STUDIES IN MONOLAYER ADSORPTION.

BY

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Publications.

A paper embodying the results of the experiments upon monolayers of sulphonated dyes has, since the compilation of this thesis, been accepted for publication in the Journal of the Chemical Society under the title 'Studies in monolayers. Part V. Monolayer formation by sulphonated azo-dyes on water and aqueous solutions' by A. Cameron and C. H. Giles. (Paper No. 7/919).

Some of the same work is also included, with results of the work of some of the author's colleagues in a review now appearing in the preprints of papers to be presented before the IInd International Congress on Surface-activity in London, April 1957. ('A Study of the Relationship between the Adsorption Properties of Dyes and their Photochemical Behaviour', by C. H. Giles).

PREFACE

Wool is generally dyed with acid dyes (e.g. dyes containing sulphonate groups) under acid or in some cases neutral conditions. In recent years a type of dye has been developed which contains an attached alkyl chain, thus making the dye surface active. These dyes ("Carbolan" dyes, I.C.I. Ltd.) are of excellent washing fastness and good fastness to light. It was reported by I.C.I., however, that chains longer than about C_{12} seriously decreased the light fastness of dyes, therefore these are not used. It was hoped by studying the spreading properties of this type of dye in monolayers on water that some correlation might be obtained between these properties and the light fastness, which was being examined by another investigator in this laboratory. The results obtained were compared with fading results obtained for the same dyes on a protein (gelatine).

Previous work in this laboratory has shown that a monolayer technique may be used to study the interactions of dyes and models of fibres. This work was continued by a study of the effect of dyes on monolayers of cellulose triacetate and proteins.

SUMMARY

The spreading properties of various sulphonated dyes containing alkyl chains have been studied, in monolayers on water. It is found that when spread on water partial or complete solution of the monolayer occurs. On decreasing the solubility of the dyes, however, by spreading on concentrated solutions of inorganic salts condensed films are obtained for all dyes with a chain length of 12 carbons or over. Dyes containing short alkyl chains (i.e. C_4 and under) generally do not form surface films, though with the larger sized molecules gaseous films are formed. Mixing of cetyltrimethylammonium bromide with the dyes before spreading causes most of the short chain dyes, which do not form monolayers by themselves, to form a stable mixed film.

It has been found that dyes which are surface-active (i.e. those dyes which form films without the aid of cetyltrimethylammonium bromide) are often less fast to light than non-surface active dyes. The inference is that the dyes which form stable monolayers at the air-liquid interface also form monolayers when adsorbed on a substrate. Those dyes which do not form surface films, on the other hand, are believed to form aggregates in the substrate. The monolayer-forming dyes then expose a much larger solid-to-air surface in the substrate, resulting in a decrease in light fastness. Thus the light fastness of a series of dyes depends to some extent upon their surface activity; those which form monolayers are often the most fugitive.

Cetyl acetate and methyl- and ethylstearyl ketones have been spread on aqueous solutions of various solutes. It is found that large dye molecules and medium-sized bifunctional molecules expand films of cetyl acetate, whereas the ketone films remain relatively unaffected. The dyes are believed to be bonded by both Van der Waals' and polar forces whereas the bifunctional molecules are bonded mainly by polar forces and each molecule cross-links two film molecules. Cellulose triacetate films have also been studied. It is believed that when these are spread on water incomplete breakdown of the micelles occurs and aggregates as well as a monolayer are formed. The dyes are found to expand these partially spread films, and it is believed that the dyes have sufficient affinity to form complexes with the monolayer, but not enough to penetrate the micelles or aggregates by breaking the interchain bonds. Substances which are strongly bonded to cellulose triacetate, e.g. urea, can penetrate the micelles by breaking interchain bonds therein.

The attachment of the non-ionic so-called 'disperse' dyes to cellulose triacetate has been studied by similar methods. A typical dye of this class, which is readily adsorbed by cellulose triacetate, when mixed with cellulose triacetate and spread as a mixed film gives no increase in the area of the film. It is suggested that the dye is oriented along the underside of the polymeric chains by polar and perhaps also by non-polar attraction.

The effect of dyes on protein films was next studied. Acid dyes in acid solution expand these films but the expansion decreases with increase in pH and at pH 7.0 it approaches zero. These results were compared with the known adsorption properties of these dyes on wool, and it was found that the effect of pH is similar in both cases.

CONTENTS.

GENERAL INTRODUCTION.

The use of surface films of oil to protect ships from waves has been known since ancient times, but the actual study of these films was not begun until 1891 when Fraulein Pockels[1] found a method of handling them. A surface film of oil was confined in a trough, filled to the brim with water, having a strip or 'barrier' lying across it and resting on the surface. The film could be compressed by moving this barrier and it was found that the surface behind the barrier was left perfectly clean. Thus a means had been found, firstly to clean the surface of the water in the trough, and secondly to expand or compress surface films. The manner in which the surface tension falls with decrease in area was investigated and it was found that provided the area exceeds a certain critical value for a given quantity of oil, the surface tension is not perceptibly different from that of clean water. It was also shown that as the area diminishes below this critical amount the surface tension falls rapidly. In 1899 Rayleigh[2] confirmed Fraulein Pockel's observations and contributed a most important idea to the theory of these films by suggesting that the critical point was one at which the molecules are crowded together, one molecule thick, touching each other over the whole surface.

In 1917 Langmuir[3] introduced new conceptions and experimental methods of great importance in the study of these films. A trough fitted with two barriers was used to measure the outward surface pressure of a film directly. The film was spread on the clean surface

between the barriers and the outward force F was measured for varying film areas. Pure substances of known constitution were used instead of 'oils' and the effect of varying their constitution was observed. Solid substances, as well as liquids, were spread by dissolving them in a volatile solvent, such as benzene, which evaporates a few seconds after spreading. The results were expressed as areas per molecule in sq. A for each surface pressure. The clearest results were obtained with films of normal saturated fatty acids and alcohols, which can stand lateral compression and give a very clearly marked critical area at which the surface pressure first appears. It was also shown that that as the area is decreased from large initial areas, no surface pressure is detected till the area reaches 22 sq.A per molecule and at 20.5 sq.A the pressure increases rapidly with further decrease in area. The most striking fact found by Langmuir was that the length of the hydrocarbon chain makes no difference to the shape of the curve provided there are more than 14 carbon atoms, though at very long chain lengths the finer details of the curve tend to be obliterated as the films are extremely rigid and do not yield readily to small lateral pressures. Since the area does not change with increase of chain length it shows that the molecules must be steeply oriented to the surface and at the same angle in all the films. It was first believed that the chains were vertical from the evidence of the films alone, but it was shown later that this may not be the case.

These results, showing that the molecules are elongated and oriented

steeply to the surface, gave at once a great deal of information as to the forces around the molecules themselves. The alcohols and acids which form stable films have an OH or a COOH group at the end of the molecule and in the lower homologues these groups confer solubility on the whole molecule and are called hydrophil/ic or water-soluble groups. In the case of the fatty alcohols and acids these groups cannot pull the whole molecule into the water, owing to the resistance of the long chains to immersion, and thus the substance spreads out as a monomolecular film on the surface. It can be seen, since long chain paraffins do not form surface films, that it is essential to have in the molecule a hydrophil/ic group as well as a hydrophobic chain and that the formation of stable monomolecular surface films may be regarded as solution of the end group of the molecule, the rest refusing to be immersed. The lateral adhesion between the long chains probably assists to keep the molecules out of the water by causing them to pack side by side. This adhesion certainly is the main factor in keeping the molecules together as a coherent film, which shows no appreciable surface pressure beyond 22 sq.A.

Langmuir also studied adsorbed surface films of shorter chain, slightly soluble, acids and found these gave 'gaseous' films in which 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 absorbed films of soluble fatty substances, which would be analogous to the evaporation and critical phenomena of liquids and vapours in three dimensions.

In 1926 Schofield and Rideal[4] showed that as the length of the hydrocarbon chains in soluble fatty acids increases so does the lateral adhesion between the molecules in gaseous films until the hydrocarbon chain contains twelve carbon atoms where there is almost enough lateral adhesion to form a coherent film. Adam and Jessop[5] in the same year, using a new sensitive instrument for measuring surface pressures, were able to trace in detail the transition between gaseous and coherent films and found that there is a very close resemblance between these transitions and the condensation of three dimensional gases to liquids.

Further complexities in the coherent type of film were found by Langmuir and were further investigated by Labrouste[6], Adam and others. They showed that there frequently exists a coherent 'expanded' state in insoluble surface films of fatty substances intermediate in the area between the very closely packed condensed films and gaseous films.

Several other methods of examining surface films have been studied and the most important of these is the measurement of surface potentials. It had been known for some time that surface films affect the contact potential between the liquid and air, but it was not until 1924 that this was first measured[7]. These measurements were continued by Frumkin[8] and in 1931 Schulman and Rideal[9] made a detailed study of several types of insoluble films and compared surface potentials over a large range of

areas. The work has been continued by Rideal, Schulman and Hughes and also by Adam and others.

It is now a common practice to measure surface pressures and surface potentials simultaneously, which is most useful, especially in giving information as to the homogenity of a film and in tracing the course of chemical reactions in films. It also affords qualitative information as to the orientation of polar groups in the molecules to the surface of the water.

Freundlich et al.,[10] Bouhet[11], and other workers have described 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 films, 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.

In 1930 another method of examining surface films was introduced by Zocher and Stiebel[12] and later modified by Adam[13]. 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 invariably settle on the surface. Although this method yields no information as to the structure of the films, it is a valuable accessory technique in that it

reveals whether or not the film is properly spread.

The most recent method of investigating the structure of monolayers is by electron microscopy[14,15]. Monolayers of synthetic linear polymers (nylon, cellulose acetate and polyvinyl alcohol) have been studied by this method and at low pressures it was found that the monolayer consists of winding microfibrils. Compression of the film shows the production of a large number of microfibrils oriented at right angles to the direction of compression. Further compression causes visible striations on the film.

(1) Insert the following paragraph after the first line of page 6.

Another important method of studying the properties of surface films is by the measurement of surface viscosity. This property was first measured quantitatively by Joly and Dervichian[158] and is dependent upon the number of film molecules per unit area of surface and also upon the orientation and attractive forces between them. An important application has recently been found for surface viscosity measurements in the study of interactions between film molecules and substances dissolved in the underlying liquid. It has been shown(123,133) that when a crosslinking network is formed by polyfunctional adsorbate molecules interacting with the film molecules, e.g. the interaction between collagen monolayers and tannic acid, large increases in the surface viscosity occur.

TYPES OF SURFACE FILMS.

It has now been established that a number of forms of surface films can exist and it has been shown that the type of film depends to a great extent on the lateral adhesion between the molecules. The present research was concerned mainly with condensed and liquid-expanded films although some of the results obtained would indicate the formation of gaseous films. The most important types are condensed, liquid-expanded and gaseous films.

Condensed Films.

These are the most important films. The molecules in these films have a great amount of lateral adhesion and if the surface is greater than can be covered by the adhering molecules a two phase system results which is detectable by surface potential measurements.

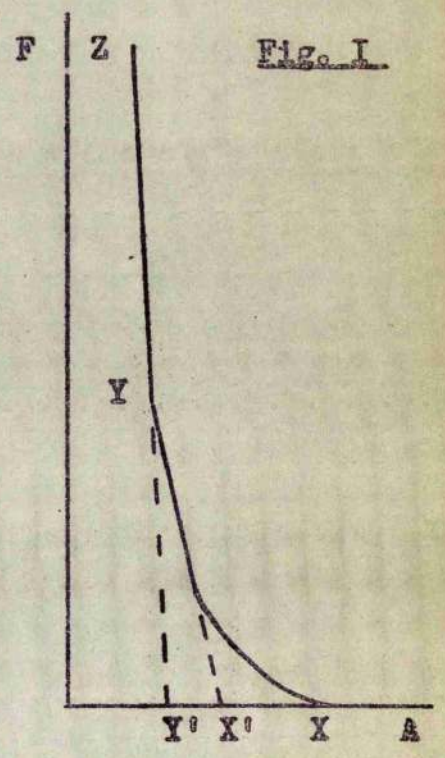


Fig. I.

With condensed films the following type of force-area curve is obtained. (Fig.I).

In some cases 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 20.5 sq.A[16] while the area at X' may extend over 30 sq.A. Numerous attempts to draw analogies between the two dimentional condensed films have been made, and it has been suggested that the regions YZ and YX correspond to the solid

and liquid states respectively.

Adams[17] suggested that the two parts XY and YZ can be attributed to close-packed heads and close-packed chains respectively. Lyons and Rideal[18] supposed that the chains are 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 as 18.5 sq.A[19], the interlocking position gives areas of 20.7 sq.A and 26.2 sq.A. for X' and Y' respectively. Adam[20], 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. With regard to the XY portion, it was shown that this 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 are rearranged by 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[21] 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.

Derivichian[22] has drawn very close analogies between monolayers and three-dimensional matter, and claimed that the lattice structure and tilt of the molecules in the different forms are the same in two and three dimensions. Alexander[23] has criticised this theory severely by pointing out, among other things, that if it was correct then solid substances at room temperature should also give condensed monolayers; this, however, is known to be incorrect in many cases. He supported the view[24] 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. Amongst other data he showed that the surface moment of condensed films of ethyl stearate requires vertically oriented chains[25]. 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) <u>The Size of the Head Group.</u>

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, amides and others. In certain cases where hydrogen bonding was expected, but prevented by steric factors, a bond through a water molecule was postulated[26].

(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 unlikely.

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 negligable 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 collisions between the moving film molecules and the floating barrier.

In the evidence outlined by Adam[27] to show that molecules of this type lie flat on the surface, it was pointed out that it is often possible to convert a coherent film into a gaseous one by introducing a second

hydrophilic group some distance from the first, e.g.

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

Adam and Jessop[5] have shown that for an ideal gaseous film,

$FA = KT$. (K is the gas constant).

This may be compared to the gas equation ($PV = RT$) and the proof follows that for the ordinary gas laws very closely.

LIQUID-EXPANDED FILMS.

This type has properties intermediate between those of the gaseous and the condensed films and is often found with long chain aliphatic substances. Langmuir's explanation[28] 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 the molecules standing upright and lying flat.

PREPARATION AND PURIFICATION OF COMPOUNDS.

PREPARATION AND PURIFICATION OF COMPOUNDS.

Most of the compounds used in this work had to be prepared and/or purified and the methods used are described below.

PREPARATIONS.

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 water bath. The acetate was then isolated from the reaction mixture by vacuum distillation.

B.p. 200°C.,15mm. M.p. 22°C.

Stearyl ethyl ketone.

This was prepared by the method used by Gilman and Nelson[29]. Powdered cadmium chloride (0.16 mole.) was stirred gradually into an ice-cold ether solution of methyl magnesium bromide (prepared from magnesium (0.35 mole.) and ethyl bromide (0.3 mole.)) and stirring was continued for 30 minutes. Stearoyl chloride was then added gradually, at first in ether (0.05 mole. in 40 c.c.) and then undiluted (0.16 mole.). Stirring was continued for one hour in the cold and for two hours on a boiling water bath. Crushed ice was then carefully added to the reaction mixture followed by water and sufficient sulphuric acid to dissolve the white precipitate which was formed. The ether layer was then removed, washed with alkali, then with water, and evaporated to dryness. The white solid residue was heated with concentrated aqueous sodium hydroxide solution, cooled and separated by

filtration; it was finally redissolved in ether and washed with water. The residue after evaporation of the ether was recrystallised from ethanol.

Colourless crystals, M.p. 53°C.

Stearyl methyl ketone.

Agaric acid (10 gm.) and sulphuric acid (100 c.c.,S.G. 1.84) were heated on a water bath for an hour, cooled in ice and then mixed with 2 litres of water. The mixture was extracted with ether and then the ether extract was shaken with aqueous potassium carbonate solution and filtered. The ether was then removed by distillation and the residue dissolved in ethanol. This solution was then decolourised with charcoal and recrystallised several times from ethanol.

Colourless plates, M.p. 56°C.

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°C. for 10 hours, while the water formed was allowed to distil off, and thereafter for a further 12 hours[30]. 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°C., 11 mm.

p-Cetylaniline → R acid.

p-Cetylaniline (0.1 mole.) is insoluble in hydrochloric acid and the diazotisation was carried out with a finely divided suspension of the hydrochloride. The suspension was placed in an ice-bath and ice was added to the mixture followed by hydrochloric acid (75 c.c. of 2N). Sodium nitrite (100 c.c. of 2N solution) was then added dropwise with constant stirring until most of the material had dissolved. Any undissolved pieces were then removed by filtration.

This solution was then coupled with R acid (0.1 mole.) dissolved in sodium hydroxide (100 c.c. of N). The dye was precipitated on coupling and was then filtered and washed with benzene to remove any unreacted amine. It was then recrystallised from water.

p-Butylaniline → N-acetyl H acid.

This dye was prepared by coupling diazotised p-butylaniline with acetyl H acid. The p-butylaniline was diazotised in the manner described for the diazotisation of aniline[31].

Acetyl H acid was prepared by dissolving H acid (0.1 mole.) in 200 c.c. of water at 50°C. containing 6 gm. of sodium carbonate. Acetic anhydride (17 gm.) was then added over a period of 15 minutes with vigorous stirring. Complete acetylation of the amino group in the H acid took place, but simultaneously the hydroxyl group was also partly acetylated. When acetylation was complete sodium carbonate (25 gm.) was added and the mixture heated for one hour at 98°C. This hydrolyses the acetyl group on the oxygen but does not attack the acetyl-

amino group. This solution was then used for the coupling reaction. The dye was then salted out and recrystallised from water.

p-Aminoazobenzene → R acid.

This dye was prepared by diazotising p-aminoazobenzene and coupling it with R acid.

p-Aminoazobenzene is insoluble in hydrochloric acid and the diazotisation was carried out with a finely divided suspension of the hydrochloride. p-Aminoazobenzene (0.1 mole.) was ground to a fine powder in a mortar and hydrochloric acid (50 c.c. of 2N solution) was added. The mixture was then ground to a fine paste and transferred to a filter flask. The flask was placed in an ice-bath and ice was also added to the mixture, followed by 75 c.c. of 2N hydrochloric acid. Sodium nitrate (100 c.c. of N solution) was then added dropwise with constant stirring until all the material had gone into solution, any undissolved lumps being removed by filtration.

This solution was then coupled with R acid (0.1 mole.) dissolved in sodium hydroxide (100 c.c. of N solution).

The dye was then salted out and recrystallised twice from water, after which a sample solution was run down an alumina column to check its homogeneity.

PURIFICATION OF COMPOUNDS.

Commercial Dyes.

All other dyes used were purified from commercial samples and unless otherwise stated were treated as follows. .The dye was dissolved

in water and then salted out; it was then recrystallised several times from water and analysed.

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

The commercial sample of this disperse dye was extracted with benzene in a Soxhlet extractor. The extract was then concentrated and the dye recrystallised from benzene. The dye was then again recrystallised twice from benzene and dried at 60°C.

4N-Ethylethyl sodium sulphate 4'-nitroazobenzene.

The commercial sample of this sulphato-ester dye was extracted with acetone in a Soxhlet extractor and recrystallised from acetone several times.

Pyridine.

The pyridine used was purified by distillation and the fraction with b.p. 115°C. collected.

Benzoquinone.

Crude benzoquinone was placed in an evaporating basin covered with a filter funnel and heated. The benzoquinone sublimed and the pure material solidified on the sides of the funnel.

PURE COMPOUNDS.

The following substances used were either Analar or purified reagents:-

ethylene glycol	2,2'dipyridyl	casein
benzene sulphonic acid	mesaconic acid	barium chloride
urea	hydroquinone (quinol)	sodium chloride
sucrose		cupric chloride

ESTIMATION OF DYES[32].

All dyes which were prepared or recrystallised from commercial samples, were estimated by reducing them to colourless substances using titanous chloride and though the principle was the same in every case the technique varied depending on the properties and structure of the dye.

Azo Dyes.

When an azo dye is titrated with titanous chloride the following reaction takes place:-

$$R.N{=}N.R' + 4TiCl_3 + 4HCl = 4TiCl_4 + R.NH_2 + R'NH_2$$

Thus each azo group requires four equivalents of titanous chloride. The titanous chloride solution was always standardised before each estimation by titration against a standard ferric ammonium sulphate solution using potassium thiocyanate as indicator and the dye estimated 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 transferred to a conical flask containing 10 c.c. of concentrated hydrochloric acid. The solution was then boiled and carbon dioxide was bubbled through to exclude air. The dye solution was then titrated with titanous chloride until the colour disappeared. From the volume of titanous chloride used the purity of the dye could be calculated.

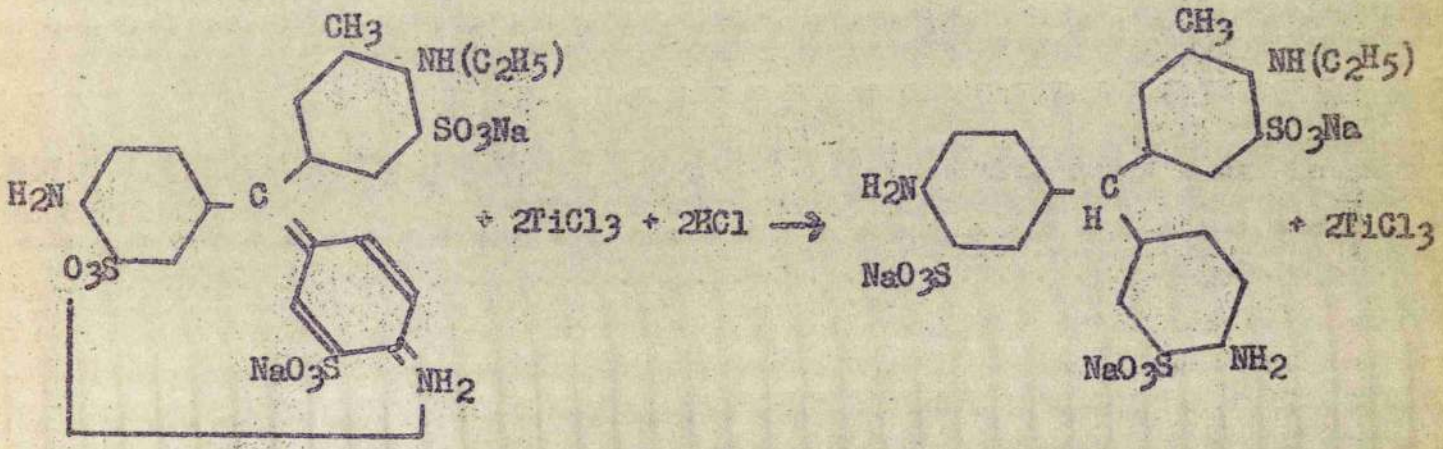
(b) If the dye was soluble in water but was precipitated by the

addition of hydrochloric acid, then the estimation was carried out using Rochelle salt instead 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 again the estimation was carried out in exactly the same way as in (a), only without the addition of hydrochloric acid.

Triphenylmethane Dyes.

The only dye of this type employed was Acid Magenta and the method used was exactly the same as (b) for azo dyes. In this case, however, the dye is not split into two compounds but forms a colourless leuco-compound.



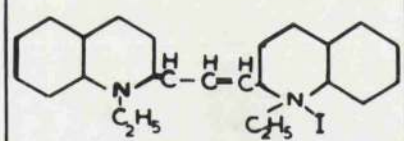
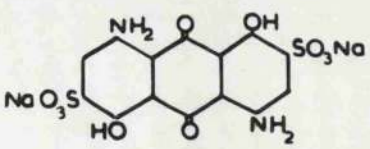
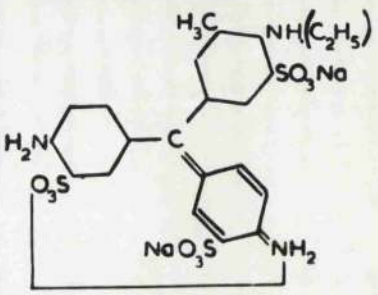
Thus in this case only two equivalents of titanous chloride are required for each dye molecule.

LIST OF COMPOUNDS USED.

