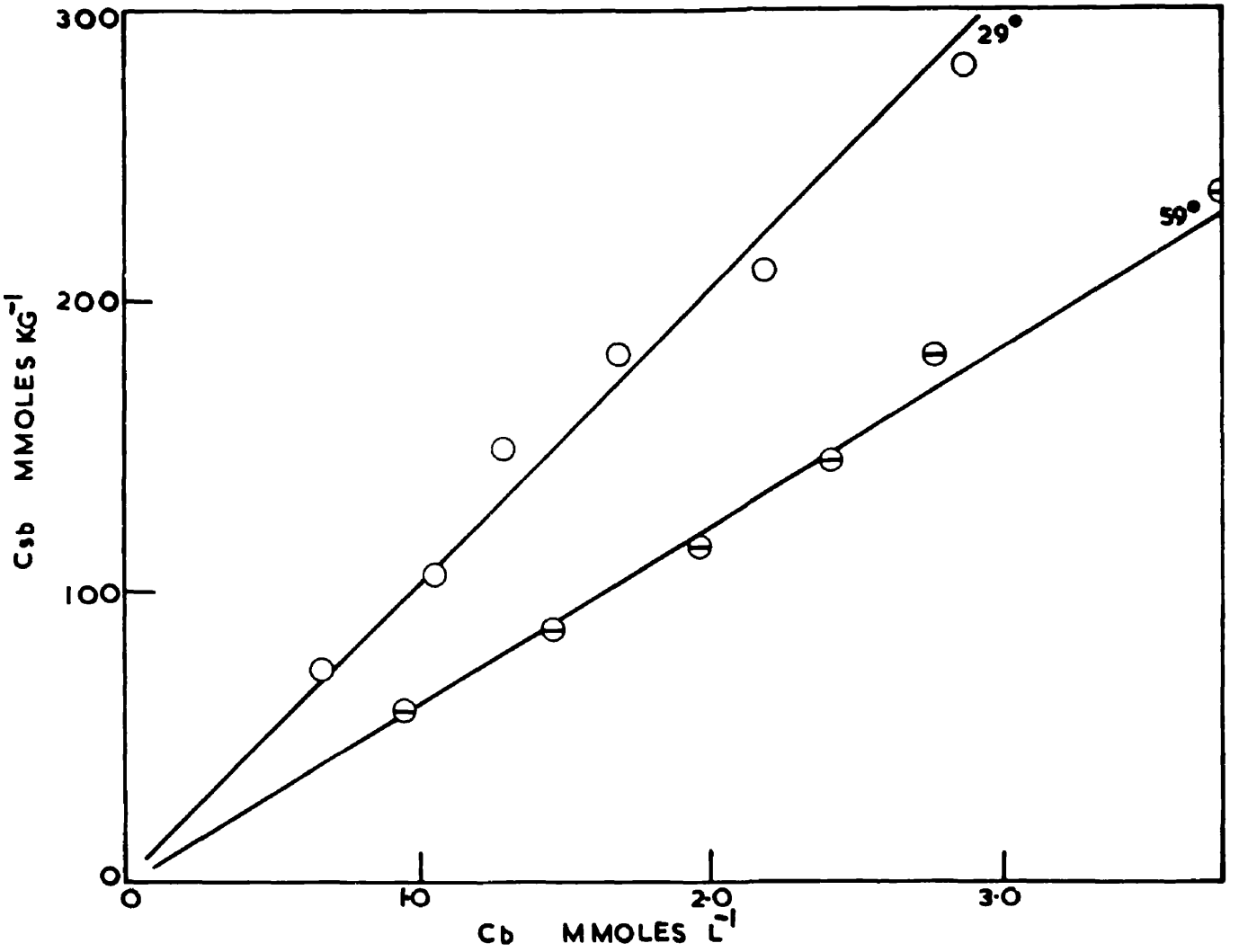
ADSORPTION OF 2:4-DINITROPHENOL ON WOOL FROM WATER

GRAPH NO.5



