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STUDIES IN THE PHYSICAL STATE OF DYESTUFFS.

by

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A Thesis submitted to the University of Glasgow  
in accordance with the regulations governing  
the award of the Degree of Master of Science  
in the Faculty of Science.

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Publications

The following papers have been prepared for publication:

- 1) "Some Statistical Relationships between Molecular Geometry of Dyes and their Fastness Properties", by C.H. Giles, K.V. Datye, N.B. Shah and D. Smith, submitted to Textile Research Journal.
  
- 2) "Association of Aromatic Solutes in Ion Exchange Adsorption", by I.A. Easton, C.H. Giles, R.B. McKay, C.C. Patel, N.B. Shah and D. Smith, submitted to Faraday Society.

SUMMARY

The first part of this thesis deals with a statistical survey of the Colour Index data on fastness properties of dyes and its relation to their molecular constitution. Both washfastness and resistance to migration of a group of acid dyes on wool rise directly with the molecular weight of the dye. Chrome mordant dyes, which may be regarded as forming 1,1 - or 2,1 - dye metal complex on the wool fibre, also display a similar trend. This may be attributed either to an increase in molecular weight by the formation of the dye-metal complex, or to the formation of firmer dye-fibre bonds through chelation with chromium.

Various attempts were made to correlate lightfastness with washfastness of acid dyes on wool and of direct dyes on cotton, but the results were not significant. There is, however, a relation between lightfastness and anionic weight for a group of acid dyes.

There is an inverse relation between molecular axial ratio and lightfastness of anthraquinone vat dyes on cotton; lightfastness decreases with increase in the ratio of molecular length to width. The molecular geometry of acid and direct dyes does not vary enough for significant trends / ...



trends to be revealed. There is, however, a significant correlation between molecular axial ratio and the proportion of fading caused by the visible spectral region (McLaren's data). Both these results are attributed to the formation of more stable aggregates with decrease in molecular axial ratio, though the result may be influenced by chemical factors.

The second part of the thesis deals with studies in the association of dyes at inorganic surfaces. Theories of solution adsorption have been applied to interpret the adsorption results. The concept of 'coverage factor' has been fully developed and a direct relation between ( $\log_{10}$ ) coverage and ( $\log_{10}$ ) ionic weight of fully conjugated dyes has been found. This relation may be used to find the suitability of a dye for specific surface area measurement. Unconjugated or imperfectly conjugated dyes do not appear to obey the relation. An empirical approach has, however, been sought to fit them to the relation and it has been shown that the size of the micelles may be governed by the average size of the individual conjugated systems in a dye molecule.

These experiments have revealed that "coated" titania (i.e. titania treated in manufacture with silica and / ...

and alumina) appears to lose its surface area and its hydrogen bonding capacity for some dyes, on ageing at room temperature. Uncoated titania does not do so. Furthermore the ageing effect on coated titania appears to be partly reversible and a part of the lost surface area can be recovered on heating the sample.

Basic triphenylmethane dyes display an endothermic adsorption effect on alumina. This anomalous effect has been explained on the basis of the theory of resonance. The amount of a dye adsorbed at room temperature is governed by its ionic weight, but at higher temperature it may be governed by the number of resonating forms by which it can be represented. The aggregates of dye molecules formed on the substrate surface at a higher temperature are supposed to be of different structure from those formed at room temperature. It is suggested that at higher temperatures the reaggregation of dye molecules on the substrate surface occurs so as to reduce the free energy to a minimum. This favours the building up of larger and more stable aggregates.

PART I

SOME STATISTICAL RELATIONSHIPS BETWEEN MOLECULAR  
GEOMETRY OF DYES AND THEIR FASTNESS

## INTRODUCTION

The aim of the present work was to examine statistically some possible relationships between the molecular geometry of dyes and their fastness properties. Several attempts have been made in the past and in recent years to correlate the chemical constitution of dyes with their fastness properties. Many outstanding discoveries in the field of organic synthetic chemistry have led to the development of innumerable colorants with a variety of structural features, and this especially has made more difficult the task of a colour chemist in trying to correlate chemical constitution with fastness properties. The difficulties are increased by the frequent introduction of new synthetic fibres with different properties. Different fibres exhibit different dyeing properties for a given group of dyes and hence the fastness properties of a particular group of dyes may vary with different fibres.

On account of the great complexity of the chemical factors involved, there is great difficulty in reducing them to order in relation to any given fastness property; a good example is the apparent impossibility of establishing any general relation between molecular constitution of dyes and their lightfastness. It was, therefore / ...

therefore, thought that an entirely new approach to the problem might be worthwhile; to attempt to relate mere geometrical shape of dye molecules to lightfastness by statistical methods. Statistical methods of analysis have been used successfully in this laboratory in the past in determining the significance of the relation between dye concentration to lightfastness.<sup>1</sup> It was hoped that the present work would be of similar value, in revealing, at least, some of the relations influencing various fastness properties.

#### Discussion of Prior Work.

The most important dyes for protein fibres are the so called acid dyes, which are sodium salts of aromatic sulphonic acids.

The early acid dyes were simple monoazo types with relatively low molecular weight and small molecular dimensions, but it was found that polyazo dyes gave much higher wet fastness.<sup>2</sup> Ultimately it was established that this observed effect was mainly due to the increase in molecular weight or rather decrease in solubility, for if the molecular weight is increased without alteration of the number of solubilising groups, the wet fastness is increased. If, however, a further solubilising group is / ...

is introduced, the fastness is decreased. The structures of the Carbolan dyes (I.C.I.) are based on this principle: the molecular weight is increased and the solubility is decreased by the introduction of long chain alkyl groups. Meggy<sup>3</sup> has developed a theory suggesting that the affinity of acid dyes for wool is largely due to the fact that the bulk of the dye and of the fibre is hydrophobic, and that on dyeing the two hydrophobic surfaces can come together with a reduction in potential energy. This fact is supported by Lemin's<sup>4</sup> work; he showed that the affinity of acid dyes on wool bears a direct relation to the molecular weight and is independent of the number of substituent groups.

The effect of a sulphonate group is to impart solubility to the dye molecule and as mentioned above, with an increase in the number of solubilising groups, wet fastness is impaired, probably because of the greater affinity of the solubilising groups for water than for the fibre. Nicholls<sup>5</sup> demonstrated that under alkaline conditions the rate<sup>of</sup> desorption of an acid dye increases with increase in number of its sulphonate groups, because of the mutual repulsion of the anionic groups in the fibre and the dye.

The rate of dyeing of wool and gelatin with acid dyes decreases with increase in the number of sulphonate groups in the dye molecule, according to Tolia et al.<sup>6</sup> Thus an increase in sulphonate groups has a retarding effect on dyeing, suggesting that the diffusion rate depends on the affinity of dye for the substrate; the greater the affinity, the slower the rate of diffusion. This relation, however, is in an opposite sense to Gilbert's<sup>7</sup> calculations; according to which the affinity decreases by about 1 Kcal./mole. for each sulphonate group added. The results of Tolia et al.'s tests could be explained on the ground that with increase in basicity the size and molecular weight of the dye increases and this may outweigh the corresponding effect due to the decrease in affinity.

Substituents reduce the diffusion rate of a dye, thus improving wet fastness on wool. Many workers have tried to relate diffusion coefficient with molecular weight or molecular size of dyes. In the case of disperse dyes on polyesters, Sekido<sup>8</sup> found a relationship between molecular volume and the square root of diffusion coefficient in films, and Glenz and co-workers<sup>9</sup> found a relation between molecular size of disperse dyes (as expressed by the maximum length / ...

length x breadth x thickness) and the reciprocal of the diffusion coefficient in polyester fibres, but in both these cases there is a wide scatter of results. Odajima<sup>10</sup> found a linear relationship between the logarithm of the diffusion coefficient and the square root of the molecular weight of the dye, for three series of data; two for anthraquinone and azo disperse dyes on secondary cellulose acetate and one for acid dyes in a co-polymer of 6-nylon and 6,6-nylon. Tolia et al.<sup>6</sup> have recently obtained a linear relationship between the number of substituent groups in the dye, or the molecular volume, and the logarithm of a simple function of the adsorption rate. In each series of dyes used the rate decreases with increase in molecular volume. They concluded that the geometry of the dye molecule and the nature and number of the substituent groups are the rate determining factors.

It has sometimes been suggested that the high fastness to washing of dyes applied to wool with chrome mordant, is due to wool-chromium-dye bonding.<sup>11</sup> Race et al.,<sup>12</sup> after finding that the lakes formed by certain chrome dyes in wool are the 2 ; 1 - dye metal complexes, suggested that the high fastness properties of all chrome-mordanted wool dyes are mainly due to the increase in molecular size and not / ...



not due to any additional dye-fibre bond through the chelated chromium atom. Later, Baxter et al.<sup>13</sup> studied the fading curves of a number of dye-metal complexes and suggested that their high fastness is due to the presence of aggregates, which would also account for their high wet fastness.

Most of the azo direct cotton dyes made from benzidine coupled with sulphonated naphthalene derivatives have very poor fastness properties, in spite of their very high substantivity for cellulose. The presence of solubilising groups is responsible for the poor wet fastness. Basic dyes, which may be regarded as very soluble 'onium' compounds also possess very poor fastness properties. Aftertreatment sometimes changes the hue of the dye completely, which is undesirable. Also, while one fastness property is improved, another may be impaired; under such circumstances a compromise between the two effects has to be made. Aftertreatments of direct dyeings with copper sulphate, formaldehyde, diazotization and development, cationic agents, resins, etc. have all been recommended.

Azoic and vat dyes, which are outstanding in all-round fastness properties are applied to cellulosic fibres / ...

fibres in a soluble form and then insolubilised in situ. Because of their special structural features they are capable of forming large aggregates which are rigidly trapped in between the fibre polymer chains,<sup>14,15</sup> and thus their accessibility to any external agency which would destroy them, is reduced to a minimum. This is the reason for their high all-round fastness properties on cellulosic fibres.

The fastness of a dye to light or other agencies does not necessarily bear any relation to the stability of the pure dye in the solid state or in solution, but to the properties of a dyed or coloured material, such as a textile fabric. The action of light on a dyed fibre depends on the constitution of the dye, the nature of the fibre, the presence of other constituents in the fibre, the composition of the atmosphere and the source of the light.

The sequence of oxidation reactions of azo dyes<sup>16</sup> in an aqueous medium is assumed to be a similar one to that in the light fading mechanism. The possible existence of a tautomeric hydrazone form of azo dyes has been reported by a number of workers.<sup>17,18</sup> Giles and Desai<sup>16</sup> have postulated that the hydrazone form is the important one in the series of reactions in light fading, and that hydrolysis of hydrazone / ...

hydrazone followed by oxidation of the products takes place; and they suggested that there is a relation between difficulty of oxidation and lightfastness. Thus, the resistance to oxidation and hence to light fading would be in the following descending order:- 2,4 - dinitro aniline > o-nitro aniline > p-nitro aniline > m-nitro aniline > aniline, which was actually proved experimentally. Atherton and Seltzer<sup>19</sup> and later Atherton and Peters<sup>20</sup> also confirmed similar effects of substituents on lightfastness. These effects were studied in more detail in this laboratory and the authors<sup>21,22</sup> showed that they are linearly related to the Hammett  $\sigma$  - constant of the substituent group.

Studying the effect of hypochlorite on dyeings with direct and vat dyes, Darye et al.<sup>23</sup> showed that dyes having an amino group ortho to an azo group in both the end components are less susceptible to oxidation than those with an amino group in a similar position in either of the two end components. Furthermore, they found that the o-hydroxyazo compounds are oxidised more easily than the corresponding o-aminoazo dyes, and that benzidine dyes are themselves less susceptible to oxidation than the corresponding o-substituted benzidine dyes.

Planar dye molecules sulphonated only at one end are surface-active and tend to have lower lightfastness than the corresponding symmetrically sulphonated ones.<sup>24</sup> Again an increase in sulphonate groups often increases the lightfastness of acid dyes on wool, possibly due to the increased strength of the ionic dye-fibre links or to the stabilization of the dye micelles in the substrate. A small increase in surface-activity, by the introduction of a short alkyl chain usually improves lightfastness, but a long alkyl chain, which increases surface-activity markedly, seems to have an adverse effect.

It has been shown that symmetry of substitution in disperse dyes reduces their solubility in water and their maximum adsorption by cellulose acetate, possibly because of the greater intermolecular forces, forming more stable crystallites.<sup>25</sup> This increased stability of the crystal structure of symmetrically-substituted anthraquinones may be the cause of their high lightfastness on Terylene (I.C.I.).<sup>26</sup> In the case of a large number of direct cotton dyes, Sekido<sup>27</sup> observed that the presence of free amino- or hydroxy-groups in the dye molecule tends to reduce fastness.

The effect of planarity on the substantivity  
of / ...

of disperse dyes on cellulose acetate and vat dyes on cellulosic fibres has been studied by Daruwalla et al.<sup>28</sup> They synthesised two series of coplanar dyes from naphthaquinones and corresponding to each dye they obtained the nonplanar compound. They confirmed the findings of Giles et al.<sup>25,26</sup> and showed that when a hydrophilic group e.g. - CH<sub>2</sub> CH<sub>2</sub>OH is present in a disperse dye molecule the affinity and saturation absorption by cellulose acetate decreases. Again in each pair of dyes the partition coefficient, affinity and saturation value were considerably higher for the coplanar dye than for the corresponding nonplanar one. Similarly they proved the importance of planarity in leuco-vat dyes for imparting substantivity to cellulosic fibres. Filippychev<sup>29</sup> showed that the colour of a dye with separated conjugated systems is mainly defined by the nature of the insulating group. If it is weak the resulting colour is merely additive because of the lack of mutual interaction between the two conjugated systems. Such dyes are less substantive and light fast than those with fully conjugated systems. Azo dyes with uninterrupted conjugation are more substantive than related compounds with interrupted conjugation. Among the straight chain polyazo dyes the most light fast structures / ...

structures are those with  $\geq 3$  azo groups. Also resistance to tautomeric change favours the light resistance of a dye molecule.

The importance of the physical state of a dyestuff on the substrate has been extensively investigated in this laboratory<sup>13,30</sup> and it has been emphasised as one of the most important lightfastness governing factors. Many of the dyes, whether soluble or insoluble, are present in the fibre as heterogeneous collections of particles ranging from a monomolecular dispersion to large aggregates of discrete particle size. Since fading of a dye on the substrate is supposed to take place at the surface, the more aggregated dye tends to be faster to light than the less aggregated one. Aggregates of the dye molecules can grow more easily in fibres of low than those of high crystallinity, so that highly porous fibres have a general tendency to show good lightfastness.

The most definite experimental evidence connecting lightfastness with the physical state of the dye in the fibre is that of Bean and Rowe<sup>31</sup> and by Weissbein and Coven<sup>32</sup>. Bean and Rowe observed that aftertreatments, e.g. soap-boiling, boiling in water, steaming, etc. applied to azoic dyes on cellulose caused crystal growth and increased the resistance / ...

resistance to fading. The increased lightfastness of vat dyes on nylon after steaming has been attributed to a similar effect. Valko<sup>33</sup> observed the existence of the aggregates of leuco-vat dyes and indigosol dyes by diffusion measurements and also observed crystallization phenomenon of these dyes in the fibre by X-ray diffraction. The direct and more recent evidence of the presence of aggregates is that of Weissbein and Coven.<sup>32</sup> They detected aggregated particles in cellulose films, dyed with dyes of good fastness, by electron microscopy, but none could be detected in those dyed with dyes of poor fastness.

The structure of the dye molecule controls the uniformity of the size of the adsorbed particles, and the structure of the fibre controls the distribution and the growth of the particles. Vat dyes, some fast-to-light direct dyes, and neutral dyeing metal-complex dyes seem to form large particles of uniform size.<sup>30</sup> Their fastness at low shade depths is generally very good. Azoic and sulphur dyes, however, form a wide range of particle sizes, increasing in size with concentration. Sumner et al.<sup>34</sup> employed a spectrophotometric method with polarized light and found that soaping of vat-dyed cellulosic material accelerates the change of leuco-dye to its oxidised form.

At / ...

At the same time leuco-vat dye molecules originally oriented parallel to the fibre axis are re-oriented in a perpendicular direction. Morton<sup>35</sup> found that certain direct dye molecules in a highly crystalline cellulosic fibre (ramie) seemed to be oriented as single molecules attached parallel to the cellulose chains.

Several authors<sup>36,37</sup> have suggested a relation between lightfastness and dye-fibre bond strength, i.e. dye affinity. The stronger this bond, the more readily can the dye molecule pass on its absorbed light energy to the substrate and therefore reduce the possibility of the primary photolytic breakdown of the dye. If this hypothesis were true, then all the reactive dyes covalently linked to the cellulose would have high lightfastness, but this is not so. There are, however, some cases in which increase in the strength of the dye-fibre bond may perhaps raise the lightfastness. These systems are: (i) basic dyes-polyacrylonitrile fibres. Wegmann<sup>38</sup> has pointed out that some basic dyes, in a given series, may show an increased tendency to form covalent bonds with the fibre and also have better lightfastness than others in the series. This effect may not be due to the suggested cause, since there is a reversal of fastness ranking at low concentration. This / ...



This can only be explained by changes in the physical form of the dyes. (ii) Direct dyes on cotton. Gill<sup>39</sup> suggested that cationic aftertreatment reduces lightfastness of direct dyes on cellulose, on the ground that cationic agents lose their close bond to the fibre molecule. The situation, however, is not so simple as this because fastness, especially in weak depths, is often improved by these agents. Also direct dyes while having the same affinity value on viscose rayon as on cotton, yet exhibit higher fastness grades on viscose.<sup>1</sup> This applies to direct, vat and reactive dyes.<sup>36</sup> (iii) Acid dyes on protein fibres. It has been already shown that increase in the number of sulphonate groups in an acid dye molecule usually increases lightfastness on wool. This may be due to increased strength of ionic dye-fibre link, but at the same time the effect of change of physical state of the dye produced by change in the relative positions of sulphonate groups cannot be ruled out.

The phenomenon of aggregation of vat dyes on the fibre is attributed to the molecular attraction (non-polar van der Waals forces as explained later) between the cellulose molecule and the dye molecule. After oxidation the monomolecular layer of the dye molecules on the walls of / ...

of the submicroscopic pores of the cellulose becomes unstable or metastable and, depending upon the adhesion strength and the magnitude of the tendency to crystallise, the monomolecular film will be disrupted to form aggregates.

The origin of affinity forces in vat dyes appear to lie in non-polar rather than polar forces.<sup>3,14,15,40</sup> The molecules in general are non-linear in shape and not all of them contain hydrogen bonding groups. In addition to the polar forces there must be present non-polar van der Waals forces, which can arise when complex aromatic molecules are brought in close contact with the substrate. These short range forces are additive and extend over the entire surface of the molecule. The results of affinity measurements confirm that affinity increases with molecular complexity, i.e. molecular weight, and it is sensitive to the planarity of the molecule. However, polar hydrogen bonding forces cannot perhaps be totally neglected, since as observed by Peters and Sumner,<sup>15</sup> simple anthraquinone derivatives are not at all substantive to cellulose whereas 1, arylamido-anthraquinones are substantive. These authors also pointed out the possible existence of the amide group in the imino form, thus setting up a conjugated chain including the whole molecule, which would account for the increased / ...

increased affinity with increase in conjugation (Shirm's hypothesis).<sup>41</sup>

The absorption of light by a molecule is related to the conjugation in the molecule. Therefore the extinction coefficient of the band of longest wavelength should be proportional to the effective area of  $\pi$ -electrons in the molecule, which in turn is the area available for the van der Waals attraction. This was shown to be true for the benzamido anthraquinones. The affinity increases with the number of condensed rings in the dye, as shown by the large affinity value of leuco-Caledon Jade Green XN. Since colour is related to the number of  $\pi$ -electrons available, so will be the van der Waals bonding forces; it must then be assumed that colour and affinity are determined by the same properties of the molecule.

Giles and Hassan<sup>42</sup> found that in the case of long conjugated direct dye molecules, the affinity values plotted against the logarithm of the number of double bonds gave a better relation than the above relation shown by Peters and Sumner.

The energy associated with light radiation is given by the equation,  $E = hv = h\frac{c}{\lambda}$ , where  $h$  = Planck's constant;  $v$  = frequency of light;  $c$  = velocity of light;  $\lambda$  = wavelength of light.

It could be seen from this equation that the energy associated with a quantum of light increases with decrease in wavelength or with increase in its frequency. Any photochemical change brought about by the absorption of light by the molecule is dependent upon the energy of the absorbed light and hence on the wavelength. Fading of a dye on the fibre is a process brought about by the absorption of ultraviolet and visible light. On general principles it might be expected that the effectiveness of light in fading would depend upon the wavelength of light, ultraviolet light being the most effective and red the least. In fact the actual relation between wavelength and fading power of a radiation of light is complex.

Recently McLaren<sup>43</sup> investigated the relative effectiveness in fading of two broad spectral regions, the blue-red and the ultraviolet, on over 100 dyes of a variety of types on different substrates. He found that wavelength is generally related to the normal lightfastness of the dye. There is a critical wavelength for each particular dye and this wavelength decreases as the resistance to fading increases. Since in daylight there is a preponderance of long wave radiations, fugitive dyes are mainly faded by the visible range of radiations and those / ...

those with high normal lightfastness are in general faded by ultraviolet and violet radiations. Luszcak and Zukriegel<sup>44</sup> found a similar relationship between fastness grade and wavelength ( $\lambda$ ) of the characteristic absorption wave band of the ultraviolet region; the shorter is this wavelength, the higher is the fastness rating; and fading is caused mainly by an absorbed wave band with a well defined upper boundary beyond which the absorbed light is ineffective.

Kebasa and Maerov<sup>45</sup> studied the effect of sunlight on the fading of basic dyes on polyester fibre and found that the most effective spectral region lies between 3500 A. and 4250 A. Light below or above this region is less effective. The main factors responsible for this effect are: (i) normal light contains a very low proportion of radiation below 3500 A. and the polymer strongly absorbs it, (ii) above 4250 A. the quantum yield in fading is very low.

Bedford,<sup>46</sup> having studied thoroughly the daylight fading of three dyeings under a series of filters, and employing a laborious method of computation for his final results, arrived at conclusions which showed good qualitative agreement with McLaren's results.