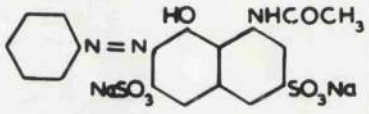
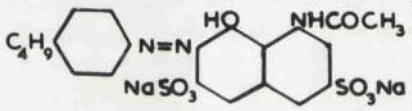
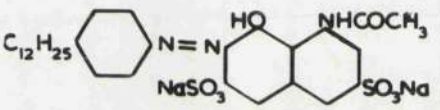
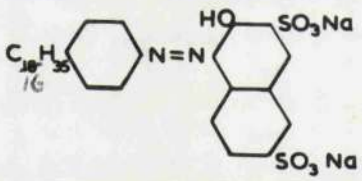
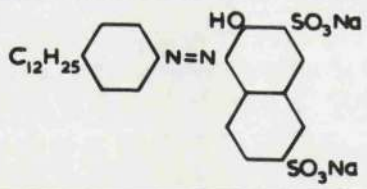
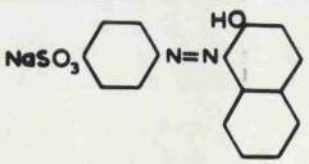
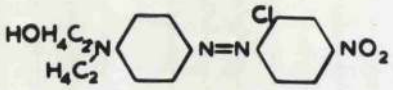
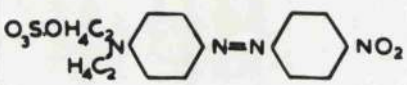
1. LONG CHAIN COMPOUNDS. (excluding dyes.)

COMMERCIAL NAME.	FORMULA.	CHEMICAL NAME.
Cetyl acetate	$C_{16}H_{33}O.C\,O.CH_3$	Hexadecyl acetate
C.T.A.B.	$C_{16}H_{33}(CH_3)_3N\ Br$	Cetyl trimethyl ammonium bromide
Stearyl methyl ketone.	$C_{17}H_{35}.CO.CH_3$	Heptadecyl methyl ketone
Stearyl ethyl ketone.	$C_{17}H_{35}CO.C_2H_5$	Heptadecyl ethyl ketone.

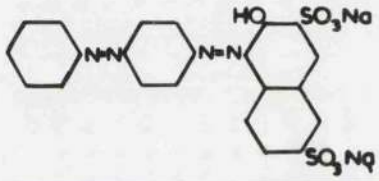
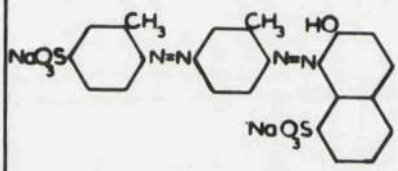
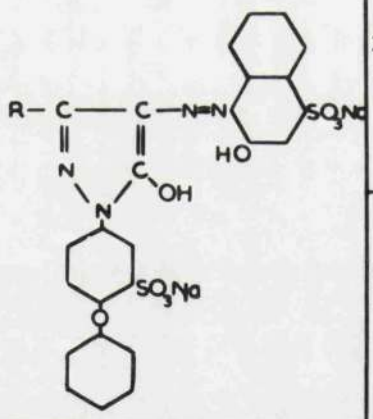
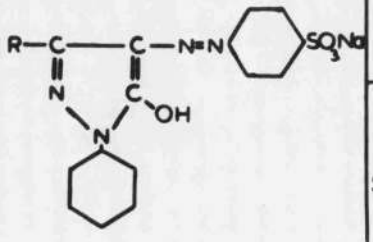
2. DYES.

COMMERCIAL NAME.	FORMULA	CHEMICAL NAME.
Pinacyanol. C.I. No. 808.		1.1' Diethyl-strepto-monovinylene-22'quinocyanine.
Solway Blue. C.I. No. 1054.		1.5. Dihydroxy-2.6-disulphonic 4.8-diamino-anthraquinone.
Acid Magenta. C.I. No. 692.		Diamino-disulpha methyl-fushonimonium sulphate.

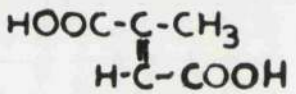
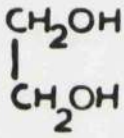
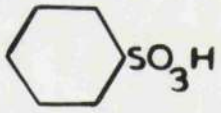
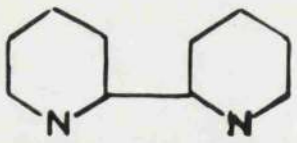
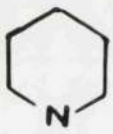
2. DYES cont.

COMMERCIAL NAME	FORMULA	CHEMICAL NAME.
Azogeranine C.I.No.31		aniline → 1 acetylamino 8naphthol-3,6.disulphonate.
p Butyaniline → ac H acid		4butylaniline → 1acetylamino — 8naphthol 3,6 di — sulphonate.
p Dodecylaniline → Ac. H acid		4dodecylaniline → 1 aaztylamino — 8naphthol 3,6 disulphonate.
p Cetylaniline → R acid.		4hexadecylaniline → 2 naphthol — 3,6disulphonate
p Dodecylaniline → R acid		4dodecylaniline → 2naphthol 3,6 — disulphonate
Orange I C.I. No. 150.		sulphanilic acid → 2naphthol
Dispersol I		4-N-ethyl-hydroxyethyl-4'nitro — 2'chloro-azobenzene.
Sulphato-ester I		4-N-ethyl sod.ethyl sulphate-4'— nitro-azobenzene.

2 DYES cont.

COMMERCIAL NAME	FORMULA	CHEMICAL NAME
Ponceau SS C.I.No253.		4-Aminoazobenzene → 2naphthol-3,6-disulphonate.
Ponceau 6R B C.I.No.286.		2',3-Dimethyl-4'-sulphonic-azobenzene → 2naphohol-8-sulphonate.
SA1—CH_3		2-Hydroxy-4-sulpho-1-naphthylamine → 1(4'-phenoxy-3'-sulpho) phenyl-3-methyl-5-pyrazolone.
SA1		2-Hydroxy-4-sulpho-1-naphthylamine → 1(4'-phenoxy-3'-sulpho) phenyl-3-heptadecyl-5-pyrazolone
SA2—CH_3		Sulphanilic acid → 1phenyl-3-methyl-5-pyrazolone.
SA2.		Sulphanilic acid → 1phenyl-3-hepta-decyl-5-pyrazolone

3. OTHER COMPOUNDS.

NAME	FORMULA.
Mesaconic acid	
Ethylene glycol	
Benzene sulphonic acid	
Urea	
2,2' Dipyridyl	
Hydroquinone	
Benzoquinone	
Pyridine	

PREPARATION OF SOLUTIONS.

(a) Solutions of Film Forming Substances.

The film forming substances used in this work were all spread from solution. The solvents varied but where possible water immiscible solutions were prepared. In all cases except casein, ca. 15 mgm. of the material was weighed accurately and dissolved in 25 c.c. of the solvent

Material.	Solvent.
Cetyl acetate	Benzene
Stearyl methyl ketone	Benzene
Stearyl ethyl ketone	Benzene
Cellulose triacetate	Chloroform
Cetyltrimethylammonium bromide	Water, ethanol and benzene mixture. (vol. ratio 1:2:2).
Sulphonated dyes.	Water, ethanol and benzene mixture. (vol. ratio 1:2:2).

Casein solutions:- 0.1 gm. of casein was shaken with 25 c.c. of water in a sealed tube for 24 hours at 40°C. in a thermostat.

In all cases two solutions were prepared to eliminate any errors in weighing.

(b) Substrate Solutions.

Aqueous solutions were used in all cases and were prepared by dissolving the required amount of material in one litre of distilled water. The pH of the solutions was adjusted in the case of protein films using acetate buffers and in Section I by the addition of the minimum amount of hydrochloric acid or sodium hydroxide. A blank buffer solution was

always used in conjunction with the buffered dye solution so that variation in film area could only be attributed to the effect of the dye. In Section 2 the ionic strength of the underlying solution was very important and would have been affected by the use of buffers.

APPARATUS

AND

EXPERIMENTAL TECHNIQUE.

SURFACE PRESSURE MEASUREMENTS.

Surface films are usually studied by measuring the surface pressure and/or surface potential of the film at various film areas. The apparatus used for measuring surface pressure is generally a modified form of the original film balance designed by Langmuir. The balance used in the present work incorporates several innovations and is described below.

Construction of the Apparatus.

The film balance originally used was one similar to that used by Alexander[33]. It was later decided to construct a new device for measuring the pressure on the barrier, using a balancing system instead of the torsion wire. This, in principle, is similar to a balance constructed by Allan and Alexander[34] for measuring low surface pressures, only in this case the balancing system is of much more robust construction calculated to give a pressure range similar to that previously obtained with the torsion wire. (Diagram 1).

The Balancing System.

The construction of 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 (C) is also fitted into the block. The calibration and counterpoise arms (F and A) are fitted 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 heavy platinum wires which pass through holes drilled in the floating Teflon (polytetrafluoroethylene) barrier (E). The balance head is fitted to the balance as shown in Diagram 1.

It has been found that this method of measuring surface pressure has several advantages over the single torsion wire previously used, e.g.

(a) The balance head can be easily removed, which facilitates the removal of the floating barrier for cleaning. Before the Teflon floating barrier was introduced a duralumin~~ium~~ barrier was used and was attached to the balance head directly. In this case the barrier was removed simply by lifting off the balance head.

(b) The sensitivity remains very nearly constant.

(c) The parts do not require renewing: Previously the torsion wire required to be replaced periodically.

(d) The sensitivity of the balance can be easily altered, if required, by addition of weights below the level of the knife-edges.

The Trough and Barriers.

The use of plastics in construction of film balances is now common practice and both perspex and Teflon[35] have been used. The material used in the construction of this balance is polythene which has been found most satisfactory. It is very similar to paraffin wax in structure and properties, and since it is water repellent does not

require to be waxed.

A block of polythene ($9\frac{1}{4}$" x $4\frac{1}{4}$" x $\frac{1}{2}$") was milled out to give the following internal dimensions, $8\frac{3}{4}$" x $3\frac{3}{4}$" x $\frac{1}{3}$" and then bolted to a brass plate to make it rigid.

The movable barrier is also of polythene and consists of a strip of this material (9" x $\frac{3}{4}$" x $\frac{1}{4}$") bolted to a brass strip (9" x $\frac{3}{4}$" x $\frac{1}{2}$"). The heads of the bolts are countersunk and heavily coated with paraffin wax. This barrier can be moved along the trough by a screw mechanism which enables it to be operated from outside the aluminium case enclosing the film balance.

The floating barrier is made of Teflon (3" x $\frac{1}{2}$" x 1/16"), chosen for its water repellent and heat resistant properties. It is also more rigid than polythene and thus requires no reinforcement. To allow the balance head to be fitted, two holes were drilled in the barrier $1\frac{1}{2}$ inches apart.

Threads.

Polythene threads were used to attach the floating barrier to the trough. These were made by heating a piece of polythene over a very small flame and quickly drawing it apart.

The Optical Lever.

The pressure exerted by the film on the floating barrier is measured by 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. The image of the light source is focussed on the

mirror in the balance head by the two biconvex lenses placed 4 cm. apart; it is then reflected first to mirror (M), and then to a centimetre wall scale placed 1 metre distant from (A). Thus any small movements of the balance head are greatly magnified on the wall scale.

Calibration Weights.

The calibration weights were phosphor-bronze rings weighing 0.1 gm., 0.075 gm. and 0.05 gm. These were made from phosphor-bronze wire and were checked periodically against standard weights.

Operation of the Instrument.

The following procedure was adopted for each experiment:-

(1) Preparation of the Balance

Trough and Movable Barrier.

The trough and movable barrier were cleaned with benzene after each experiment and then, after checking that all bolt heads were well coated with paraffin wax, were thoroughly washed with distilled water.

Periodically the bolt heads were rewaxed, but any other waxing was unnecessary.

Floating Barrier.

The duralumin~~ium~~ barrier used in the earlier part of the work was cleaned and rewaxed after each experiment. Periodically the mica strip attached to the underside by collodion adhesive to prevent metallic contact with the solution became detached and required to be renewed.

The Teflon barrier now used, requires much less attention and only needs to be cleaned with benzene and washed with distilled water after each experiment.

Attachment of the Floating Barrier to the Trough.

Polythene threads were attached to the edges of the floating barrier and trough (as shown in Diagram 4), using paraffin wax. New threads were used for each experiment.

(2) Cleaning the Surface.

The movable barrier was moved to within 1 cm. of the floating barrier. The solution was then introduced behind the movable barrier until it was level with the edges of the trough. The threads were then carefully inspected to check that they were lying on the surface and that there were no gaps through which leakage of the film could occur.

The surfaces between the barriers and behind the floating barrier were then carefully cleaned with a suction pump, the solution level being kept constant by additions behind the movable barrier. The movable barrier was then drawn back, sweeping any surface contamination before it and leaving a clean surface between the barriers.

(3) Testing for Surface Contamination.

The cleanliness of the surface was then tested. This was done by reducing the area of the cleaned surface by three-quarters. The surface was assumed clean if a pressure of less than 0.1 dynes/cm. was developed.

(4) Calibration of the Instrument.

After the surface was clean the barrier was again retracted and the instrument was calibrated. This had to be carried out to ascertain the relationship between movement on the wall scale and dynes/cm. pressure on the float. Calibration weights were hung on the notch on the calibration arm and the corresponding deflections on the wall scale noted. From these readings the sensitivity of the instrument was calculated.

(5) Spreading of the Film.

The material was dissolved in a suitable solvent (page 23) and spread by ejecting a known volume of the solution on to the surface using an Agla Micrometer Syringe (Burroughs Wellcome & Co.). This instrument is now in general use for measuring accurately small volumes of solutions and is graduated to deliver any volume of solution up to 0.5 c.c., accurate to 0.0002 c.c.

A few minutes were allowed to elapse before compression of the film to allow the solvent to evaporate.

(6) Compression of the Film.

The film was compressed by moving the movable barrier towards the float and readings on the wall scale, at different values of surface area were taken. Hence by knowing the amount of material spread on the surface the area occupied by each molecule can be calculated. The pressure at different molecular areas can also be calculated from the deflections on the wall scale and a force-area curve can be constructed.

(7) Detection of Leakage.

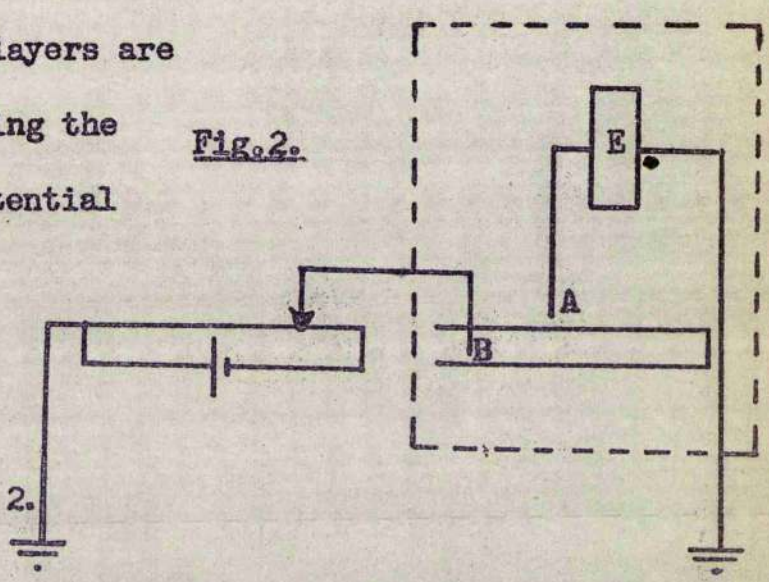
Leakage past the barriers and threads is made apparent by a rapid fall in the pressure. The position of leakage can be detected by dusting fine powder on to the surface behind the float in the vicinity of the threads and noting the movement of the powder on increasing the pressure.

SURFACE POTENTIAL MEASUREMENTS.

Chemical reactions in monolayers are generally carried out by measuring the surface pressure and surface potential simultaneously.

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

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 main difficulty in the measurement of air-liquid potentials is that the air is normally non-conducting. This difficulty is overcome by ionising the air -gap by coating the tip of the air electrode with a 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.

METHODS USED FOR MEASURING SURFACE POTENTIALS.

Two methods using d.c. electrometer units were employed for measuring surface potentials. The first incorporating a triode valve was not completely satisfactory as the circuit was unstable. Hence it was decided to construct another unit containing a balanced double tetrode. Unfortunately it was not until near the end of this work that the second unit was completed and only preliminary tests were carried out.

Method 1. - Triode Electrometer.

Construction of the Apparatus.

The circuit used originally was that designed by Adam and Harding[36] incorporating a triode valve (Diagram 5).

The electrometer unit and the Langmuir trough were enclosed in separate aluminium earthed cases. The potential of the air electrode was transmitted to plate A of the valve, via Y, by a polythene-insulated screened cable. E was a mercury switch in which the contacts were well insulated by paraffin wax. This switch allowed A to be connected to either the guard ring or the standard cell and potentiometer P. The air electrode was a platinum wire coated with polonium fitted into a brass holder containing an aluminium window. The non-polarisable electrode was a calomel half-cell and was connected to the electrometer unit through X.

Calibration of the Instrument.

The potentiometer P was calibrated in the normal fashion using a standard cell. The switch E was set to position 1 (i.e. joining plate A to G.R.) and the current through the galvanometer was balanced out using R.3. Readings of the galvanometer were calibrated in terms of potential on the plate by switching to position 2 (i.e. joining the lower cups of E) and noting deflections of G for given settings of P; the voltage S was subtracted from the reading of P.

The galvanometer calibration was found to be 3 div./mv.

Surface Potential Measurements.

The surface was carefully cleaned and the air electrode set 2 - 3 mm. above the surface of the liquid in the trough. The calomel half-cell was then immersed in the solution and E set to position 3 (i.e. leaving all cups on E disconnected) after calibration of the instrument. The greater part of the surface potential was balanced out by applying a potential using potentiometer P, and amounts less than 30 mv. were found from deflections of G. The surface was then tested for contamination by reducing the area and if an increase of less than 15 mv. was obtained the surface was assumed clean. Variation of potential over the clean surface was less than 5 mv.

The film was then spread and the increase or decrease in potential was measured by adjusting P. The film was then compressed and fluctuations were obtained over the surface until it was completely covered by film molecules. (i.e. until the surface pressure first appeared).

Readings were then taken at several points over the surface and averaged. Readings were then taken as the film was compressed and a ΔV-area curve was drawn.

Method 2. - Double Tetrode Electrometer.

The disadvantage of the triode circuit is its relative instability. It therefore requires considerable adjustment during the experiment and hence it was decided to build another unit using a circuit designed by Few and Pethica[37] incorporating a balanced double tetrode. This valve considerably reduces the instability of the electrometer circuit since it is relatively insensitive to variation in supply voltages and ambient temperature.

Construction of the Apparatus.

The valve (Ferranti BDM 20.) used in the circuit has an indirectly heated cathode, the advantages of which are summarised by Little[38]. The electrometer assembly (Diagram 7) 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 earthing switch and the reversible electrode are the same as previously used in the triode circuit.

Operation of the Instrument.

The filament current is adjusted to 125 ma. and the valve passes 250 μa. plate current in each half, with the screen and cathode potentials as shown in Diagram 7. The potentiometer is

then calibrated and with the air electrode out of circuit, R3 and R4 are adjusted to give zero deflection on the galvanometer.

The air electrode is then switched into the circuit and the deflection in G is balanced out by applying a potential from P.

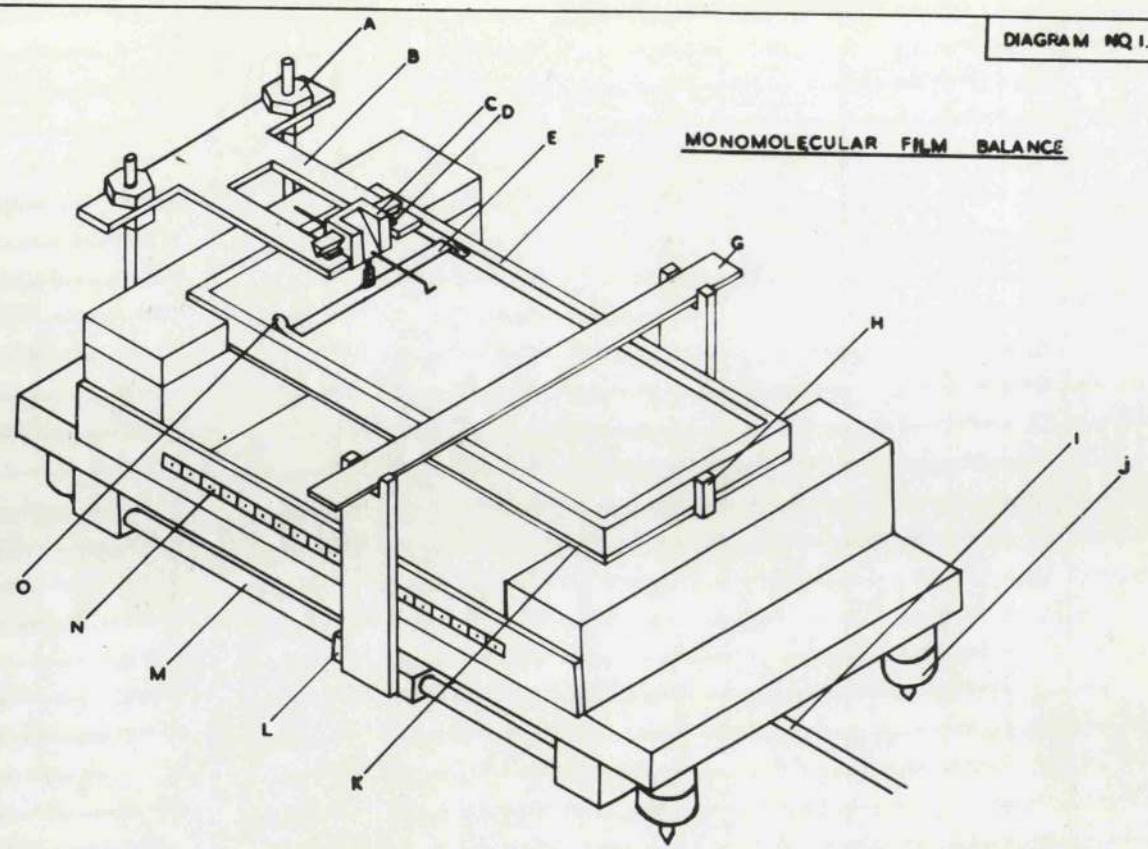
The calibration of G is then carried out by applying a known potential from P and noting the deflection of G. The reading of the galvanometer is then returned to zero and a film is spread. The procedure for measuring the surface potential of the film is then exactly the same as that used with the triode electrometer.

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 was as shown in Diagram 6, C and D in this circuit being connected to corresponding points in the electrometer circuit (the same in both electrometer circuits). 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 has a 470 ohm shunt in parallel and the galvanometer terminals on the potentiometer are then connected to complete the circuit. A brass plate was also inserted under the tapping key to give a fixed contact.

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 — DURALUMINIUM 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.

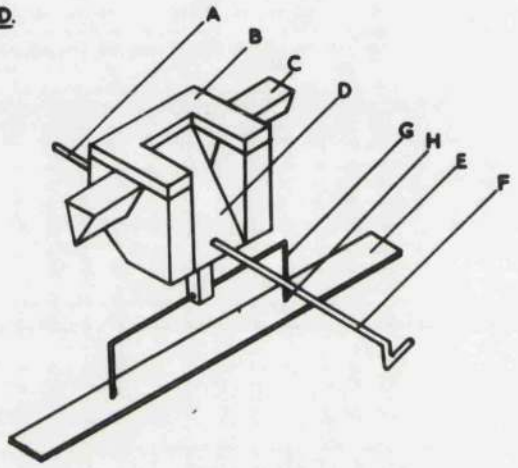
M — SLIDE FOR L.

N — CENTIMETRE SCALE.

O—TERYLENE THREADS.

DIAGRAM NO.2.