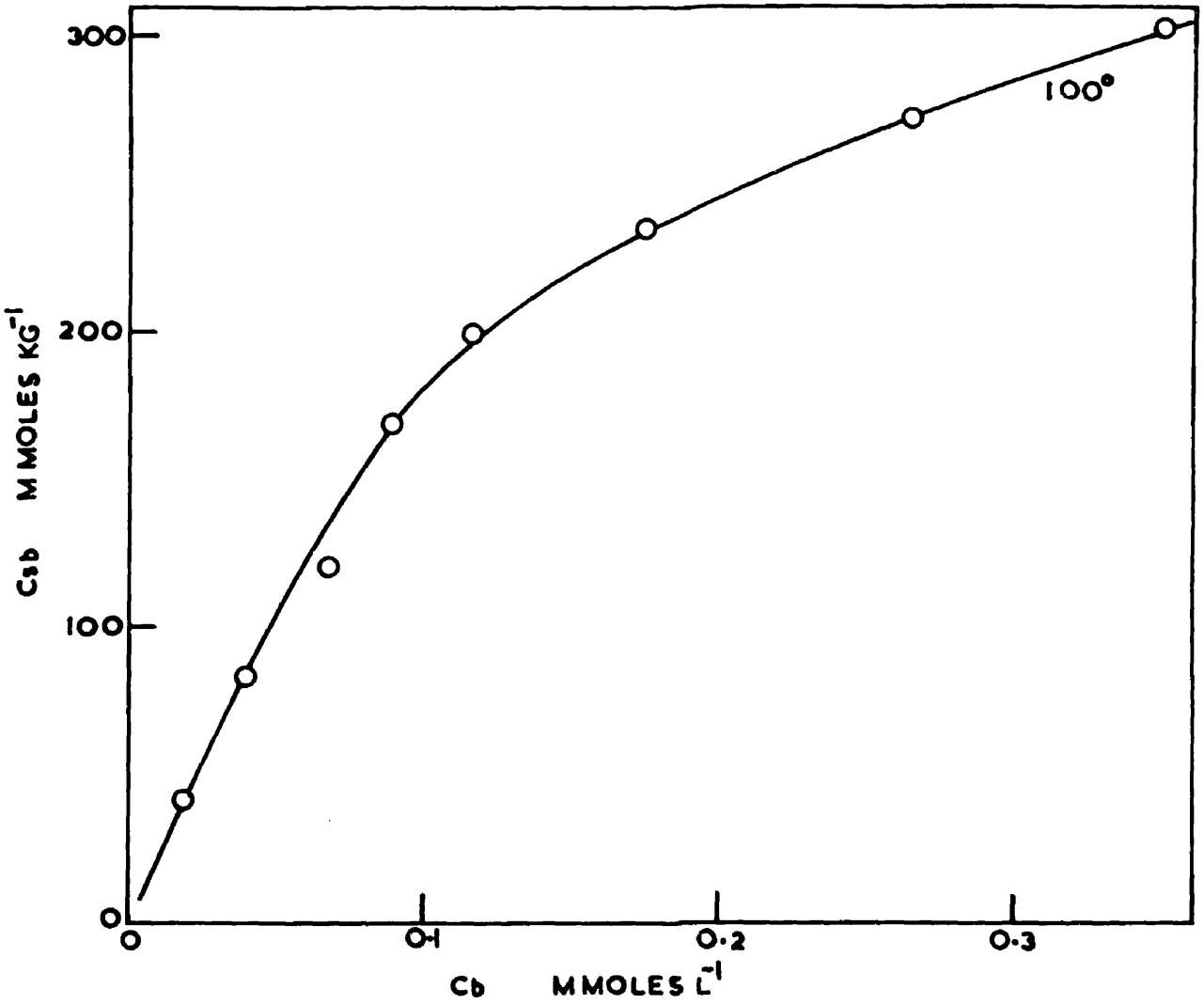
ADSORPTION OF PHENOL ON STEARYL ALCOHOL FROM WATER (●), & FROM 10% AQ. Na_2SO_4 (○)