EXPERIMENTAL

All the lightfastness tests are the British (B) or Continental (C) tests for normal shade depths taken from the Colour Index.<sup>48</sup> For a note on washfastness of acid dyes and chrome mordant dyes on wool - see reference number 48b; the figures for "alteration" are used here. For the measurement of molecular axial ratio of all the dye molecules in the present work, Catalin (Stuart type) molecular models are used. The "molecular axial ratio" of a dye molecule, in its most probable orientation, has been defined as the ratio of the maximum axial length to the width and is denoted by  $x/y$ , where  $x$  stands for the axial length, and  $y$  for the axial width. Since planarity of a dye molecule is one of the most important factors determining substantivity<sup>28</sup> and the physical state<sup>36</sup> of the dye, all the planar or nearly planar molecules are examined for lightfastness data ( Figs. 1A, B). All sulphonate groups are considered to be ionised. For other purposes all the dyes for which full molecular constitutions are shown in the Colour Index (volumes III and V) have been used. All the statistical data analysed by the standard method are presented in the Appendix, and the details of the Colour Index numbers, various fastness data and other data / ...

data used for the statistical analysis are given in tables.

## RESULTS AND DISCUSSION

### Relation between Molecular weight and Washfastness:

A - Acid dyes on wool. A direct relationship between molecular volume of an acid dye and its rate of dyeing on wool was previously established in this laboratory.<sup>6</sup> The larger the molecule the slower is the rate at which it can penetrate the fibre. This result was obtained by experiments of the dyeing rate of wool and gelatin with a limited number of acid dyes. Fern<sup>49</sup> also showed that there is a direct relationship between diffusion coefficient and washfastness for some acid dyes on wool. From the above results we might expect a direct relation of molecular size or weight against washfastness and an adverse relation against ease of migration. Thus it was decided to study the expected relations statistically, including all acid dyes. Following the observation of Nicholls,<sup>5</sup> that under alkaline condition the rate of desorption of acid dyes from wool increases with increase in the number of sulphonate groups, because of the negative affinity produced by the alkaline solution, it was decided to make the present comparison by grouping the dyes according to their degree of sulphonation. It will thus be expected that the larger the dye molecule the slower will be its desorption / ...



desorption during washfastness tests and the higher its washfastness.

To test this hypothesis, the structure and fastness of a variety of acid dyes were examined with the help of the Colour Index. The washfastness numbers and migration numbers were compared with the anionic weights of all the dyes. Washfastness values plotted against anionic weight are shown in Fig. 2. These data were statistically analysed, the statistical analysis being presented in the Appendix. It is seen that there is indeed a relation between the molecular weight and washfastness: the washfastness increases with increase in molecular weight. The results are highly significant statistically, accounting for 35% of the total regression. The rest of the significance must be due to other factors, perhaps, e.g., the crystalloidal or colloidal nature of the dye or its chemical constitution.

The plot of migration number on wool, for acid dyes with two or more sulphonate groups in the molecule, against molecular weight, is shown in Fig. 3. As expected, there is a relationship between these parameters: the migration number decreases with an increase in molecular weight. Statistical analysis of the data, presented in the Appendix / ...

Appendix, show that the relation accounts for 20% of the total regression. The other groups of acid dyes not shown gave no significant relation; probably they contained relatively too few dyes to give results of any significance.

B - Chrome mordant dyes on wool. After a direct relationship between anionic weight of acid dyes and their washfastness on wool had been established, it was thought that the washfastness of chrome mordant dyes on wool would show a similar trend. For the present purposes, chrome mordant dyes are included amongst acid dyes by doubling the anionic weight and adding the weight of one chromium atom. Inclusion of the chrome mordant dyes in the results in this way, is shown in Fig. 2. The statistical analysis presented in the Appendix shows that their inclusion does in fact increase the significance of the regression line, which accounts for 45% of the total regression. For the present investigation only those chrome mordant dyes with washfastness less than the maximum (grade 5) are included, because those graded 5 might in a more severe test have a higher grading.

Therefore the present results are quite consistent with the hypothesis that the high all-round fastness properties of chrome mordanted dyes are due to their high molecular / ...

molecular weights. Just recently, however, it has been pointed out that there is no definite evidence for the formation of only 2 : 1 dye-metal complexes by chrome mordant dyes on wool.<sup>50</sup> The complex may be either 2 : 1 - or 1 : 1 - dye-metal complex and the high all-round fastness properties of chrome dyes on wool may be due to the formation of firmer dye-fibre bonds through chelation with chromium. It can be seen from the fig. 2 that some of the metal complex dyes, in spite of having very high washfastness on wool, have comparatively low molecular weight. Their high washfastness may be attributed either to an increase in molecular weight by the formation of the complex or to the formation of firmer dye-fibre bonds.

#### Relation between Dye Affinity and Lightfastness:

It has been suggested, as stated above, that there is a relation between lightfastness of a dye on the fibre and the dye-fibre bond strength, i.e., the affinity of the dye for the fibre.<sup>36,37</sup> It is suggested that the energy absorbed by the dye molecule can more easily be transferred to the fibre, with an increase in the dye-fibre bond strength. On this reasoning Schaeffer<sup>51</sup> has traced a relation between washfastness and lightfastness in a variety of dye-fibre systems.

In the present investigation several attempts were made to find such a relation, but the results were quite disappointing. In fact there was no such relation found between washfastness and lightfastness in all the groups of dyes examined. In one case, however, there is a significant relation between lightfastness of a group of acid dyes on wool, and their anionic weight as shown in Fig. 4. Some other groups of dyes do not show this relation (Figs. 7,8).

The hypothesis is not confirmed, however, by the significant result shown in Fig. 4. The high significance, which accounts for 25% of the total regression, might be due to  $\frac{a}{\lambda}$  high degree of dye aggregation.

Relation between Molecular shape and Lightfastness:

In order to examine the working hypothesis that with shortening of the longest molecular axis of the dye, either (a) the number of possible points of attack by an oxidising agent is decreased, or (b) the crystal structure is strengthened, it was found necessary to plot molecular axial ratio of a dye molecule against its lightfastness. Since it is supposed that the dyes are present as aggregates in the fibre the effect (a) may well be masked by (b).

Jeffreys<sup>52</sup> found that certain cyanine dyes in methanol / ...

methanol solution fade more rapidly with increase in length of the polymethin chain; and that Hayashi and Shibata<sup>53</sup> showed that compactness and symmetry in the molecular structure of vat dyes are factors in improving their lightfastness on cotton.

Molecular axial ratio, i.e. the symmetry of shape of the dye molecule, and lightfastness, for a variety of groups of dyes, were plotted. The groups included direct dyes on cotton, anthraquinone and azo acid dyes on wool, and anthraquinone and indigoid vat dyes on cotton. The results are presented in Figs. 5, 6, 7, 8, 9. Statistical analysis of the data shows that there is a significant relation between symmetry of shape of anthraquinone vat dyes and their lightfastness on cotton. The regression line accounts for 26% of the total regression.

The statistical analysis shows that the geometrical factor is one of possibly many other factors influencing lightfastness. The chemical constitution of a dye molecule and the nature of its substituent groups are obviously important factors. The present relation, however, could not be detected in acid wool dyes or in indigoid vat dyes. This may be because they show only a limited range of ratios; in such cases the chemical nature of the substituent groups would / ...

would be more noticeable. Anthraquinone and azo acid dyes are all derived from much the same basic structures, with different substituent groups. Therefore it is conceivable that with a limited range of ratios, the nature of the substituent group rather than molecular symmetry would be more important in affecting lightfastness. In the case of direct cotton dyes the absence of such a relation could be explained on the ground that they almost all have similar basic structures. Again here also the chemical nature of the substituent group may well be more important, in their effect on lightfastness. 94 out of 136 bisazo direct dyes and 40 out of 54 trisazo dyes tested are in fact based on benzidine, and thus have very similar molecular shapes, but probably widely varying chemical reactivity due to the many different types of substituent group present.

Relation between Molecular Geometry of Dyes and Fading in different Wavebands:

McLaren<sup>43</sup> found, as stated, that wavelength is generally related to the normal lightfastness of the dye. Fugitive dyes are mainly faded by the visible range of light and those with high lightfastness are faded mainly by violet and ultraviolet light. The reason for this may be more physical than chemical. It was decided to examine the relation / ...

relation between molecular axial ratio and percentage fading caused by the blue-red region of the spectrum (McLaren's results), for all the dyes with planar molecules of given constitution, used by McLaren. The results are shown in Fig. 10. Statistical analysis presented in the Appendix shows that the relation is highly significant and accounts for 52% of the total regression. Thus it can be seen that with an increase in the molecular axial ratio of a dye molecule the proportion of fading caused by the visible region of the spectrum increases.

McLaren's results show that the fast dyes are faded mainly by only a narrow band in the violet and ultra-violet region of the spectrum. This, however, does not take into account the relative quantum efficiencies of the different wavebands. So it is very difficult to suggest any fundamental reason for the differences. Faster dyes appear to be more aggregated than the less fast. Thus it is possible that the geometrically symmetrical molecules come into closer contact with each other, as a result of which a closer packing in the crystal lattice can occur, resulting in greater stability. It is here assumed that such a close packing of the dye molecules actually takes place in the fibre. Now as the fading is caused by the absorption of energy / ...

energy in the form of light, it is conceivable that the breaking down of stable dye crystals requires very high energy short-wave radiation. This is a suggested explanation of the observed fact that symmetrical dye molecules are faded more by high energy short-wave radiations and unsymmetrical or less symmetrical molecules are faded more by the low energy visible radiation.



PART II

SOME ASPECTS OF THE ADSORPTION AT INORGANIC SURFACES

INTRODUCTIONAdsorption<sup>54,55,56</sup>

The atoms or molecules constituting solids are held together by different forces: electrostatic or coulombic forces, exchange or homopolar valence forces, van der Waals forces, etc. In most solids several of these are operative, with one or the other predominating, but an atom located inside the body is subjected to equal forces from all directions whereas an atom on the surface of a solid is subjected to unbalanced forces. It is attracted inwards and to each side by its neighbours, but there is no outward attraction to balance the inward pull. As a result of these unbalanced forces the surface of a solid is in a state of strain or unsaturation. It is the existence of this unsaturation at a solid surface, which is responsible for the phenomenon of adsorption. When a solid is in contact with any gas or solute in solution a considerable amount is taken up and concentrated on the surface of the solid, thereby saturating some of the unbalanced forces of the surface. A substance is said to be "adsorbed" if the concentration of the substance in a boundary region is higher than in the interior of the adjoining phase (usually a solid). The solid that adsorbs the / ...

the substance is called the "adsorbent", the substance which is taken up the "adsorbate". During the process of adsorption either of two things may happen; there may be either a weak interaction between the adsorbent and adsorbate, similar to condensation, or a strong interaction, similar to a chemical reaction. The former is called physical or van der Waals adsorption and the latter is called chemical adsorption or chemisorption.

### Interfaces:

In a system with an assembly of phases, the boundary between any two adjacent phases comprises an interface. The interface can be considered as a two-dimensional region with an accompanying restriction of molecular motion within this region. The interfaces formed by two phases may be: liquid-gas; liquid-liquid; solid-gas; solid-liquid; and solid-solid interfaces. All these interfaces are characterised by molecular thickness,<sup>54</sup> (i.e. ca. 100 A.), but are extended in length and breadth. Both the area and the thickness of the interface are of importance in the study of adsorption phenomenon.

Interfaces may be classified as mobile or immobile. Mobile interfaces include liquid-liquid and gas-liquid types. These are characterised by an effective interfacial tension under / ...

under which the surface always tends to contract spontaneously.<sup>57</sup> The molecules at a mobile interface are free to move continually and under the influence of orienting forces they set up an equilibrium. The phase so formed is a homogeneous one parallel to the interface.

Immobile interfaces, which include solid-liquid, solid-gas and solid-solid types may have different properties from those of mobile interfaces, in particular, properties mainly due to free molecular motion are more or less absent in immobile interfaces owing to the rigidity of the solid surface. Thus solid surfaces cannot contract spontaneously, and liquids do not spread over solid surfaces as easily as over surfaces of other liquids. The immobility of the surface particles of a solid causes the surface to be very uneven unless it is polished. The atoms in a solid surface stay where they are when the surface is formed. No two adjacent atoms or molecules can have the same adsorption characteristics. As a result the interface is normally heterogeneous.

Adsorption takes place in the interface. The substance adsorbed may originate in one or more continuous phases. The molecules of adsorbate pass from one phase into the interface, where they remain for a period of time. In / ...

In a reversible process the molecules can return to the phase from which they came or can reversibly pass into another phase, their place in the interphase then being taken by other molecules. At equilibrium the number of molecules entering the interface in a given time is the same as the number of molecules leaving the interface. The requirement for adsorption is, according to the definition, that the concentration of the substance in the interface is greater than its concentration in the continuous phase.

#### FORCES OF ADSORPTION

Whatever the nature of the force holding the atoms or molecules of a solid together, it can be regarded as a field of force around each ion, atom or molecule. Since at the surface of a solid the atoms or molecules are subjected to unbalanced forces, the field of force reaches some distance beyond the surface, attracting the molecules of a liquid (wetting and solution adsorption) or the atoms, molecules or ions of another solid (adhesion) or gas molecules (gas adsorption) and unless the molecules of the attracted substance possess a field of force, no attraction could occur.

The forces of attraction involved in the physical adsorption of gases or vapours are electrostatic in origin. There are three electrostatic effects which jointly account for the attractive van der Waals forces as follows:

(a) The orientation effect. Many uncharged molecules have dipole moments, and it was suggested by Kesson<sup>58</sup> that interaction between the dipoles is responsible for van der Waals attraction forces. The dipole molecules exert forces upon each other and tend to orient parallel to each other, the positive end of one being closest to the negative end of the other. On an average the attractive forces between two unlike poles of the molecules predominate over the repulsive forces between like poles, thus the net effect of orientation is that of attraction between two dipole molecules.

(b) The induction effect. Debye<sup>59</sup> showed that the orientation effect alone cannot account for van der Waals forces of attraction, because all the attracting molecules cannot always be permanent dipoles. He considered the influence of the field of a polar molecule on the field of a nonpolar one, and depending upon the degree of polarization of the latter, he calculated the magnitude of the attractive forces / ...

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forces between them. Since, in this case, the non-polar molecule is polarized under the influence of the field of the polar molecule, the effect is called a polarization or induction effect.

(c) The dispersion effect. The electrostatic origin of the forces of attraction between two molecules without a permanent dipole moment was discovered by F. London.<sup>60</sup>

In a non-polar molecule the dipole moment is constantly fluctuating in magnitude and direction. However, the average dipole moment is zero. The fluctuating dipole moment creates a fluctuating electric field around the atom which produces a corresponding displacement of charge in a neighbouring atom. The displacement is in phase with the fluctuations and so leads to attraction. The magnitude of the force of attraction was calculated by London with the aid of quantum mechanics and because of its close resemblance to the frequency of optical dispersion, the effect is called dispersion effect.

#### Forces involved in Solution Adsorption.

Since most of the work done by the author has involved solution adsorption, we shall now discuss the forces involved therein.

Van der Waals forces. The importance of van der Waals forces in solution adsorption and in the dyeing of textile fibres (which is a special case of solution adsorption) has been studied by a number of workers from time to time.

Van der Waarden<sup>61</sup> found that planar aromatic hydrocarbons are adsorbed with flat orientation on the surface of carbon black. Similar results have been obtained by Galbraith et al.<sup>62</sup> who found that non-ionic azo dyes are adsorbed from an aliphatic solvent by graphite with flat orientation. Benzene as a solvent reduces adsorption, by itself competing for the surface. Acid wool dyes are considerably adsorbed from water at the surface of graphite. In all these cases the origin of the forces of attraction between chemically inert surfaces of graphite and charcoal on the one hand and non-ionic and anionic dyes and aromatic hydrocarbons on the other, appears to be the van der Waals forces.

Anions of acid dyes are adsorbed to a much greater extent than inorganic anions by wool and nylon from weakly acid solution.<sup>40</sup> Lemin<sup>4</sup> has shown that the affinity for wool of a series of acid dyes and of certain organic acids rises almost linearly with increase in molecular / ...



molecular weight. This must be attributed mainly to van der Waals attraction between the aromatic nuclei of the dye and the hydrophobic parts of the wool protein. Chipalkatti et al.<sup>63</sup> have found that dry wool and nylon under certain conditions can adsorb from dry solvents appreciable amounts of certain aromatic compounds, e. g. benzene or stilbene. This is probably due to van der Waals forces.

There are <sup>a</sup><sub>λ</sub> number of facts which seem to indicate the operation of physical forces of adsorption in the dyeing of cellulose with direct and vat dyes.<sup>14,15,40,64</sup> For instance the affinity of dyes for cellulose has no relation to their content of potential hydrogen-bonding groups. It has been shown<sup>65</sup> that substantivity of direct dyes is very much dependent on the length of their molecules and the presence of an extended conjugate chain therein. In the case of vat dyes there is a linear relation between affinity for cellulose and the logarithm of the number of conjugated bonds in the longest axis of the dye molecule.<sup>42</sup> Experiments made in absence of water show that cellulose adsorbs phenol from a dry solvent (iso-octane); it does not do so from water. The reason seems to be that cellulose can form intermolecular hydrogen bonds only in / ...

in absence of water; in presence of water cellulose is highly hydrated and the surrounding water molecules prevent it forming hydrogen bonds with phenol; and phenol molecules are too small to produce high van der Waals attraction. Dye molecules are large enough to produce high van der Waals attraction even in presence of water and so they are adsorbed. Acid wool dyes, which have no appreciable affinity for cellulose in water, dye cellulose from alcoholic solution.<sup>35</sup>

Non-polar van der Waals forces and dipole-dipole forces certainly contribute to the adsorption of disperse dyes by cellulose acetate fibres. The evidence for van der Waals forces is the tendency for the partition coefficient between cellulose acetate and water to rise with molecular weight.<sup>66</sup>

Hydrogen bonding. Many adsorption processes depend on hydrogen bond formation. Low molecular weight non-ionic solutes are very little adsorbed by any inorganic or organic polar solid unless they can form hydrogen bonds with it. Compounds such as o-nitro phenol, in which the phenolic group is intramolecularly hydrogen-bonded, are not adsorbed by the anodic oxide film on aluminium, whereas other solutes with free hydroxyl or amino-groups are readily adsorbed / ...

adsorbed.<sup>67</sup> Adsorption of non-ionic anthraquinone and azo compounds on alumina columns (judged by speed of travel) is weaker when any amino-, hydroxy, etc. groups they contain are internally bonded, than when they are free. Proton donors are readily adsorbed and proton acceptors are adsorbed weakly or not at all.<sup>68</sup> The shapes of the isotherms are also consistent with the hypothesis of hydrogen bond adsorption.<sup>69</sup> Polar solvents, e.g. water and ethanol, which associate with the solute by hydrogen-bonding, compete with the alumina for the solute and favour elution.

Acetate dyes have several polar groups, e.g. hydroxyl, amino-, nitro, chloro-, etc., but no strongly ionic groups in their molecules. The acetate groups of cellulose acetate can act both as proton-donors and proton-acceptors in hydrogen-bond reactions with polar groups.<sup>70</sup> Thus all the polar groups in an acetate dye molecule may form hydrogen-bonds with acetate groups.

Adsorption of phenol and aniline by nylon from water takes place probably by hydrogen-bonding.<sup>63,71</sup> Phenol, with a powerful hydrogen bonding group, has more affinity for nylon from aqueous solution than benzoic acid has. The adsorption by protein and polyamide fibres of various / ...

various polar solutes are in the following order, phenol > benzoic acid > aniline, a sequence which is in good agreement with the hydrogen bonding affinities. Acetone and pyridine are not adsorbed from water by these fibres, presumably because of the protective action of the solvent.

There is a linearity in the saturation values of some disperse dyes on nylon, polyesters and cellulose acetate. This leads us to believe that a mechanism of hydrogen bonding, which operates on acetate fibres, may also operate on the other two fibres.

Covalent bond formation. Several systems are known in which adsorption takes place by formation of a covalent bond between adsorbent and adsorbate. It was shown by Giles et al.<sup>67</sup> that when the anodic film is treated with chromic acid, the adsorption of sulphonated dyes is temperature-dependent and exothermic, and whereas when the film is treated with hydrochloric acid it is temperature-independent. On the observation that ion exchange reactions between ions of the same valency have very low temperature coefficients and temperature has very little effect on them,<sup>72,73</sup> it was suggested that the mechanism of dyeing of the chromic acid treated anodic film by sulphonated dyes is by the formation of covalent bond between them.

Covalent bonds are formed between mordanting metal and mordant dyes in the fibre. When a water-insoluble dye is applied to a mordanted fibre, the formation of covalent bond between metal and dye is responsible for the adsorption of the dye.

One of the most important examples of adsorption by covalent bond formation is provided by dyeing of cellulose with reactive dyes.<sup>74</sup> All these dyes contain a reactive system capable of forming a covalent bond with the secondary hydroxyl group of cellulose. Typical reactive systems present in reactive dyestuff molecules are the triazinyl group and vinyl sulphone group.

Ion exchange. As discussed above, an ion-exchange reaction is often temperature-independent. A number of examples can be given of ion exchange adsorption mechanisms. Examples are: adsorption of cationic dyes by graphite,<sup>62</sup> in which the dyes exchange their cation with hydrogen ion in the electrical double layer surrounding the graphite particles. Adsorption of cation dyes by silica is also by cation exchange,<sup>75</sup> as evidenced by the very low apparent heat of adsorption. Other examples of adsorption by ion exchange are those of sulphate esters by the anodic film on aluminium<sup>67</sup> and of anionic dyes by protein and polyamide fibres / ...

fibres in presence of acid.<sup>76</sup>

Chelate bonding. When a suitable mordant dye is applied to alumina powder or anodic film a marked change in colour of the dye takes place. It is now recognised that aluminium atoms form a complex with the dye molecules. Recently Kiel and Heertjes<sup>77</sup> have shown that the alizarin-aluminium complex has a 2 : 1 ratio. Datye and Giles<sup>78</sup> have recently put forward a new hypothesis for the adsorption of alizarin by alumina and have suggested that the initially formed 1 : 1 - complex is set free into the solution and then forms a negatively charged 2 : 1 - complex which in turn forms anionic micelles, which are strongly adsorbed by the positively charged surface of the alumina.<sup>79</sup>

Salt formation. Adsorption of acid dyes and strong electrolytes by wool and nylon takes place by strong electrovalent linkages; this has been fully explained by Vickerstaff.<sup>47</sup> Giles and McKay<sup>80</sup> have suggested another type of  $\pi$ -electron complex formation between polynuclear hydrocarbons (in non-aqueous solvents) and charged aluminium atoms exposed by mechanical damage at the surface of alumina powder. In the adsorption of organic compounds by alumina, a similar type of molecular complex formation mechanism has / ...

has been suggested by Basu.<sup>81</sup> By the application of the LCAO method he calculated the energy of the top filled orbitals of five condensed ring aromatic hydrocarbons and four  $\alpha, \omega$ , diphenylpolyenes and showed that adsorption power increases with the lowering of the orbital energy. Adsorption is favoured by high electron affinity of one component and low ionisation potential of the other.