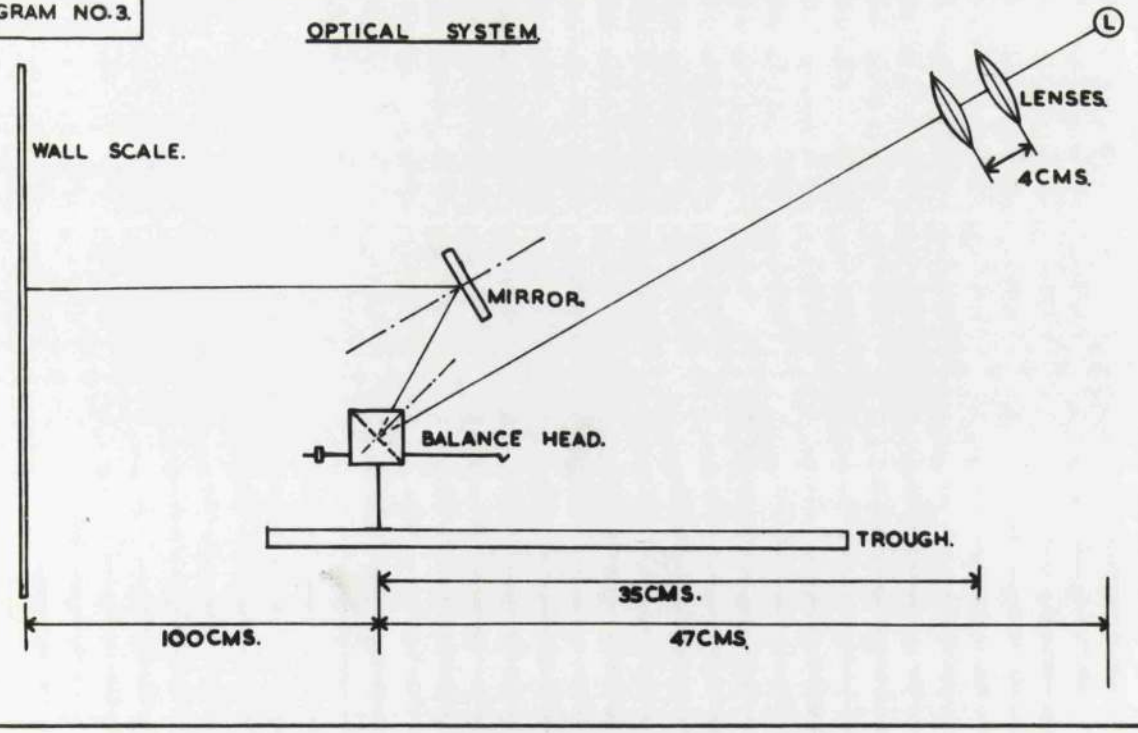
BALANCE HEAD.



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.



TRIODE ELECTROMETER.

KEY TO VALVE CIRCUIT.

R1..... 25 ohm w.w. potentiometer.

R2..... 10,000 ohm.

R3..... 500 ohm w.w. potentiometer.

M..... 1 - 200 ma. milliammeter.

B1..... 2v. lead accumulator.

B2..... 4v. lead accumulator.

B3..... 3v. grid bias battery.

T..... triode valve (E.T.1.).

G..... Galvanometer.

E.....Paraffin block switch.

S..... Standard cell.

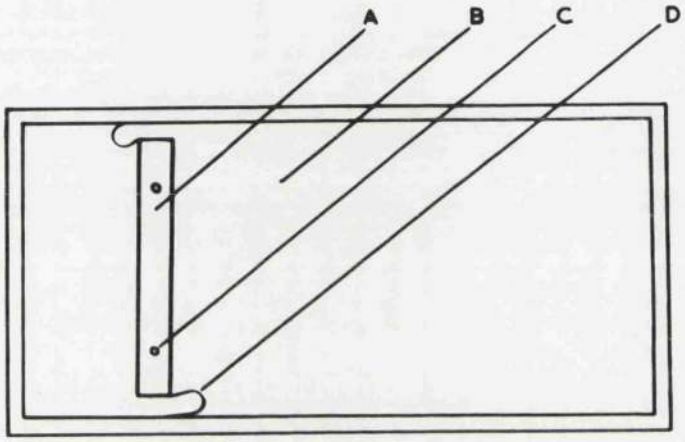
X..... Calomel half cell connection.

Y..... Air electrode connection.

P..... Accurate 2v potentiometer.

DIAGRAM No.4

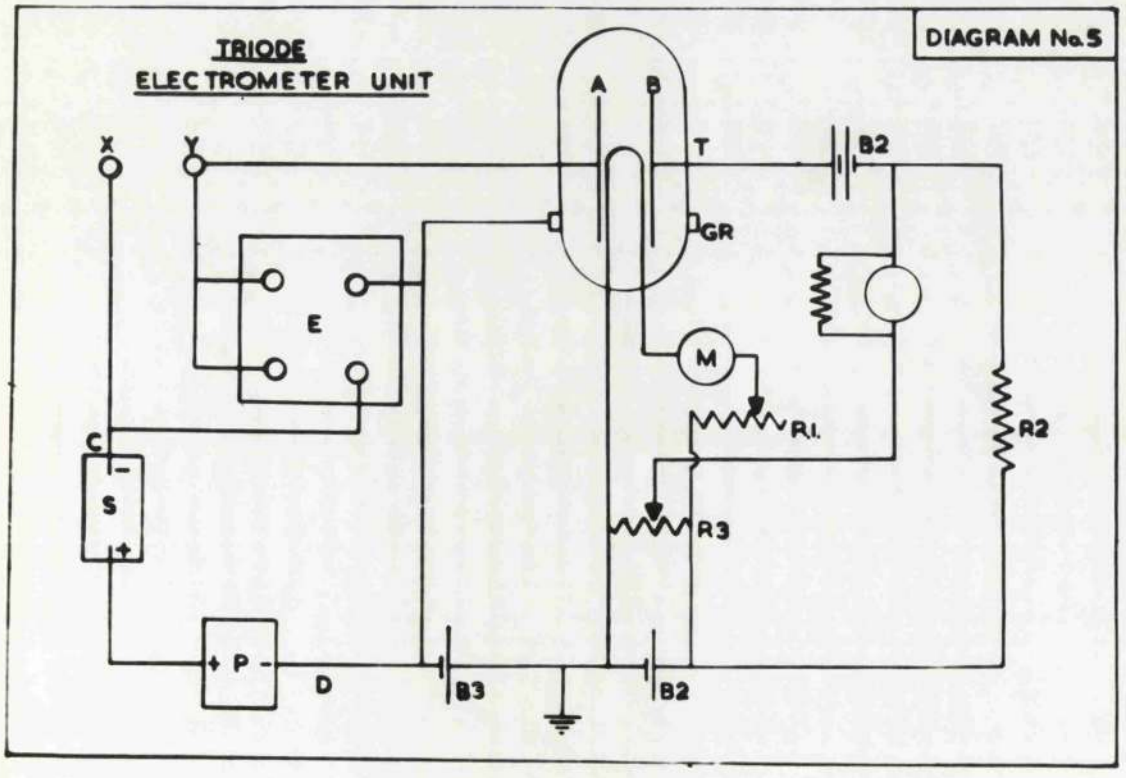
ATTACHMENT OF FLOATING BARRIER TO THE TROUGH.



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

DIAGRAM No.5

TRIODE
ELECTROMETER UNIT



DOUBLE TETRODE ELECTROMETER.

KEY TO VALVE CIRCUIT.

R1 and R2.....25 kΩ w.w. 5w.

R3.....5kΩ w.w. Berko potentiometer.

R4.....250Ω w.w. Berko potentiometer.

R5.....3kΩ w.w. Berko potentiometer.

M1.....0 - 1 milliammeter.

M2.....0 - 200 milliammeter.

E1.....29v NiFe battery.

E2.....10v lead accumulators.

T.....Balanced double tetrode (Ferranti BDM 20 with internal and external guard rings earthed).

R6.....470Ω.

R7.....0 - 20Ω 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. 6.

POTENTIOMETER CONNECTIONS.

SWITCHES SET FOR SURFACE POTENTIAL MEASUREMENT.

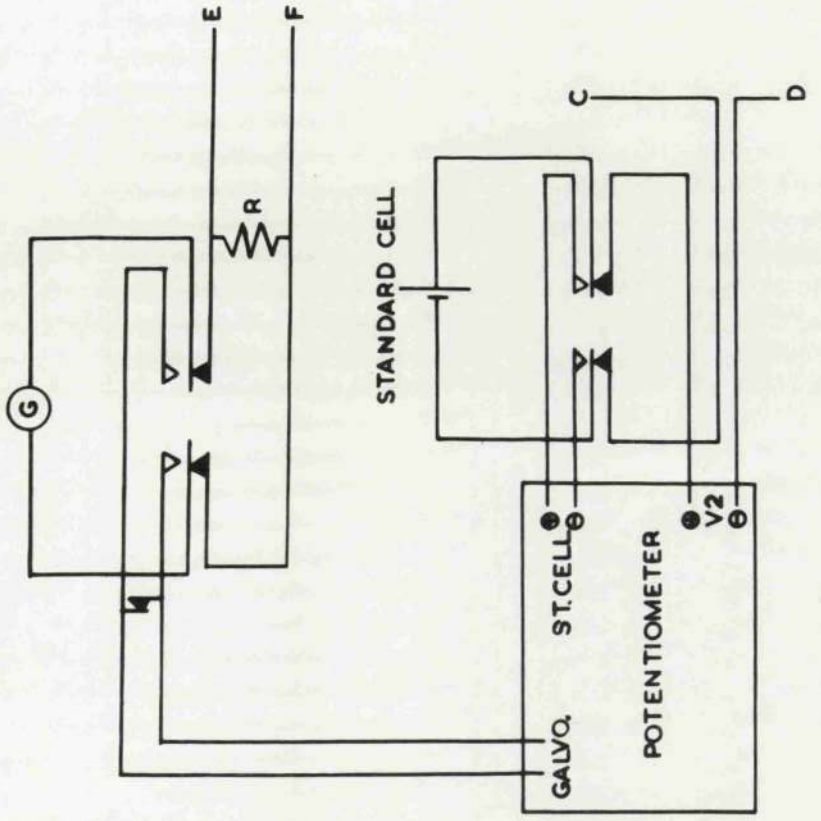
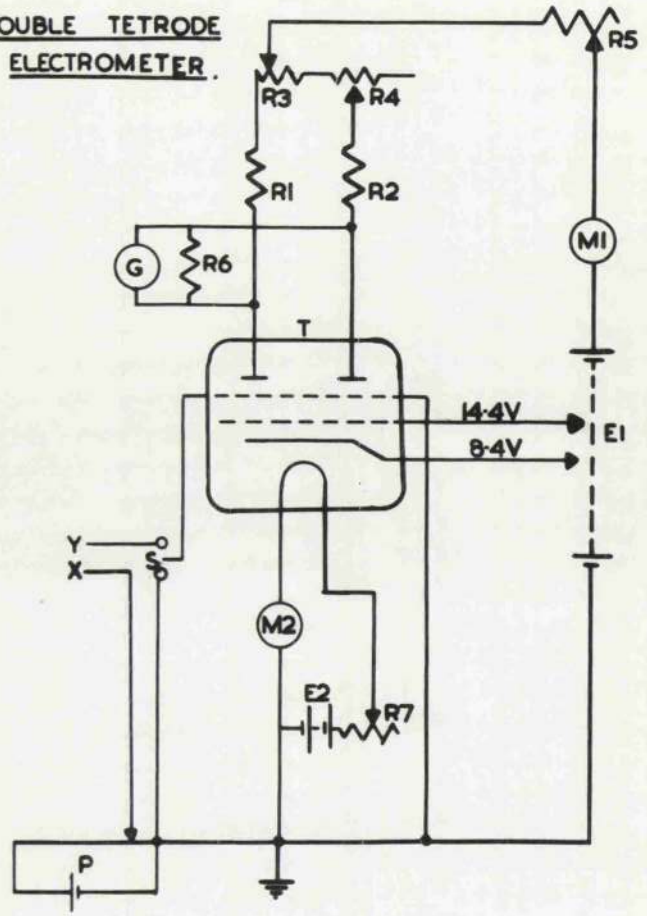


DIAGRAM NO.7.

DOUBLE TETRODE ELECTROMETER.



SECTION I.

MONOLAYERS OF WATER SOLUBLE DYES.

INTRODUCTION.

Nearly all fibres are dyed from aqueous solution and hence commercial dyes must all be to a certain extent soluble in water, at least during the actual dyeing operation. This water solubility is generally conferred upon the molecule by the introduction of ionic groups (e.g. sulphonate) which, in many cases, also play an important role in bonding the dye to the fibre.

This section of the work was carried out to investigate the film-forming properties of sulphonated dyes and an attempt has been made to relate these properties to the light fastness of the dyes, because parallel work in this laboratory[39] has demonstrated an apparent relationship between light fastness and the length of an alkyl chain attached to a dye molecule.

Work on dye monolayers has only recently been reported[40,41] and the only work carried out to date has been with water-insoluble dyes.

Insoluble Dye Films.

A systematic study of water-insoluble dye films was carried out in 1952 by Giles and Neustädter[41]. A series of 22 aromatic azo-compounds was prepared containing straight alkyl chains (C_{12}- C_{18}) and, in most cases, with one hydroxy group either o- or p- to the azo group. These compounds were spread on water and it was found that in all cases

where a hydroxy group was present and the alkyl chain had 16 carbon atoms, condensed films were formed. Condensed films were also formed in many cases where the alkyl chain contained only 12 carbon atoms. It was also shown that in the absence of a hydroxy group it required at least two azo groups to confer the necessary water attraction for the formation of stable films. In all cases the molecules appeared to be oriented in the films with the plane of the aromatic nuclei vertical, but the longer axis of this plane was in many cases tilted from the perpendicular at an angle depending upon the nature and the relative position of the substituent groups.

The effect of acid or alkali on the molecular areas and compressibilities of aromatic hydroxy-azo compounds containing long alkyl chains was then investigated[42]. It was hoped that by a study of these films it would be possible to determine the presence of a chelate link in o-hydroxy-azo compounds or the quinone hydrazone tautomer in either type of azo-compound. It was found that p-hydroxy-azo compounds exist almost completely in the azo form whereas o-hydroxy-azo compounds contain much of the hydrazone form.

The effect of mono- and di-hydric phenols, dissolved in the substrate, on monolayers of certain long chain aromatic compounds has also been investigated[43]. It was shown that azo, hydroxy and quinone groups in monolayers on water form a hydrogen bond with the hydroxy group in the monohydric phenols dissolved in the water phase. The increased water attraction thus imparted, e.g. to the azo-group,

causes an expansion of the film by a change in the angle of tilt of the film molecules. Dihydric phenols in water behave in a different manner and were found to be able to act in one of two ways:-

(a) If there are two suitably placed bonding groups in the monolayer molecule a 1:1 complex is formed in which each of these groups is bonded to the corresponding hydroxy groups in the phenol; the two molecules probably stand side by side and parallel to each other. A small increase in area may result with a decrease in the compressibility of the film.

(b) If the solute hydroxy groups are too far apart for (a) to take place then they may form cross-links between the monolayer molecules, leading to a considerable increase in film area and compressibility.

Monolayers of proteins which have been diazotised and coupled have also been studied for film forming properties[44]. The behaviour of these films was found to be very little different from that of the parent protein and this was believed to be due to the azo-group lying under the protein, and having very little effect on the area of the film, but increasing its thickness.

The Effect on Monolayers of Inorganic Ions Dissolved in the Underlying Liquid.

The effect of inorganic ions on monolayers has been known for a considerable time. It was first observed by Adam[45] in 1921, when he noticed that palmitic acid spread on freshly distilled water from a

quartz still gave an area which was much greater than that obtained when it was spread on distilled water which had been left in the trough or kept in a glass bottle. No explanation was given for this, but it is now believed that the condensation was due to calcium ions from the glass, or zinc and copper ions from the trough interacting with the palmitic acid to form soaps[46-48]. This was shown to be the case in 1936 when Langmuir[49] spread films of fatty acids on barium and calcium hydroxide solutions. The films were removed and analysed and were found to be the calcium and barium soaps.

The different types of monolayers which can form complexes with inorganic ions are limited and the most studied of these compounds are the carboxylic acids. Sasaki and Matuura[50] studied the effect of various metal ions on stearic acid monolayers and showed that calcium, barium, and magnesium condensed the film on alkaline solutions. This was believed to be due to bivalent bonding, joining two molecules of stearic acid and forming a stoichiometric compound of the type $M(St.)_2$. This causes close-packing of the chains and gives an area of 20.5 A^2 per molecule of stearic acid. Stearic acid films spread on solutions of thorium, aluminium, iron, copper, zinc, mercury, cobalt, and nickel ions were found to be expanded and also much more compressible, which suggested that they may form types of soap of a much more complex structure than those from calcium or barium. Since McBain[51] reported for the first time the non-existance of the aluminium trisoap many

workers have investigated the properties and structure of aluminium soaps, but co-ordinated results have not been obtained as yet[52-56]. The properties of the soap depend greatly upon the method of preparation especially upon whether or not water takes part in the process[53,57], a sure indication of the complicated structure of aluminium soaps. Eigenberger[58], McGee[52], Gray and Alexander[53] all agree that aluminium soaps have a polymeric structure although they disagree about the details. It is generally believed, however, that the aluminium atoms are joined through oxygen atoms and this explains the expansion of stearic acid films and, since the Al - O - Al chain is considered flexible, it also accounts for the compressibility of the film. Matuura also studied the rigidity of stearic acid films spread on various substrates over a range of pH values. When spread on calcium, barium, and magnesium substrates the films had no measurable rigidity, while on the other hand thorium, aluminium, iron, copper, zinc, mercury, cobalt, and nickel conferred great rigidity on the film. This gives additional proof of the conclusions previously reached that calcium and barium soaps are simple stoichiometric substances whereas the thorium, aluminium, and iron soaps have a complex polymeric structure.

The study of fatty acids was continued by Wolstenholm and Schulman[59] using myristic acid, which on solutions containing no metallic ions forms liquid-expanded films. Complex formation is shown by solidification of the monolayer and this solidification takes place in a pH range

characteristic for each metal. The overall range of pH studied was from 2.0 - 10.0 and a knowledge of the various degrees of association of myristic acid over this pH range leadsto the formulation of different types of bonding as follows:-

(1) COOH COOH (2) COOH COOH (3) COO^- COO^- (4) COO^- COO^-

M^{++} M^+ M^+ M^+ M^+ M^{++}

..O-H...O-H.. ..O-H..O-H..

Induced dipole -ion interaction. | Induced dipole - basic ion, interaction. | Ion-basic ion aggregate interaction. | Ion - ion interaction.

Complex formation with branched chain fatty acids[60] and metal ions was then studied and it was shown that if the cross-sectional area of the branch chain acid is greater than the area occupied by the basic metal ion, no complex formation takes place: The steric effect of the branch chain acid prevents hydrogen bonding between the metal ions and liquefaction of the monolayer takes place.

Competitive adsorption of metal ions by fatty acid monolayers has shown that the bonding of the metal ion must be essentially covalent[61,62]. Stearic acid films were spread on solutions containing various concentrations of calcium, magnesium, copper, and hydrogen ions. The films on reaching equilibrium were removed and analysed and it was found that calcium was bound to the layer in preference to magnesium and also that copper was bound more strongly than calcium. It was shown by measuring the amount of calcium interacting with the monolayer on substrates of varying pH that the pH in the immediate vicinity of the monolayer is less than in the substrate

which agreed with theoretical considerations[63].

Spreading of myristic acid monolayers on copper sulphate and ferric chloride solutions[64] resulted primarily in the formation of undissociated normal and basic soaps. In carbonate buffer solutions cupric salts react with the monolayer through complex copper carbonate ions. Monolayer soaps have also been formed by spreading myristic acid on uranyl nitrate[65].

Fatty acid and amino-acid monolayers are capable of being 'tanned' using chromium ions[66]. In this case the interaction is accompanied by a large increase in the area per molecule of fatty acid with solidification of the monolayer. With the straight chain fatty acids, one chromium ion is attached to each fatty acid molecule but, should the fatty acid have a branched chain, then instead of liquefaction of the monolayer one more chromium ion per acid molecule is anchored to the monolayer thus keeping it solid. The structure of this two dimensional lattice is due to hydrogen bonding between the hydroxy groups of the basic chromium ion and the C=O of the carbonyl group.

Another type of substance which can form monolayer complexes with inorganic ions is a long chain sulphate. Sodium cetyl sulphate monolayers have been studied on substrates of varying ionic strength and pH[67]. It was found that interaction between the ionised film molecules and simple metal ions has little effect on the properties of the monolayer and that the monolayers on neutral or alkaline substrates

occupy a smaller area than on acid substrates. This is directly opposite to the effect of pH on acid monolayers[68]; the explanation is that on alkaline or neutral substrates the sodium cetyl sulphate dissociates and partially dissolves whereas fatty acid monolayers on substrates of high pH are more dissociated and repulsion takes place between the charged head groups. Solidification of the monolayer occurred only in the presence of complex metal ions which stabilise the monolayer soap by hydrogen bonding. The condensing effect of barium and calcium ions on films was not observed with long chain sulphates, probably because the barium salt of the ester group is water soluble; thus the presence of barium ions does not affect the ionisation and hydration of the ester sulphate head group.

The effect of polyvalent metal ions on film molecules containing only dipoles is very small[69].

Light Fastness.

One of the most important properties of dyes is their resistance to exposure to light. This is not only affected by the nature and intensity of the light, but also by several other factors namely:-

(a) the presence of oxygen and/or water.

(b) the chemical structure of the dye.

(c) the physical nature of the dye.

(d) the chemical structure of the substrate.

(e) the physical nature of the substrate.

Although fading is affected by all these factors, the variation in

light fastness of a series of dyes (e.g. dyes containing various lengths of alkyl chain), adsorbed on the same substrate and irradiated under identical conditions, will only depend upon either the chemical and/or physical nature of the dye.

The Influence of Aggregation on Light Fastness.

Since the fading reaction involves oxygen and/or water then it must clearly be influenced by the size and nature of the air-dye interface. The smaller the surface exposed the less rapid should be the fading. It has been shown by Bean and Rowe[70] that this must be the case because, if the dyed fibre is subjected to after-treatments, e.g. soap boiling or steaming, which cause microscopically visible crystal growth, the light fastness increases considerably. These tests were carried out with water-insoluble azo dyes on cellulose fibres and the results were confirmed by Macauley[71] examining this type of dye on 'Cellophane' films.

The very low light fastness of vat dyes on nylon, compared with their fastness on cellulose has likewise been attributed to their much smaller particle size on the former substrate, occasioned by the restriction of the dye crystal growth by the greater compactness of the fibre[72,73].

Sumner, Vickerstaff and Waters[74] examined the effect of soaping on vat dyeings on 'Cellophane' and found that in this case no significant increase in light fastness is obtained. Electron photo-micrographs of aged colloidal suspensions showed that the treatment changes

the dye from amorphous particles to long needle-shaped crystals, but there is no convincing evidence from these results that the surface area is actually decreased by the crystallisation process as it undoubtedly is in the azo-dye systems examined by Bean and Rowe.

All these investigations were made upon water-insoluble dyes. Baxter et al.[75] have examined a number of water soluble dyes, studying their rate of fading when irradiated on a variety of substrates, over ranges of concentrations. They have developed the interpretation of their results on the basis of a theory which postulates the presence in all dyed fibres of dye in a heterogeneous state, partly monolayer and partly multilayer or aggregate material. The aggregates may be formed during dyeing or when the water is removed in the subsequent drying, or both. From the argument given above it will be clear that dye in the form of a monolayer should fade more rapidly than in an aggregated state.

The Influence of Alkyl Chains on Light Fastness.

It has been shown[76,77], that fading results in the oxidation or reduction of dyes depending upon the type of substrate on which they have been adsorbed. Dyes adsorbed on proteins usually are reduced on fading whereas dyes adsorbed on non-proteins are usually oxidised. The relative rates of fading of certain series of dyes on appropriate substrates fall in the same order as the relative rates of oxidation or reduction but it has been found that the introduction of a long alkyl chain, while it does not increase the rate of oxidation or reduction

appreciably in some cases increases the rate of fading to a large extent. This effect has been known for a considerable time but it is only recently that a systematic study of this subject has been carried out[71]. On what may be called the 'classical' theory of fading, i.e. that all water-soluble dyes in fibres are present as monolayers, it would not be expected that the addition of a saturated alkyl group in a position where it does not interfere with a conjugate chain, could influence their light fastness, because it cannot much affect the chemical reactivity of the molecule. On the new theory of Baxter et al.[75], however, light fastness can vary with the surface activity of the dye because this may determine the proportion of monolayer and aggregate formed by the dye in the substrate. In particular as the surface activity of the dye rises with increase in chain length, so may its tendency to form a monolayer on the internal surface of the substrate when the material dries out. The surface area of the dye is thereby increased and the fastness decreased.