GRAPH NO.6



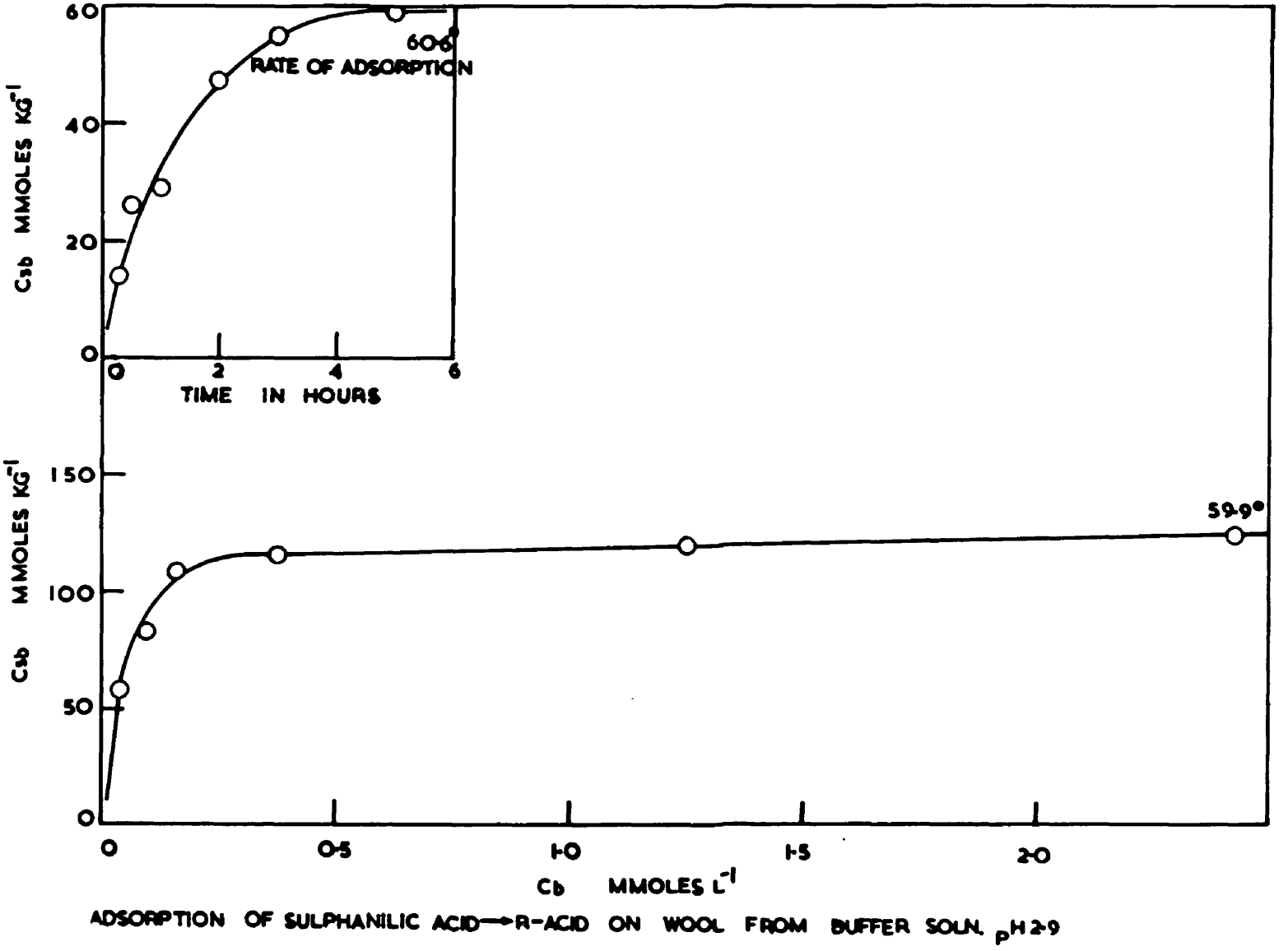
ADSORPTION OF PHENOL ON CELLULOSE TRIACETATE FROM ISOOCTANE

GRAPH NO.7



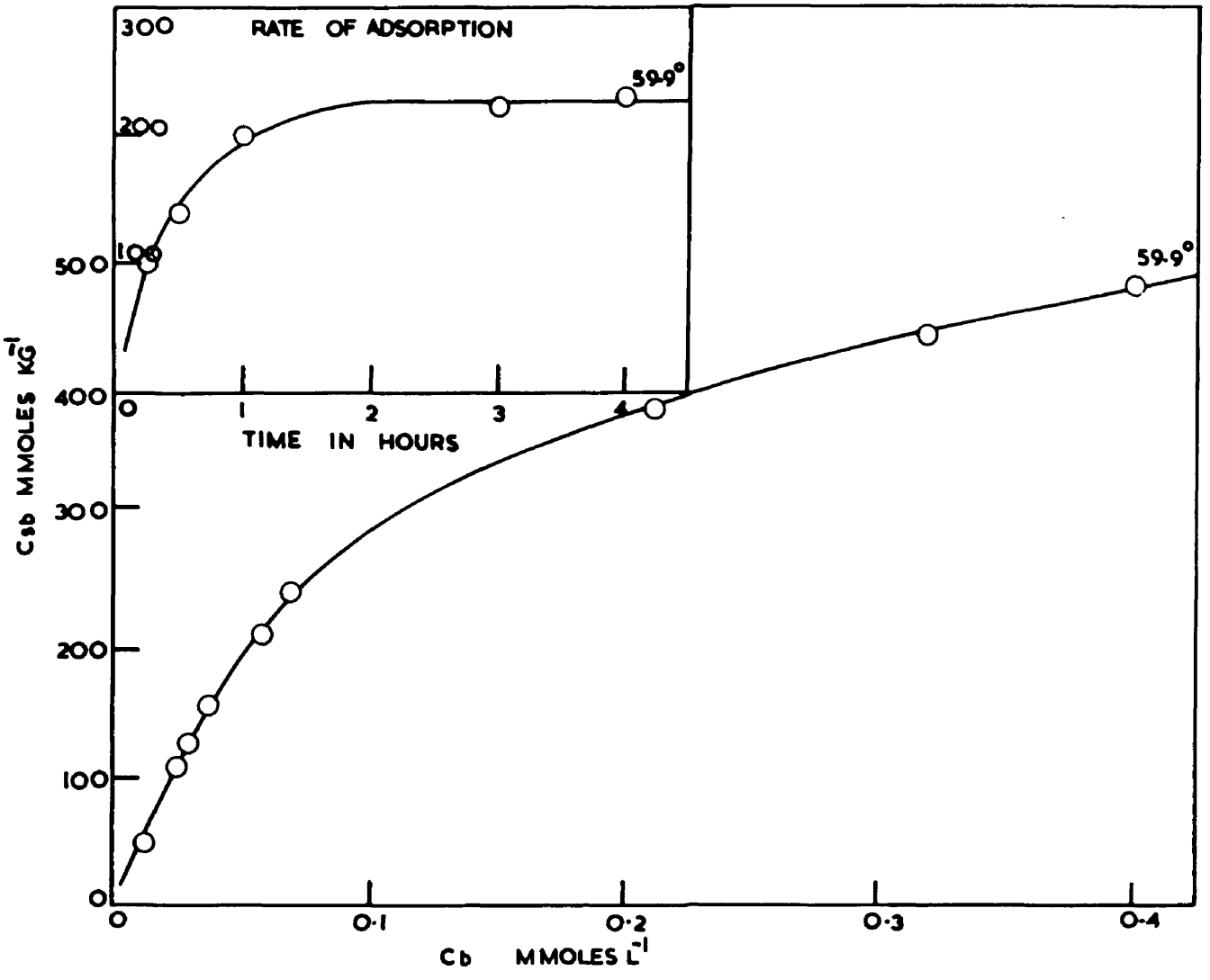