### FACTORS AFFECTING ADSORPTION

#### Structure of Solute and Adsorption:

Chromatography, which in many forms is a special case of adsorption, has been developed to such an extent that it has become the most important method for the separation and identification of different constituents of highly complex solute mixtures. For the adsorptive power of different solutes by alumina a comprehensive survey is given by Roosens.<sup>82</sup> For sulphonated azo dyes the adsorptive power increases with increase in the number of azo groups; amino - or hydroxy groups in the 2-position of the naphthalene nucleus in azo dyes are more effective than in 1-position; o-hydroxyazo compounds are more strongly adsorbed than their para isomers; dyes with thio- or hydroxyl groups / ...

groups are more strongly adsorbed than dyes without these groups; adsorption increases with increase in number of sulphonate groups or vinyl groups in the molecule and also with increase in molecular weight.

Adsorbability of chain molecules has been studied by Ruggli and Jensen,<sup>83</sup> who showed that in a chromatographic analysis of various organic molecules having a long carbon chain or a multiplicity of rings the substance of greater molecular weight is the more strongly adsorbed. Baum and Broda,<sup>84</sup> and Broda and Mark<sup>85</sup> showed that in the case of long chain molecules the adsorbability tends to increase with increase in chain length, independent of the sign of the heat of adsorption.

The polarity of a molecule is important in adsorption phenomena, as shown by Richard and Arnold.<sup>86</sup> Polarity determines the order of adsorption of a mixture on a polar medium (alumina). Picric acid with three nitro groups is more strongly adsorbed on alumina than o-nitrophenol or 4-methyl-2-nitrophenol. Internally chelated compounds are less strongly adsorbed than those without internal chelation. In the case of isomeric compounds with the same number and kind of functional groups, those with larger dipoles are the more strongly adsorbed on polar media.

Selective / ...



Selective adsorption of polar organic molecules on polar surfaces has been studied by Dintenfass.<sup>87</sup> He showed that when a number of polar compounds with identical polar groups are adsorbed, the amount of each component adsorbed is proportional to the molecular concentration of that component in the solution. There is no preferential adsorption of long chain compounds; a long chain molecule may be replaced by a short chain one having identical polar groups. He also suggested that selective adsorption can take place only when the active sites on the adsorbent surface correspond to the polar groups of the adsorbate.

Configuration of an adsorbate molecule may affect its adsorptive power.<sup>88</sup> Thus cis-azobenzene is more strongly adsorbed by alumina than the trans-isomer. Planarity of a molecule also favours adsorption. In polynuclear aromatic compounds adsorbability increases with an increase in number of aromatic rings. Basu<sup>81</sup> explained the adsorption of polynuclear aromatic compounds by the formation of molecular complexes.

Several cases are known in which a compound is catalytically changed, on an alumina column, or isomerised. Adsorption colours provide a good example of this catalytic effect; they are especially useful as indicators in volumetric / ...

volumetric analysis. Spiropyrans<sup>89</sup> are thermochromic, being colourless in cold benzene solution, but coloured when heated or adsorbed on alumina. Both these effects are attributed to ionic dissociation with the formation of a heteropolar molecule. 1,3-diketohydrindene becomes coloured on alumina; the effect is attributed to enolisation.

Adsorption of inorganic compounds has been studied by Oden and Anderson,<sup>90</sup> who showed that in the compounds of alkalis and alkaline earths with the same anionic group adsorption on charcoal increases with the increase in molecular weight of the cation, thus,  $\text{Na} < \text{K} < \text{Rb} < \text{NH}_4 < \text{Cs}$ . They further showed that adsorption of these metal compounds with the same cation increases in the order of increasing molecular weight of the anion, thus,  $\text{OH} > \text{I} > \text{Br} > \text{Cl} > \text{F}$ .

#### Effect of Solvent on Adsorption:

Amongst various factors affecting adsorption of a solute from a solvent by a solid substrate, the effect of the solvent is the most pronounced. A solvent molecule may either interact with the solute or with the solid substrate, or both.

The effect of the solubility of fatty acids in petroleum ethers upon their adsorption by various carbons has been pointed out by Harold and Cassidy,<sup>91</sup> who showed that / ...

that the higher the solubility, the lower the adsorption. From a mixed solution of acids, each exerts an effect on the adsorbability of the other. Bhatnagar et al.<sup>92</sup> studied the effect of solubility on adsorption and found the following order for adsorption of benzoic acid on dried phenol-formaldehyde resin from different solvents: methanol < benzene < ethanol < acetone < carbon tetrachloride < carbon disulphide < water. The order of solubility of benzoic acid in these solvents is, methanol > ethanol > acetone > benzene > carbon disulphide > carbon tetrachloride > water. Patrick and Jones<sup>93</sup> found that adsorption of benzoic acid and acetic acid on silica from different solvents also falls in the order of their solubility. Adsorption decreases in the following order, kerosene > carbon disulphide > gasoline > carbon tetrachloride > toluene > nitrobenzene, solubility decreases in the reverse order. Thus adsorption increases as solubility decreases.

It has been shown previously<sup>86</sup> that polarity of the solvent is an important factor in determining the order of adsorption of a solute mixture on a polar medium (alumina). There is always a competition between polar solvent and solute molecules for sites on a polar substrate. Phenol is not adsorbed at all by cellulose from aqueous solution, but readily / ...

readily adsorbed from organic non-polar solvents. The effect of solvent on the adsorption can be seen from the shape of the isotherm<sup>94</sup> when solute molecules meet strong competition from solvent molecules for substrate sites, S-isotherm occurs. Thus, phenols usually give S-curves, when adsorbed on a polar substrate, e.g. alumina, from a polar solvent such as water or ethanol, but not from a non-polar solvent such as benzene or iso-octane (2,2,4-trimethylpentane), which does not compete for the adsorption sites. Kipling<sup>95</sup> studied adsorption from binary mixtures on silica and found that adsorption of organic acids is related to the ease of formation of a hydrogen bond between the carboxy group and the solid surface, and he gave the following order for adsorption, palmitic acid < propionic acid < acetic acid < formic acid. Further, it has been shown that<sup>96</sup> the adsorption of any one of these acids decreases as the hydrogen-bonding power of the solvent increases, viz. carbon tetrachloride < toluene < nitrobenzene < dioxane < water.

Bartell<sup>97</sup> measured the effect of adhesion tension of various solvents against carbon and silica and showed that adsorption should be a maximum from those solvents which have the lowest adhesion tension against the solid surface / ...

surface. On this basis he showed that silica adsorbs best from organic liquids and carbon from aqueous solution. Firth<sup>98</sup> confirmed Bartell's result by showing that water could be replaced from silica gel by alcohol.

Earlier research workers showed that during adsorption of an electrolyte by a charcoal, the ions are not adsorbed in equivalent amounts, and thus the solution is left either acidic or basic. Later Bartell,<sup>99</sup> from a series of experiments on activated ash-free charcoal, demonstrated a hydrolytic mechanism of adsorption of electrolytes; concluding that hydrolysis is a considerable factor in the adsorption, especially of acid and basic dyes by activated ash-free charcoal. Charcoal selectively adsorbs acids or bases set free by hydrolysis of the electrolyte in aqueous solution, thus disturbing the equilibrium and causing more hydrolysis of the dissolved substance. Confirmation of the hydrolytic mechanism of adsorption is provided by Miller.<sup>100</sup> He found that strong inorganic bases are not adsorbed by pure activated sugar charcoal. Benzoic acid is more readily adsorbed than any other acid. Further, during adsorption of alkali salts of inorganic acids in aqueous solution by activated sugar charcoal, it was observed that when alkali is set free in salt / ...

salt solution during adsorption there exists on the charcoal, after adsorption, an equivalent amount of adsorbed acid . The amount of hydrochloric acid adsorbed by an activated charcoal increases with an increase in the concentration of electrolyte (KCl). Addition of electrolyte to an alkaline solution does not cause an alkali to be adsorbed by charcoal.

The effect of ionisation on the adsorption of weak acids by pure charcoal has been studied by Phelps et al.<sup>101</sup> According to them, adsorption proceeds predominantly through the unionised molecules. Ionisation is an important factor in determining adsorption, but it is the unionised molecules that are adsorbed. If this is true; it is possible to show that bases tend to be most adsorbed from alkaline solution. The adsorption results with two amines, n-propylamine and n-butylamine show that the adsorption does increase with increase in pH, which confirms the general view that adsorption increases with decreasing ionisation.

Properties of Solids:

Because of the lack of mobility of the particles of solids, solid surfaces are likely to be very complex in structure. Even in a comparatively simple material such as metal / ...

metal, a single crystal may have different types of surface. The various surfaces, edges and corners will all have different properties. Unlike amorphous solids, crystalline solids are characterised by a sharp melting point. In an unstrained crystalline substance all the lattice parameters are the same at a given temperature, but in an amorphous substance all the lattice parameters are lost and the particles show random disorder. There is much evidence to show that a perfect crystal lattice is rare and most crystals show imperfections. Heterogeneity of solid surfaces is revealed by many phenomena of adsorption and catalysis.

As far as the catalytic activity of a solid is concerned, it is now universally accepted that most solid surfaces consist of patches of widely different activity. Only a very small part of the whole surface is very active, responsible for any catalytic activity. Armstrong and Hilditch<sup>102</sup> pointed out that the amount of poison required to suppress catalytic activity is far less than that required to cover the whole of the surface. That some degree of irregularity in a surface is often necessary for catalytic activity was earlier shown by Palmer,<sup>103</sup> who found that electrolytic copper is inactive in the dehydrogenation / ...

dehydrogenation reaction of alcohols to aldehydes, whereas copper formed by reduction of oxide is active. The effect of sintering on the catalytic activity of a solid provides strong evidence for the presence of active centres on the surface. Garner<sup>104</sup> and his co-workers found that a film of cuprous oxide on heating was reduced in area by a factor of five, but its power of catalysing the reaction,  $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$  diminished by a factor of hundred thousand.

Adsorption provides another means of studying the activity of solid surfaces. There is a great variation in the energy of adsorption of gases by different parts of the surface of a solid. Garner and Blench<sup>105</sup> found that oxygen adsorbed on charcoal evolves up to 220 Kcal per mole for the first portions adsorbed and much smaller amounts for later portions. The effect of the different crystal faces on physical adsorption has been treated theoretically by Barrer,<sup>106</sup> who calculated that the heat of adsorption on the basal surfaces of graphite is larger than on the prismatic surfaces. Beebe<sup>107</sup> observed that an active adsorbing centre for one gas may not necessarily be an active centre for another; different substances favour different regions of the surface for their adsorption.

As there are differences in heat of adsorption at different / ...



different faces of a crystal, so some faces may adsorb very much more than others. A crystal will sometimes adsorb one dye on one set of faces and another on a second set, no adsorption of the first dye occurring on the second set of faces, and vice versa. Lead nitrate<sup>108</sup> adsorbs Methylene Blue on one set of faces and picric acid on the other. These different adsorptions are of great importance in determining the habit of crystals, for if a substance is adsorbed on a particular set of faces, growth of the crystals perpendicular to these faces is retarded.

The surface of a solid may be porous, as is silica gel, or non-porous, as silica dust. The activity of a solid<sup>109</sup> depends upon its porosity and so upon its specific surface area. The activity of a solid surface often varies according to the treatment it has received. For example, the ignition of a sample of calcite at 900°C. yields highly active lime whereas when ignited at 1400°C. only an inactive lump of stone is obtained.

#### THE ADSORPTION ISOTHERM

The results of solution adsorption can be conveniently represented in the form of an isotherm, which is a plot of the amount of solute adsorbed by a solid against / ...

against the equilibrium concentration of the solute in solution. Adsorption from solution is often complicated because of the presence of more than one component in the liquid phase, which may be either a mixture of liquids or a solution of a solid in a liquid, which can interact with each other or compete with each other for the available sites on the adsorbent surface. When the liquid phase contains two components, e.g. two miscible liquids A and B, or a solution of a solid C in a liquid D, both the components will be adsorbed to differing extents so that the concentration of one component relative to the other will change in the bulk of the solution. Hence the isotherm of an individual component from a binary system is an absolute one. Kipling and Wright<sup>110</sup> have shown that in solution adsorption a component of low solubility seems to meet very little or no competition from the solvent, and in dilute solutions the composite isotherm could represent the adsorption of solute alone, but the two isotherms diverge with increasing concentration. The present work is confined to adsorption from dilute aqueous solutions of dyestuffs.

All the isotherms for vapour phase adsorption were classified into five main types by Brunauer et al.<sup>56</sup>

An / ...

22

An outline system of classification for the solution adsorption isotherms has been given by Giles et al.<sup>94</sup> in which all the available types of isotherm are divided into four main classes according to the initial slope of the isotherm and each class is divided into sub-groups depending upon the shape of the later portion of the isotherm. From the experimental facts these authors<sup>94</sup> interpreted all the four classes of isotherms and have shown how they could be used to study the mechanism of solution adsorption, solvent-solute interactions, the nature of the solid surface, and also for the measurement of specific surface areas of powders.<sup>111</sup> The four main classes are designated "S", "L", "H", and "C".

The L-isotherms are the normal Langmuir type. To start with the amount of a solute adsorbed is high from dilute solution, but progressively decreases with increase in concentration of the external solution because of the reduced chances of solute molecules finding a suitable adsorption site. In this case there may be little competition between solvent and solute molecules, and the latter are normally oriented flat on the surface. When solute molecules are adsorbed in the form of large micelles often L-isotherm is obtained.

S-isotherms are similar to Brunauer's types III and V. Initially there is very little or no adsorption, but it increases with increase in the concentration of the external solution. The more solute there is already adsorbed the easier it is for an additional amount to be adsorbed. This is called "co-operative adsorption". There is a strong competition between solvent and solute molecules for the available sites on the adsorbent surface; the solute molecules are monofunctional and have moderate intermolecular attraction, causing them to pack vertically on the adsorbent surface.

The H-isotherm is a special case of the L-type, in which solute molecules have very high affinity for the substrate and in dilute solution the solute is completely adsorbed. The solute molecules may be adsorbed as ionic micelles, polymeric molecules or as single ions. Finally, C-isotherms are obtained with non-ionic or some mono-ionic solutes on hydrophobic polymers from inert liquids, i.e. those which do not swell the substrate. In this case the available sites may be constant at all concentrations up to saturation.

Almost all complete curves have either a plateau or an inflection (knee). The plateau or the beginning of the / ...

the linear portion beyond the knee corresponds to Brunauer's "Point B" and represents a so-called "first degree saturation" of the surface,<sup>94</sup> when all possible sites are filled. This first degree of saturation may correspond to the formation of a complete layer, a monolayer. This layer may be solvated or may consist of isolated patches of solute molecules or of ionic micelles either packed or well scattered. Sometimes there appears a second inflection beyond the first plateau. This indicates that a second layer has started building up on the first one. Generally the molecules in the second layer are oriented as in the first layer, but sometimes it happens that molecules forming a monolayer of flat orientation are forced, by the entry of more of the adsorbed molecules, into a vertically orientated monolayer which then appears as an inflection in the isotherm.

## EXPERIMENTAL

Dyes. Of the sulphonated azo dyes listed in Table IX, some were obtained as commercial "batch" samples without the addition of diluent, others were laboratory-prepared samples. All of them were purified by one of two methods: either by sodium acetate method or by recrystallisation from water-ethanol mixture, as recommended by Giles and Greczek.<sup>112</sup> Care was taken to remove any foreign coloured impurities and to check this, the one-dimensional paper chromatographic technique<sup>113</sup> was employed. A mixture of equal proportions (v/v) of benzyl alcohol, dimethylformamide, ethylmethyl ketone and water was used as an eluent. Further, it was found necessary to pretreat the chromatographic paper with a mixture of benzyl alcohol, dimethylformamide, and water (3:2:2, v/v), in order to reduce the affinity of the dye for cellulose and to assist elution. Crystallisation of the dyes was continued until no coloured impurities appeared on the chromatogram. Finally the dyes were dried at 60-70°C, and then cool, in a vacuum dessicator in presence of potassium hydroxide, over-night. The metal complex dye used was an already purified sample.

Substrate and adsorption procedure. The graphite sample used for the experiments was an electric furnace material / ...

material. It was found to have a specific surface area of  $2.5 \text{ m}^2/\text{g}$ . as calculated by the author's colleague C.C. Patel by p-nitrophenol adsorption. Coated and uncoated titania samples were obtained from British Titan Products Ltd.

Samples (0.05 to 0.25 g.) of the substrate were weighed in soda glass test tubes, a series of 10 c.c. aliquots of adsorbate solutions of increasing concentration were introduced and the tubes sealed in a flame. The tubes were then fixed by spring clips to an electrically driven horizontal shaft revolving at 35 r.p.m., with a thermostat arrangement. This apparatus has been described by Clunie and Giles.<sup>114</sup>

It was found that 30 minutes were more than enough for equilibrium to be established. After equilibration the solutions were separated from the substrate by centrifuging, and decanting the supernatant liquor.

The amount of solute adsorbed was calculated from the difference in initial and final concentrations of the solution. For the measurement of the concentration of the solutions the Unicam SP 500 photoelectric spectrophotometer was used. For the analysis of solutions, readings / ...

readings were taken at a wavelength of maximum absorption for the solute. In order to work to maximum precision (i.e. at O.D. between 0.2 and 0.7) it was necessary to dilute the solutions 50-100 fold. The calibration curve was obtained by plotting optical densities against concentrations and this was used as a standard for analysing the test solutions.

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



## RESULTS AND DISCUSSION

### Adsorption of Anionic Dyes on Graphite:

The graphite surface is negatively charged in water<sup>62</sup> and adsorbs cationic compounds by the exchange of their cations with hydrogen ions in the electrical double layer. The adsorption of non-ionic compounds in dilute solution may be by van der Waals forces between the surface of graphite and the hydrophobic portions of the solute molecules or ions; anionic compounds might be expected to be adsorbed similarly, but there is some evidence from the work of the author and colleagues that ion exchange of micelles is involved in their case.

$\pi$ -electron interactions are mainly responsible for the origin of powerful van der Waals forces on the surface of graphite. The arrangement of carbon atoms in the space lattice of graphite is similar to that of aromatic hydrocarbons, in which layers of six-membered carbon rings are separated from one another by a distance of 3.41 Å. However this distance is too large to form any chemical bonding between carbon atoms of the two successive layers, but they are held together by weak van der Waals forces. Each carbon atom is joined laterally to three neighbouring carbon atoms in the same layer by covalent / ...

covalent ( $\sigma$ ) bonds and a  $\pi$ -electron of each carbon atom, being mobile, forms delocalised  $\pi$ -electron orbitals, which give double bond character to the C-C bonds. This graphite surface with delocalised  $\pi$ -electron orbitals has a great affinity for the aromatic condensed ring systems with similar delocalised  $\pi$ -orbitals, the energy of interaction between them obeys the simple London law.<sup>115,116</sup> This clearly explains that the adsorption of non-ionic solutes by graphite is purely physical.

Three of the four main types of solution adsorption isotherms have been reported for adsorption on graphite,<sup>69</sup> viz., S-, L-, and H. In fact L- and H-curves have been obtained in the present work (Figs. 11,12). An increase in the hydrophobic nature of the solute increases its attraction for the graphite surface and changes the shape of the isotherm in the direction L→H. The tendency for the hydrophobic portion of the solute molecule to approach as closely as possible to the graphite surface, which in turn itself is hydrophobic, will favour flat orientation for non-ionic solute molecules and end-on orientation for monosulphonates, when adsorbed mono-disperse, the sulphonate group being directed towards the water and the unsulphonated end of the molecule being nearest to the graphite / ...

graphite surface. When there are two ionic groups situated along one side or at opposite ends of the dye molecule, it is oriented edge-on, but if they are both at one end, it is oriented end-on as with the monosulphonates. When there are more than two sulphonate groups present in a molecule, they are normally scattered along the periphery of the dye molecule and the orientation is flat. Furthermore with a polysulphonated dye the hydrophilic nature of the ionic groups considerably reduces its adsorption, the van der Waals forces are not strong enough to attract solvated dye molecules. Hence in the case of a polysulphonated dye there may be very little or no adsorption by graphite. Orientation of cationic dyes can also be explained in a similar way.

A few of the adsorption isotherms, instead of showing a flat plateau, display a maximum and then a minimum, e.g. Fig. 12. This is a behaviour of some detergent solutions in which individual detergent ions are present as single ions up to the Critical Micellar Concentration. Thus it is possible that the direct adsorption of preformed dye micelles will take place at room temperature.

The plateau or beginning of the linear portion  
above / ...

above the 'knee' (Point B)<sup>56</sup> in the isotherms may in some cases represent the formation of a complete monolayer<sup>94</sup>. Recently Sing<sup>117</sup> has shown that calculation of specific surface from the Point B in vapour phase adsorption isotherms is generally more correct than the use of the BET equation. Hence from a knowledge of the orientation of the solute molecule on the surface and its projected cross-sectional area in that orientation, it should be possible to calculate the surface area of the substrate. However it is not always that a complete monolayer with close-packed single molecules or ions is formed on the surface of the substrate. Generally the layer may contain, solvent as well as solute molecules, or clusters of solute molecules adsorbed only on the most active sites, or ionic micelles, either closely packed or isolated. In all these cases the "first degree" saturation values may give only apparent but not true surface area values. However, the authors<sup>94</sup> have suggested that p-nitrophenol and some sulphonated dyes, e.g. Solway Ultra Blue B (C.I.62055) form a closely packed layer on polar surfaces and the specific surface area values are in close agreement with those obtained by the nitrogen adsorption method. Here the concept of "coverage factor" is introduced to account for the deviation / ...

deviation of the apparent surface area values from the true values. The hypothesis underlying this factor has been important in present work, for the measurement of specific surface area, for finding a relationship between molecular weight of an adsorbate and the amount adsorbed, and also for studying the effect of conjugated and unconjugated systems on adsorption. The coverage factor is defined as the apparent specific surface area (SSA) divided by the true area, i.e.  $\frac{\text{SSA (apparent)}}{\text{SSA (true)}}$ . The

"true" SSA may be obtained by any one of the standard methods and the "apparent" value is calculated from either the first "knee", the Point B, or the maximum of the isotherm. Greenland and Quirk<sup>118</sup> in adsorption tests of cetylpyridinium bromide on clay found that where an isotherm with a maximum is obtained, calculation of specific surface at the maximum gives an area agreeing with nitrogen values, consequently in the present work, where maxima are obtained, they are taken to correspond to a completed monolayer.