RESULTS AND DISCUSSION.

A water-soluble dye containing a long alkyl chain would be expected to exhibit surface activity, as the molecule contains a hydrophobic tail and a hydrophilic head. Thus it would be expected that provided such a dye molecule does not dissolve completely in the underlying liquid then it should spread out as a monolayer. Consequently the present work was carried out to investigate the possible film-forming properties of dyes containing sulphonic acid groups and various lengths of alkyl chain. The effect of certain inorganic salts dissolved in the underlying liquid and variation in pH were also investigated, and also the effect of cationic surface-active agents. This is because the presence of a cationic dispersing agent, e.g. cetyltrimethylammonium bromide, decreases the light fastness of dyes[74] and on the Baxter et al. theory[75] the inference is that the cationic agent assists the dye to spread as a monolayer. It was hoped to confirm this hypothesis by showing that the addition of cetyltrimethylammonium bromide to dyes, which do not spread by themselves, would result in their spreading as stable mixed monolayers.

Spreading of Sulphonated Dyes on Distilled Water.

A typical long chain sulphonated dye, 'SA1', was spread on distilled water (graph No. 1). The results showed that the dye formed a condensed film but the area at zero compression was considerably lower than was predicted from measurements carried out on

molecular models. The area was found to be 40 sq.A. whereas the predicted area, allowing for solvation of the sulphonic acid groups was ca. 95 sq.A. This represents only 42% spreading, attributable to partial solution of the dye. This effect is similar to that found in investigations carried out on long chain sulphates[67] on water and it was found that in this case the sulphate group occupies 8 sq.A. instead of the expected 34 sq.A.

Two other long chain dyes, 'SA2' and p-dodecylaniline →N-acetyl H acid, were also spread on distilled water (graph No. 4). It was found that partial solution of the dye also occurred in these cases and areas of 23 sq.A. and 16 sq.A. respectively were found instead of the calculated areas of 74 sq.A. and 55 sq.A. In tests with homologues of these dyes, viz. p-butylaniline →N-acetyl H acid and Azo Geranine 2G (lower homologues of p-dodecylaniline →N-acetyl H acid) and also 'SA1-CH_3' and 'SA2-CH_3' (lower homologues of 'SA1' and 'SA2' respectively), it was found that if the chain length is below 12 carbon atoms no surface films are apparently formed even at very low surface areas. The shorter chain dyes are much more soluble than their higher homologues and it is concluded that complete solution takes place, resulting in no monolayer formation.

Thus in general as the length of the alkyl chain increases so do the spreading properties of the dye, and possibly at very long chain lengths complete spreading will occur on water.

The Effect of Sodium Chloride in the Underlying Solution.

The introduction of sodium chloride into the underlying solution would be expected to influence the spreading of sulphonated dyes, because salt tends to decrease the solubility of the dye and it might be expected that complete spreading would be obtained on strong solutions of sodium chloride.

This was investigated by spreading the dye 'SA1' on solutions of sodium chloride of varying concentrations (graph No. 1) and it was found that as the concentration increased so did the area of the monolayer, until at a concentration of 1.0M the area was the same as the calculated value, i.e. ca. 94 sq.A. Further increase in salt concentration produced no change in the molecular area at zero compression or in the characteristics of the curve.

The effect of sodium chloride on the dye, p-dodecylaniline → N-acetyl H acid was similar (graph No. 5), except that a more concentrated salt solution was needed to produce complete spreading. The relative effect of sodium chloride on these two dyes may be seen on graph No. 6. The dye, 'SA2', was also spread on sodium chloride solution of a suitable concentration to produce maximum spreading and the area at zero compression was found to correspond to the calculated area (table 1).

TABLE 1.

DYE.	Molecular Area in Surface Layer(sq.A)	
	Calculated	Found (max).
'SA1'	95	94
'SA2'	74	72
p-dodecylaniline → N-acetyl H acid	55	53

No ~~spreading~~ film was obtained when p-butylaniline → N-acetyl H acid and Azo Geranine 2G were spread on very concentrated salt solutions; sufficiently so, in fact, to precipitate them completely. Thus these dyes cannot be considered surface active and it must be assumed that they form aggregates rather than monolayers on the surface of the salt solutions.

Experiments with other dyes then showed that as the size of the dye molecule increases, without alkyl chains being present, gaseous films tend to be formed. The dyes used were 'SA1-CH_3', 'SA2-CH_3', Ponceau SS, and Ponceau 6RB and in these, the molecules contain hydrophilic groups arranged a considerable distance from one another in the molecule. They might therefore be expected to form gaseous films, and it was, in fact, found that when they were spread on 4M sodium chloride solution (graph No. 7) a pressure of ca. 0.5 dynes/cm. was produced at very large areas. On compression, the films of 'SA1-CH_3' and 'SA2-CH_3' collapsed at pressures of 11 dynes/cm. and 12 dynes/cm., respectively, but if the tangents of the curves are extrapolated to the X-axis the areas approximate to the areas at zero compression of 'SA1' and 'SA2'. Thus, these dyes when compressed in the monolayer appear to be oriented in the same manner as their higher homologues. In the case of the Ponceau dyes the collapsed pressure is much lower (ca. 5 dynes/cm.) and the areas obtained by extrapolating the tangents to the X-axis show that neither dye is completely spread.

The Effect of pH.

Certain acid dyes will precipitate in acid solution. Thus, the use of acid in the water phase was considered as a possible means of obtaining complete spreading of some sulphonated dyes. The dye 'SA1' was spread on solutions of varying pH (graph No. 3) to test this hypothesis: These tests showed that pH does influence the spreading properties of the dye. Complete spreading of this dye was obtained at pH 1.2. On the acid side of pH 1.2 the area at zero compression remained the same i.e. 94 sq.A., but on the alkaline side the area decreased with increasing alkalinity. It was found, however, that a slightly more compressible film was obtained on acid solutions than on concentrated salt solutions.

The Effect of Barium Chloride in the Underlying Solution.

The introduction of barium chloride into the underlying solution would be expected to have a similar effect to sodium chloride, resulting in the 'salting-out' of the monolayer. The concentration of barium chloride required, however, would be expected to be much lower as the barium salt is much less soluble than the sodium salt. 'SA1' was thus spread on solutions of barium chloride of varying concentrations at pH 6.0 (graph No. 2) and it was found that the above prediction is correct except that the area at zero compression of the completely spread dye is 85 sq.A. instead of 94 sq.A., as previously obtained with sodium chloride. This condensing effect was further studied by spreading 'SA2' and p-dodecylaniline→N-acetyl-H acid on solutions of barium

chloride at a concentration suitable for maximum spreading (graph No.4). These dyes were found to give areas which are considerably lower than the areas obtained on sodium chloride, and it may be seen from these results that the decrease in area is constant in each case (table 2).

TABLE 2.

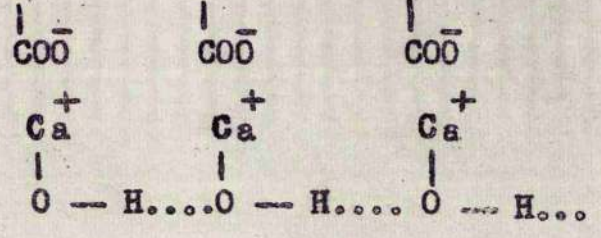
Dye	Area on Barium Chloride.	Area on Sodium Chloride	Difference.
'SA1'	85 sq.A.	94 sq.A.	9 sq.A.
'SA2'	64 sq.A.	72 sq.A.	8 sq.A.
p-dodecylaniline N-acetyl-H acid.	45 sq.A.	53 sq.A.	8 sq.A.

The constant decrease in area must depend upon the different influences on the monolayer of sodium and barium ions. When sodium ions are in the underlying liquid it is believed that each ion is attached by ionic forces to one sulphonic acid group, which is hydrophilic and is surrounded by an envelope of water molecules. Thus each dye molecule acts independently and is separated from the ajoining molecules by water molecules. On the other hand when the dye is spread on barium chloride each barium ion will attach itself to two sulphonic acid groups, as barium is divalent. Two of the dyes used were disulphonates, but the positions of the sulphonate groups were such as to sterically prevent one barium ion being attached to two groups

in the one molecule. Thus, each barium ion must link up with two dye molecules, probably forming a dimer rather than a cross-linking network, since the compressibility of the film is not altered as would have been expected if cross-linking had taken place. The solvated water molecules round each sulphonic acid group will be affected by the formation of the dimer and those between the dye molecules will be ejected into the underlying liquid. The water envelope surrounding each molecule is therefore replaced by a water envelope surrounding each dimer and the area occupied becomes less. The formation of dimers in this manner may be compared to the formation of barium soaps[50] on molecules in which a stoichiometric compound of the type $Ba(St)_2$ has been detected, and there is no alteration in the compressibility of the film.

The Effect of pH on 'SA1' Films Spread on 0.0005M Barium Chloride Solutions.

'SA1' was spread on 0.0005M barium chloride solutions of varying pH (graph No. 8) to determine whether the formation of the basic barium ion influences the rigidity of the film. It is known that in the pH range 5.5-10.5 basic calcium ions are formed and it has been shown that these ions solidify a myristic acid monolayer by cross-linking[59], thus:-



The present investigation was therefore carried out to find out

if this effect also applies to sulphonated dyes. Thus 'SA1' films were spread on 0.0005M barium chloride solutions at pH values both inside and outside the range for the formation of basic barium ions. It was found that identical curves were obtained at all pH values studied, and so the effect must be due to simple 'salting out' of the dye. Further, the rigidity of the film is not affected by this treatment with barium, at any pH, presumably because the large size of the dye head group prevents cross-linking by barium ions. Another possible explanation is that the presence of barium ions does not affect the hydration or ionisation of the sulphonic acid group, present in the dye, as the barium salt is to a certain extent water-soluble. This is believed to be the case with long chain sulphates[67].

The Effect of pH on 'SA1' Films Spread on .001M Cupric Chloride Solutions.

Myristic acid films are converted from liquid-expanded to solid films when spread on cupric solutions in the pH range 4.2 - 7.7 which is believed to be due to the basic copper ions, formed in this pH range, being bonded to the carboxylic acid groups by ionic forces and to one another by hydrogen bonding.[59] A similar effect has been observed with long chain sulphates spread on complex copper carbonate ions[67] and the present experiments were carried out to study the effect of these ions on films of 'SA1'.

'SA1' was spread on 0.001M cupric chloride solutions, saturated with carbon dioxide at various pH values in the range 3.1 - 6.2 (graph No.9).

It was found that very incompressible films are formed between pH 4.4 and pH 6.1, the area of the film increasing with pH. At pH 3.1, however, the film has a compressibility similar to that obtained on sodium chloride solutions which seems to indicate that the complex copper carbonate ions only influence the film in the pH range 4.4 - 6.1. The areas obtained at the various pH values are given below (table 3) and it appears that in all cases partial solution of the film is taking place.

TABLE 3.

pH	Molecular area of monolayer (A^2).
3.1	46
4.4	35
5.2	48
6.1	52

The decreased compressibility obtained in the pH range 4.4 - 6.1 is possibly due to the complex copper carbonate ions interacting with the sulphonate groups in the dye molecules. This results in the formation of a rigid cross-linking network.

The Effect of Mixing Cetyltrimethylammonium Bromide with Dyes before Spreading.

Cetyltrimethylammonium bromide was next used to form ionic complexes with the sulphonated dyes, mixed before spreading, in the expectation that thus some dyes might be induced to form stable monolayers, which would not otherwise do so. The amount of cetyltrimethylammonium bromide mixed with the dye was made equivalent to the number of sulphonate groups present, e.g. a dye containing two such groups was mixed with two molecular equivalents of cetyltrimethylammonium bromide.

'SA1' mixed with two molecular equivalents of cetyltrimethylammonium bromide was spread on water (graph No. 10) and it was found that a stable mixed film was formed. The area at zero compression was found to be 134 sq.A., i.e., 86% spread, since the calculated area for one molecule of 'SA1' + two molecules of cetyltrimethylammonium bromide is 155 sq.A. This decrease in area is possibly due to partial solution of the dye and/or the cetyltrimethylammonium bromide, but it is much less than when 'SA1' is spread on water by itself, where only 42% spreading is observed. The difference is almost certainly due to the 'SA1' and cetyltrimethylammonium bromide interacting and causing a decrease in the solubility of both. When 'SA2' and the cationic agent were spread on water similar results were obtained, 84% spreading being obtained. In both cases, however, the compressibility of the mixed films is the same as for the dyes alone. Complete spreading was obtained when 'SA1' and cetyltrimethylammonium bromide were spread on 0.2M barium

chloride, 2M. sodium chloride, or 4M sodium chloride solutions (graph No. 10) and also when 'SA2' and cetyltrimethylammonium bromide were spread on 0.2M barium chloride and 2M sodium chloride solutions (graph No. 11). In these cases the areas on barium chloride and sodium chloride are the same. This must be due to the cetyltrimethylammonium bromide preferentially interacting with the sulphonate groups and preventing the formation of the dimers which occurs when these dyes are spread by themselves on barium chloride solutions.

In the next series of experiments dyes containing no alkyl chains were mixed with cetyltrimethylammonium bromide and spread on water (graph No. 12). It was found that considerable spreading was obtained with all the dyes used. 'SA1-CH_3' and Ponceau 6RB were found to have an area at zero compression of ca. 120 sq.A. This is larger than the area of two cetyltrimethylammonium bromide molecules, and hence the latter must be anchored to the sulphonate groups and so held apart. (The distance between the sulphonate groups in these two dyes are the same namely, 14A.). The calculated area for two cetyltrimethylammonium bromide molecules + one 'SA1-CH_3' molecule and for two cetyltrimethylammonium bromide molecules + one Ponceau 6RB molecule are 135 sq.A. and 132 sq.A. respectively. Hence the films are 89% and 91% spread and thus partial solution of the dyes and/or cetyltrimethylammonium bromide has taken place. In the case of Azo Geranine 2G the sulphonate groups are much closer together than in 'SA1-CH_3' and Ponceau 6RB, so close in fact that if the cetyltrimethylammonium bromide molecules

were attached to the sulphonate groups in Azo Geranine 2G they would also touch one another and thus form a condensed film; the dye molecule ~~would~~ would then possibly be adsorbed under the film. In fact, a much more incompressible film is formed with Azo Geranine 2G then with 'SA1-CH_3' and Ponceau 6RB (graph No. 12). The adsorption of the dye under the cetyltrimethylammonium bromide film neutralises the charge on both anionic and cationic molecules, thus decreasing the solubility of both. The area obtained is slightly less than the area of two cetyltrimethylammonium bromide molecules alone and is possibly due to partial solution of the dye and/or cetyltrimethylammonium bromide. A similar effect to that observed with 'SA1-CH_3' is obtained when 'SA2-CH_3' mixed with one molecular equivalent of cetyltrimethylammonium bromide was spread on water (graph No. 12).

When these dyes were spread on 4M sodium chloride solutions, in the presence of the cationic agent, complete spreading is obtained (graphs Nos. 13-14), and the compressibility of these films is much greater than that of the long chain dyes in the presence of cetyltrimethylammonium bromide. This is to be expected, since dyes with no alkyl chains hold the cetyltrimethylammonium bromide molecules apart only at the head groups and not also along the whole length of the chain. In the case of Azo Geranine 2G the increase in area when spread on 4M sodium chloride solutions in the presence of the cationic agent must be due to the dye being completely precipitated on the surface instead of being adsorbed underneath. Thus the condensed film of cetyltrimethylammonium bromide is penetrated and a more compressible film is obtained.

The Relationship between Light Fastness and the Spreading Properties of Dyes.

The light fading of all the dyes used in this work has been studied by Baxter [39] and in order to correlate the fading results with the spreading of the dyes his results are considered. The light fastness of dyes depends upon various factors as discussed above and it is only possible, of course, to study the effect of alkyl chains by using dyes which have the same basic structure and differ only in the length of the attached alkyl chain.

Three different series of dyes were investigated by Baxter namely:-

(a) 'SA1' Series.

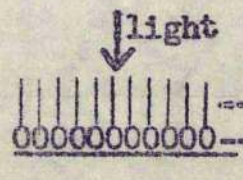
(b) 'SA2' Series.

(c) Aniline → N-acetyl H acid.

Unfortunately only the methyl and stearyl homologues of the 'SA1' and 'SA2' series were available and hence the results with these dyes do not show the effect of several variations in the length of the alkyl chain.

Dye 'SA1' was found to be fairly fugitive by normal standards for dyes when faded on a gelatine film. The time taken at a relative concentration of 0.1 for a 10% fade was found to be 15 minutes. This poor fastness is believed to be due to the dye largely forming a monolayer on the internal surfaces of the substrate as discussed above. Its lower homologue ('SA1-CH_3') was expected to be considerably faster to light, because it was thought that it would form aggregates rather

than monolayers. It was, however, less fast to light than the higher homologue. An explanation may lie in the fact that it forms a gaseous film on water and may retain this spreading tendency inside the substrate, and so a monolayer may be formed therein. The presence of long alkyl chains in the higher homologue may protect, to a certain extent, the chromophoric head groups from the light, thus increasing the light fastness.



The 10% fade time, at the equivalent concentration, for p-dodecylaniline → N-acetyl H acid was 11 hours. The corresponding time for the p-butyl homologue was found to be 27 hours and it is therefore assumed that the dodecyl homologue is forming a monolayer, whereas the butyl homologue is forming aggregates. This is consistent with the fact that no evidence of monolayer formation is obtained on aqueous solutions with p-butylaniline → N-acetyl H acid. No fading results have been obtained with Azo Geranine 2G but from surface film results it may be predicted, since no monolayer formation is observed, that its light fastness should be of the same order as the butyl homologue.

Further indication that the light fastness depends upon the spreading properties of dyes has been obtained by studying the fastness of dyes mixed with cetyltrimethylammonium bromide. It has been found that this cationic dispersing agent decreases the fastness of almost all the dyes used.

Therefore there is some ground for believing that the fastness of dyes to light depends upon their physical nature in the fibre and hence upon their surface activity.

CONCLUSIONS.

The dyes used may be conveniently divided into two classes and are discussed separately below.

(a) Sulphonated Dyes with Long Alkyl Chains (i.e. 12 carbons and over).

It was found that these dyes form condensed monolayers on water but the area at zero compression is considerably less than measured with molecular models. Partial solution of the monolayer occurs because on decreasing the solubility of the dyes complete spreading is obtained. This can be effected by spreading on concentrated sodium chloride solution, acid solutions and barium chloride solutions, though in the latter case a slightly smaller than calculated area is obtained. This is believed to be due to barium ions forming a complex of the type $(Dye^{-})_2Ba^{++}$.

The effect of the basic barium ion on these films was shown to have no influence on their F-A curves and is believed to be due to steric factors preventing the formation of a cross-linking network. Complex copper carbonate ions, on the other hand, considerably affect these films and increase their rigidity. This is possibly due to the complex copper ions cross-linking the dye molecules and forming a more rigid structure.

Mixing cetyltrimethylammonium bromide with the dyes was also found to decrease their solubility and allowed more complete spreading on water with the formation of stable mixed films. Complete spreading

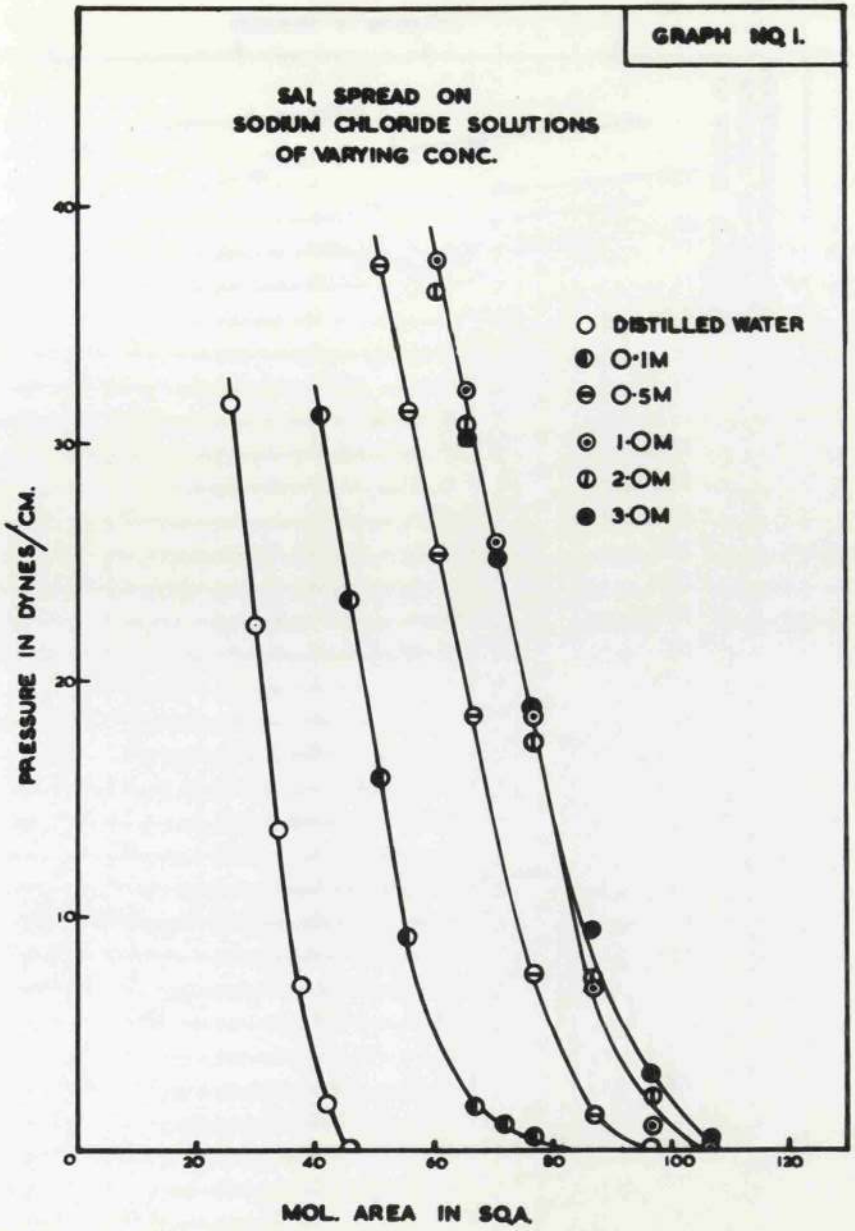
of these mixed films was obtained on concentrated sodium chloride solutions.