ADSORPTION OF SOLWAY BLUE BN ON WOOL FROM BUFFER SOLN. $_{p}$H 1

GRAPH NO. 8



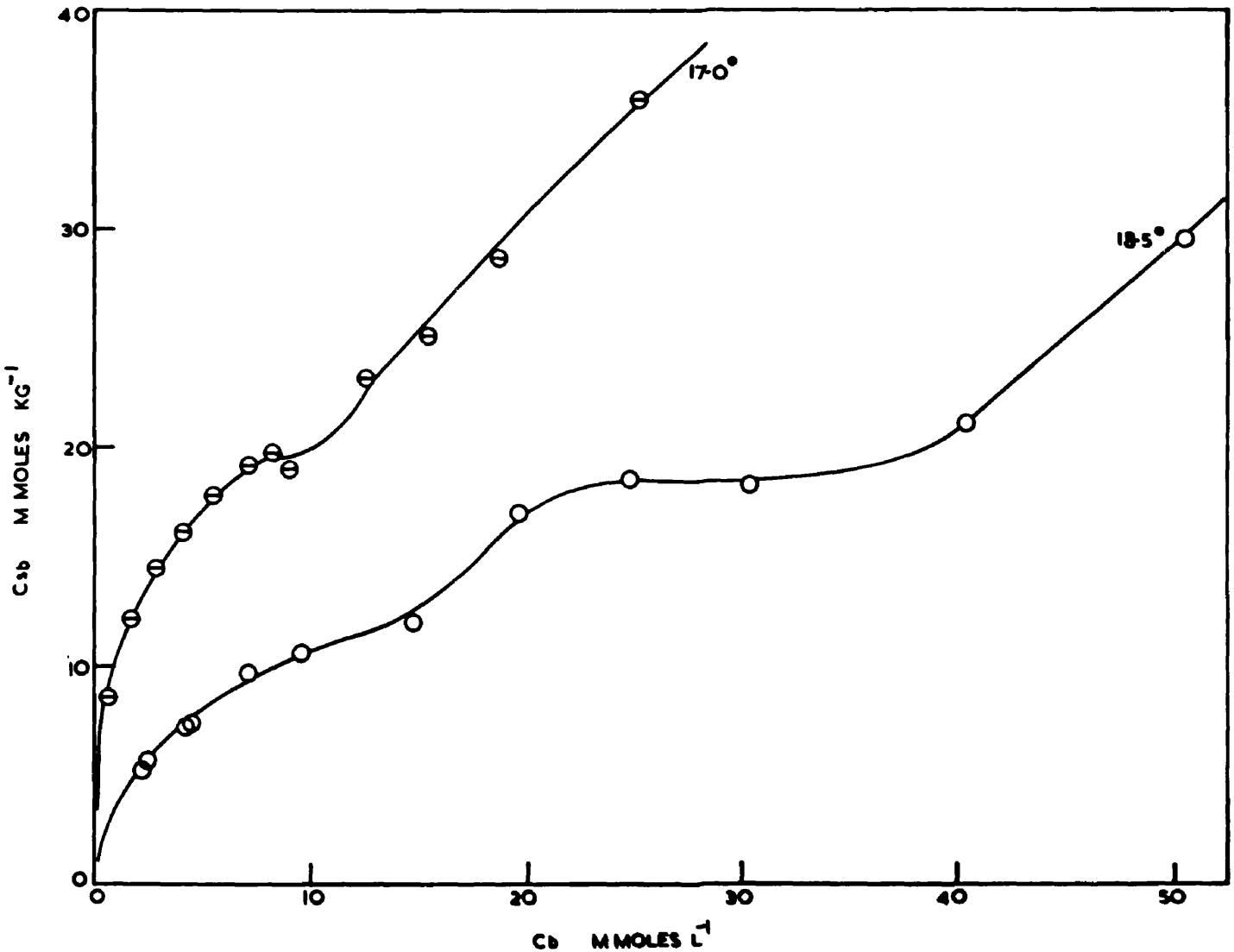
ADSORPTION OF SULPHANILIC ACID → R-ACID ON WOOL FROM BUFFER SOLN. pH 2·9

GRAPH NO.9