Apart from the author's own coverage factor results on graphite, results from the author's colleague C.C. Patel and also from earlier work,<sup>68,75,119,120,121</sup> for a variety / ...

variety of substrates, viz. fixed yeast cells, alumina, silica, and graphite, were included to find the statistical significance of the results. McKay pointed out that using a series of basic dyes the coverage factor on fixed yeast cells increased with increase in molecular weight of the dye. The author continued to work on this subject, but on a different substrate in order to discover whether there existed the same relation, and he has now observed that (with a few exceptions, to be discussed, involving anionic dyes on graphite), there exists a linear relation between ( $\log_{10}$ ) coverage factor and ( $\log_{10}$ ) ionic weight. First of all, coverage factor data for different substrates were plotted separately and in all cases straight lines parallel to each other with very high significance were obtained (Fig.13). Analysis of variance revealed that the regression coefficients and positions of the separate regression lines for the different systems are not significantly different. Thus all the data could be combined to give an overall regression line (Fig.14) with very high significance. The relation may be expressed as:

$$\log_{10}c = b \log_{10}w + \log_{10}a$$

$$\text{or} \quad c = aw^b,$$

where  $c$  is the coverage factor,  $w$  the ionic weight of the solute / ...

solute and a and b are constants. The values of a and b which fit the line are shown to be  $1.2 \times 10^{-7}$  and 2.93 respectively. Therefore it is highly probable that the coverage factor is independent of the nature of the surface and rises with the third power of the ionic weight. Thus each solute has a characteristic coverage factor which is independent of the nature of the surface. The significance of this relation is that any dye with a single ionic group can be used readily for the specific surface area measurements.

During the course of the present investigation, it was found that some very high molecular weight anionic dyes gave coverage factor values which were too low to be fitted into the observed relation. Initially it was thought that some factors unknown to the author were responsible for this anomalous effect, but after a close examination of the chemical constitution of all the anionic compounds, which were behaving anomalously, a possible interpretation of the observed effect was found. Examination of the formulae (Fig.18) shows that all these dyes have molecules consisting of two or more aromatic units imperfectly conjugated, whereas all other dyes have perfectly conjugated systems. The effect of conjugation on the substantivity of direct / ...

direct cotton dyes has already been discussed in the first part. Here there appears to be a somewhat similar effect of conjugation on the adsorbability of an acid dye.

In these anomalous cases, the molecules are divided into their individual conjugated sections, thus A-B or A-c-B, where c is a small insulating group (the sulphonate group may be in any one of the sections), and the ionic weight is assumed to be  $\frac{A + B}{2}$ . After applying

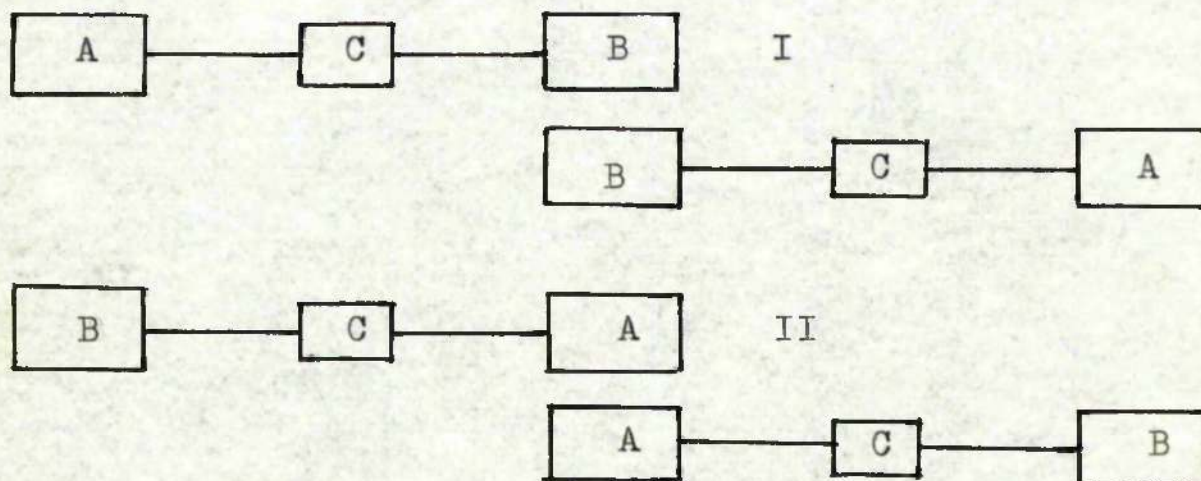
this correction to all the imperfectly conjugated systems, the values of ionic weight are in good agreement with the relation established for the fully conjugated systems (Fig.15). From this it appears that the effective ionic weight is approximately 2 - 2.5 times less than the full molecular weight. It thus appears that the size of the micelles can be governed by the average size of the individual conjugated systems. This qualitative treatment is entirely empirical, but the results must have some physical cause. The coverage factor is a measure of the tendency of the dye to associate. There is a dynamic equilibrium between single ions and micelles in solution or on the adsorbent surface, and collisions cause continual formation and breakdown of micelles. The maximum number of ions / ...



ions which can combine to form a micelle depends upon the balance of attractive forces and disruptive (solvation) forces on each ion. The intermolecular attractive forces arise from  $\pi$ -bond interaction and increase with the size of conjugated molecule.<sup>115,116</sup> Coulson and Davis have calculated the long range interaction energy between pairs of conjugated polymer molecules of different lengths and at different relative positions. They found that at large distances compared with the length of the molecule the total interaction energy obeys the normal London law, i.e. interaction energy is inversely proportional to the sixth power of the distance, and also to the fifth power of the length of the molecule. However at short distances as compared with the molecular length, the London law is beginning to break down and the interaction energy becomes nearly proportional to the length of the molecule. Furthermore they calculated the contribution of  $\pi$ -electrons to the total energy as compared to those of  $\sigma$ -electrons and found that the  $\pi$ -electron contribution increases with the square of the length of conjugated molecule. These results clearly indicate that long chain molecules have powerful interaction energy which increases with increase in the chain length. Here it may be assumed that in a long chain molecule / ...

molecule formed by the union of two conjugated molecules by an insulating group, the interaction energy between two such molecules will be dependent on the length of the individual conjugated systems and not the length of the whole molecule. Calculations by Davis<sup>116</sup> for the polarizability of long chain molecules are comparable to the coverage factor data. He showed that polarizability of long chain molecules is proportional to the third power of the molecular length, i.e. with approximately the third power of their molecular weight, since the cross-section is constant. Furthermore he showed that contribution by electrons to the total polarization effect is very great and their freedom of movement is mainly responsible for large polarization effect. Therefore any factor that reduces the mobility of  $\pi$ -electrons reduces its polarizability and so the energy of interaction. From these calculations it appears that there is some relation between the polarizability of long chain molecules and size of the adsorbed micelles, i.e. the coverage factor, both being proportional to the third power of molecular weight. The long range forces emanating from the adsorbent surface may be responsible for the polarization of the bombarding solute molecules, and the greater the polarizability of a solute / ...

solute molecule the easier for it to be readily adsorbed. The polarized solute molecules may then interact with other solute molecules to form micelles and become adsorbed or may, after being adsorbed singly, form micelles on the surface interacting with other bombarding solute molecules. It is assumed that in the case of fully conjugated molecules the intermolecular forces cause any bombarding molecule (say A) which is retained by a micelle, to align itself completely alongside a molecule already in the micelle surface, thus giving, e.g. the dimer AA, and larger micelles. However, imperfectly conjugated molecules behave somewhat differently;  $\pi$ -bond interaction takes place mainly between like units of the interacting molecules, so that several possible micellar forms may result, depending on the orientation of the bombarding molecules relative to those in the micelle. Thus a dye molecule with three divisions, A, B, and C may give the dimers I or II



and corresponding large micelles. In the present case, C, is always in the central portion: (C and C do not combine for steric reasons). The coverage factor is then a mean value determined by the portions A and B individually.

The present relation holds only for adsorption where no bond is formed with the surface. If a bond is formed then the coverage cannot be greater than unity. An example is provided by the adsorption of Solway Ultra Blue B (C.I.62055) on alumina, silica and titania; the coverage is unity assuming end-on orientation with the formation of a hydrogen bond to the surface.<sup>111</sup> On graphite, this dye cannot form such a bond, and the coverage value of 5.6 agrees with its anionic weight of 393. The relation also fails to hold where, even though no bond is formed to the surface, powerful intermolecular forces favour face-to-face packing of dye molecules, forcing them to orient vertically on the surface. This gives a coverage of unity. Examples are two Rhodamine dyes on alumina<sup>121</sup> and many cyanine dyes on silver halides.

#### Adsorption of a Cyanine Dye on Graphite and Alumina:

Adsorption of a cyanine dye (1,1'-diethyl,2,2'-cyanine) on graphite provides a very good example of preferential adsorption by van der Waals forces, even from  
a / ...

a very dilute aqueous solution. The cyanine dye molecule is fully conjugated; the charge is not localised, but oscillates between two nitrogen atoms, so giving rise to abnormally high van der Waals forces. The extraordinarily high affinity of cyanine dye molecules from a very dilute solution, for the graphite surface, becomes evident from the shape of the isotherm (H- or high affinity type, Fig.16A). The dye molecules are obviously oriented flat on the surface with the completion of a monolayer, the coverage value being 1.4 calculated from the horizontal portion of the isotherm and taking 136 sq.A. as the area of each molecule. From the general relation, if this dye were adsorbed as cationic micelles, its coverage factor would be 4.

Face-to-face orientation is favoured by powerful intermolecular forces. Cyanine dye molecules possess very high attraction for themselves and in absence of more powerful van der Waals forces, the dye molecules are forced to orient vertically with a close face-to-face packing, on a polar surface, where the adsorption is by ion exchange. Adsorption of a cyanine dye on alumina provides an example of face-to-face packing with vertical orientation. The initial portion of the isotherm as shown in the Fig.16B is of / ...

of S-shape, indicating vertical orientation. The latter portion of the isotherm could not be studied because of the limited solubility of the dye in water.

#### Ageing of Titanium Dioxide:

The surface of titanium dioxide, like silica, is negatively charged<sup>122</sup> and adsorbs oppositely charged ions by an ion exchange mechanism. However, it has been shown that<sup>123</sup> even an anionic dye, Solway Ultra Blue B (C.I.62055), is readily adsorbed by titania, but by hydrogen bonding. Solway Ultra Blue B appears to form a monolayer with face-to-face packing and vertical orientation and the measured surface area value from the isotherm is very close to the nitrogen value.

In order to confirm these facts, four samples of titania, used here by the previous workers,<sup>123</sup> and three more new samples were used for the present work. Out of these seven samples, two give S-isotherms (Fig.17) with Solway Ultra Blue B, thus confirming the previous results. The surface area values of these two samples calculated from the isotherms are in close agreement with the nitrogen values. The remaining five samples, unlike the first two, behave quite abnormally with very little or no adsorption. All of them seem to have lost their potential hydrogen-bonding power / ...

power with the dye. Also their surface area values by the basic dye adsorption method show a considerable reduction in area (measured by C.C. Patel).

Technical details given by the manufacturer, for all these samples show that the first two are "uncoated" titanium dioxide, whereas the latter five are "coated" with small percentages of silica, alumina and other oxides, to improve the durability of the pigments. From the history of all the samples, it appears that since none of them is a fresh one, they have undergone an ageing effect, as could be seen from the reduction in their surface area. This ageing effect seems to be specific and only the coated samples have been affected, whereas uncoated samples have retained their original surface properties. At this stage it is very difficult to propose any theoretical explanation for this ageing effect at room temperature, the experimental evidence is far too limited. However, the author's colleague, C.C. Patel, has shown that this ageing effect is partly reversible and after heating the samples at various temperatures for various periods, the surface area, as measured by basic dye adsorption, increases gradually, but it never reaches its original value. The uncoated samples are not affected by heating treatment, at least up to 200°C. Further / ...

Further work on this problem may provide a useful method for distinguishing coated titania samples from uncoated ones and also for determining their approximate date of preparation.

Anomalous Adsorption of Triphenylmethane Dyes on Alumina:

Adsorption is an exothermic reaction and so the amount adsorbed should decrease with increase in temperature. Ion-exchange adsorption reactions, however, which have a very low heat of adsorption, since no chemical bonds are formed, usually show no change in the amount adsorbed at two temperatures. Very little is known of systems showing a reversed temperature effect, i.e. where rise in temperature increases the saturation adsorption. Recently several anomalous results have been reported in which ion-exchange adsorption was shown to increase with increase in temperature.<sup>120,123</sup> It was suggested that this anomalous behaviour was peculiar to solutes which form large aggregates. At higher temperature there is a large proportion of monomers, which then build up into large aggregates, on or immediately after adsorption, possibly with a different structure.

More recently a similar anomalous endothermic adsorption effect has been reported by the author's colleague / ...

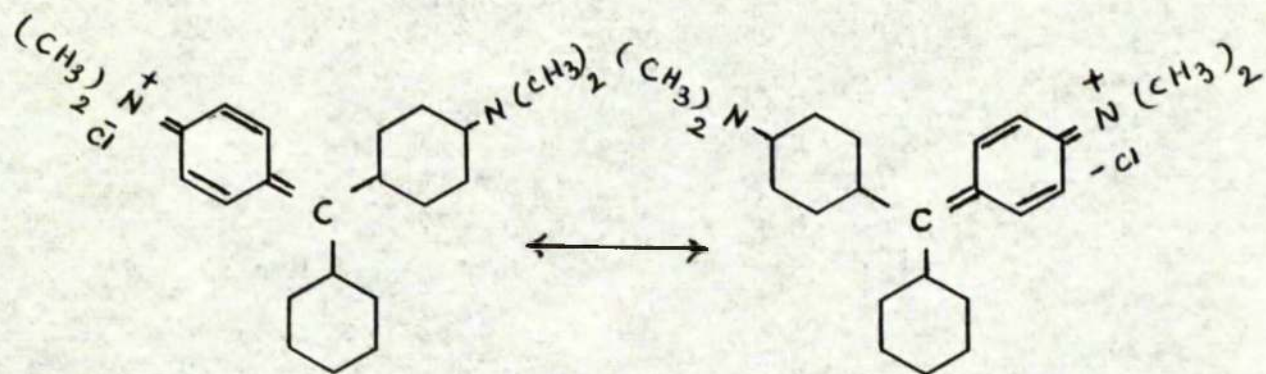


colleague, I.A. Easton, in which a series of triphenylmethane dyes on alumina were adsorbed more at 60°C. than at room temperature. He suggested that these anomalies are a result of aggregation effects, and since the structure of the aggregates in solution and at the surface is unknown, no prediction could be made as regards the magnitude of the heat of adsorption.

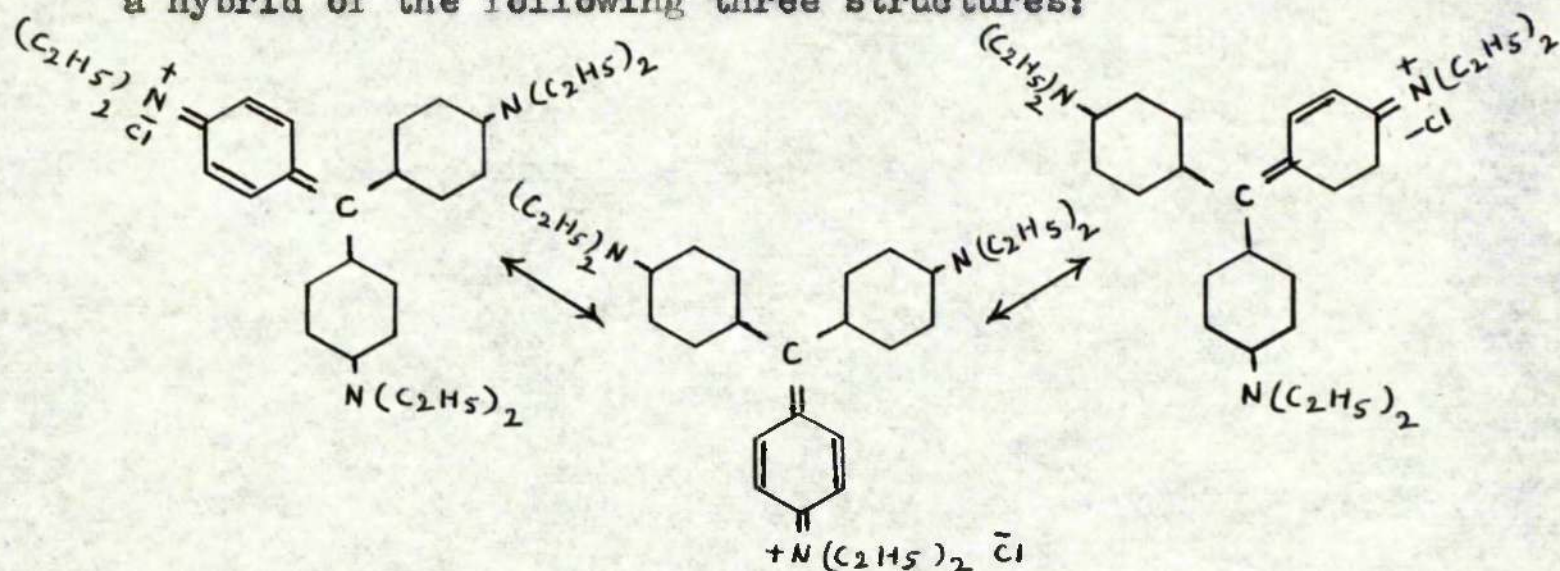
When only triphenylmethane basic dyes were shown to behave anomalously, it was thought that a possible explanation of the observed effect could have been sought from the special structural features possessed by the triphenylmethane dyes. Here in this part of the discussion an attempt is made to explain this anomaly on the ground of the fundamental theory of resonance.<sup>124</sup>

Any conjugated system which is a resonance hybrid of a number of equivalent forms, shows a chromophoric effect. This chromophoric effect is intensified (bathochromic effect) with an increase in the number of equivalent resonating forms.

A molecule of Malachite Green has been shown to be a resonance hybrid of the following two structures, in which the charge is delocalised and oscillates between two nitrogen atoms,



whereas a molecule of Ethyl Violet has been shown to be a hybrid of the following three structures:



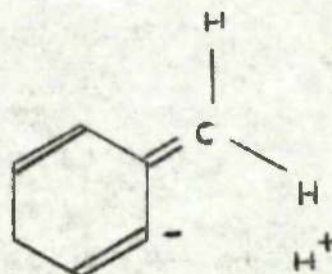
(Only symmetrically substituted aromatic residues of a T.P.M. dye molecule can enter into resonance). This resonance effect is mainly responsible for high intermolecular forces and so for the aggregation of the dye molecules in solution. Even at room temperature these dyes are highly aggregated as shown by the very high coverage / ...

coverage factor value. At higher temperature a greater proportion of dye is present monodisperse. In a monomeric molecule the process of charge transfer is greatly increased and makes the ionic groups more active; thus they are more active at high temperature than at normal temperature, and are then capable of exchanging their cations with those of the alumina surface. Once a dye molecule is adsorbed by cation exchange, it arranges itself and also forces the bombarding molecules after they are adsorbed to arrange themselves on the surface in such a way as to form aggregates which are very stable. This would account for very high adsorption even at high temperature. The re-arrangement of the individual molecules to form stable aggregates on the surface could be explained as follows:

Consider a compound system formed by the coupling of two resonators, resonating with the same frequency but out of phase. The resultant frequency  $\nu + \epsilon$  of this system will be greater than  $\nu$ . When the two resonators are in the same phase the resultant frequency  $\nu - \epsilon$  will be less than  $\nu$ . In the former case the energy of the compound system increases, whereas in the latter case it decreases. According to the laws of thermodynamics the latter case will be more stable in that the free energy of the system is reduced to a minimum / ...

minimum. Accordingly we may consider that aggregating dye molecules arrange themselves in such a way that they resonate in the same phase which reduces the free energy to a minimum and favours the building up of even larger aggregates.

The experimental results have been reproduced here<sup>121</sup> and some predictions have been made. From the table (Table X) it is seen that the ratio of the coverage factor at two temperatures increases with an increase in the number of resonating forms in a molecule. In the case of Magenta P, the number of resonating forms is the same as in Ethyl Violet, but the ratio increases from 2 to 3. This can be explained on the ground that in Magenta P, the extra methyl group in one of the nuclei of its molecule, may enter into resonance and increase the number of resonating forms. This suggestion can be supported by the fact that a methyl group in a phenyl nucleus<sup>125</sup> can donate an electron and assume the following structure:



in the phenomenon called hyperconjugation, whereby the methyl group activates the phenyl ring. This can explain the increased activity of Magenta P at higher temperature.

## APPENDIX

### Statistical Analysis of Results presented in Part I:

I.A. Relation between anionic weight and washfastness on wool, of disulfonated acid and monosulphonated chrome dyes (Fig. 2).

$$n = 173, \quad \Sigma x = 108792, \quad \Sigma y = 542.5, \quad \Sigma xy = 359062.0,$$

$$\Sigma x^2 = 73052308, \quad \Sigma y^2 = 1854.75$$

$$b = 3.8615 \times 10^{-3}$$

$$y = 3.8615 \times 10^{-3}x + 0.7072$$

Source of variance.	Degree of freedom.	Sum of squares.	Mean square.
1) Due to regression	1	69.156	69.156
2) About regression	171	84.4018	0.4936
3) Total	172	153.5578	

$$F = 140.11 \text{ with } N_1 = 1 \text{ and } N_2 = 171$$

Therefore the straight line is highly significant for the regression and accounts for 45% of the total regression.

I.B.

$$n = 139, \quad \Sigma x = 80255, \quad \Sigma y = 399.5, \quad \Sigma xy = 238949,$$

$$\Sigma x^2 = 48278743, \quad \Sigma y^2 = 1248.75$$

$$b = 4.2687 \times 10^{-3}$$

$$y = 4.2687 \times 10^{-3}x + 0.4095$$

Source of variance.	Degree of freedom.	Sum of squares.	Mean square.
1) Due to regression	1	35.38	35.38
2) About regression	137	65.17	0.476
3) Total	138	100.55	

$$F = 74.3 \text{ with } N_1 = 1 \text{ and } N_2 = 137$$

Therefore the straight line is highly significant for the regression and accounts for 35.2% of the total regression.