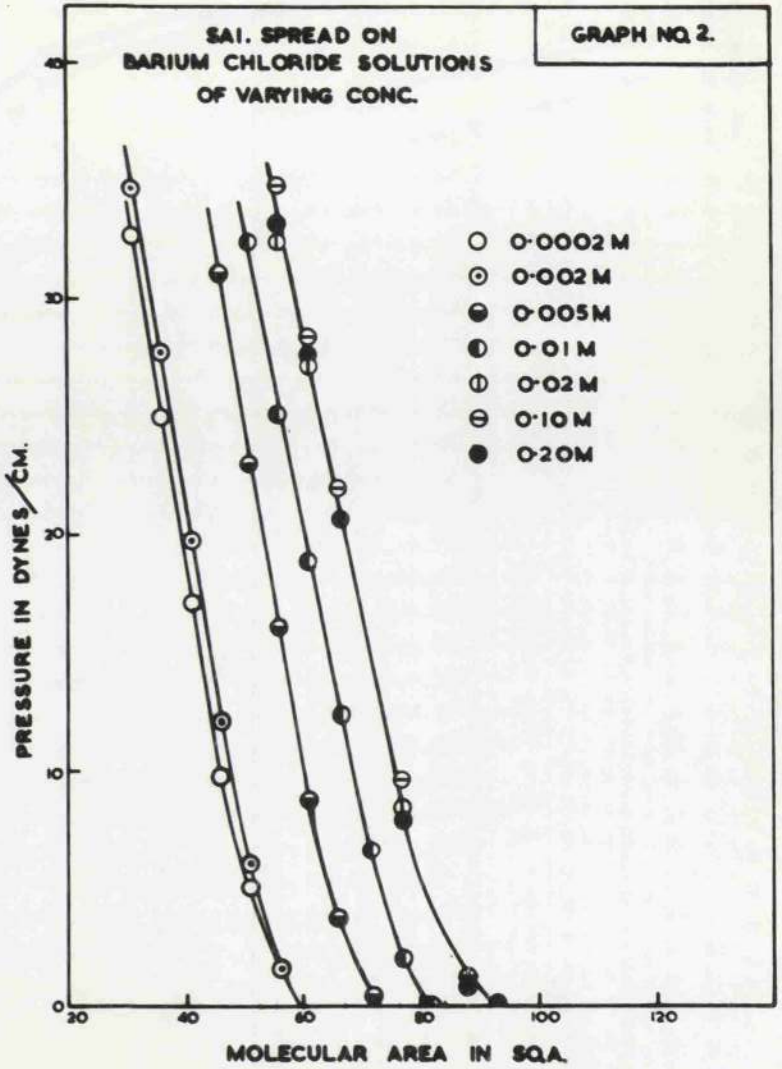
(b) Sulphonated Dyes with Short Alkyl Chains (i.e. 4 carbons and under).

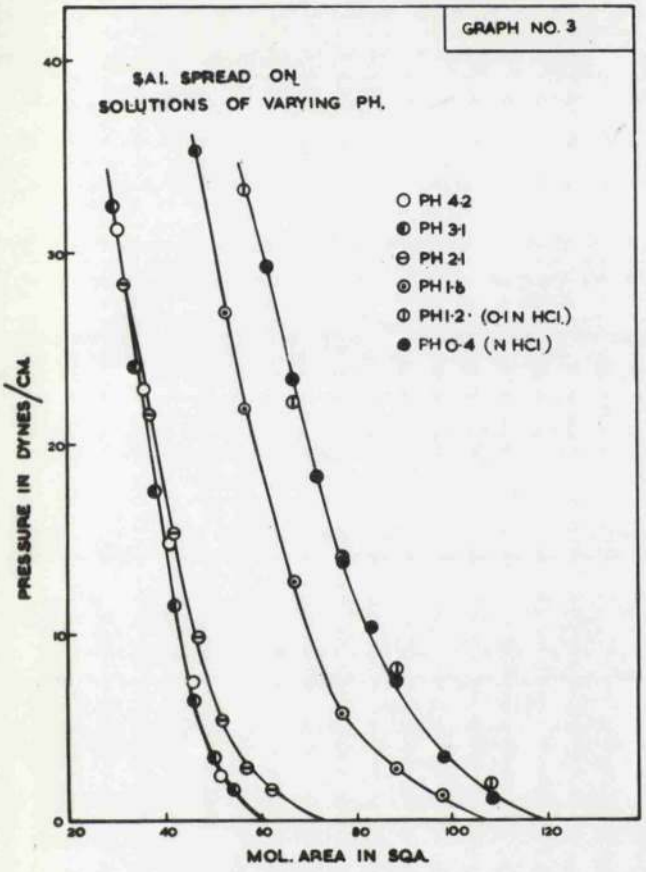
All these dyes dissolved completely when spread on water. Spreading, however, was obtained with the larger sized molecules on concentrated sodium chloride solutions resulting in the formation of gaseous films. As the size of the molecules decreases no films are formed and this is believed to be due to the dyes forming aggregates on the surface rather than monolayers.

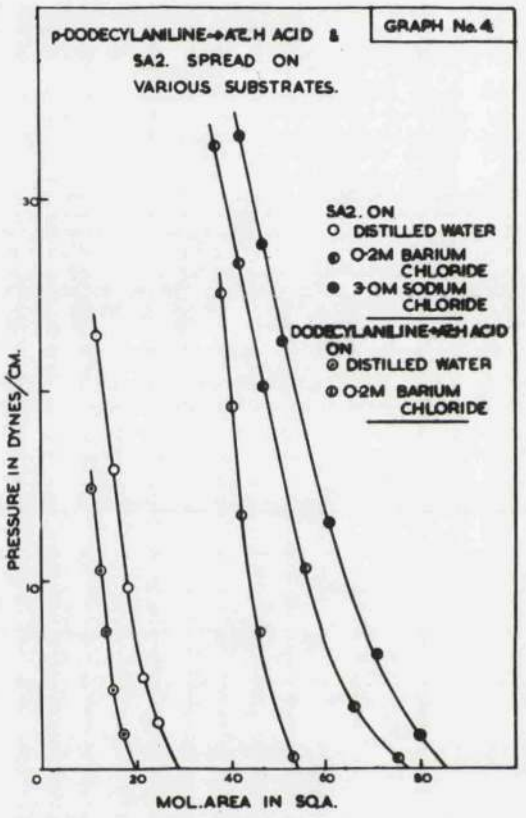
Cetyltrimethylammonium bromide mixed with the dyes, however, spreads them on water and sodium chloride solutions, showing that the cetyltrimethylammonium bromide is attached to the dye molecules and acts as a spreading agent.

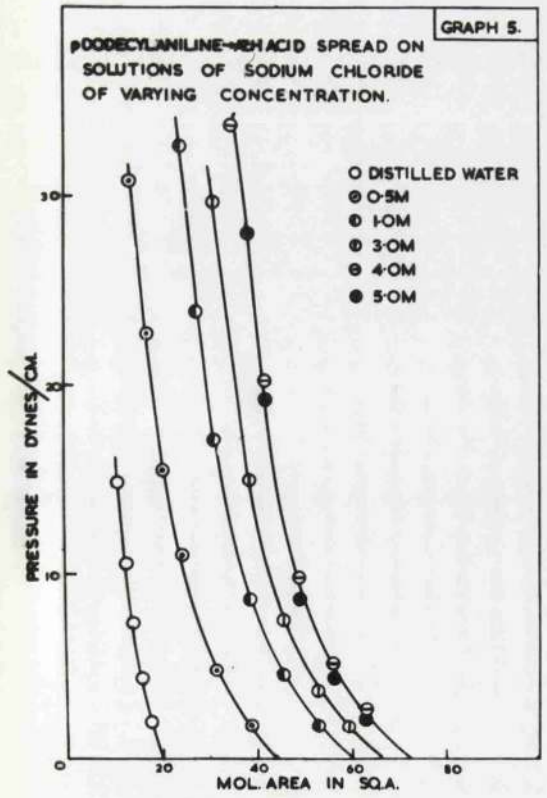
It has been found that dyes which are surface active (i.e.those which form films without the aid of cetyltrimethylammonium bromide) are often less fast to light than non-surface active dyes. The inference is that the dyes which form stable monolayers at an air-liquid interface also form monolayers when adsorbed on a substrate. Those dyes which do not form surface films, on the other hand, are believed to form aggregates in the substrate. The monolayer forming dyes have a much larger solid-to-air surface resulting in a decrease in light fastness. There is thus some reason to believe that the light fastness of a series of dyes depends upon their surface activity; those which form monolayers are generally the most fugitive.

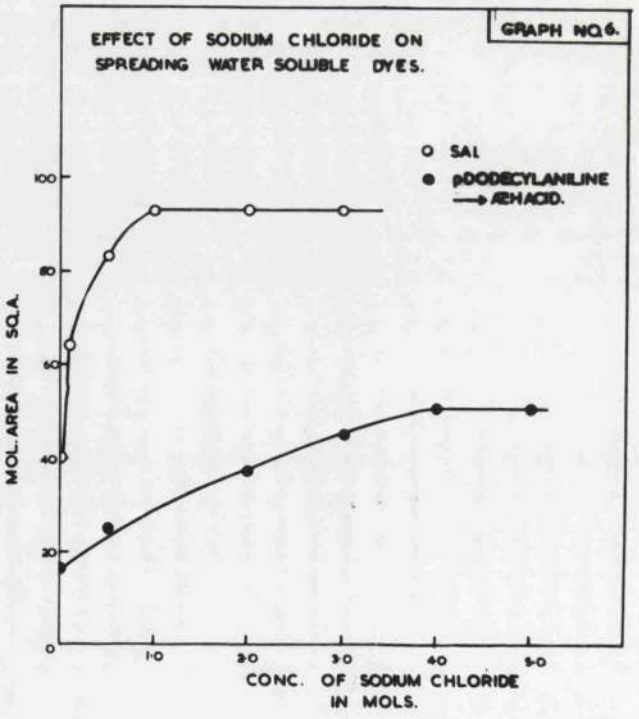

GRAPH NO 1.
SAL SPREAD ON
SODIUM CHLORIDE SOLUTIONS
OF VARYING CONC.
DISTILLED WATER
0·1M
0·5M
1·0M
2·0M
3·0M
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.
0
10
20
30
40
20
40
60
80
100
120

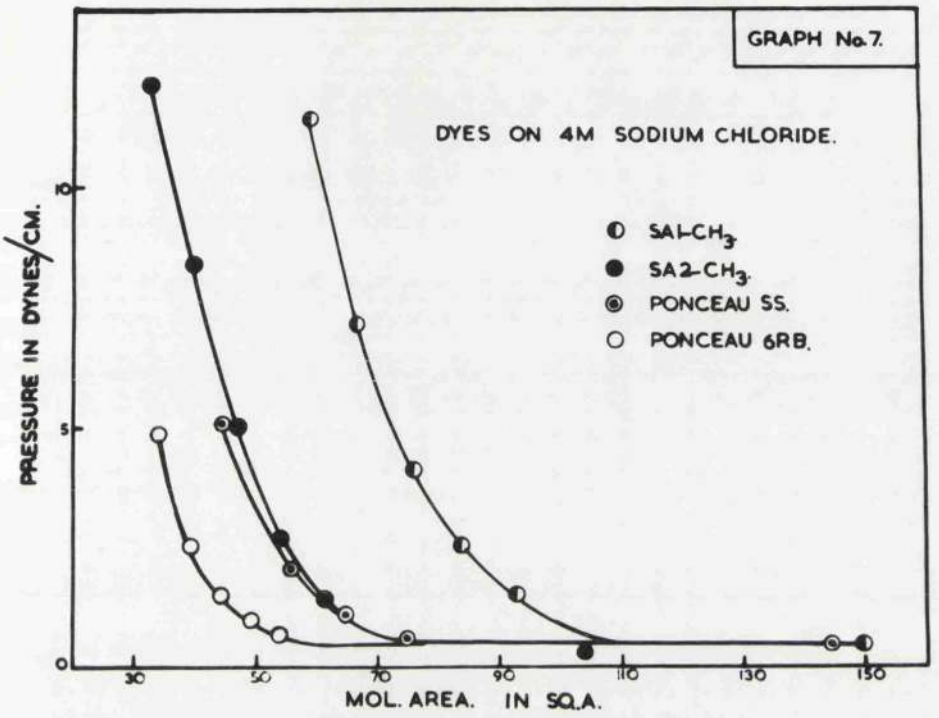

GRAPH NO. 2.
SAL. SPREAD ON
BARIUM CHLORIDE SOLUTIONS
OF VARYING CONC.
0·0002 M
0·002 M
0·005M
0·01 M
0·02 M
0·10 M
0·20M
PRESSURE IN DYNES/CM.
MOLECULAR AREA IN SQ.A.
0
10
20
40
20
40
60
80
100
120

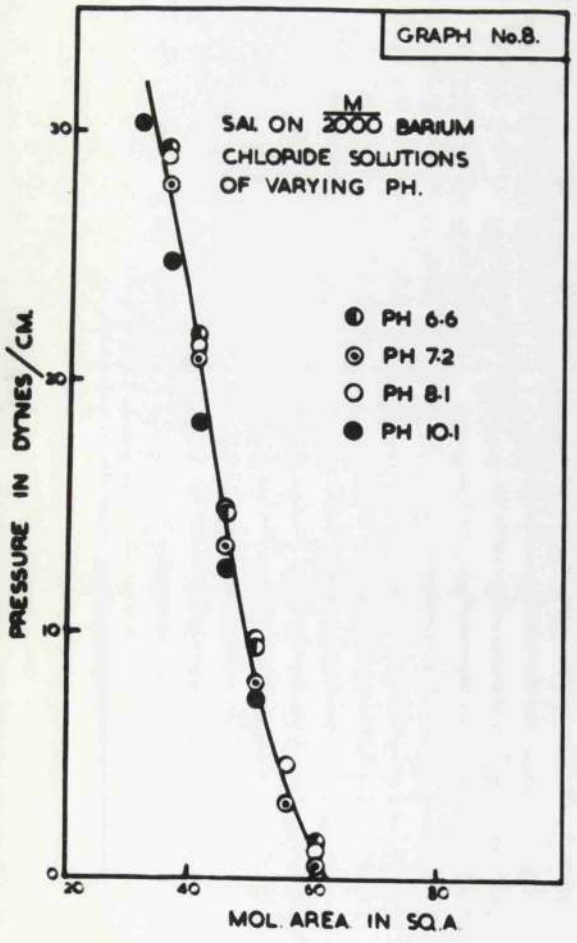

GRAPH NO. 3
SA1. SPREAD ON SOLUTIONS OF VARYING PH.
PH 4·2
PH 3·1
PH 2·1
PH 1·5
PH 1·2 · (0·1 N HCl.)
PH 0·4 (N HCl)
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

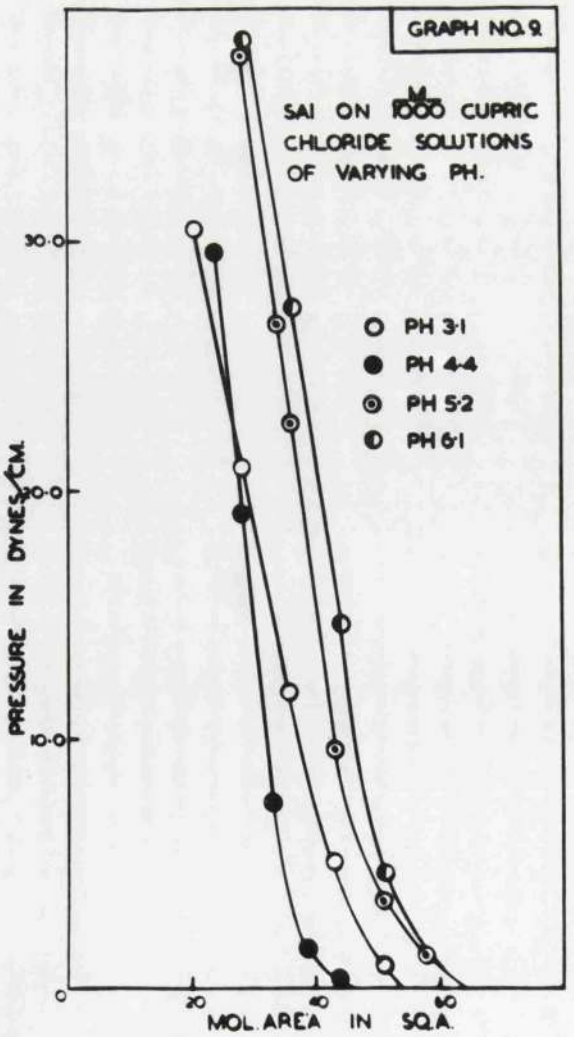

GRAPH No. 4
p-DODECYLANILINE→ATE.H ACID & SA2. SPREAD ON VARIOUS SUBSTRATES.
SA2. ON
DISTILLED WATER
0·2M BARIUM CHLORIDE
3·0M SODIUM CHLORIDE
DODECYLANILINE→RH ACID ON
DISTILLED WATER
0·2M BARIUM CHLORIDE
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

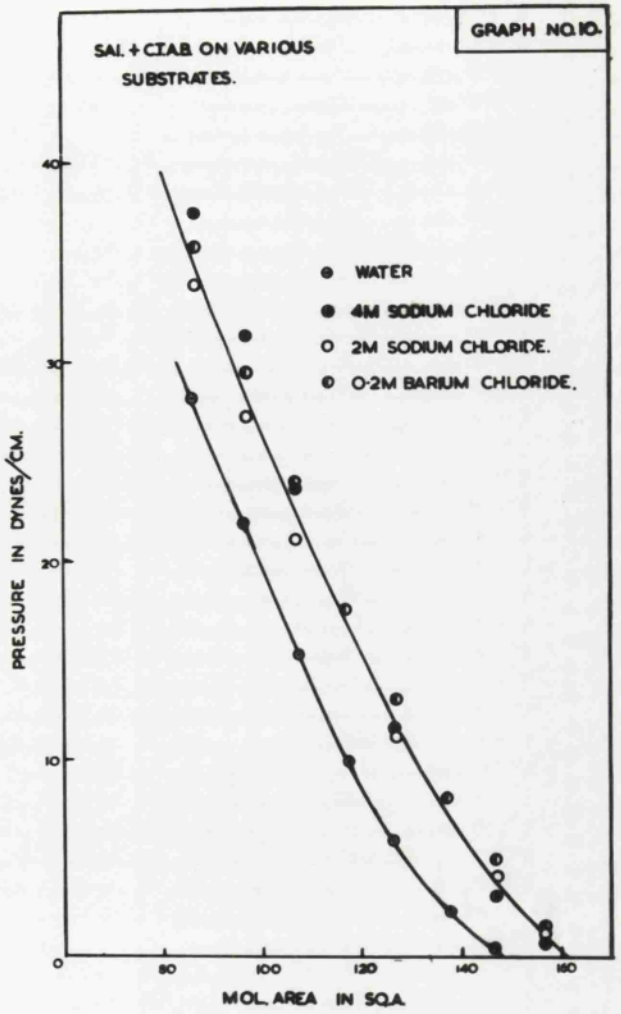

GRAPH 5.
p-DODECYLANILINE→RH ACID SPREAD ON SOLUTIONS OF SODIUM CHLORIDE OF VARYING CONCENTRATION.
DISTILLED WATER
0·5M
1·0M
3·0M
4·0M
5·0M
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

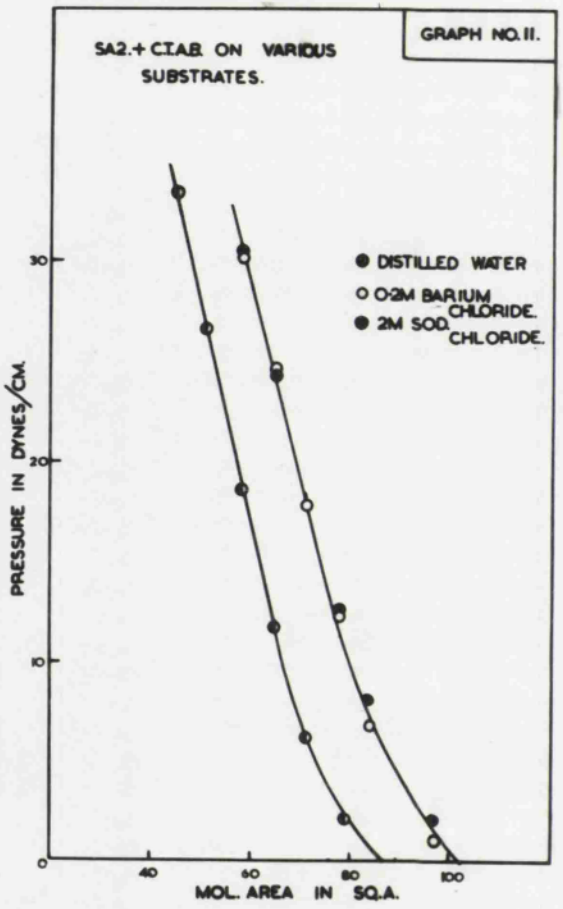

GRAPH NO. 6.
EFFECT OF SODIUM CHLORIDE ON SPREADING WATER SOLUBLE DYES.
SAL
p-DODECYLANILINE →RH ACID.
MOL. AREA IN SQ.A.
CONC. OF SODIUM CHLORIDE IN MOLS.

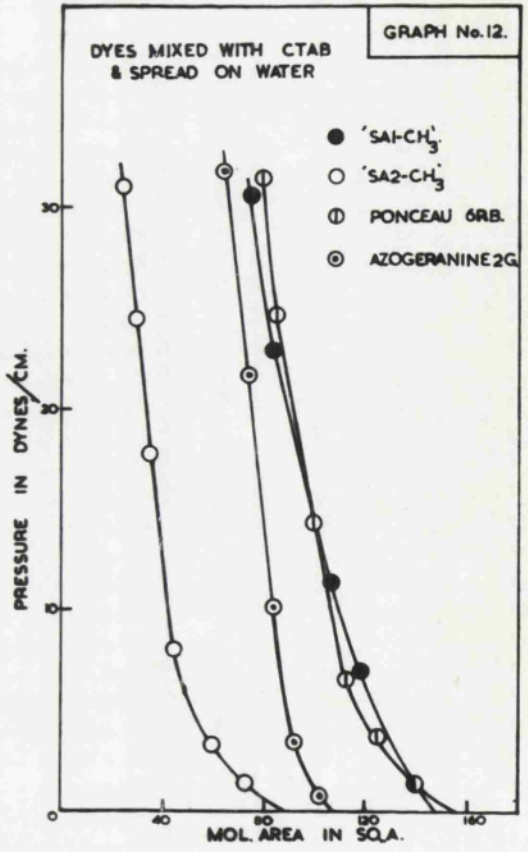

GRAPH No.7.
DYES ON 4M SODIUM CHLORIDE.
SA1-CH3.
SA2-CH3.
PONCEAU SS.
PONCEAU 6RB.
PRESSURE IN DYNES/CM.
MOL. AREA. IN SQ.A.