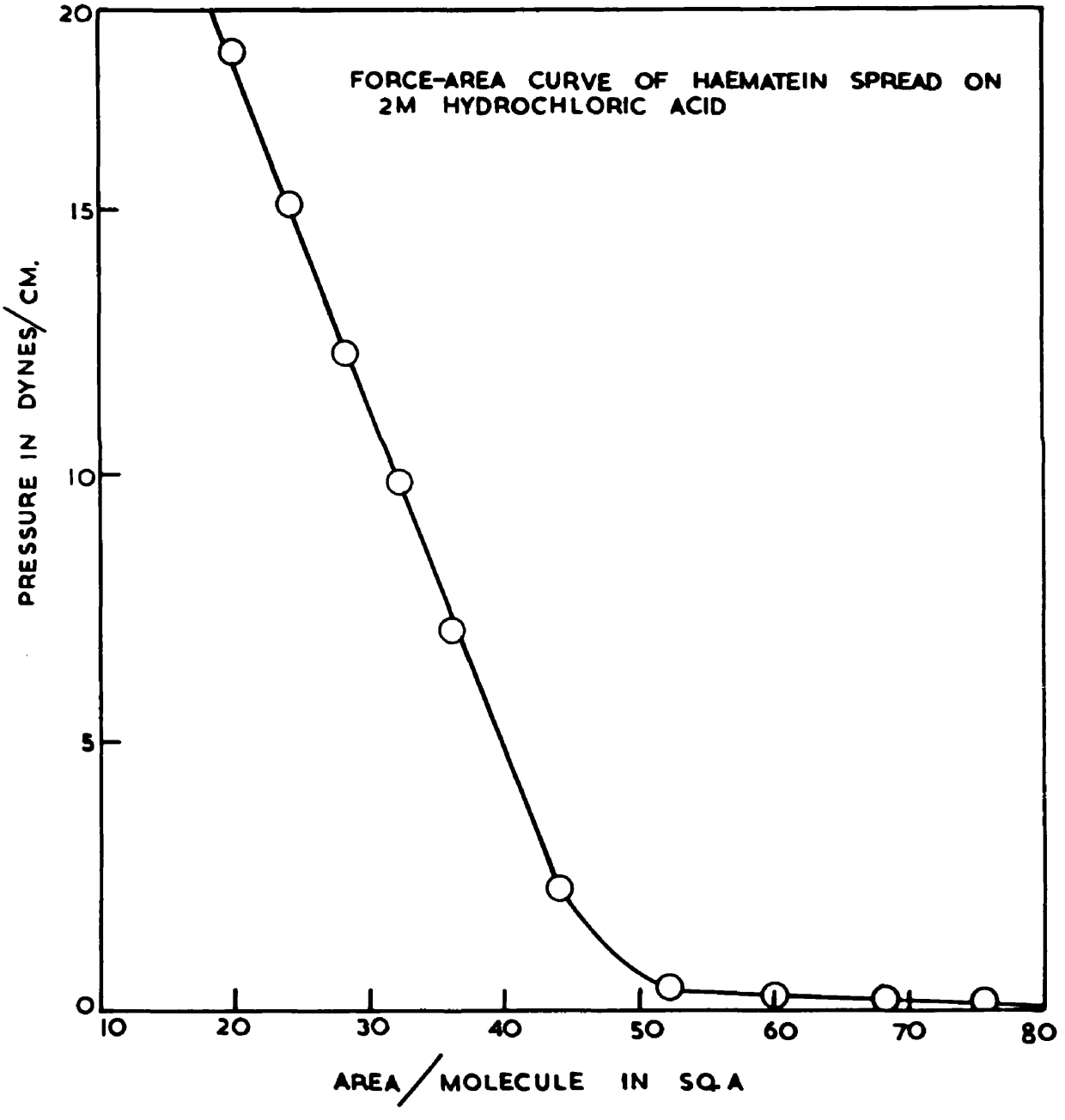
ADSORPTION OF ORANGE II ON WOOL FROM BUFFER SOLN. pH2·8

GRAPH NO.10

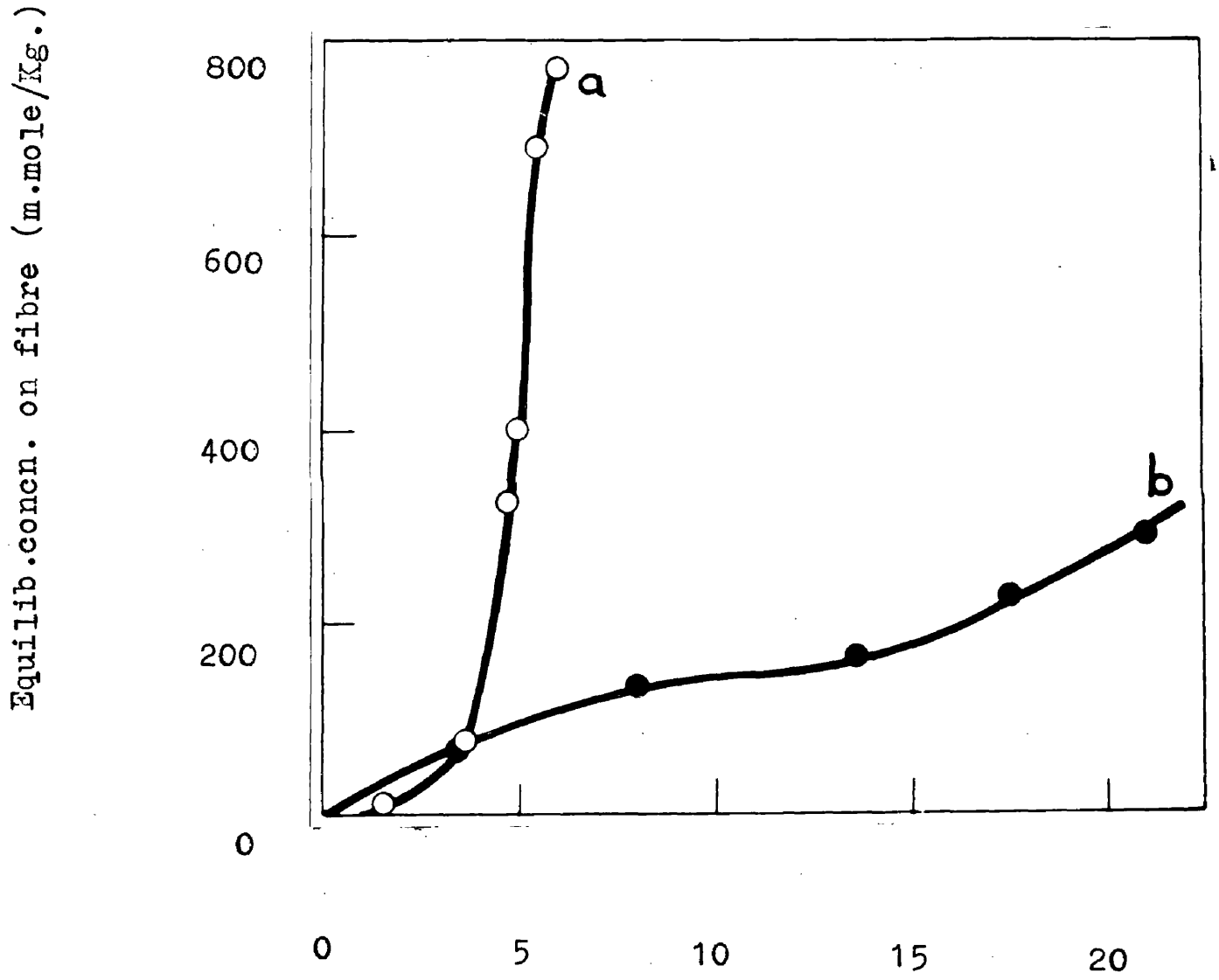


ADSORPTION OF PHENOL (Q), & p-NITROPHENOL (θ) ON GRAPHITE FROM WATER

GRAPH NO.11


FORCE-AREA CURVE OF HAEMATEIN SPREAD ON 2M HYDROCHLORIC ACID
PRESSURE IN DYNES/CM.
0
5
10
15
20
10
20
30
40
50
60
70
80
AREA/MOLECULE IN SQ.A

Graph No.12. Adsorption isotherms of (a) haematein (after Macneal[132]) and (b) haematoxylin (after Arshid*)[133] on wool at 60°C.



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