## II. Relation between anionic weight and migration number (Fig. 3).

$$n = 62, \quad \Sigma x = 36886, \quad \Sigma y = 160.5, \quad \Sigma xy = 91998.5,$$

$$\Sigma x^2 = 22796286, \quad \Sigma y^2 = 483.75$$

$$b = -4.09708 \times 10^{-3}$$

$$y = -4.09708 \times 10^{-3}x + 5.0262$$

Source of variance.	Degree of freedom.	Sum of squares.	Mean square.
1) Due to regression	1	14.29	14.29
2) About regression	60	54.97	0.92
3) Total	61	69.26	

$$F = 15.53 \text{ with } N_1 = 1 \text{ and } N_2 = 60$$

Therefore the straight line is highly significant for the regression and accounts for 20% of the total regression.

III. Relation between lightfastness and anionic weight  
(Fig. 4).

$$n = 47, \quad \Sigma x = 20101, \quad \Sigma y = 199, \quad \Sigma xy = 87586.5,$$

$$\Sigma x^2 = 8917201, \quad \Sigma y^2 = 919$$

$$b = 7.7344 \times 10^{-3}$$

$$y = 7.7344 \times 10^{-3}x + 0.9262$$

Source of variance.	Degree of freedom.	Sum of square.	Mean square.
1) Due to regression	1	19.1659	19.1659
2) About regression	45	57.2596	1.2724
3) Total	46	76.4255	

$$F = 15.06 \text{ with } N_1 = 1 \text{ and } N_2 = 45$$

Therefore the straight line is highly significant for the regression and accounts for 25% of the total regression.

IV. Relation between total number of atoms and lightfastness on cotton of tri- and tetrasulphonated direct dyes (Fig. 8).

$$n = 65, \quad \Sigma x = 5301, \quad \Sigma y = 182, \quad \Sigma xy = 15156.5,$$

$$\Sigma x^2 = 436743, \quad \Sigma y^2 = 666.5$$

$$b = 7.0876 \times 10^{-2}$$

$$y = 7.0876 \times 10^{-2}x - 2.9802$$



Source of variance.	Degree of freedom.	Sum of square.	Mean square.
1) Due to regression	1	22.23	22.23
2) About regression	63	134.67	2.14
3) Total	64	156.90	

$$F = 10.4 \text{ with } N_1 = 1 \text{ and } N_2 = 63$$

Therefore the straight line is highly significant for the regression, but it accounts for only 14.2% of the total regression.

V. Relation between molecular axial ratio and light-fastness on cotton of tri- and tetrasulphonated direct dyes (Fig. 8).

$$n = 65, \quad \Sigma x = 176.69, \quad \Sigma y = 182, \quad \Sigma xy = 490.32,$$

$$\Sigma x^2 = 498.4857, \quad \Sigma y^2 = 666.5$$

$$b = -2.4258 \times 10^{-1}$$

Source of variance.	Degree of freedom.	Sum of square.	Mean square.
1) Due to regression	1	1.07	1.07
2) About regression	63	154.83	2.46
3) Total	64	156.90	

$$F = 0.43 \text{ with } N_1 = 1 \text{ and } N_2 = 63$$

Therefore the straight line is insignificant for the regression.

VI. Relation between molecular axial ratio and light-fastness of anthraquinone vat dyes on cotton (Fig.9).

$$n = 50, \quad \Sigma x = 104.84, \quad \Sigma y = 325.5, \quad \Sigma xy = 668.355,$$

$$\Sigma x^2 = 235.2016, \quad \Sigma y^2 = 2168.75$$

$$b = -0.92066$$

$$y = -0.92066X + 8.4404$$

Source of variance.	Degree of freedom.	Sum of square.	Mean square.
1) Due to regression	1	13.0304	13.0304
2) About regression	48	36.7146	0.7649
3) Total	49	49.7450	

$$F = 17.3 \text{ with } N_1 = 1 \text{ and } N_2 = 48$$

Therefore the straight line is highly significant for the regression and accounts for 26.19% of the total regression.

VII. Relation between effectiveness of blue-red spectral region in causing fading and molecular axial ratio of dyes with planar molecules (Fig.10).

$$n = 31, \quad \Sigma x = 62.46, \quad \Sigma y = 1075.0, \quad \Sigma xy = 2505.42,$$

$$\Sigma x^2 = 134.8504, \quad \Sigma y^2 = 6188.5$$

$$b = 37.7037$$

$$y = 37.7037X - 41.289$$

Source of variance.	Degree of freedom.	Sum of squares.	Mean square.
1) Due to regression	1	12799.2016	12799.2016
2) About regression	29	11807.5725	407.1576
3) Total	30	24606.7741	

$$F = 31.4 \text{ with } N_1 = 1 \text{ and } N_2 = 29$$

Therefore the straight line is highly significant for the regression and accounts for 52% of the total regression.

TABLE I

Colour Index Numbers and Various Fastness Data for  
Monosulphonated Acid Dyes.

C.I. Designation Number.	Anionic Weight.	L.F. Number.	W.F. Number.	x/y	Migration Number.
Yellow 4	357	5.5	-	-	-
6	442	3	2	-	-
7	381	2	1	-	-
11	357	5.5	1.5	-	-
12	371	5	2.5	-	-
14	425	5.5	-	-	-
21	341	5.5	2.5	2.05	-
25	527	5.5	2	-	4.5
29	547	6.5	2	-	3.5
36	352	3	2	-	4
40	561.5	4.5	2.5	-	3.5
41	439	6	2	-	-
53	490.5	4.5	2	-	-
65	535	4	3	-	2
66	270	4	3	1.7	-
76	527	5	3.5	-	-
Orange 5	352	3	1.5	-	-
6	293	4.5	3	-	-
8	341	3	1	1.6	1.5
23	372	4	2.5	1.6	-
25	397	2.5	3	2.15	-
30	418.5	5	3	2.2	-
Red 4	357	5	2.5	1.65	-
6	488	4	3	-	-
9	376	2	3	-	-
10	377	3	2.5	1.9	-
32	582	6	3	-	4.5
42	482	6	2	1.85	-
68	531	4.5	3	-	-
80	445	5.5	3	1.55	-
81	431	5.5	3	1.45	-
83	466.5	6.5	2.5	1.45	-
88	377	2.5	1	1.6	1.5
104	457	5	4	1.8	1.5
135	355	3	3	1.8	-
141	377	2.5	2	1.8	1.5
148	459	4.5	3.5	2.4	-
151	431	4	4	2.35	-

C.I. Designation Number.	Anionic Weight.	L.P. Number.	W.P. Number.	x/y	Migration Number.
Violet 11	540	5	3	-	2
14	553	6	3.5	1.75	4
27	385	3	2.5	1.45	-
36	387	6	2	1.4	2
39	446	5	3	1.55	-
41	409	5	2.5	1.8	-
43	408	5	1	1.75	4
63	544	5.5	3	2.3	-
Blue 25	416	5.5	3.5	1.6	-
27	421	4.5	2.5	1.5	-
40	450	6	1	1.9	3.5
41	465	5.5	1	1.9	4.5
43	349	5	2	1.3	3
47	421	5	2	1.7	3.5
51	465	6	2.5	1.9	-
53	404	5.5	2.5	1.6	-
55	401	5.5	3	1.35	3
62	399	5	2.5	1.6	-
78	480	5.5	3	1.7	-
111	569	5.5	4	2	-
117	570	5	3	-	-
Brown 2	493	5.5	3	-	2
3	341	2	2	1.75	-
4	342	3	3.5	1.9	-
6	377	2	2.5	1.6	-
8	361	4.5	3	1.9	-
20	547	4	3	-	-
Black 31	493	6	3	-	-
14675	355	4	3	1.7	-

TABLE II

Colour Index Numbers and Various Fastness Data  
for Disulphonated Acid Dyes.

C.I. Designation Number.	Anionic Weight.	L.F. Number.	W.F. Number.	x/y	Migration Number.
Yellow 9	355	3	1	1.9	2
17	505	7	2	-	4
18	484.5	6	2	-	-
44	746	4	3.5	-	1
55	534.5	4.5	3	-	-
Orange 9	491	6	3	2.1	-
10	374	4.5	1	1.45	4.5
14	406	4	2	1.45	3
27	463	5.5	1.5	2.2	-
28	545	4.5	3.5	-	2
45	723	4.	4.5	-	1
49	784	4.5	4	-	-
51	799	6	4.5	-	1
79	713	4	3.5	-	-
Red 1	463	5	3	1.7	4
3	456	3	2	1.9	3
5	436	5	2	1.8	4.5
7	463	4	2	2.35	4
8	434	5	2.5	2.05	-
12	456	3	4	1.85	3
13	456	3	2.5	1.75	-
14	580	3	2	1.85	3.5
16	456	4	2.5	2.25	-
17	456	3	3	1.5	-
19	450	5	3	2	-
21	436	5.5	1	1.6	-
22	450	4	4	1.65	-
23	463	3	2.5	1.7	-
24	420	1.5	2	1.45	-
25	456	3.5	1	1.55	-
29	422	4.5	2	1.95	-
30	478	6	2.5	1.6	4
31	422	4	2	1.75	-
33	421	2	2.5	1.95	-
34	436	6.5	2.5	1.8	-
35	477	4.5	2	1.75	3

C.I. Designation Number.	Anionic Weight.	L.F. Number.	W.F. Number.	x/y	Migration Number.
Red 37	478	5.5	2	2	3
44	456	3	2.5	1.7	-
54	452	6	4	1.65	-
66	510	3.5	4	2.35	-
70	510	4	2.5	2.4	-
71	538	5.5	2.5	2.4	-
73	510	6	3	2.2	2
76	588	4	4	-	-
82	510	6	3	1.45	-
85	756	4.5	3	-	1
86	912	2	3.5	2.25	-
89	680	4	3	2.45	1
97	652	4	3	2.6	1
99	680	5	3.5	3	1
102	456	3	3	2.1	3
111	770	5	4	-	1
114	784	3	4	-	-
115	536	4.5	3	1.95	-
128	816	5	4	-	-
133	722	4.5	4	-	1.5
142	510	4	4	2	-
150	510	4	1.5	1.9	-
157	664	5	3	-	-
161	675	4.5	3.5	-	-
164	713	4	3.5	-	-
173	680	4	4	2.65	-
Violet 1	466	4.5	1	1.85	3
3	437	2	3	2.05	2.5
6	479	4	3	2.15	-
7	520	4	2	1.9	4.5
12	493	4	2	1.55	-
13	472	4	2	1.95	-
15	624	1.5	2	-	2
17	738	1	3.5	-	2
20	479	4.5	2	2.15	-
34	576	6	3	2.5	-
34	576	6	3	1.75	-
42	580	6	3	1	-
49	710	1.5	3	-	-

C.I. Designation Number.	Anionic Weight.	D.F. Number.	W.F. Number.	x/y	Migration Number.
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Blue	1	543	1	2	-	5
	3	559	1	2.5	-	-
	4	451	2	2	2.05	2
	6	481	3	2.5	1.95	-
	7	665	1	3	-	3
	13	608	1	3	-	3.5
	15	752	1	3.5	-	2
	18	733	3	3	-	3
	23	529	6	2	1.8	2.5
	29	556	6	2	2.3	-
	34	606	1.5	2	-	-
	35	658	5.5	3	1.03	-
	45	428	5.5	2	1.3	-
	49	499	5	3	1.7	2
	56	396	5.5	1.5	1.3	-
	59	647	3	2	-	3
	61	676	4	2	-	3.5
	80	632	6	3	1	1
	83	802	2.5	4	-	2
	87	523	3.5	2.5	2.15	-
	90	830	3	3	-	2
	96	565	6.5	3	1.7	-
	98	729	5	2	-	2
	102	676	3.5	3	-	3
	113	635	5	3	-	2
	114	669.5	5	3	-	2
	116	635	5	3.5	-	-
	118	649	5	3	-	1
	120	649	5	3.5	-	-
	128	720.5	4.5	3.5	-	-
	135	547	4.5	3.5	-	-
	145	486	5.5	3	1.7	-
	147	515	2	2	-	4
	150	782	6.5	4.5	2.7	-
Green	3	667	2	1	-	-
	7	571	2	2	-	3.5
	9	701.5	2	2	-	3
	11	608	6.5	3	1.2	-
	19	643	3	3	2.35	2
	20	540	4	3	2.25	4
	25	576	6	3	1.1	2



C.I. Designation Number	Anionic Weight.	L.F. Number.	W.F. Number.	x/y	Migration Number.
Green 27	660	6	5	1.35	-
36	702	6	4	1.25	-
38	592	6	3	1.25	-
42	698	6	3.5	1.55	-
44	742	6	4.5	1.2	-
50	553	2.5	2	-	3
Brown 9	480	4	3	2	-
15	526	3	3	2.4	-
16	623	4	3.5	-	-
26	587	6	4.5	3	-
Black 1	570	5	3	2.3	3
5	576	6.5	3	2.2	-
16	570	6	3	2.4	-
17	575	5.5	3	2.35	-
21	699	6	5	-	-
24	685	6	3.5	-	2
26	651	4	3.5	-	3
26A	665	4	3.5	-	3
28	582	5	3	2.3	-
14955	-	5	-	1.5	-
19145	414	4	3	-	-
19180	434.5	4	3	-	-
61135	826	-	4	-	-
61550	581	4	3	1.6	-

TABLE III

Colour Index Numbers and Various Fastness Data for  
Acid Dyes with Three or more Sulphonate Groups.

C.I. Designation Number.	Anionic Weight.	L.F. Number.	W.F. Number.	x/y	Migration Number.
Yellow 13	465	6	2	-	-
23	465	4	2	-	3
Red 18	534	4	2	-	-
41	613	4.5	2.5	-	-
47	732	4	2.5	-	-
60	551	4.5	-	-	-
112	668	3.5	2.5	-	-
145	863	5	5	-	-
152	879	4	3.5	-	-
Violet 2	672	2	2.5	-	-
Blue 89	640	5	3	-	-
92	626	5	1	-	1.5
Brown 32	732	3.5	4	-	-
Black 3	768	6	3	-	-
18	654	6.5	4	-	-
32	785	4	4	-	-
41	649	5	2	-	3

TABLE IV

Anionic Weight (Anionic Weight x 2 + 52) and  
Colour Index Data for Chrome Mordant Dyes.

C.I. Designation Number.	Anionic Weight.	Washfastness on wool.
Mordant Yellow 3	790	4
9	856	4.5
10	690	4.5
14	646	4
18	532	4.5
32	790	4.5
33	904	4.5
Mordant Orange 2	692	4
14	620	4.5
26	774	4.5
37	796	4
Mordant Red 15	912	3.5
27	1030	4
34	916	4.5
Mordant Violet 11	1016	4.5
15	920	4.5
27	978	4
41	732	4.5
Mordant Blue 14	706	4
24	592	4
29	1152	4
50	623	3
Mordant Green 12	1194	4
24	756	4.5
28	992	4.5
Mordant Brown 11	868	3.5
18	938	4
25	936	4
48	756	4.5
69	962	4.5
Mordant Black 10	1076	4.5
15	826	4.5
19	758	4
56	838	4.5

TABLE V

Molecular Axial Ratios and Colour Index Data  
for Mono- and Disulphonated Direct Dyes.

C.I. Designation Number.	L.F. Number.	Total Number of Atoms.	x/y	
Yellow	1	4	52	3.1
	2	5	58	2.94
	10	4	55	3.5
	12	4.	70	3.3
	14	2	65	3.0
	15	4.5	63	2.86
	17	2.5	68	3.05
	20	3	58	2.77
	24	1.5	54	2.83
	26	4.5	58	3.44
	33	6	98	4.3
	48	5	64	2.77
	49	4	64	3.05
Orange	3	3	69	3.33
	4	3	64	2.63
	6	1	65	2.8
	6	1	65	2.7
	7	2	68	2.7
	8	1	60	2.94
	10	1.5	72	2.7
	13	3	73	2.34
	17	2	55	2.75
	18	2	56	2.55
	25	1.5	61	2.95
	29	2	74	3.44
	30	3	72	3.1
	31	3	69	3.1
	33	4	72	2.9
Red	1	3	60	2.27
	2	1	74	3.1
	3	2	59	2.2
	7	1	76	2.95
	8	4	59	3.06
	10	2	67	3.1
	13	2.5	69	2.45

C.I. Designation Number.	L.F. Number.	Total Number of Atoms.	x/y	
Red	14	3	78	3.44
	16	2	58	2.88
	17	1.5	67	2.9
	18	1.5	61	2.13
	20	2	52	2.4
	21	1	74	2.52
	22	1	74	2.3
	23	3	79	3.66
	24	2.5	82	3.15
	28	1	68	3.1
	33	3	60	3.05
	37	2	70	2.57
	39	2	72	2.8
	45	2	52	2.5
	47	3	52	2.25
	50	2	61	2.9
	51	2	58	2.25
	52	3	59	3.0
	53	2	60	3.05
	59	4	69	3.28
	61	1	68	3.1
	64	3	61	2.45
	65	3.5	60	2.65
	67	1.5	74	2.4
	68	1.5	65	2.95
	69	2	64	3.22
	70	1.5	64	2.6
	77	5	62	3.06
	81	4.5	63	3.47
	85	5	69	3.47
	88	4	66	2.9
	90	4.5	66	3.47
	108	4.5	63	3.47
	110	5.5	75	3.42
Violet	1	3	70	2.52
	4	3	70	2.45
	5	3	61	1.83
	10	2	65	1.92
	12	1	70	3.1
	13	1	72	2.52
	21	2	73	3.1

C.I. Designation Number.	L.F. Number.	Total Number of Atoms.	x/y		
Violet	28	1	72	3.1	
	32	1.5	75	2.95	
	38	3	80	3.9	
	39	1.5	72	3.1	
	42	2	68	2.4	
	43	1	66	3.1	
	63	5	67	3.27	
	64	5	76	3.1	
Blue	3	1	74	3	
	8	1	74	2.95	
	12	2	76	2.95	
	19	1	68	2.9	
	22	1	76	2.7	
	42	1	68	2.9	
	45	1	76	2.6	
	50	1.5	74	3.0	
	58	2.5	70	2.85	
	60	2	76	2.95	
	Green	1	1.5	74	2.75
		6	1.5	76	2.9
7		1.5	77	2.82	
8		3	78	2.9	
9		2	78	2.8	
10		2	74	2.75	
11		3	69	2	
12		4.5	74	2.85	
19		2	80	2.9	
22		3	81	2.7	
Brown		1	1	68	3.15
		1A	1	71	3.0
	2	3	60	2.8	
	5	3	65	3.3	
	6	2.5	65	3.1	
	7	2	75	2.95	
	17	2	75	2.8	
	21	3	71	3.15	
	27	4	81	2.15	
	32	3	72	2.9	
	56	3	62	3	
	57	1	75	2.85	
58	3	66	2.62		

C.I. Designation Number.	L.F. Number.	Total Number of Atoms.	x/y
Brown 60	1	60	2.27
61	1	76	3.15
68	3	80	2.85
79	2	71	3.15
80	2	71	3.35
86	2	61	2.94
99	4.5	78	2.6
101	5	73	2.75
154	2.5	74	2.85
158	2.5	71	3.0
Black 3	3	54	2.1
4	3	80	2.8
11	3	77	2.8
17	5	57	2.37
20	3	101	3.05
21	2.5	81	3.15
29	3.5	70	2.75
38	3	77	2.74
40	2	77	3.10
48	3	71	2.48
49	3	78	2.44

TABLE VI

Molecular Axial Ratios and Colour Index Data  
for Tri- and Tetra Sulphonated Direct Dyes.

C.I. Designation Number.	L.F. Number.	Total Number of Atoms.	x/y
Yellow 34	6.5	90	2.65
50	6.0	82	2.9
51	5.0	86	2.77
Orange 24	2	76	3.1
49	5	90	2.3
Red 4	2.5	75	3.72
15	2	77	2.3
26	2	85	3.15
34	1	77	2.3
36	2.5	90	3.95
42	1	72	2.54
43	2	72	2.26
46	2	76	2.26
49	3	86	2.16
54	2	90	3
56	2	80	2.3
60	1	72	2.35
62	2	81	3.15
75	4	82	2.45
79	6	92	2.6
101	4.5	82	2.34
103	4.5	75	2.05
113	5	78	3.82
Violet 3	1	69	3.22
22	1	69	2.75
27	2.5	71	3.1
36	1	69	2.6
45	2	72	2.65
62	5	84	2.45
Blue 1	1	84	3.16
2	1	73	2.9
6	1	76	3.05
9	2	77	2.3
10	3	82	3
11	2	88	3.1
14	1	82	3.2
16	1	71	2.67



C.I. Designation Number.	L.F. Number.	Total Number of Atoms.	x/y	
Blue	21	1	77	2.9
	25	2	80	3.2
	26	2	96	2.7
	27	1	75	2.9
	30	3	98	2.95
	31	2	76	3.05
	35	2	77	3.1
	36	2	77	2.9
	37	1.5	80	3.1
	39	2	96	2.85
	43	2	89	2.75
	48	3	73	3
	49	1.5	74	3.2
	51	4	85	3
	53	1.5	82	3.16
	63	3	96	2.95
	65	4	79	2.7
	71	5	87	2.3
	72	5.5	78	2
	82	5	81	2.1
	96	5	63	2.25
Green	3	4	101	3.05
	20	2	85	2.9
	33	5	98	2.35
Brown	69	3	80	2.85
Black	14	3.5	87	3.05
	15	2	79	3.2
	24	3	95	2.95
	27	3	86	2.9
	74	5	90	1.9

TABLE VII

Molecular Axial Ratios and Colour Index Data  
for Vat Dyes.

C.I. Designation Number.	L.F. Number.	x/y	C.I. Designation Number.	L.F. Number.	x/y	
<b>Anthraquinone</b>			<b>Blue</b>			
Yellow	1	5.5	4	7.5	2.15	
	3	6	6	7.5	1.65	
	4	5.5	11	7.5	1.65	
	12	5	13	7	1.9	
	13	4.5	20	6.5	2.3	
	20	7	21	6.5	1.4	
	23	5	22	6.5	2.3	
	26	5.5	26	6.5	1.6	
	29	6	32	7	1.5	
	31	6	33	7.5	1.55	
	58950	4	2.8	<b>Green</b>		
65400	5.5	2.2				
65435	4.5	2.85				
Orange	3	7.5	1			
	9	5.5	3	8	2.3	
	13	7.5	4	7	1.75	
	16	7	9	6	2.55	
	17	7.5	11	7.5	1.8	
Red	18	6.5	69515	8	2.45	
	19	7	Brown	31	6	2.05
	21	7	<b>Indigoid</b>			
	29	6	Orange	5	4.5	3.05
	32	5	73640	5	5	1.5
	33	7	Red	1	5	2.4
	35	8	2	5	2.0	
	39	7.5	5	6	2.4	
	42	7	6	6.5	2.4	
	61655	7	26	4.5	3.05	
	Violet	9	5.5	41	6.5	2.2
13		7	45	5	1.65	
14		8	47	5.5	2.55	
15		6	73330	4	2.5	
17		6.5	73345	3.5	3.3	
		73625	3	2.0		
		73650	5	1.35		
		73680	6	1.75		

C.I. Designation Number.	L.F. Number.	x/y
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Indigoid

Violet	2	5	2.05
	4	5.5	2.1
	18	5	1.95
73370		4	1.85
73380		5	2.25
73390		5	2.7
73595		5.5	2.05
73810		5	1.85
Blue	1	4	2.0
	2	3.5	2.2
	3	4	2.2
	5	4.5	2.05
	8	5.5	1.65
	35	4.5	2.4
	36	5.5	1.75
	37	4	1.95
	40	5	1.85
	41	4.5	2.05
	48	4	1.75
73030		5	2
73315		5.5	1.95
73420		4.5	2.4
73425		5	1.8
73815		5	1.85
73820		4	2.2
73825		3.5	2.2
73840		3	2.0
73845		3.5	2.35
73850		4.5	2.0
Green			
73415		4	2.95
Brown	5	6.5	1.95
	42	6	2.05
73655		3	1.45
Black	1	6.5	2.05

TABLE VIII

Relation between Percentage Fading caused by Blue-Red region of the Spectrum (McLaren's data) and Molecular

Axial Ratio.