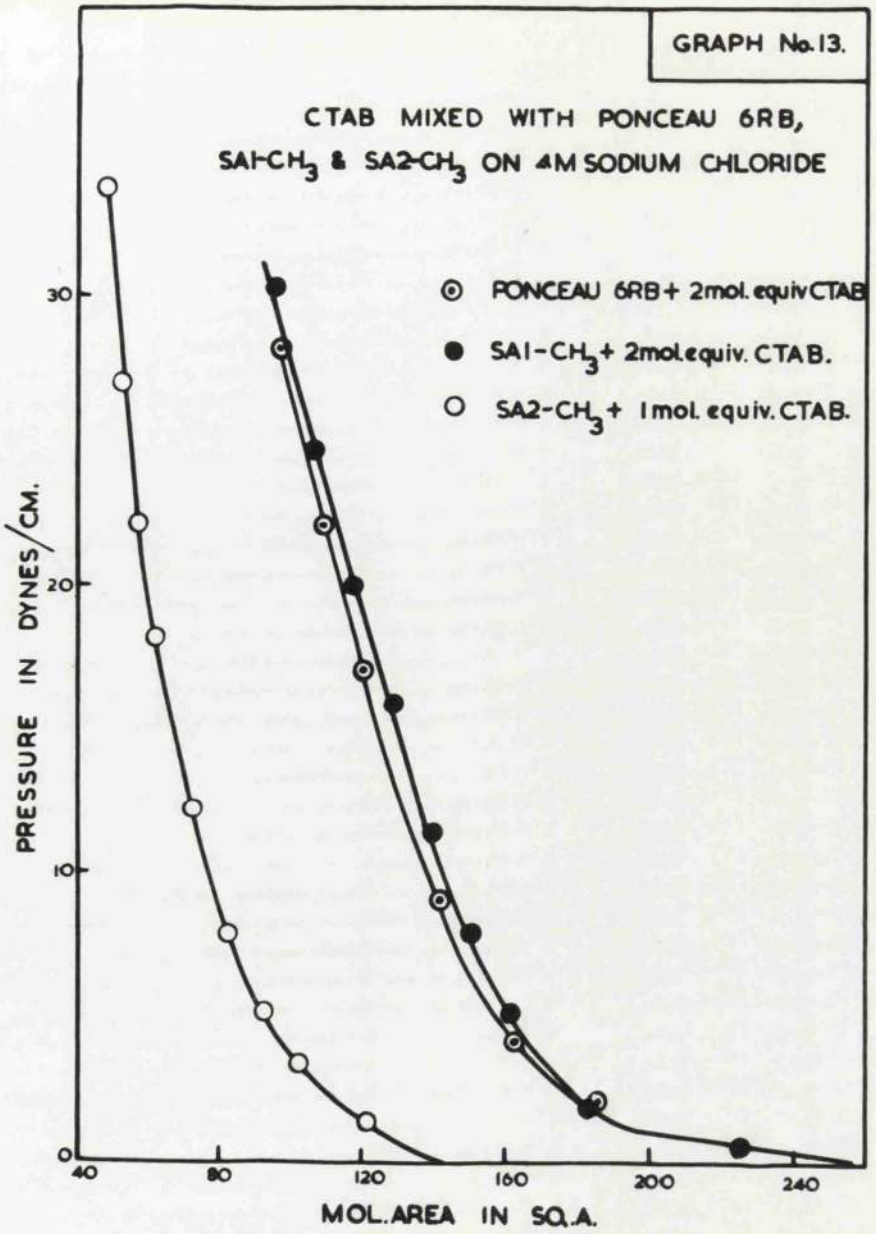

GRAPH No.8.
SAL ON M/2000 BARIUM CHLORIDE SOLUTIONS OF VARYING PH.
PH 6.6
PH 7.2
PH 8.1
PH 10.1
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

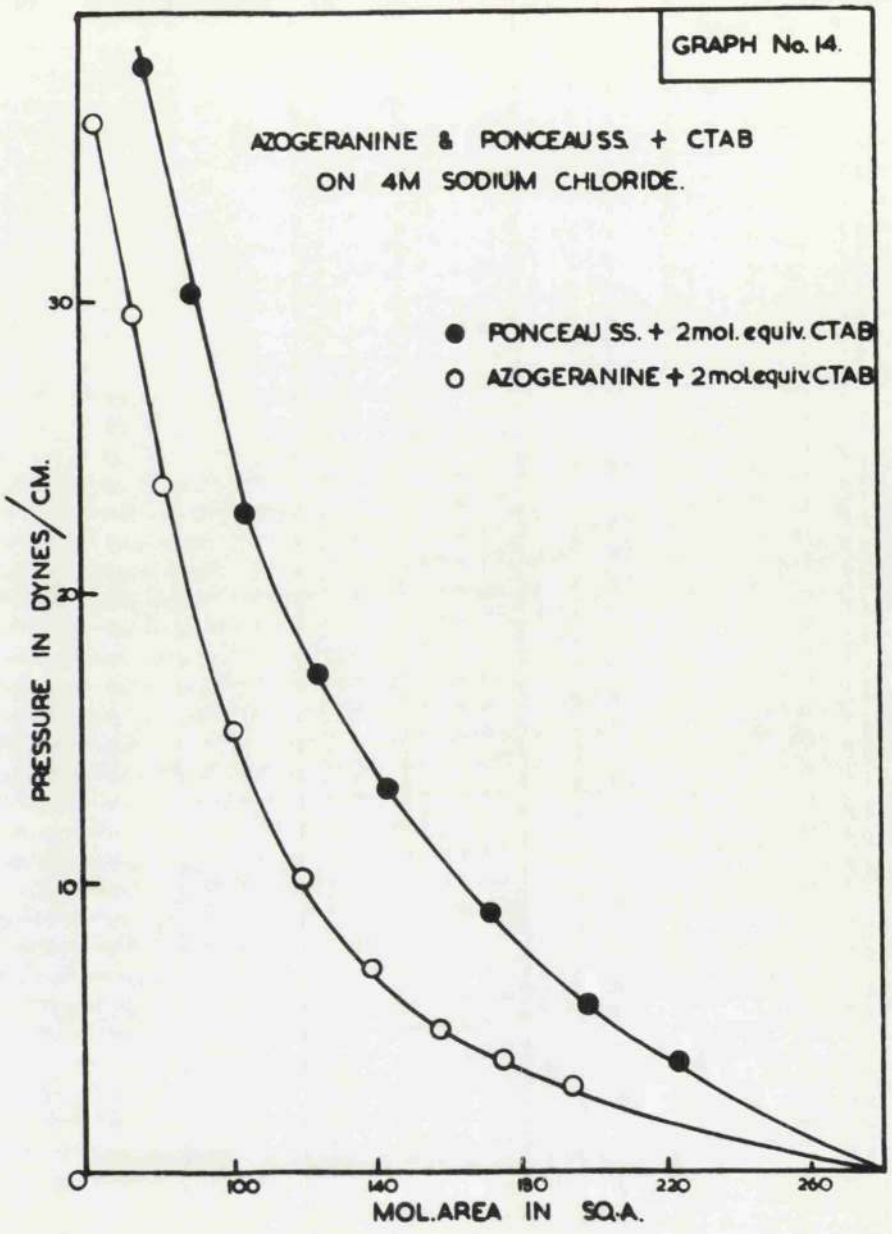

GRAPH NO.9.
SAI ON M/1000 CUPRIC CHLORIDE SOLUTIONS OF VARYING PH.
PH 3.1
PH 4.4
PH 5.2
PH 6.1
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.


GRAPH NO.10.
SAI. + CTAB. ON VARIOUS SUBSTRATES.
WATER
4M SODIUM CHLORIDE
2M SODIUM CHLORIDE.
0·2M BARIUM CHLORIDE.
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.


GRAPH NO.11.
SA2. + CTAB. ON VARIOUS SUBSTRATES.
DISTILLED WATER
0·2M BARIUM CHLORIDE.
2M SOD. CHLORIDE.
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.


GRAPH No.12.
DYES MIXED WITH CTAB & SPREAD ON WATER
'SAI-CH3'.
'SA2-CH3'
PONCEAU 6RB.
AZOGERANINE 2G.
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.


GRAPH No. 13.
CTAB MIXED WITH PONCEAU 6RB,
SA1-CH3 & SA2-CH3 ON 4M SODIUM CHLORIDE
PONCEAU 6RB + 2mol. equiv CTAB
SA1-CH3 + 2mol. equiv. CTAB.
SA2-CH3 + 1mol. equiv. CTAB.
PRESSURE IN DYNES/CM.
0
10
20
30
40
80
120
160
200
240
MOL. AREA IN SQ.A.


GRAPH No. 14.
AZOGERANINE & PONCEAU SS. + CTAB
ON 4M SODIUM CHLORIDE.
PONCEAU SS. + 2mol. equiv. CTAB
AZOGERANINE + 2mol. equiv. CTAB
PRESSURE IN DYNES/CM.
0
10
20
30
100
140
180
220
260
MOL. AREA IN SQ.A.

SECTION 2.

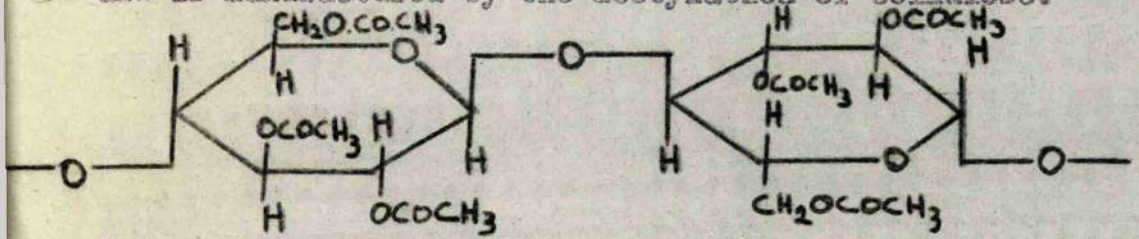
INTERACTIONS BETWEEN DYES AND MONOLAYERS OF ACETATES AND PROTEINS.

INTRODUCTION.

Studies in complex formation in monolayers have yielded much important information regarding complexes between such pairs of substances as proteins and tanning materials and also between certain biological substances. Very little work, however, has been reported on interactions between dyes and monolayers of fibrous substances and this section of the work was carried out to study this type of interaction with a view to determining some details of the mechanism by which dyes are bonded to cellulose triacetate, and to protein fibres.

THE STRUCTURE OF CELLULOSE TRIACETATE.

Cellulose acetate has a considerable value as a textile material and is manufactured by the acetylation of cellulose.



As may be seen from the formula, cellulose is made up of repeating glucose units arranged in an alternating manner. Thus any particular group is in the same position every second unit, corresponding to a spacing of 10.3A. Each glucose unit has three hydroxyl groups available for acetylation but the material used commercially approximates only to the diacetate. The acetate fibre is obtained by spinning a concentrated solution of the acetate dissolved in acetone which readily dissolves the 'diacetate' (but not the triacetate). It has been

found that for the diacetate, acetylation is fairly uniform along the chain and thus most of the glucose units contain two acetyl groups. The triacetate, on the other hand, is almost completely acetylated.

It has been shown by X-ray examination[78] that commercial cellulose acetate has a very low degree of orientation, yielding an ill-defined and probably composite photograph. However, from more highly oriented specimens it was shown that the molecular period along the fibre axis is practically the same as for cellulose itself.

Cellulose acetate has very different properties from cellulose and this is due, to a great extent, to changes in the surface characteristics of the fibre on acetylation. The acetate is hydrophobic whereas cellulose is hydrophilic and thus little swelling of the acetate takes place in aqueous solutions. The intermicellary canals are thus narrow and the passage of dye ions into the interior of the fibre is difficult. The negative surface potential of the acetate is also much higher than that of cellulose which results in the repulsion of anionic dye ions.

Dyeing of Cellulose Acetate.

The dyeing behaviour of cellulose acetate is very much different from that of cellulose, as would be expected on consideration of their physical and chemical properties.

A hypothesis has been put forward by Kartaschoff[79], that the dyeing of cellulose acetate with disperse dyes is a process of solid solution. This was supported by the observation that this fibre is dyed when it

comes in contact with dry dye powder. Knoevenagel[80] has found that with increasing concentration a constant partition ratio is observed for the distribution of phenol and aniline between the fibre phase and the solution in exactly the same 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 the isotherm also will be expected to give a constant partition coefficient at low concentration. Therefore the discrimination between adsorption and solution is not possible on the basis of these results alone.

Marsden and Urquhart[81] have investigated the adsorption of phenol by cellulose acetate and suggested that it may be by hydrogen bonding through the carbonyl oxygen of the acetate group. 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 highly improbable that the bulky dye molecules of even larger size than phenol will be able to diffuse through the unswollen fibre substance and thus these experimental results tend to disprove the solid solution theory.

The absence of any dichroic effect with dyed cellulose acetate has led to the suggestion that the dyes are not adsorbed by the main cellulose

chain, but are hydrogen bonded to the carbonyl oxygen of the acetyl side chain[82].

Recent work has resulted in the formulation of several new theories to explain the dyeing mechanism of cellulose acetate. Allingham, Giles and Neustädter[83] have suggested, that since proton acceptors, e.g. azobenzene, are adsorbed by cellulose acetate, the dyeing mechanism is by hydrogen bonding through the methyl residue of the acetyl group. Thus,the methyl group acts as a proton donor, and the -C-H..O bond formed would be expected to be weak. This is consistant with the low affinity of solutes for cellulose acetate.

Recent investigations on hydrogen bond formation[84] support this theory and it has in fact been found that there is no conclusive evidence of a carbonyl oxygen atom forming a hydrogen bond in water.

Majury[85] 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[86]. From these results it has been suggested that a dye molecule penetrating cellulose acetate undergoes alternate adsorption by the acetate and solution by the water.

Derbyshire and Peters[87], on the other hand, have explained the dyeing mechanism in terms of non-polar bonding between the hydrophobic surfaces of the dye and fibre. This theory has been used by them to explain also the dyeing mechanism of other fibres, and helps to explain their increased affinity for dyes containing long saturated alkyl chains which cannot be interpreted in terms of polar forces.

Campbell and Cathcart[88], in this laboratory have recently shown that neither a -C-H..O- nor a -C=O..H-O- bond is likely to be formed in water, but a bond of the form -O-H...O< can exist. They have therefore suggested that proton-donors bond with cellulose acetate in water at the ether oxygen atoms of the substrate. The -C-H... bond which is probably a weaker one, is therefore likely to be formed only with proton-acceptors.

Structure of Proteins.

All protein fibres consist essentially of polypeptide chain molecules formed by the linear condensation of α amino acids.

$$-NH-\underset{\displaystyle R_1}{\underset{|}{CH}}-CO.NH-\underset{\displaystyle R_2}{\underset{|}{CH}}-CO-$$

The nature of the protein depends upon the nature of the side groups (R) which may be classified as follows:-

(a) Non-reactive Side Chains. These groups contain hydrocarbon residues but also included in this section are substances containing polar groupings such as hydroxyl. These groupings, however, are much less reactive

than the members of other classes.

(b) Acidic Side Chains. These acidic groups all terminate with a carboxyl group and play an important part in bonding the peptide chains and also in attaching the dye to the fibre.

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

(d) Cross-Linking Groups. The only member of this class is cystine, and it is capable of linking two peptide chains. Cystine is found abundantly in wool and in other similar animal fibres and plays a very important part in determining their properties as compared with other proteins.

Extensive investigations by Speakman[89] and Astbury[90] have elucidated the structure of the wool fibre, and Pauling[91] 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 molecules more or less in one plane. These planes are themselves held together by hydrogen bonds or weak Van der Waal forces. The micelles are regarded as lamellar in shape, about 200A thick and 2,000A long.

The intermicellar space has pores of the order of 6A in the dry unswollen state and about 40A 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.

The dyeing properties of wool have been very widely studied and a brief review of the theories which emerged from this work are given.

A chemical theory of the dyeing of wool by acid dyes has been proposed by Knecht[92] and developed by Fort in which it is assumed that the wool on immersion in the dye bath first combines with the colourless acid to form a protein salt. This is then followed by the formation of a protein-dye salt and the overall reaction may be expressed by the following equation.

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

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

This view has been confirmed by Eldd[93] who measured quantitatively the replacement of chloride ions in the wool fibre by dye anions. Speakman and Stott[94] have established that wool has a maximum combining capacity of 0.82 equivalents of monobasic acid per kilogram at pH 1.00 which corresponds closely to the number of amino groups in the wool. Therefore it is obvious that if the chemical theory of wool dyeing is correct then dyed wool would have a smaller combining capacity for acid than undyed wool and this has been shown to be the case[93]. Further evidence in support of this theory has been afforded by Speakman and Stott[94], who have shown 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 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 there exact nature is still undetermined. Vickerstaff[95] and Meggy[96] have drawn attention to the importance of Van der Waals' forces in this connection. It has been shown that there is 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[97] 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 hydrogen bonding must be responsible for their attachment to the fibre. Chipalkatti et al.[98] have studied the adsorption on wool of aliphatic and aromatic non-ionic compounds from a variety of solvents and found that from non-aqueous solutions hydroxy compounds appear to be adsorbed by the formation of hydrogen bonds, perhaps with the enolic forms of the amide or peptide groups in the fibres.

Gilbert and Rideal[99] have offered a thermodynamic treatment of wool

dyeing in which they assume that the anions and the cations are adsorbed on specific sites in the substrate, and that the fibre contains equal numbers of positive and negative sites possessing the same properties. The adsorbed ions in this theory are free to occupy any site irrespective of whether or not the adjacent sites are occupied.

Peters and Speakman[100], on the other hand, have suggested 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.

Both theories agree to a large extent with experimental observations but they do not enable an equivocal picture of the mechanism of dye adsorption by wool to be obtained.

PENETRATION AND COMPLEX FORMATION IN MONOLAYERS BY ORGANIC MOLECULES.

The most important observation prior to 1935 on mixed films was the 'condensing' effect of large molecules on smaller molecules when both were present in a mixed unimolecular layer[101]. It has been shown that cholesterol condenses myristic acid films. This is believed to be simply due to the reduction of the vibratory movements of the hydrocarbon chain by the presence of large inert molecules and not to complex formation, since the two dimensional vapour pressure is not reduced more than would be expected from the proportion of cholesterol molecules present in the film. A similar observation, that cholesterol condenses an expanded film of lecithin, was made by Leathes[102] and it was shown by Hughes[103] by surface potential measurements that the condensation in this case

is not accompanied by any appreciable change in the dipole moments of the two components. Schulman and Hughes[104], 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 A can be completely replaced by a monolayer of B.

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

(3) Neither replacement or penetration takes place.

A tentative explanation was given 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 to an extent dependent upon the relative adhesional forces of A to A, and 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, the stability of which is related to the stability of the complex.

Harkins and Myers[105] investigated another type of mixed film, by spreading a mixture of Nujol (a low volatile, liquid hydrocarbon) and a

saturated fatty acid, and found that in the expanded region the Nujol affected the F-A curve of the acid most markedly. As the pressure was applied the Nujol was squeezed to the top of the film where it no longer exerted any further influence on the film. This is similar to the effect observed with mixed films of stearic acid and phenanthrene[106].

The effect of injecting substances under a monolayer of oriented molecules was more thoroughly investigated[107, 108, 109] and it was found, that if the injected molecules were similar in structure to the film molecules (i.e. having a polar head group and a hydrophobic tail) then the following could occur:-

(a) If association took place between the polar head groups of the film and the injected molecules and none between the hydrophobic tails then adsorption of the injected molecules occurred below the monolayer with a consequent change in the surface potential. In some cases where the injected molecules were polyfunctional rigid films were obtained due 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 portions of the respective molecules. The term complex was used to designate a combination of measureable stability in a stoichiometric ratio between the two reactants.

(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.

Further research was then undertaken to ascertain the extent electrical forces play in governing the stability of complexes in mixed monolayers[110]. Mixed films containing molecules having the same hydrophobic portions but different polar groups were studied and it was shown that the attractive and repulsive forces in these films were due to coulombic forces acting between polar groups in the following systems:-

(1) ion-ion, unlike sign.

(2) ion-dipole.

(3) dipole - dipole.

(4) ion - ion, like sign.

In many cases it was possible to regard the association of molecules in a mixed film as due to a system of co-ordinating hydrogen or hydroxyl bonding as in solution, though it was necessary to assume that the bonds are resonant and that the substrate ion can be considered to be attached to several film molecules, since the films are always solid.

Complex formation in mixed monolayers has also been observed by Harkins and Florence[111], by studying mixed films of long chain acids, alcohols and amines. The stability of the mixed monolayer is decreased

by the introduction of a double bond into the acid. It was shown that oleic acid (cis-form) is completely ejected from mixed monolayers of the acid and long chain amines and alcohols. Eladic acid (trans-form) on the other hand, is only partially ejected and stearic acid gives a very stable mixed film. Thus as the energy of binding between the chains decreases so does the stability of the mixed film. Further evidence that the configuration of the hydrocarbon chain plays an important part in the stability of these films was shown by Goddart and Schulman[112]. The interactions between sodium cetyl sulphate and alcohols containing hydrocarbon chains of different configurations were examined and it was shown that molecular association was greatest when the alcohol contained a straight chain.

It has already been shown that substances containing polar groups with a small non-polar residue do not penetrate films but are adsorbed as a double layer causing no change in the film characteristics. Further work, expecially at low pressures, showed that substances, such as carboxylic acids, with a small non-polar portion can penetrate the layer but are ejected on increasing the pressure[113], forming the previously observed double layer. Similar effects have also been observed by Adam, Askew and Pankhurst[114], who studied the effect of simple capillary active substances on insoluble monolayers. It has been shown that substances such as butyric acid or phenol disrupt the cohesion of the insoluble film converting it usually into a vapour expanding film

at low pressures. On increasing the pressure the penetrant is displaced from the surface. This penetration becomes more powerful by increasing the chain length of the penetrant and the subsequent displacement of these molecules then becomes more difficult[115].

Schulman and Stenhagen[116], by studying the interaction between saturated and unsaturated hydrocarbon chain and aromatic ring structures found that several general types of complexes can be obtained:-

(1) Ring penetrated by ring (1:1).

(2) Ring penetrated by chain (1:1, 1:2, 1:3).

(3) Chain penetrated by chain (1:1, 1:3).

(4) Chain penetrated by ring (2:1).

It was found that the 1:1 and 1:3 complexes are stable and though the existence of the 1:3 complex was doubted by Harkins[117] it was confirmed by Jolly[118]. Matalon[119], studying the effect of the conditions under which the above experiments were carried out, found that the discrepency in the results was due to the use of a phosphate buffer by Schulman and Stenhagen. When no phosphate buffer was used the kinks in the curve representing the three different complexes disappeared. Further work by Goddart and Schulman[120] has shown that cetyl sulphate and cholesterol form a stable 1:1 complex and also that complexes are formed between cholesterol and digitonin.

The interactions studied so far have been between substances in which

one injected molecule has combined with one molecule in the monolayer. It has been shown, however, that if a film of a long chain amine is spread on a substance containing numerous acidic groups, e.g. tannic acid, a large number of film molecules are attached to one tannic acid molecule, resulting in the formation of a very rigid film. In particular, the importance of leather tanning stimulated an investigation of the effect of tanning materials on protein films[121 - 123]. When the acid was either injected under the monolayer[121], or dissolved in the underlying liquid[122, 123], it produced less compressible and more rigid films. The development of tanning properties during polymerisation of certain non-tanning monomers, such as benzoquinone, showed that as polymerisation proceeded the film became more rigid, proving that the rigidity of the film is due to multipoint association.

The interation between detergents and proteins has also been studied. The injection of detergent molecules under a protein film caused penetration of displacement of the film[124, 125], but it has been found difficult to interpret the results quantitatively. Doty and Schulman[126] injected proteins under monolayers of detergents to avoid structural alterations of the protein which occur by spontaneous spreading. It was possible by this method to distinguish three distinct processes, namely adsorption, penetration and solution. If the layer was maintained at constant area adsorption took place. On the other hand, if the pressure was kept constant, solution or penetration occurred characterised by the rate of the

expansion.

The effect of dyes on monomolecular films has also been studied. Matuura[55] showed that dyes expand stearic acid films and that different forces operate depending on the type of dye used. Acid dyes, in the acid region in which both the film and the penetrant are anions, expand stearic acid films. This expansion decreases with the size of the dye molecule and is believed to be due to adsorption of the dye by Van der Waals' forces. On the other hand basic dyes expand the film by adsorption of the dye by ionic forces. Allingham, Giles and Neustädter[40 and 83] have shown that dyes expand films of long chain compounds containing groups which are present in fibres.

RESULTS AND DISCUSSION.

The precise mechanism by which dyes are bonded to cellulose acetate, though of considerable commercial importance, has remained uncertain in spite of many attempted explanations. The present investigation was carried out to study this problem by examining the penetration of solutes into films of these substances.

Previous work carried out in this laboratory has shown that certain dye molecules dissolved in the underlying solution penetrate films of cetyl acetate[83]. This substance was used as a model compound to represent cellulose triacetate and from the results obtained a dyeing mechanism has been suggested. The present work was carried out to extend these initial investigations and to study the effect of dyes and related compounds on cellulose triacetate monolayers.

Preliminary experiments were carried out on cetyl acetate and stearyl ketones. These substances were spread on various solutes to study the effects of these solutes on keto- and acetyl-groups. These two substances have almost identical non-polar attraction for solutes introduced into the water phase, and any difference between their films in penetrability or expansion by the solute will thus be attributable to differences in polar attraction of the keto and the acetyl groups. That of the keto group is, in fact, likely to be very low because ketones do not appear to form complexes by polar

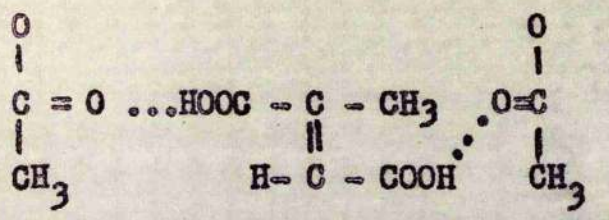
attraction with other solutes in water, whereas acetates do so.

It has been shown[108], that before penetration of a monolayer can take place there must be present in the penetrant both polar and non-polar attraction for the film molecules. Thus the penetration of monolayers is very specific and it would be expected that substances with both polar and non-polar attraction would expand films of cetyl acetate, but not films of the stearyl ketones. The solutes used in this work are water-soluble compounds of varied molecular size and shape and may be conveniently classified according to the size of the hydrophobic residue in their molecules.

The Effect of Small Solute Molecules on Acetate and Ketone Films.

It has been shown that substances with polar groupings and very little hydrophobic character are often adsorbed under the monolayer and cause no change in the molecular area or characteristics of the F-A curve[108]. It has been found, however, that the adsorbed molecules alter the surface potential of the film[109]. Unfortunately, the apparatus for measuring surface potentials was not completed until near the end of the work and all of the results were obtained by Force-Area measurements and hence the conclusions must be tentative.

The present tests were carried out with small sized solutes containing two polar groups and it was hoped that each solute molecule would cross-link two film molecules and possibly expand the film thus:-



The solutes used were ethylene glycol and mesaconic acid and it was found that when cetyl acetate films were spread on 0.1M solutions of these substances at room temperature very little increase in area was observed (graph No. 1). This slight increase in area may be due to the solute molecules being adsorbed under the monolayer and holding the head groups slightly apart by cross-linking. The mesaconic acid and ethylene glycol molecules adsorbed under the monolayer possibly affect the cohesional properties of the film, which explains the larger area at which the surface pressure first appeared.

Stearyl methyl ketone spread on 0.1M ethylene glycol gave an almost identical curve to that obtained on water, but because of the reasons previously stated it is believed that no interaction is taking place in this case.

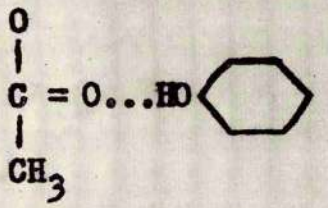
The Effect of Medium Sized Molecules on Acetate and Ketone Films.

Cetyl acetate was spread on 0.1M pyridine and 0.1M sucrose solutions in which it was expected that polar attraction would be weak. The F-A curves (graph No. 2), give areas at zero compression of 26 sq.A. and therefore it appears that no interaction is taking place. A similar result was obtained with cetyl acetate spread on 0.1M benzoquinone and the areas at which the surface pressure first appeared are slightly

greater than on distilled water, which is possibly due to the solute molecules penetrating the film at low pressures. On increasing the pressure, however, the molecules appear to be ejected into the underlying solution.

Cetyl acetate was then spread on 0.1M quinol sulutions and it was found that the area at which the surface pressure first appears is very much greater than is obtained with benzoquinone. On increasing the pressure the quinol molecules are not ejected from the monolayer and an expanded and more compressible film is formed. The area at zero compression was found to be 62 sq.A, which may be accounted for by the cross-linking of two acetate groups by each quinol molecule.

Benzoquinone and quinol have a similar structure and vary only in their polar groupings. It therefore appears that the quinol molecules are bonded to the acetate groups by hydrogen bonding through the hydroxy-groups in the quinol molecules. This is similar to the mechanism suggested by Marsden and Urquhart[81] for the bonding of phenol to cellulose acetate:-



Recent work[88] has suggested that the bonding may take place at the ether oxygen in the acetyl group but from surface pressure

measurements it is not possible to say which mechanism is operative.

Quinol was found to expand ketone films (graph No. 6), possibly due to the solute molecules, which have a slightly higher non-polar attraction than ethylene glycol, interacting with the non-polar portions of the ketone, or to the more powerful proton-donating power of phenolic than of alcoholic groups. Compression of the film ejects the quinol molecule into the underlying solution but the film collapses before the quinol is completely ejected. Thus it appears that in this case only a weak interaction is taking place.

The Effect of Large Molecules on Acetate and Ketone Films.

Cetyl acetate was spread on solutions of dyes and other large molecules and it was found that, in all cases, expansion of the film occurred if polar groups were present in the molecule. Cetyl acetate was spread on 0.002M Pinacyanol and it was found that an expanded and more compressible film was formed, giving an area of 84 sq.A. at zero compression. This area and compressibility are similar to those obtained by Allingham et al.,[83] for cetyl acetate spread on a similar cyanine dye. The expansion may be due to the cyanine dye cross-linking the acetate groups through the two nitrogen atoms in the dye. These nitrogen atoms, because of resonance, are considered equally able to form a hydrogen bond with a proton-donor group in the monolayer. Alternatively it may be due to dipole-dipole interaction at these cationic centres. Cetyl acetate spread on 0.01M Acid Magenta also gave an

expanded film with a molecular area of 90 sq.A (Graph No. 3).

The effect of pinacyanol on stearyl methyl ketone films is similar to that obtained with quinol (graph No. 5) and again it appears that very little interaction is taking place between the dye and the film.

The Effect of Dyes and Related Compounds Dissolved in the Water Phase on Cellulose Triacetate Films.

The behaviour of cellulose triacetate films has been studied by Borgin and Johnston[127] who found that they do not completely spread on water. The area occupied by each glucose residue was found to be 37 sq.A instead of 67 sq.A, which is believed to be due to the residual hydroxy-groups in the triacetate binding the polymeric chains into micelles which do not spread as a monolayer when ejected on to the surface. When cellulose triacetate, however, was spread on urea or guanidine hydrochloride solutions it was found that complete spreading occurred, which is believed to be due to these substances acting as hydrogen bond breaking agents by preferentially combining with the residual hydroxy-groups in the fibre. Thus the attractive forces between the polymeric chains are considerably reduced and this allows the material to spread completely as a monolayer.

The cellulose triacetate used in this work was almost completely acetylated. Preliminary tests carried out on distilled water and 4.9M urea solution (graph No. 7) gave results in complete agreement with those of Borgin and Johnston.

Dyes and related compounds were then used in the water phase (graphs Nos. 7 and 8) and from the results (Table 1) it may be seen that these substances expand the films.

TABLE I.

Area at Zero Compression (sq.A).	Substrate
37	Water
43	0.1M Quinol
48	0.1M 2,2' Dipyridyl
60	0.002M Pinacyanol
77	0.01M Acid Magenta.

In all cases, except acid magenta, the area obtained is lower than that of the completely spread material (i.e. 67 sq.A. per glucose unit) and thus it appears that the dissolved substances are interacting with the partially spread material, causing an expansion between, and not within the micelles. The area of the film increases with the size of the solute molecules and thus the area obtained with acid magenta is possibly also due to the expansion of the partially spread material.

The Effect of Mixing the Dye 'Dispersol I' with Cellulose Triacetate Before Spreading.

Disperse dyes, which are unsulphonated and contain non-ionic

polar groups, are used commercially for dyeing cellulose acetate. Because of their very low water-solubility it was decided to study their effect on triacetate films by spreading mixed films from a mutual solvent. It was found that when 'Dispersol I' was mixed with cellulose triacetate (in the ratio of 2 glucose units per dye molecule) and spread on water the F-A curve is the same as that of the triacetate alone on water. This result is somewhat surprising, because the dye used is very substantive to cellulose acetate, and it should therefore be powerfully bonded to the film. The only explanation which appears to fit the facts is that adsorption does take place, but because of the planar nature of the dye molecule it can fit exactly under the glucose units in the film and does not affect the area of the film. The bonding is probably caused by polar and non-polar forces but from the other experimental work described here the polar forces appear to be the most important.

Adsorption Tests on Cellulose Triacetate Powder.

The adsorption of substances by cellulose acetate powder was investigated by studying their adsorption isotherms. Phenol was adsorbed on cellulose acetate powder at 30°C. and 58°C. and it was found that straight line isotherms were obtained (graph No. 15) .

Quinol was also adsorbed on cellulose triacetate powder and it was also found to give an approximate straight line isotherm (graph No. 16).

Other adsorption tests were carried out with pinacyanol, acid magenta and pyridine but in all these cases no adsorption could be detected.

The linear isotherms have often been considered as evidence of "solid solution" but they may in more general terms be taken as implying that the solute has higher affinity than the solvent for the substrate[128], i.e. that the solute and not the solvent is the more active swelling agent. This is the reverse of the conditions in adsorption from water by hydrophilic substrates, e.g. cellulose and proteins, where the solvent is the active swelling agent and in which normal Langmuir isotherms are usually observed. In these systems the excess of solvent breaks a high proportion of intermolecular bonds between the polymer chains in the substrate, so that these are then attached only to water. This ensures that any solute will be adsorbed provided it has sufficient affinity to form a complex with the substrate polymer in the isolated state.

In adsorption from water by hydrophobic substances in the solid state, on the other hand, the solvent has too low an affinity to release many of the polymer molecules from their inter-chain bonds in this way and only solutes which have a high enough affinity to do so will therefore be adsorbed.

In the present work it was found that pinacyanol and Acid Magenta expand the film but are not adsorbed by the solid. These dyes are hydrophilic and because the substrate is hydrophobic they are not

adsorbed. These dyes also have large molecules, too large, presumably to penetrate the pores of the fibre without breaking the inter-chain bonds.

Cellulose triacetate is largely hydrophobic, but it has some hydrophilic character, because it spreads on water as a monolayer. The hydrophilic groups, which are responsible for spreading, must lie on the water surface when the material is spread, and thus dyes dissolved in the underlying liquid will have easy access to them. Interaction therefore occurs, resulting in the expansion of the film. A film of cellulose triacetate, when spread on water is believed to be an incomplete monolayer but consists of a mixture of completely spread material and aggregates. Interactions with dyes appear to take place with the completely spread material and not with the aggregates. These dyes, therefore, do not have sufficient affinity to break the inter-chain bonds and penetrate the aggregates themselves as do phenol or urea, but have enough affinity to penetrate the film between the aggregates.

The Effect of Organic Substances Dissolved in the Underlying Liquid on Casein Films.

The spreading of proteins has been widely studied and it has been found that the most reliable method of spreading is to allow the protein to spread on to the surface from a protein-coated waxed fibre

Amendments

(1) Omit last paragraph on page 90 and replace with the following.

The two methods originally used for spreading films of proteins used either concentrated aqueous solutions or solid material. It was found by Gorter and Grendel[132] that if the drops of the solution are small enough and of the correct concentration the protein spreads over the surface after a time to give a homogeneous layer. Solid particles of proteins were found by Rideal and his collaborators[128] to spread very rapidly over a clean surface when a protein-coated waxed quartz fibre was dipped into the surface of the liquid. The amount of protein spread was determined by weighing the fibre before and after spreading. This method is now considered to be unreliable and proteins are generally spread from solution.

Two other methods of spreading from solution have been devised more recently. Langmuir and Schaefer[134] have spread the protein solution on a thin metal strip nearly as long as the width of the trough and then dipped this strip slowly into the water. The dissolved protein was easily carried away over the surface as the water rose up the face of the strip. Another method of spreading from solution has been used by Stallberg and Teorell[135] who dissolved the protein in a 60% aqueous solution of propanol containing 0.5M sodium acetate. Spreading from this solution has the advantage that when applied to a water surface it does not penetrate the space nearly as much

as/

as the pure aqueous solution.

It has been shown by Gorter and Grendel[18] that casein forms a homogeneous layer when spread from a concentrated aqueous solution and this method was adopted in the present work.

The Effect of Tannic Acid on Casein Films.

Casein films were spread on an acetate buffer solution at pH 4.4 and then on the same buffer solution to which had been added 15 mgm./l. of tannic acid. It was found that the tannic acid caused a condensation of the film, which is believed to be due to hydrogen bonding between the hydroxy-groups in the tannic acid and the side-chain groups in the protein. This causes the peptide chains to orient in such a manner that the side-chains are vertical to the surface instead of lying flat on the surface; those under the surface are anchored to the tannic acid molecules.

This explains the condensation of the film and also its increased rigidity; the effect has also been observed with other proteins[123].

The introduction of a simple hydrogen bonding agent, e.g. urea, into the underlying solution causes no alteration in the area or characteristics of the film (graph No. 9), which may be due to the urea being adsorbed under the film (cf. the action of the dispersed dye on the cellulose triacetate film).

The Effect of Azo Geranine 2G on Casein Films.

The effect of change of pH on casein films has been studied by Gorter and Grendel and from the areas at zero compression on various buffer solutions, the following type of curve was constructed (Fig.1). As may be seen from the figure the film area decreases with increasing pH to pH2.8, after which it increases to a maximum at the isoelectric point. Further increase in pH causes a decrease in film area.

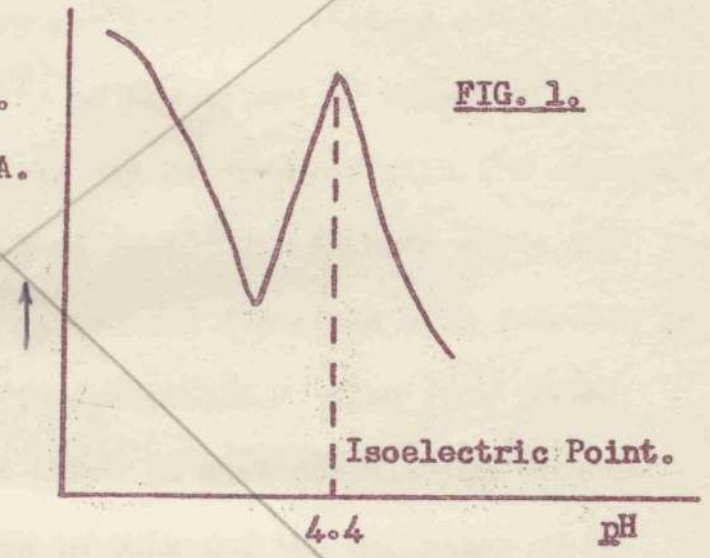


FIG. 1.

The effect of Azo Geranine 2G on casein films was studied at various pH values by spreading casein films on buffered 0.001M Azo Geranine 2G solutions over the pH range 1.2 - 6.0. Simultaneously casein was spread on blank buffer solutions and the results obtained are tabulated below.

TABLE 2.

pH	Film Area at Zero Compression in $M^2/mg.$		Difference in Area.
	Buffer Solutions.	Buffered Azo Geranine 2G solns.	
1.5	0.580	0.740	0.24
2.4	0.360	0.590	0.23
3.2	0.415	0.625	0.21
4.4	0.505	0.695	0.19
5.1	0.410	0.580	0.17
6.6	0.265	0.375	0.11

From these results it may be seen that in all cases the presence of the dye causes an expansion of the film and that the increase in area decreases with increasing pH (graph 14). The film area in all cases was calculated in sq. metres per milligram instead of sq.A. per molecule because of the uncertainty of the molecular weight of casein.

The lower curve in graph No. 14 may be compared with the adsorption of another acid azo dye, Orange II on wool[131]. In both cases the adsorption is greatest at low pH values and decreases with increase in pH until at pH 7.0 no adsorption is detectable. Thus from these preliminary tests it appears that there is some correlation between the adsorption of dyes by proteins in bulk and the expansion of a protein film by dyes.

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(2) Omit Fig. I and first paragraph on page 92. Insert the following paragraph between the first and second paragraphs on page 93.

The curve obtained for casein on buffer solutions of varying pH (graph No. 14) is similar to that obtained by Gorter and Grendel.[18] The variation in the film area at the different pH values is believed to be due to insufficient time being allowed for complete spreading to occur.[18a] Unfortunately, it was not possible in the available time to pursue experiments to obtain complete spreading at all pH values but it is hoped that one of the author's colleagues may continue this work.

(2) Insert between pages 93 and 94.

SURFACE POTENTIAL MEASUREMENTS[x]

The following surface potential measurements were made with the triode electrometer unit but owing to a considerable zero drift of the galvanometer they cannot be considered very reliable:-

x The sentence "It has been found..." beginning on line 15 of page 82 should have the reference No. 108 added.

29.3	1328	429
25.4	1280	471
21.5	1206	545
17.6	1132	619

Large fluctuations in the surface potential were observed until the molecular area of the film reached 40.6 A^2, which corresponds to the area at which the surface pressure first appears. Thus until the surface between the two barriers is completely covered by the film no steady value for the surface potential is obtainable.

Surface Potentials of Casein on an Acetate Buffer Solution (pH 1.5)

(Clean surface : 840 m.v.)

(0.0025 ml. of 5.085 g./l. casein solution spread)

Film Area (m^2/mg.)	Potential (m.v.)	ΔV (m.v.)
0.709	620	220
0.656	590	250
0.595	570	270
0.539	550	290
0.487	540	300
0.429	515	325
0.372	503	332

Again large fluctuations were observed until a film area of 0.709 $m.^2$/mg. was reached, but even then considerable zero drift of the galvanometer made precise measurements impossible.

The double tetrode electrometer was then built to eliminate zero drift and also to give a more stable circuit. Unfortunately, this instrument was not completed in time to investigate the effect of adsorbed molecules upon the surface potentials of acetate and protein films.

CONCLUSIONS.

The effect of various solutes on monolayers of cetyl acetate (a model for cellulose triacetate) and methyl- and ethylstearyl ketones shows that only cetyl acetate films are greatly affected by many solutes. Those which affect the films are either large-sized dye molecules or smaller bifunctional molecules. In all these cases, expansion ofthe film occurs, probably due to the solute molecules being bonded to the film molecules. The dyes are possibly bonded by polar and non-polar forces whereas the smaller bifunctional molecules are bonded mainly by polar forces, forming cross-links.

A powerful hydrogen bonding agent, e.g. urea, can break the inter-chain bonds of floating micelles of cellulose triacetate and so allow it to spread completely, which it does not do on distilled water.

Many solutes which expand cetyl acetate films do not break the bonds in the micelles themselves but simply expand the material between the micelles.

The dyes used are not adsorbed by the solid cellulose triacetate probably because the small pore size of the solid and its hydrophobic character prevent penetration. When spread as a film, however, the hindrance of the small pores of the material is eliminated and the active groups are all exposed at the film-water interface. Thus the dyes have easy access to these groups and have sufficient affinity

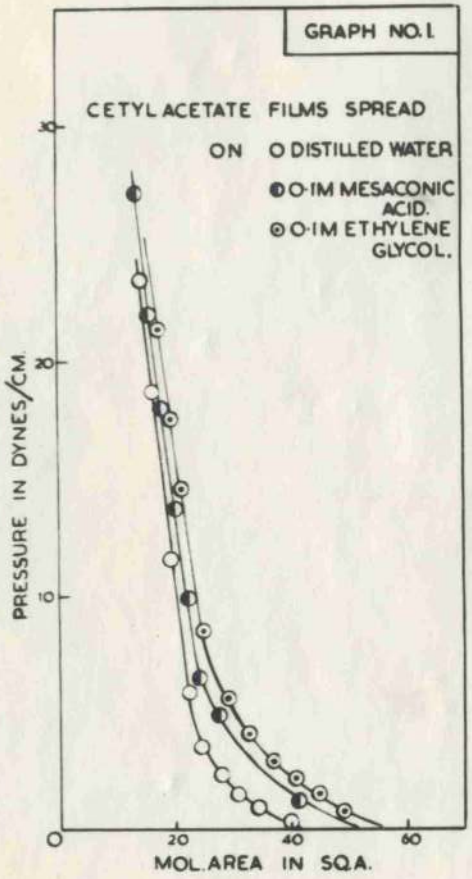
to form a complex with the spread material and penetrate the film. They still do not penetrate the micelles which are mixed with the film.

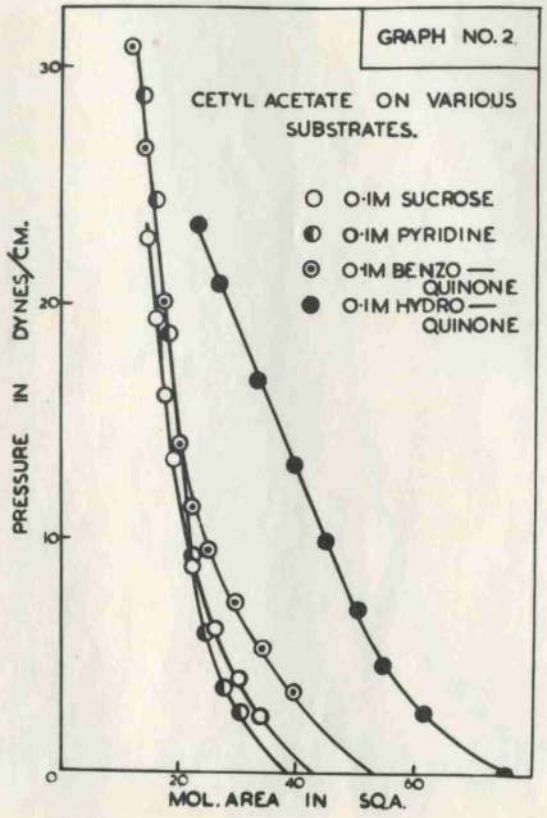
The attachment of disperse dyes to cellulose triacetate appears to be due to both polar and non-polar forces because a dye of this type, which is readily adsorbed by the cellulose acetate in the solid, when mixed with cellulose triacetate and spread as a mixed film gave no increase in film area. It is suggested that this dye fits exactly to the underside of the polymeric chains perhaps by Van der Waals' forces and polar forces.

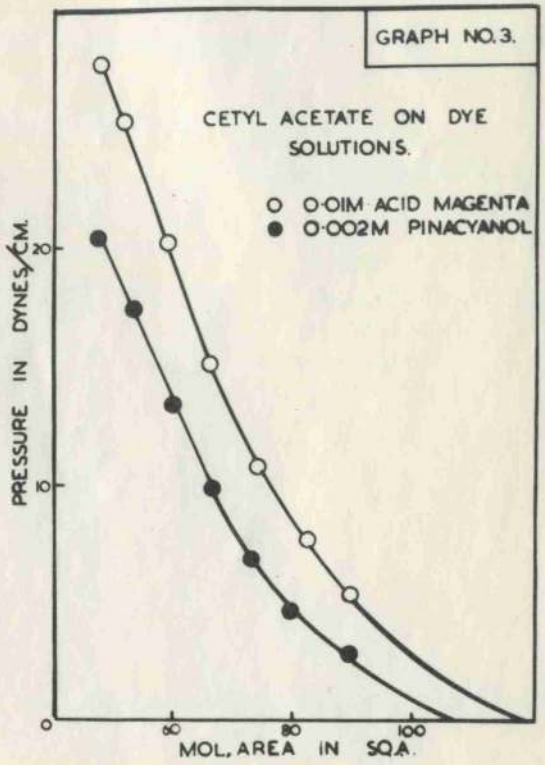
Acid dyes in acid solution expand casein films. With increase in pH the expansion decreases and at pH 7.0 approaches zero. This behaviour resembles the bulk adsorption of acid dyes by wool; the effect of pH is similar in both cases.

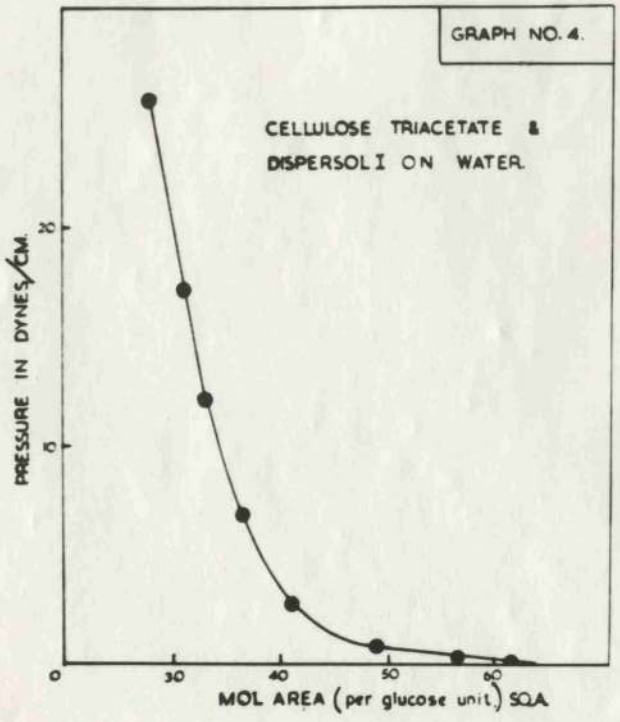
Note on use of molecular models.