C.I. Designation                      (%) Fading by                      x/y  
Number.                      Blue-Red region.

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Acid Dyes

Violet	1	3	1.83
Black	24	12	1.95
Blue	78	20	1.68
Green	19	75	2.5
Green	20	32	2.26
Orange	10	17	1.45
Blue	113	75	1.96
Violet	41	5	1.82
Blue	40	3	1.9
Blue	27	29	1.52
Green	27	17	1.37

Direct Dyes

Green	6	68	2.9
Violet	22	83	2.75
Blue	1	87	3.16
Blue	10	83	3
Black	38	68	2.74

Vat Dyes

Violet	17	16	1.92
Violet	9	46	2.3
Green	9	39	2.53
Green	1	20	1.86
Violet	13	1	2.3
Violet	2	55	2.06
Brown	5	71	1.95
Violet	14	1	1.68
Red	1	53	2.4

Disperse Dyes

Blue	7	8	1.18
Violet	8	26	1.3
Blue	3	16	1.28
Blue	24	22	1.43
Violet	4	18	1.28

TABLE IX

A List of Imperfectly Conjugated Dyes used in the Present Work.

Name.	C.I.Designation	C.I.Number.	Molecular Weight.	Area (sq.A)	Anionic Coverage factor.
	Number.				(o.f.)
1) Solophenyl Brilliant Green 5 GL.	Direct Green 28	14155	832	434	2.7
2) Direct Brown BBN	Direct Brown 58	22340	609	280	3.2
3) Chlorazol Brown BS.	Direct Brown 59	22345	657	295	2.3
4) Diazo Brilliant Orange GRN	Direct Orange 90	28660	690	315	2.1

Note to Tables I to IX: In all the tables for Colour Index data, where C.I. designation numbers are not available in those cases C.I. numbers (from Colour Index Vol.III) are given.

TABLE X

Coverage Factor and Resonating Form Data for  
Cationic Dyes.

C.I. No.	Cationic Weight.	Coverage Factor		$c.f. 60^{\circ}C$	Number of Resonating Forms.
		$20^{\circ}C$	$60^{\circ}C$	<del><math>c.f. 20^{\circ}C</math></del>	
42595	478	11	16.2	1.5	2
42600	456	6.9	14.2	2	3
42510	302	1.9	5.3	3	3 1
42555	372	6	<u>12</u>	<u>2</u>	3
44045	470	<u>11</u>	<u>16</u>	<u>1.5</u>	2
42000	329	-	-	-	2

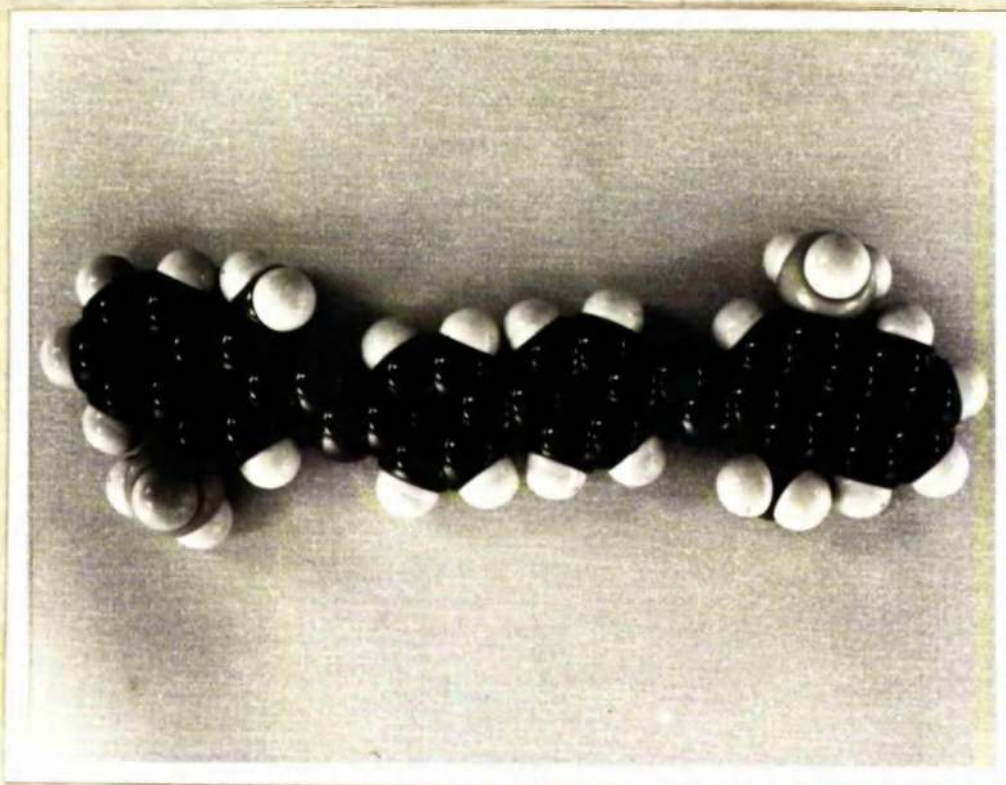
Underlined values in the table are  
predicted values.

LEGENDS TO FIG.I

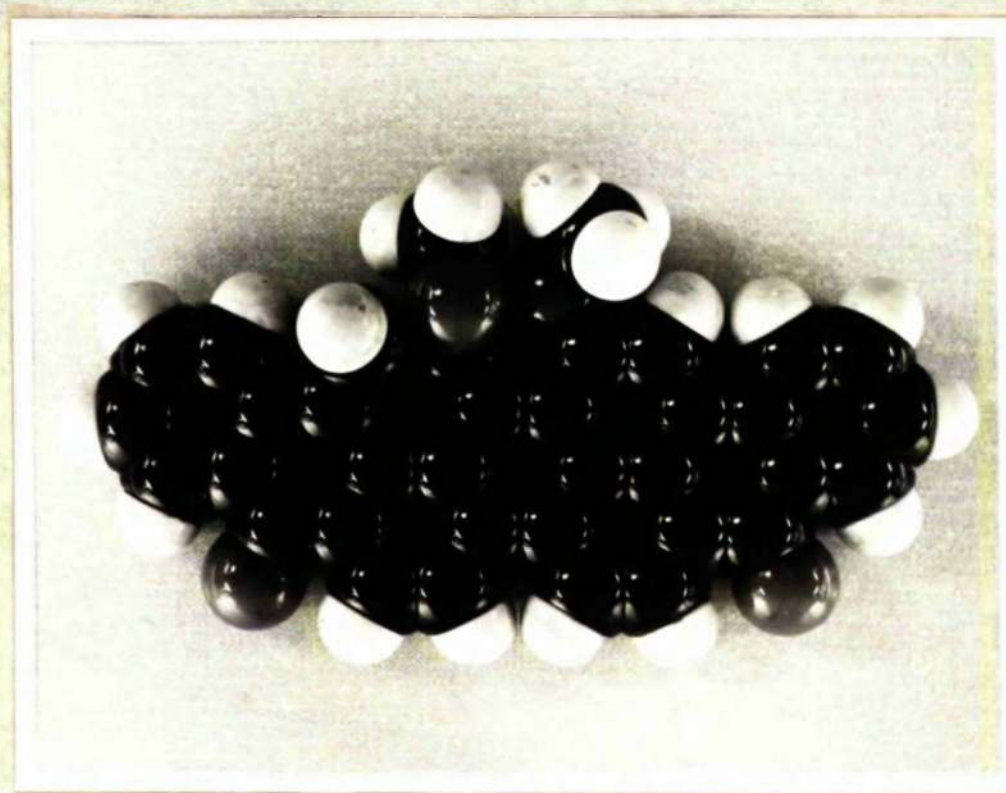
Molecular models of two planar dyes.

A. Direct Red 28 (C.I. 22120).

B. Vat Green 1 (C.I. 59825).



A. Direct Red 28 (C.I. 22120).



B. Vat Green 1 (C.I. 59825).

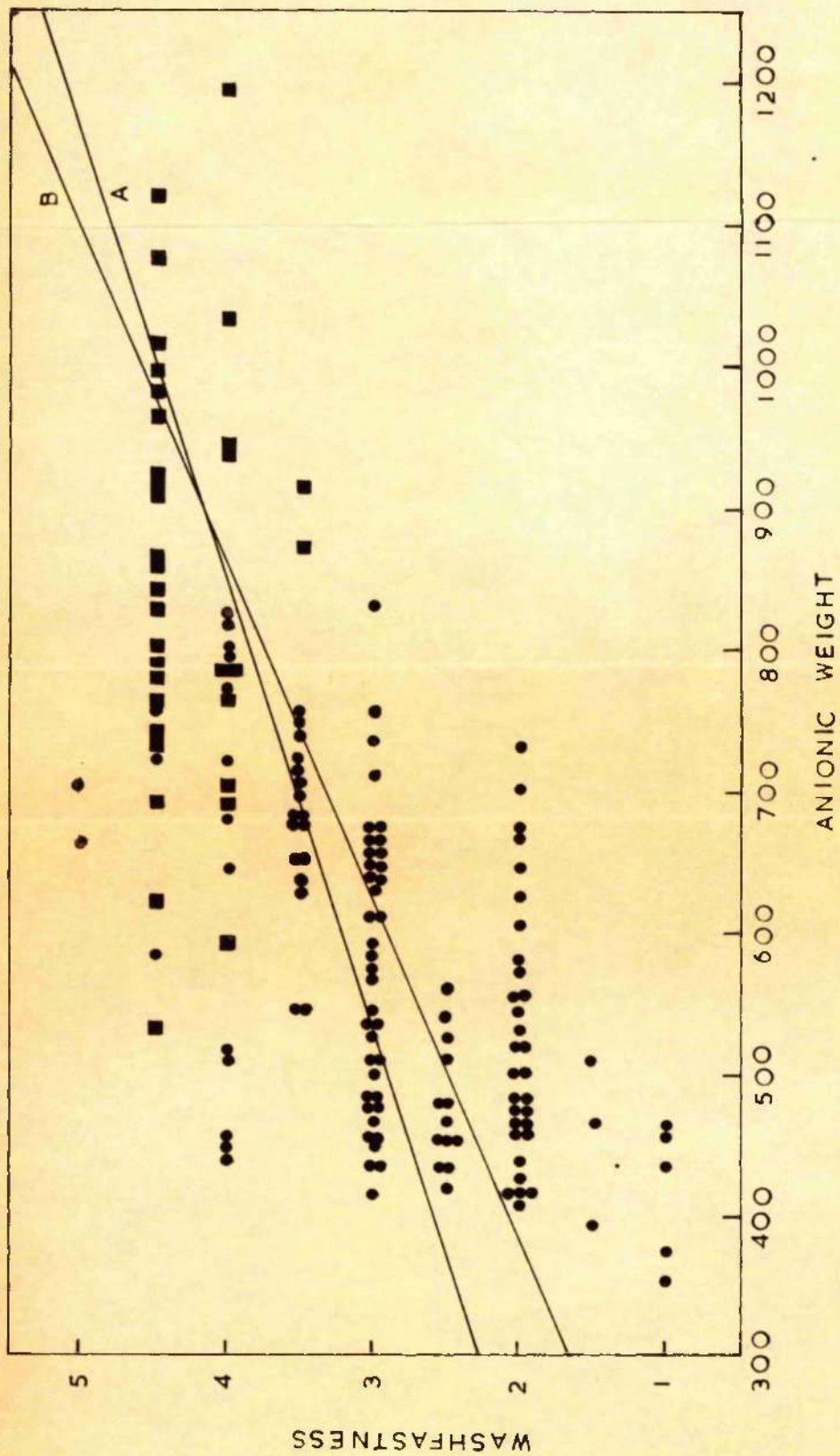


LEGENDS TO FIG.2

Relation between anionic weight and washfastness  
on wool, of disulphonated acid dyes (circles)  
and monosulphonated chrome dyes (squares).

A. For all dyes.

B. Only disulphonated acid dyes.



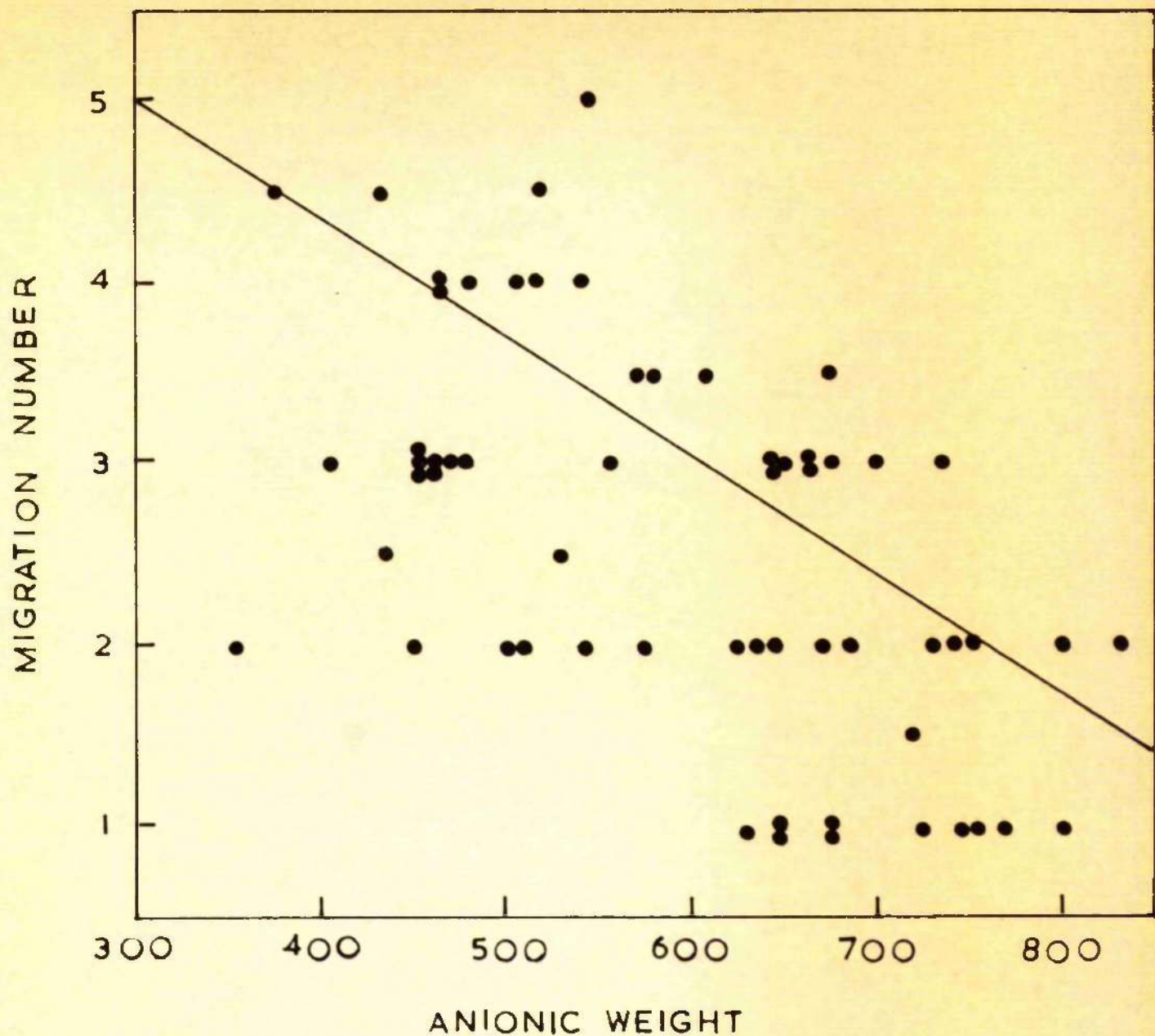
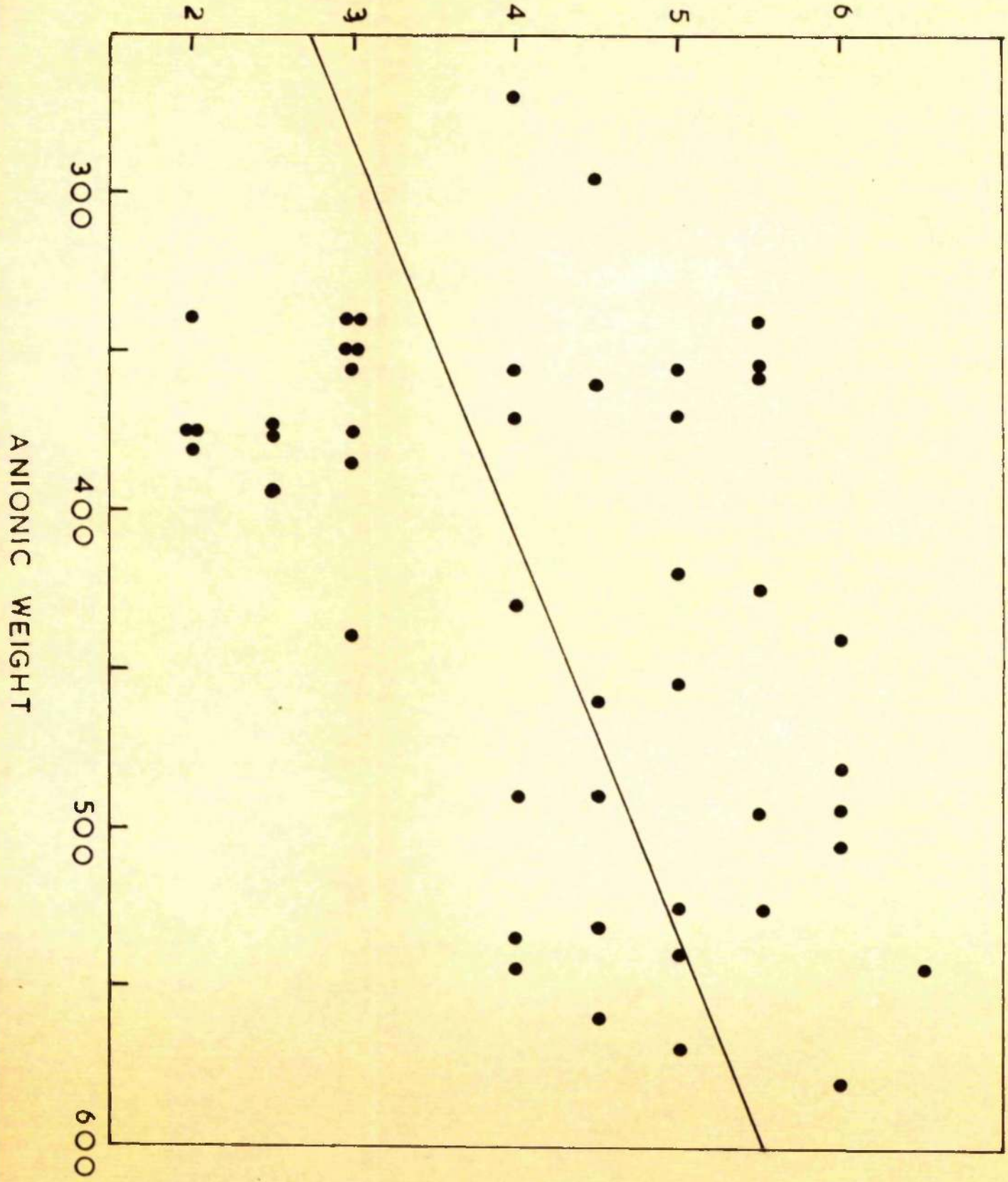


Fig.3. Relation between anionic weight and migration number on wool, of acid dyes with two or more sulphonated groups.

LEGENDS TO FIG.4

Relation between lightfastness and anionic  
weight of monosulphonated acid dyes on wool.