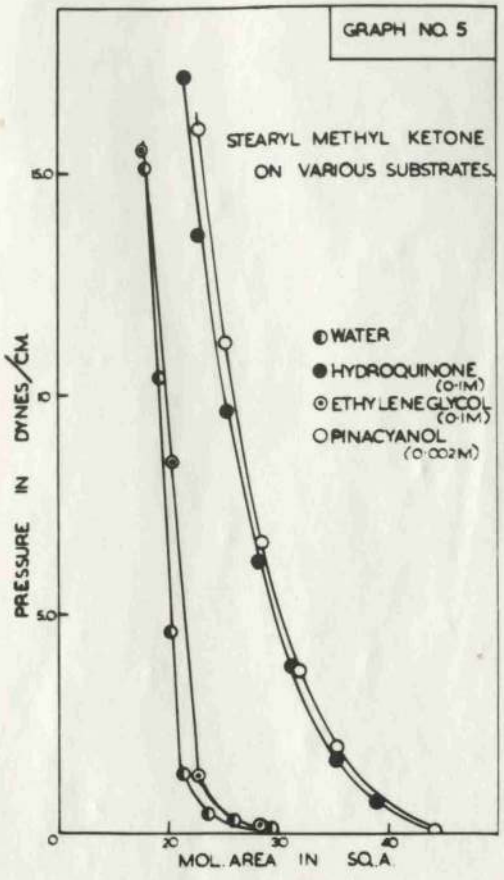
The approximate dimensions of the molecules were estimated by use of Stuart-type models (Catalin Ltd.). It appears from a study of these models that the aromatic portions of all the azo dye molecules are planar, and the theoretical values quoted, which are given to the nearest 5Å, represent the smallest rectangle enclosing the projection of the model, no allowance being made for solvated water molecules around the sulphonate groups.

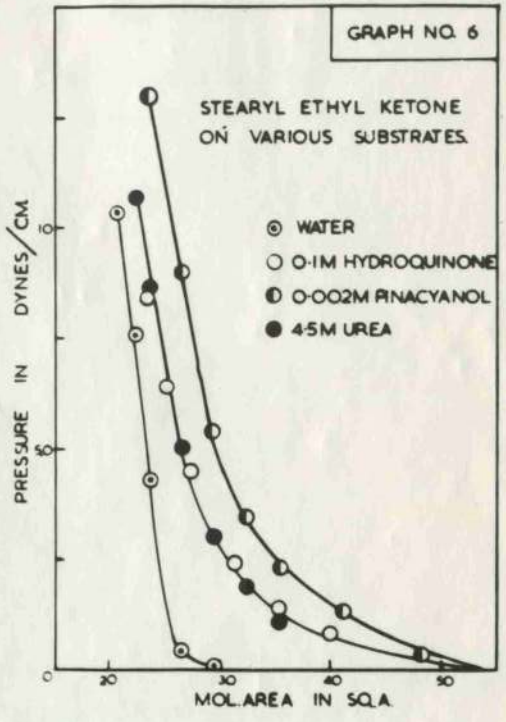

GRAPH NO. 1.
CETYL ACETATE FILMS SPREAD
ON O DISTILLED WATER
O·1M MESACONIC ACID.
O·1M ETHYLENE GLYCOL.
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

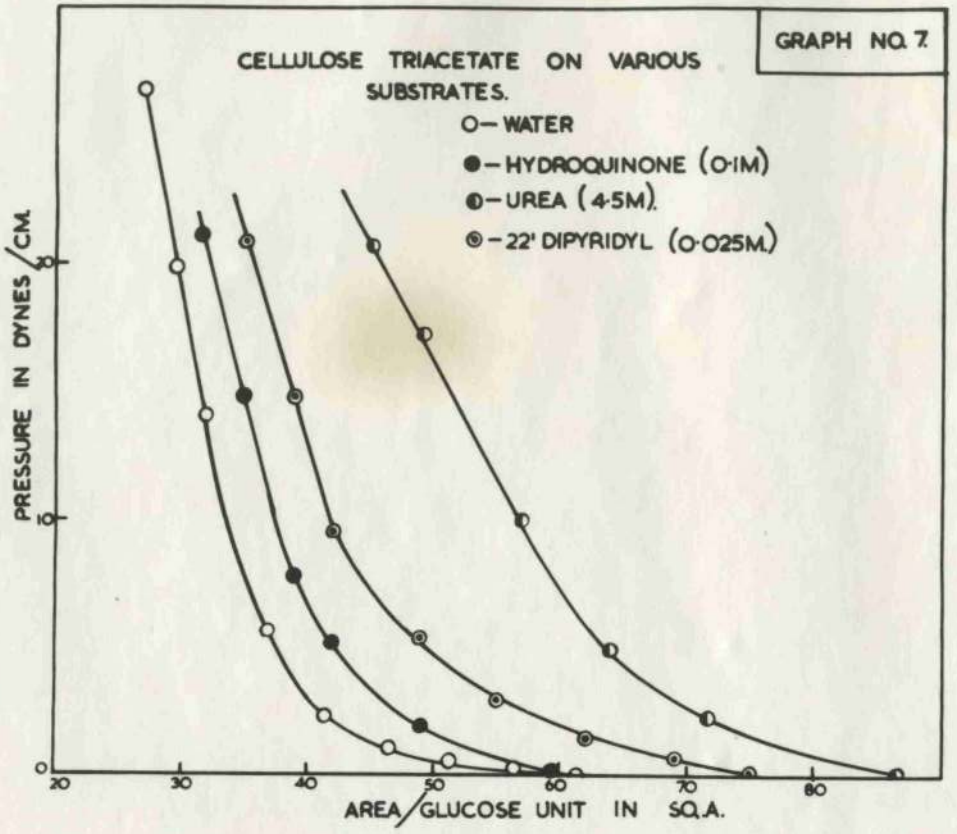

GRAPH NO. 2.
CETYL ACETATE ON VARIOUS SUBSTRATES.
O·1M SUCROSE
O·1M PYRIDINE
O·1M BENZO — QUINONE
O·1M HYDRO — QUINONE
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

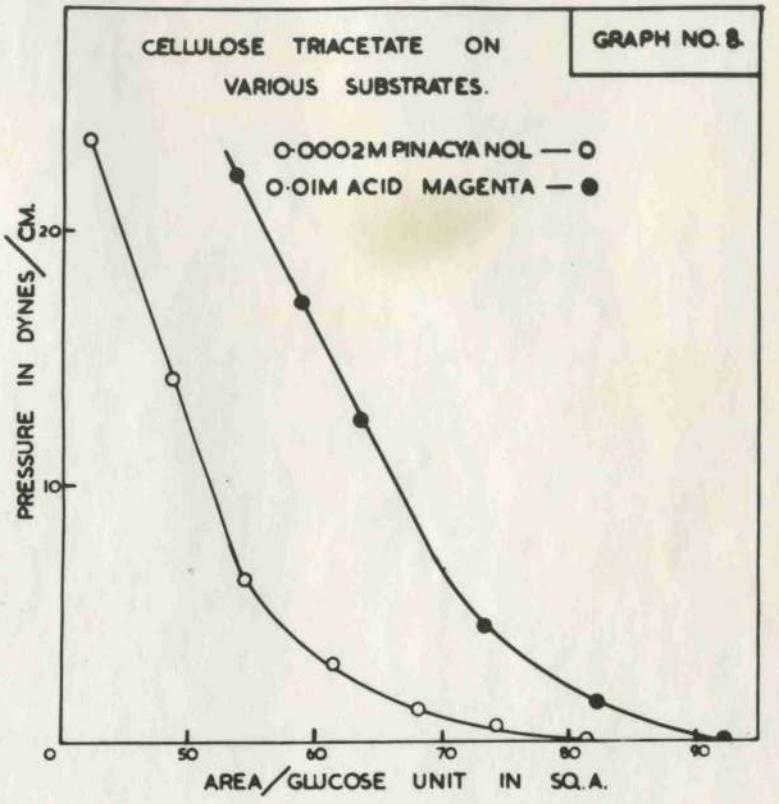

GRAPH NO. 3.
CETYL ACETATE ON DYE SOLUTIONS.
O·01M ACID MAGENTA
O·002M PINACYANOL
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

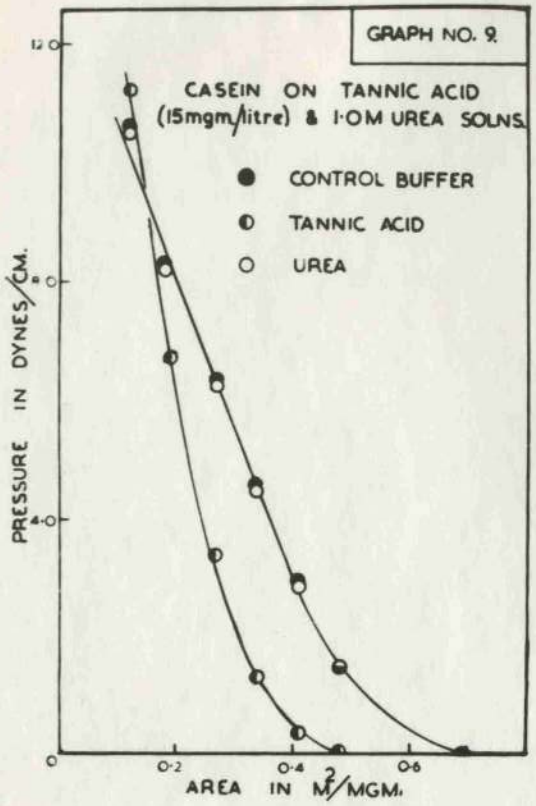

GRAPH NO. 4.
CELLULOSE TRIACETATE &
DISPERSOL I ON WATER.
PRESSURE IN DYNES/CM.
MOL AREA (per glucose unit.) SQ.A.

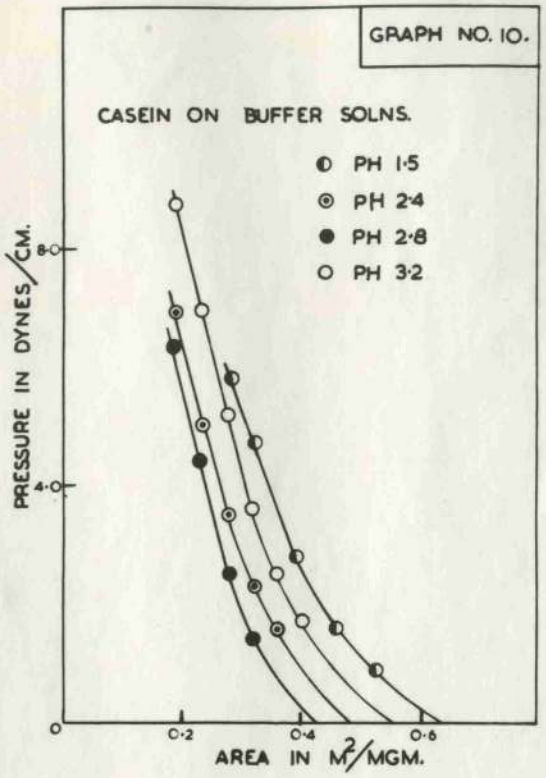

GRAPH NO. 5
STEARYL METHYL KETONE
ON VARIOUS SUBSTRATES.
WATER
HYDROQUINONE (0·1M)
ETHYLENE GLYCOL (0·1M.)
PINACYANOL (0·002M)
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

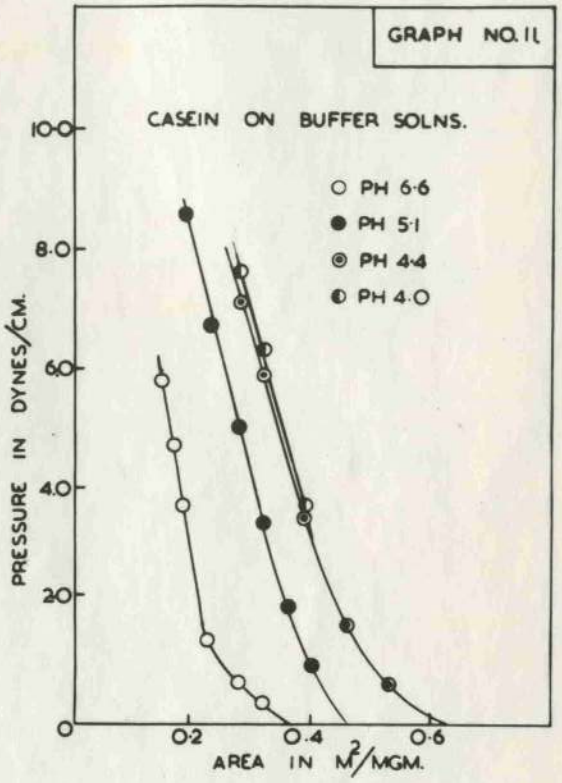

GRAPH NO. 6
STEARYL ETHYL KETONE
ON VARIOUS SUBSTRATES.
WATER
0·1M HYDROQUINONE
0·002M PINACYANOL
4·5M UREA
PRESSURE IN DYNES/CM.
MOL. AREA IN SQ.A.

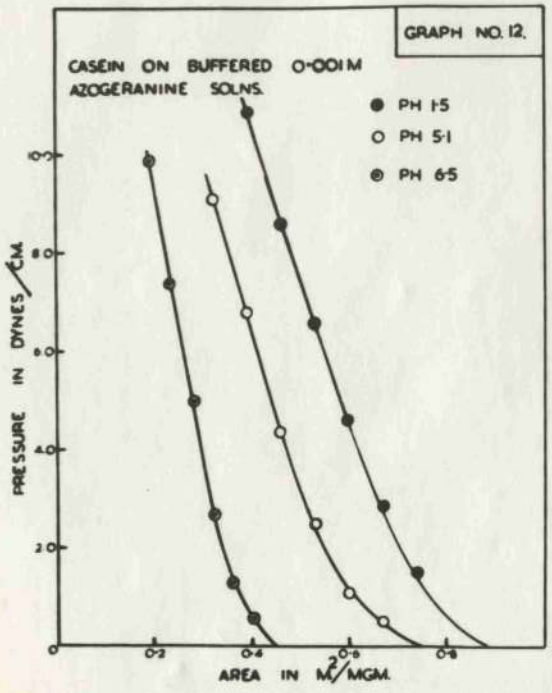

GRAPH NO. 7
CELLULOSE TRIACETATE ON VARIOUS SUBSTRATES.
O— WATER
●— HYDROQUINONE (0·1M)
◐— UREA (4·5M).
◎— 22' DIPYRIDYL (0·025M.)
PRESSURE IN DYNES/CM.
AREA/GLUCOSE UNIT IN SQ.A.

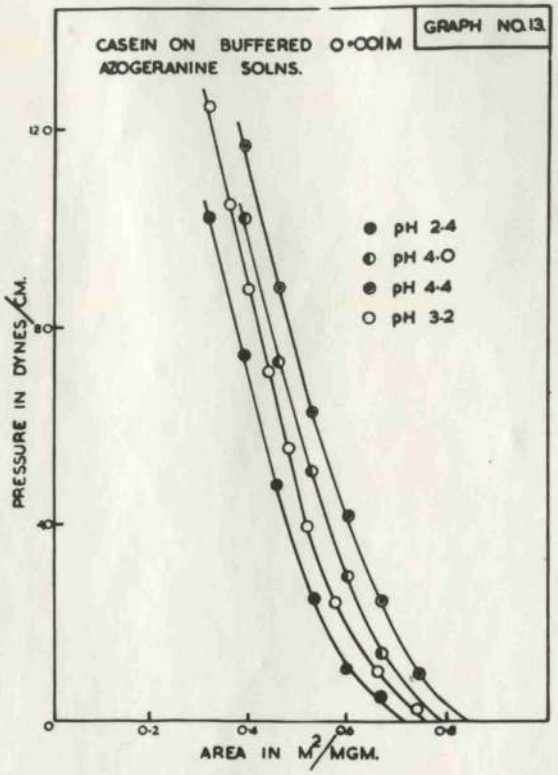

GRAPH NO. 8.
CELLULOSE TRIACETATE ON VARIOUS SUBSTRATES.
0·0002M PINACYANOL — O
0·01M ACID MAGENTA — ●
PRESSURE IN DYNES/CM.
AREA/GLUCOSE UNIT IN SQ.A.

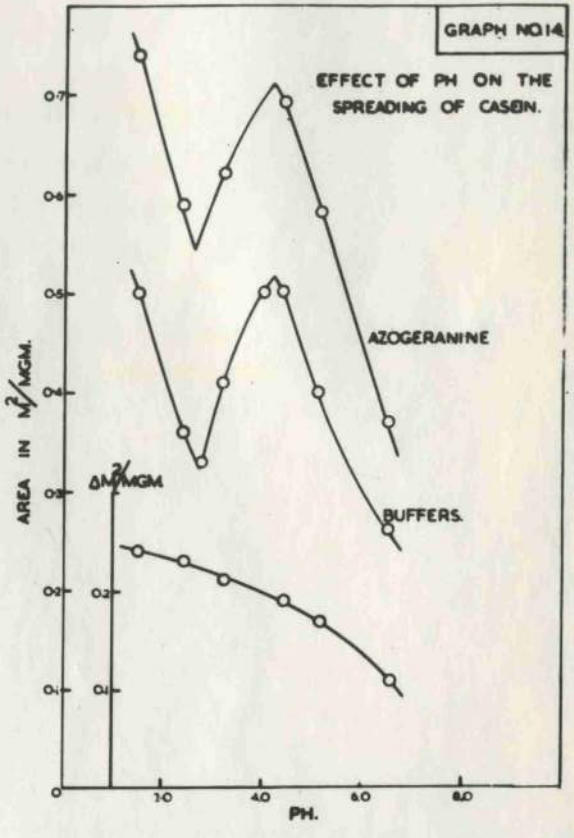

GRAPH NO. 9.
CASEIN ON TANNIC ACID
(15mgm/litre) & 1·0M UREA SOLNS.
CONTROL BUFFER
TANNIC ACID
UREA
PRESSURE IN DYNES/CM.
AREA IN M²/MGM.
0·2
0·4
0·6

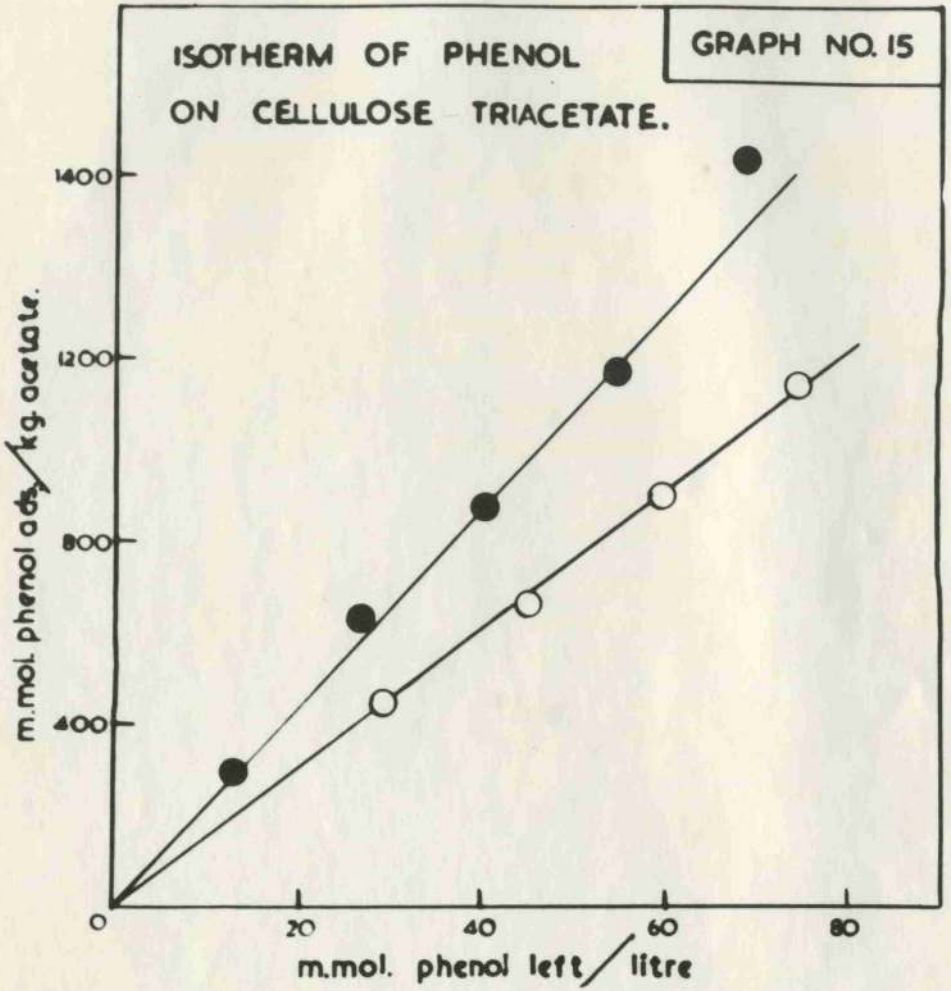

GRAPH NO. 10.
CASEIN ON BUFFER SOLNS.
PH 1·5
PH 2·4
PH 2·8
PH 3·2
PRESSURE IN DYNES/CM.
AREA IN M²/MGM.
0·2
0·4
0·6

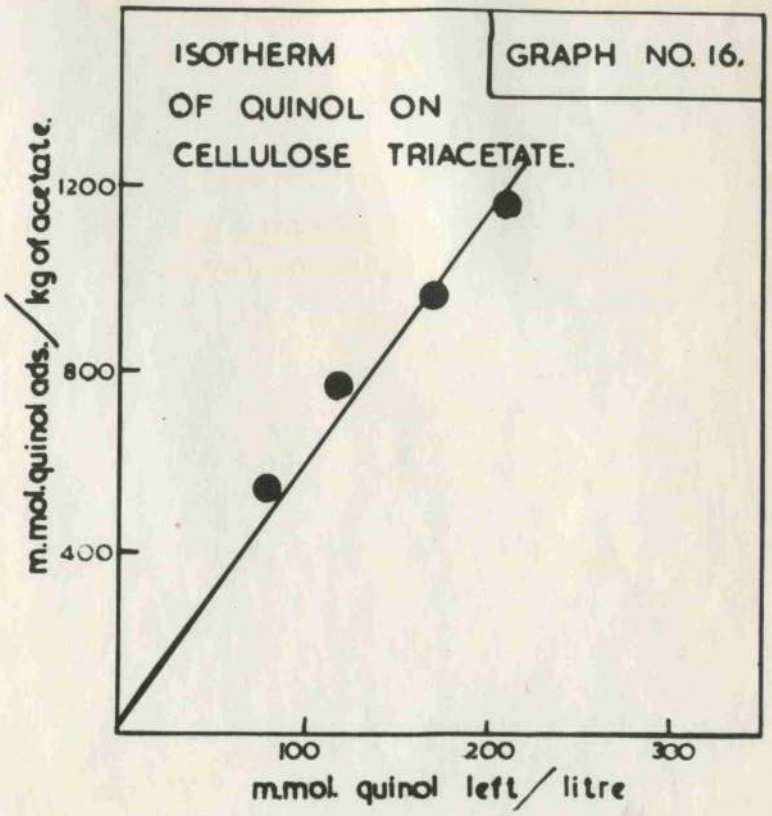

GRAPH NO. 11.
CASEIN ON BUFFER SOLNS.
PH 6·6
PH 5·1
PH 4·4
PH 4·0
PRESSURE IN DYNES/CM.
AREA IN M²/MGM.
0·2
0·4
0·6


GRAPH NO. 12.
CASEIN ON BUFFERED 0·001M AZOGERANINE SOLNS.
PH 1·5
PH 5·1
PH 6·5
PRESSURE IN DYNES/C.M.
AREA IN M²/MGM.


GRAPH NO.13.
CASEIN ON BUFFERED 0·001M AZOGERANINE SOLNS.
pH 2·4
pH 4·0
pH 4·4
pH 3·2
PRESSURE IN DYNES/C.M.
AREA IN M²/MGM.


GRAPH NO.14.
EFFECT OF PH ON THE SPREADING OF CASEIN.
AZOGERANINE
BUFFERS.
AREA IN M²/MGM.
PH.


ISOTHERM OF PHENOL
ON CELLULOSE TRIACETATE.
GRAPH NO. 15
m.mol. phenol ads./kg. acetate.
1400
1200
800
400
0
20
40
60
80
m.mol. phenol left/litre


ISOTHERM
OF QUINOL ON
CELLULOSE TRIACETATE.
GRAPH NO. 16.
m.mol. quinol ads./kg of acetate.
1200
800
400
100
200
300
m.mol. quinol left/litre

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