# LIGHT FASTNESS



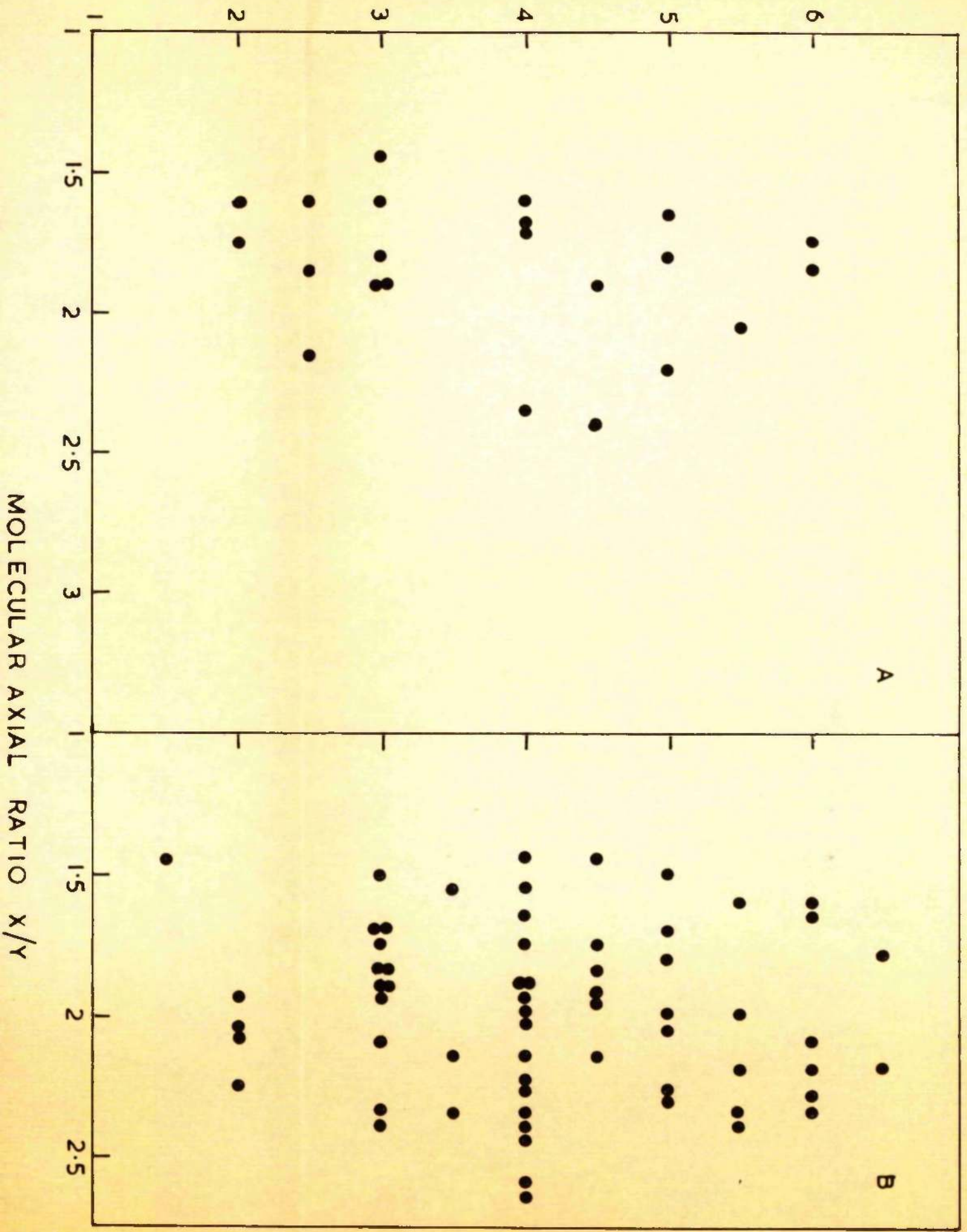
LEGENDS TO FIG.5

Plots of lightfastness on wool against  
molecular axial ratio for acid dyes.

A. Monosulphonated azo dyes.

B. Disulphonated azo dyes.

# LIGHT FASTNESS



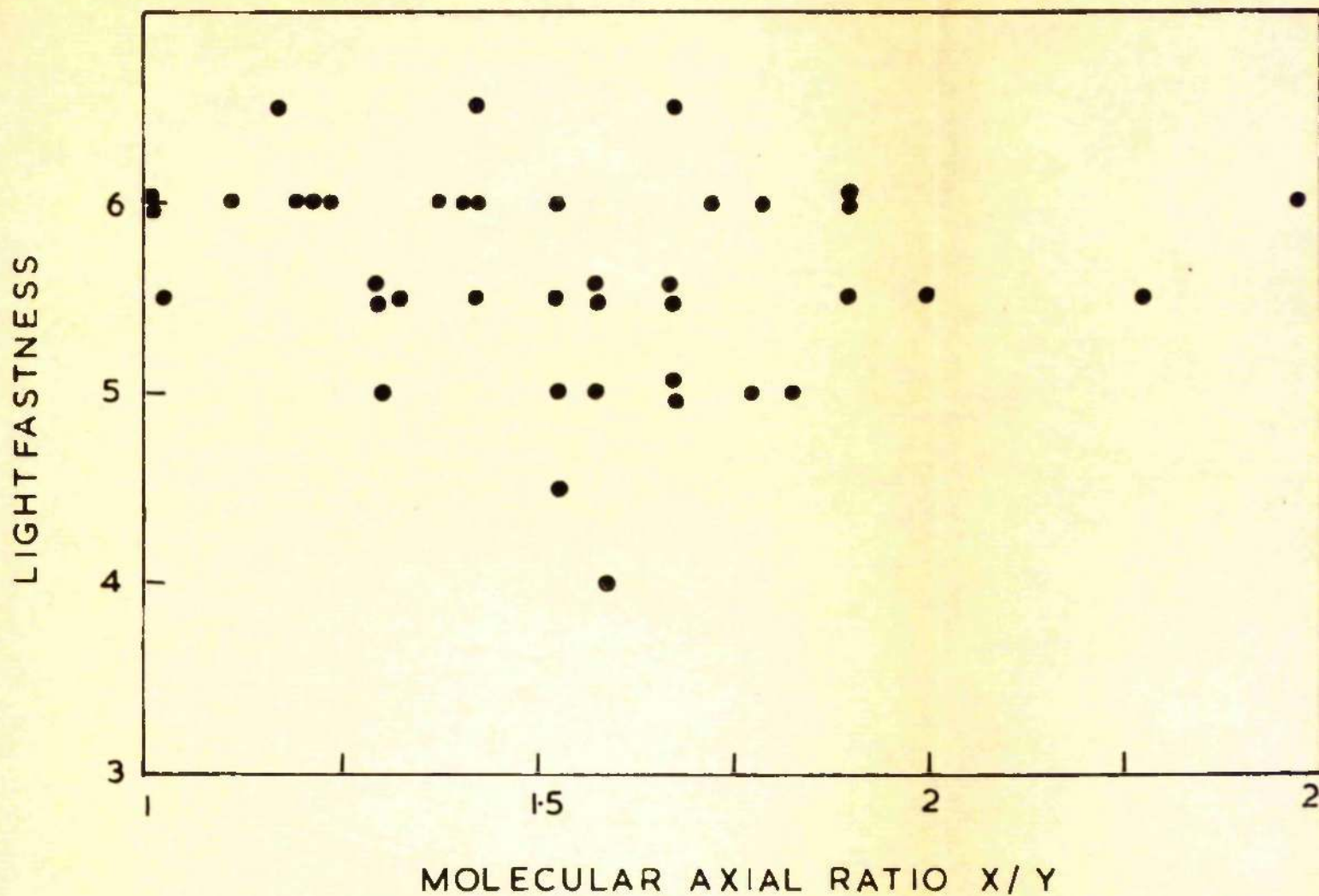


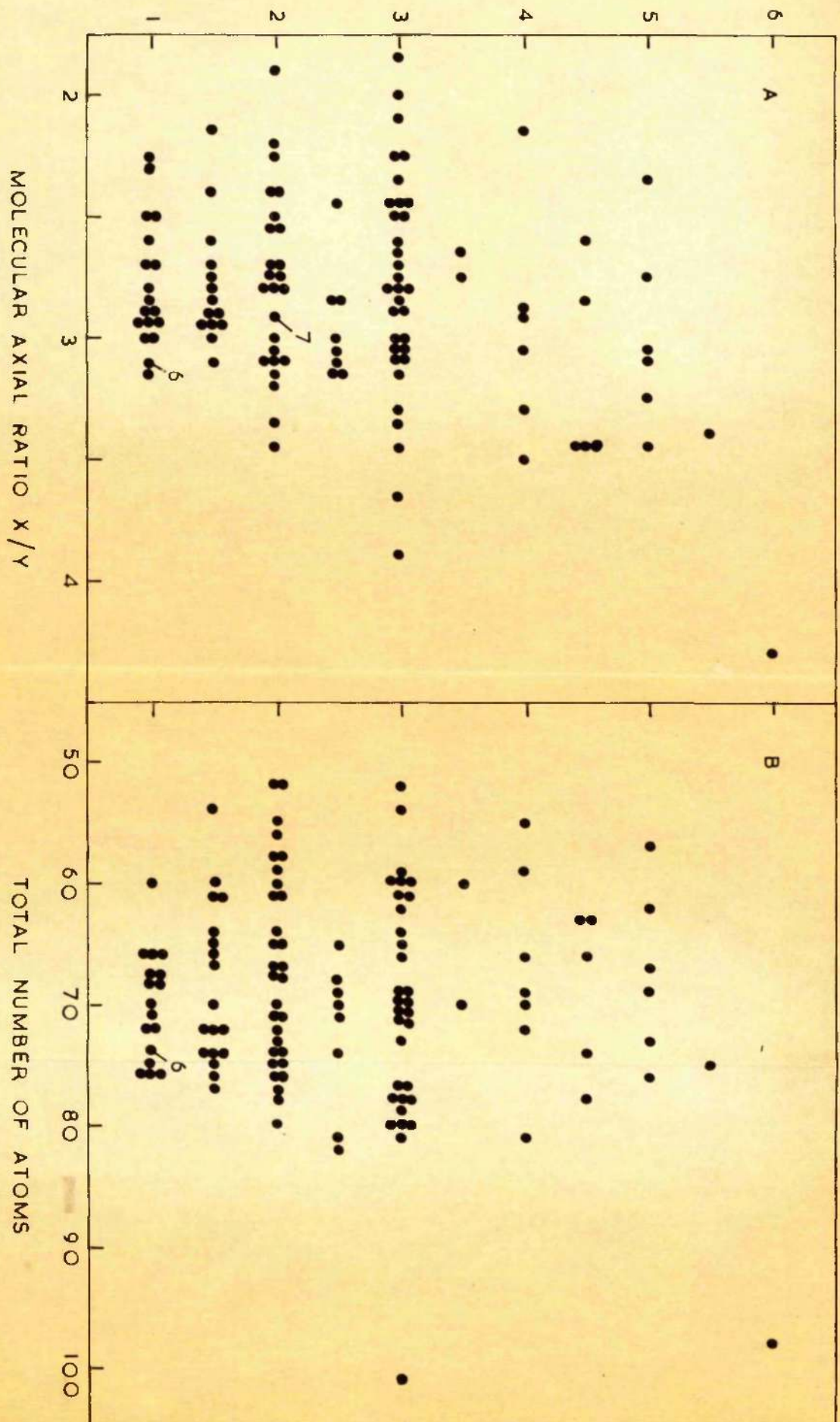
Fig.6. Plot of lightfastness on wool against molecular axial ratio for anthraquinone dyes.



LEGENDS TO FIG.7

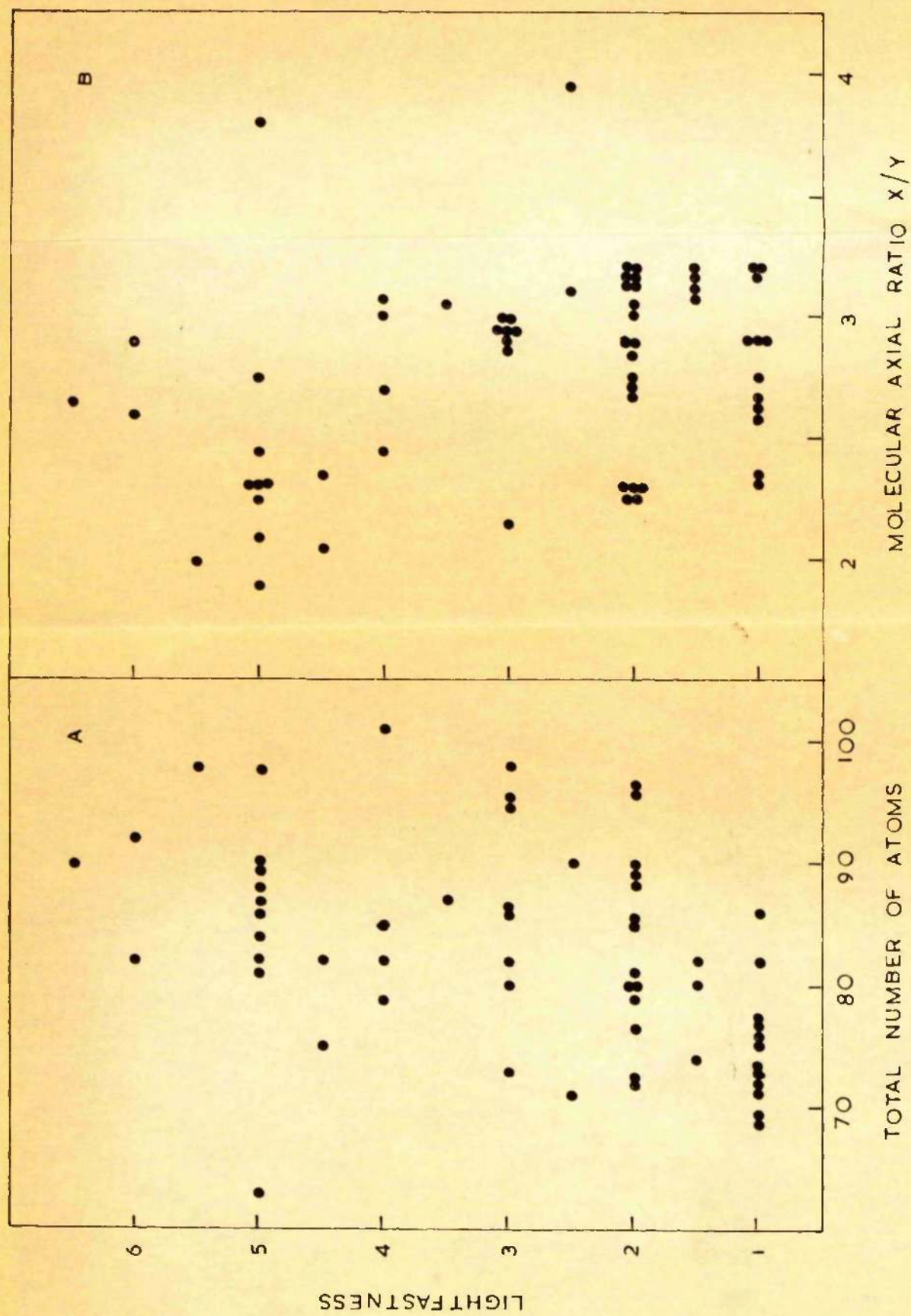
Plots of lightfastness on cotton  
against molecular axial ratio and  
total number of atoms in the dye  
molecules for mono- and di-  
sulphonated direct dyes.

LIGHT FASTNESS



LEGENDS TO FIG.8

Plots of lightfastness on cotton  
against molecular axial ratio and  
total number of atoms in the dye  
molecule for tri- and tetra-  
sulphonated direct dyes.

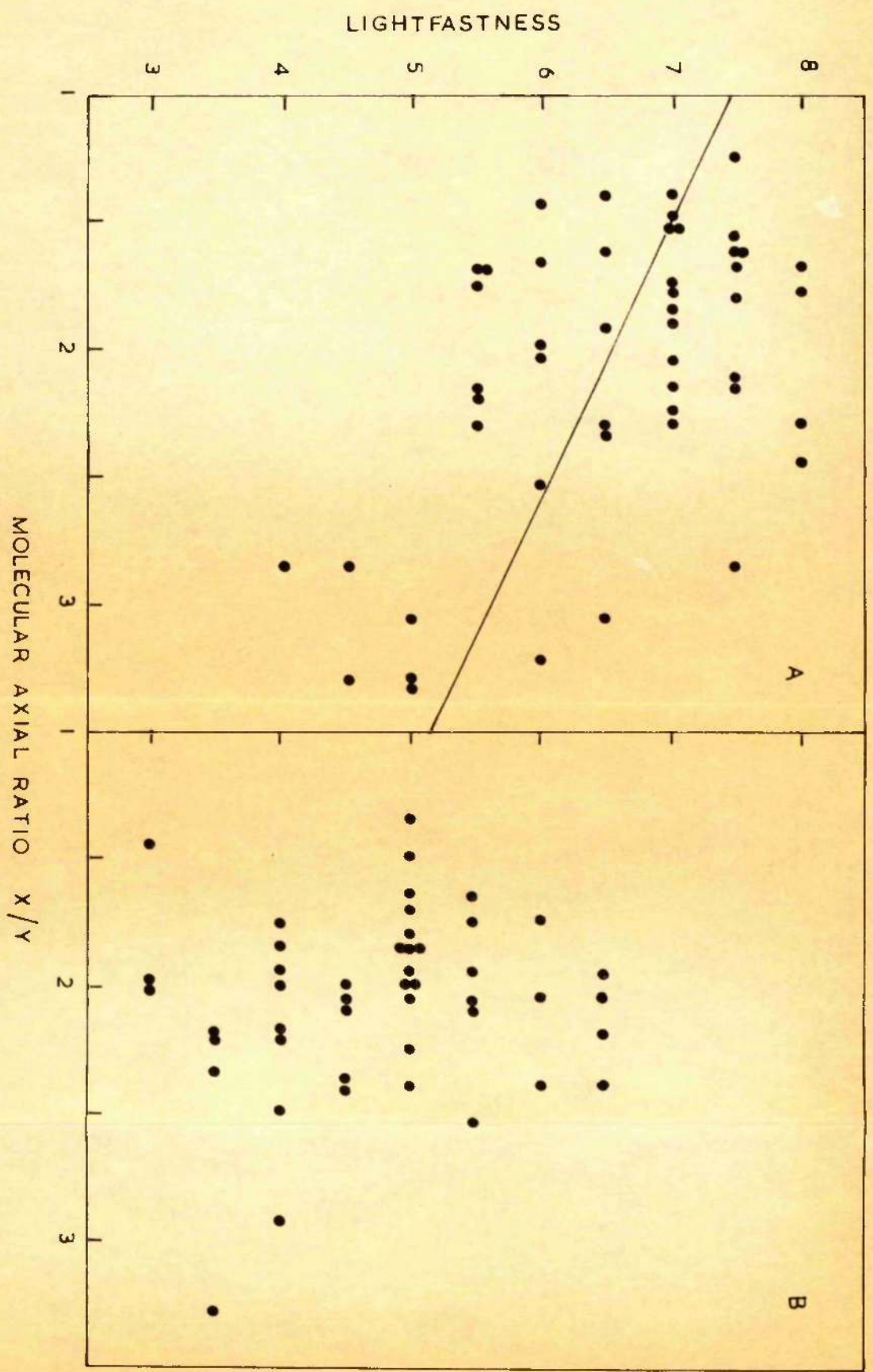


LEGENDS TO FIG.9

Plots of molecular axial ratio  
against lightfastness of vat  
dyes on cotton.

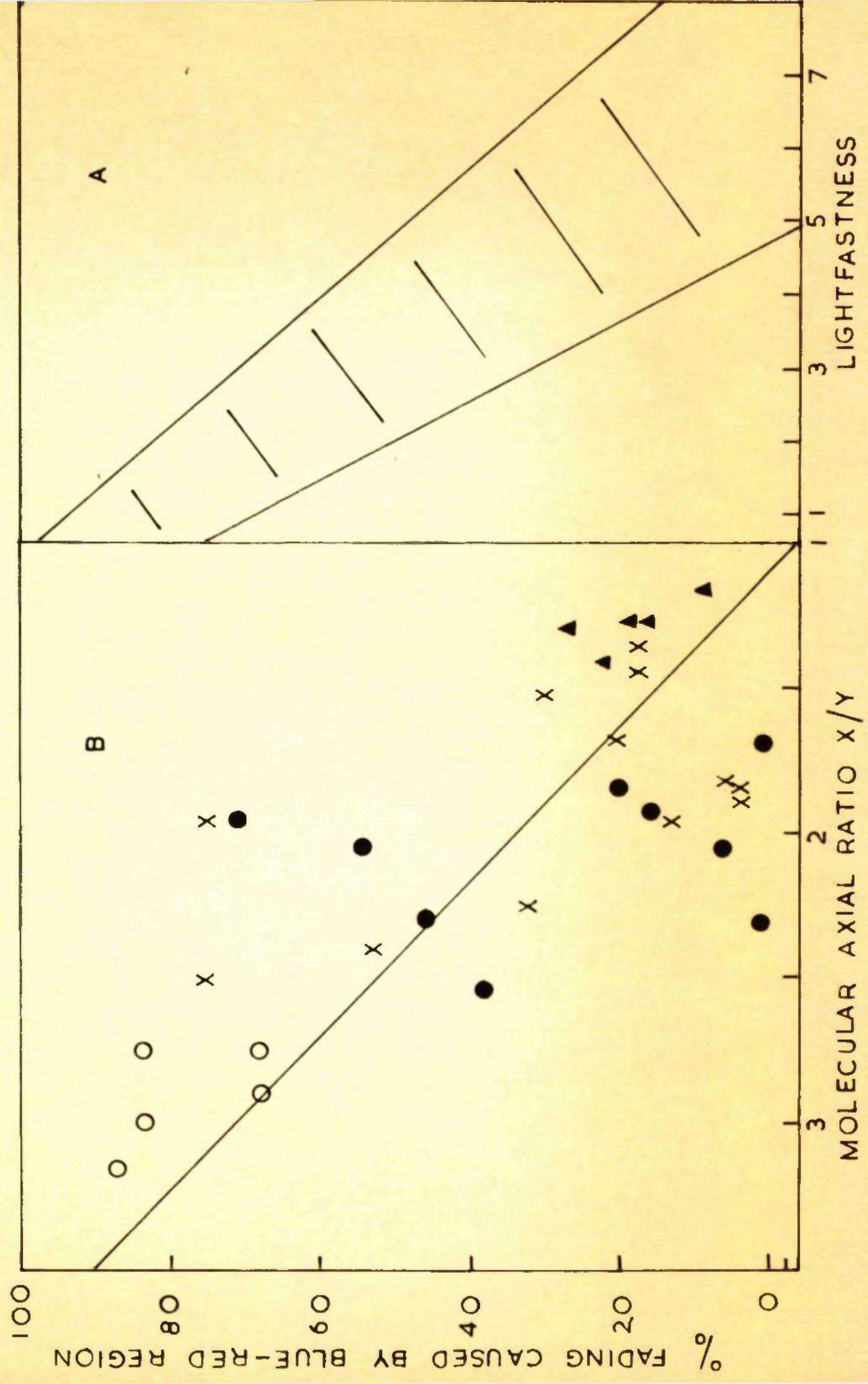
ANTHRAQUINONE

INDIGOID



LEGENDS TO FIG.10

Relation between effectiveness of the blue-red spectral region in causing fading and (A) lightfastness, McLaren's data, omitting experimental points and (B) molecular axial ratio of dyes with planar molecules.





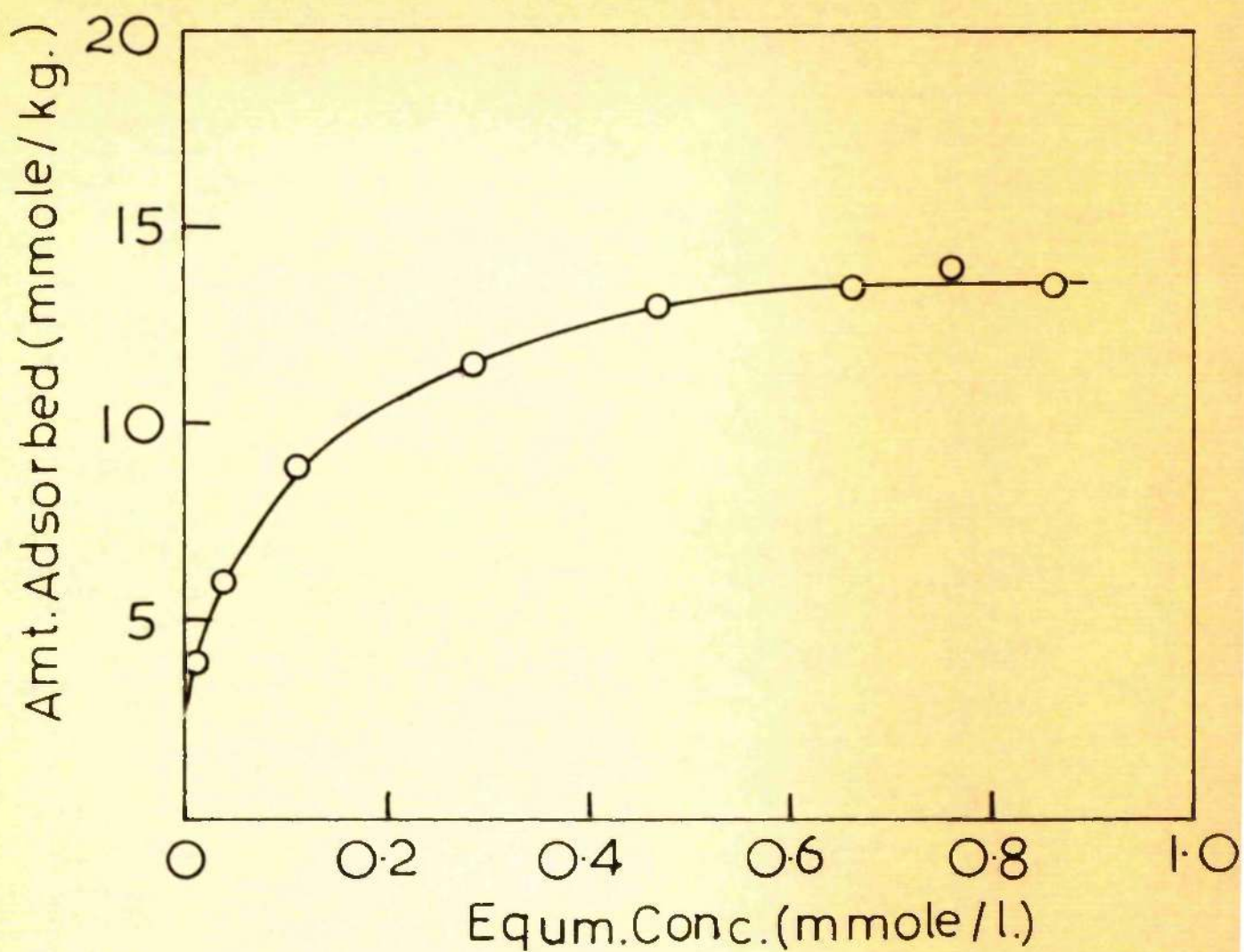
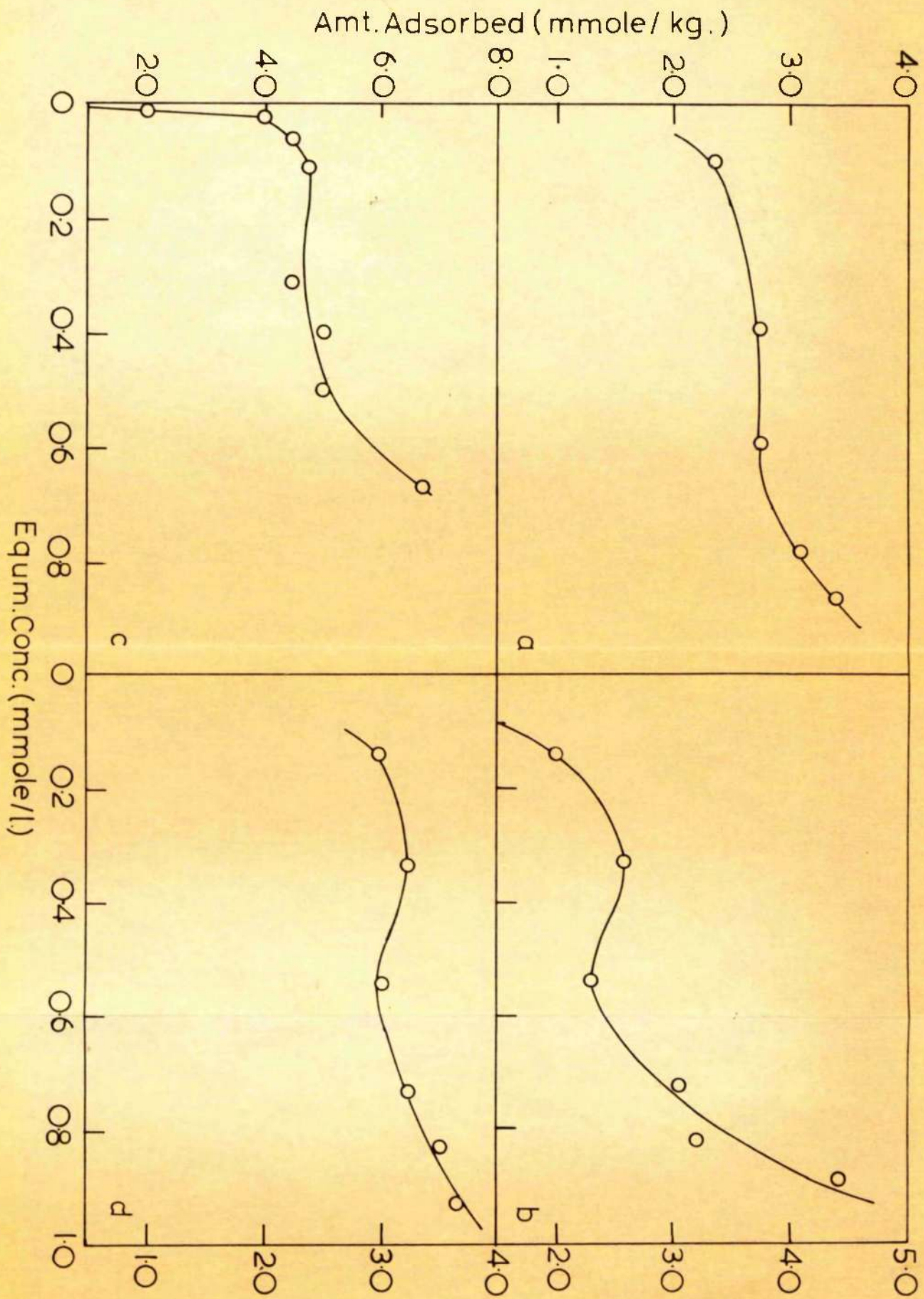


Fig.11. Adsorption isotherm of Direct Brown 138 (C.I. 31500) on graphite.

LEGENDS TO FIG.12

Adsorption isotherms of imperfectly  
conjugated dyes on graphite.

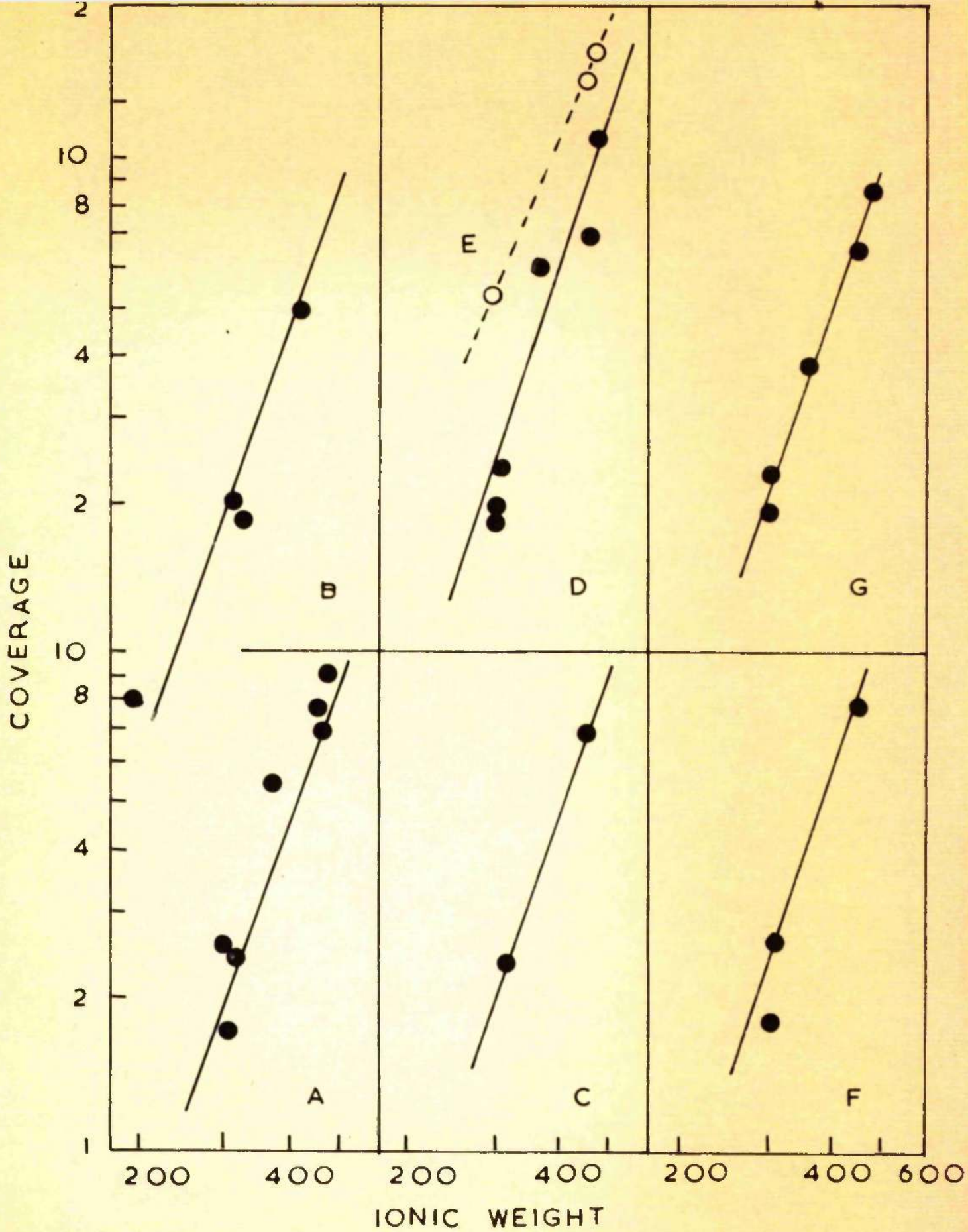
- a. Direct Orange 90 (C.I.28660).
- b. Direct Green 28 (C.I.14155).
- c. Direct Brown 58 (C.I.22340).
- d. Direct Brown 59 (C.I.22345).



LEGENDS TO FIG.13

Plots of ( $\log_{10}$ ) coverage against ( $\log_{10}$ ) ionic weight for cationic dyes (at 20°C except for E).

A. yeast; B. silica; C. calcium carbonate; D. alumina at 20°C;  
E. Alumina at 60°C; F. titanium-dioxide; G. graphite.



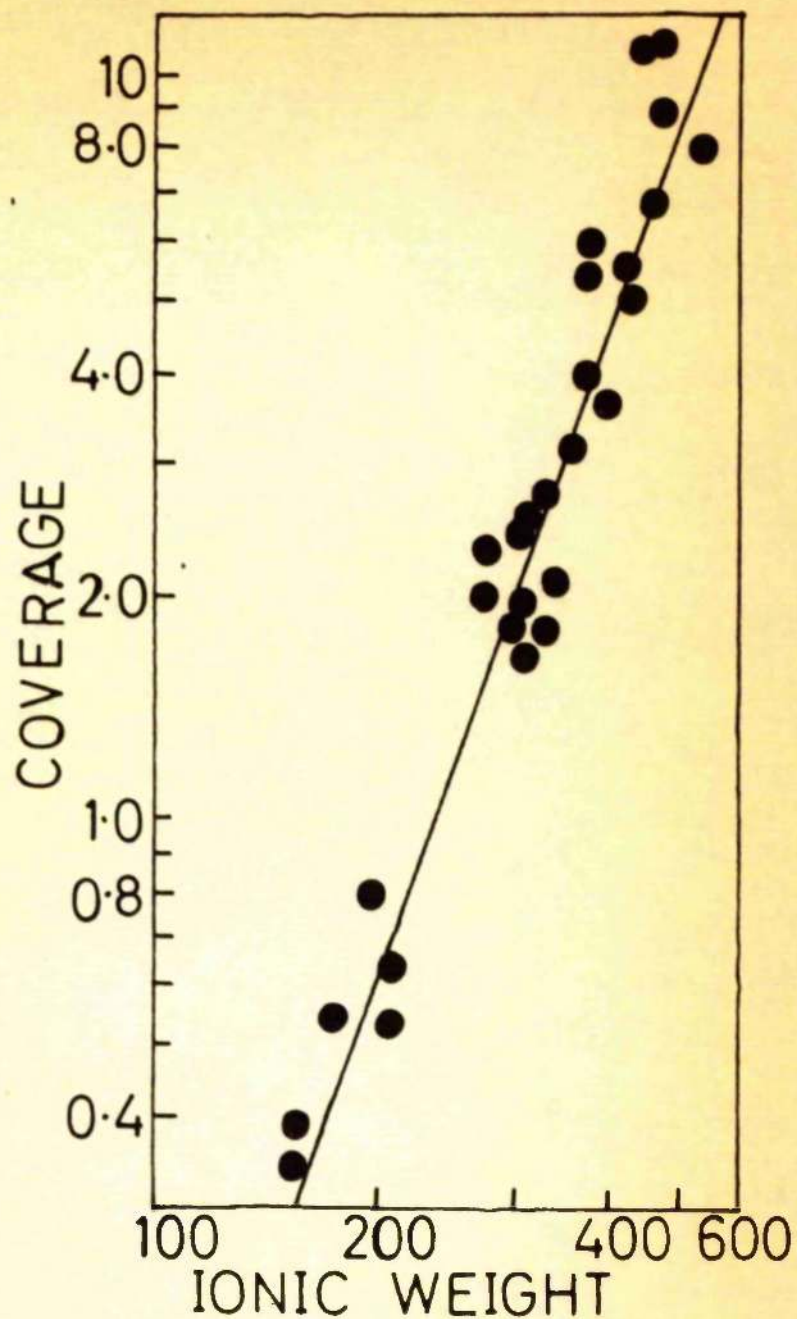


Fig.14. Relation between  $(\log_{10})$  coverage and  $(\log_{10})$  ionic weight for cationic and anionic solutes on various substrates.

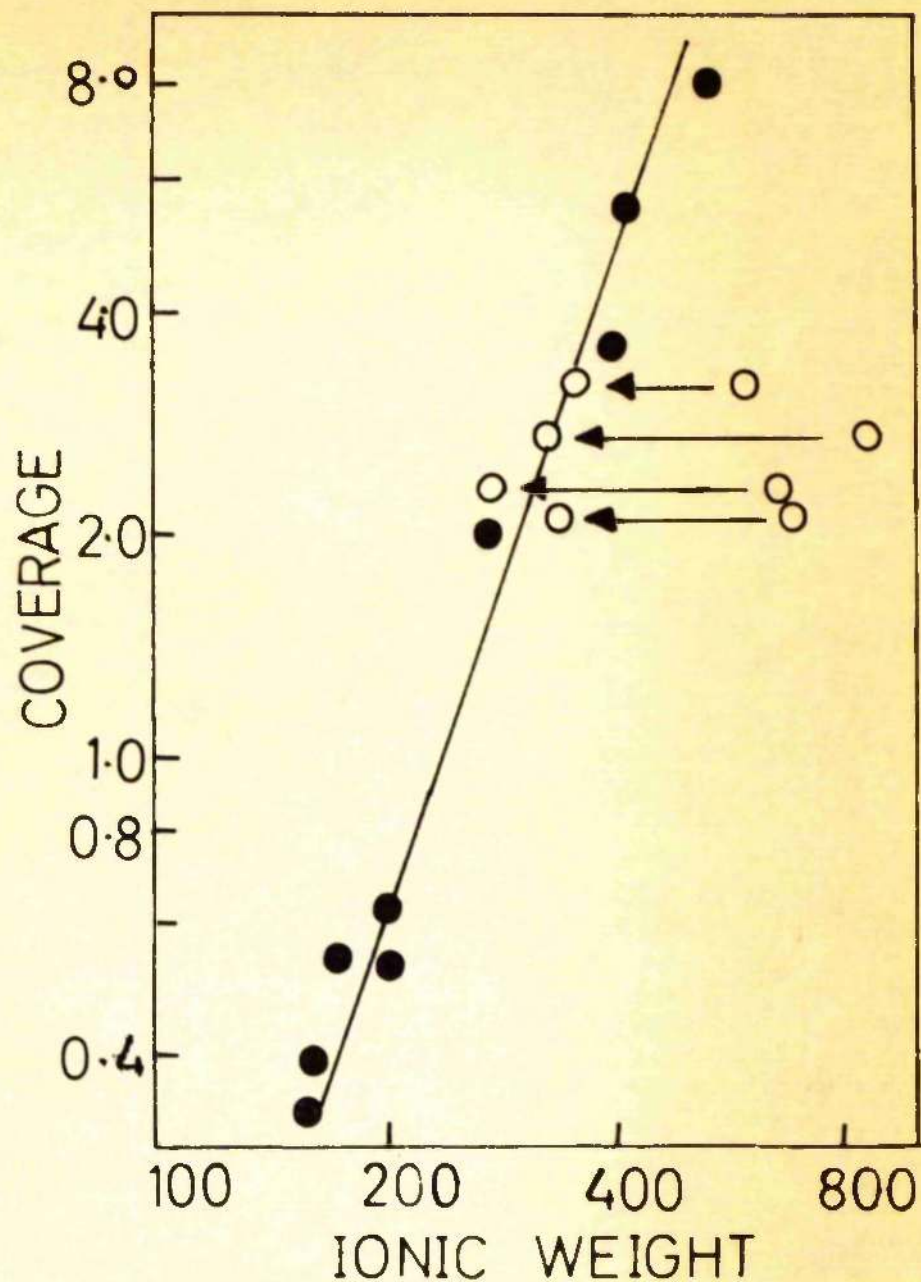


Fig.15. Relation between  $(\log_{10})$  coverage and  $(\log_{10})$  ionic weight for anionic solutes on graphite and alumina at  $20^{\circ}\text{C}$  (least square line). For the imperfectly conjugated solutes, the coverage is plotted against both actual and corrected ionic weight as indicated by arrows.

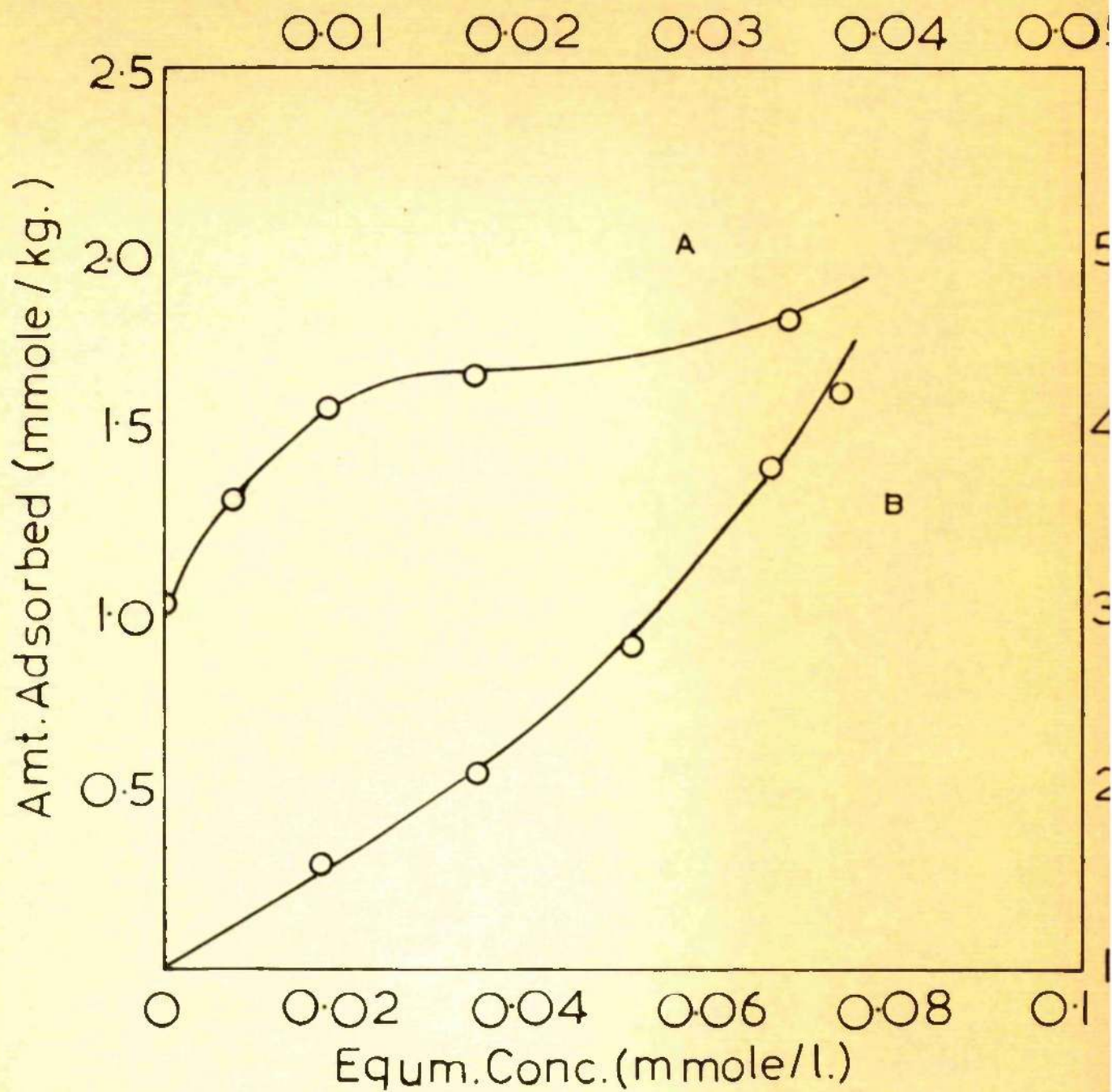


Fig.16. Adsorption isotherms of a cyanine dye on  
 (A) graphite and (B) alumina.



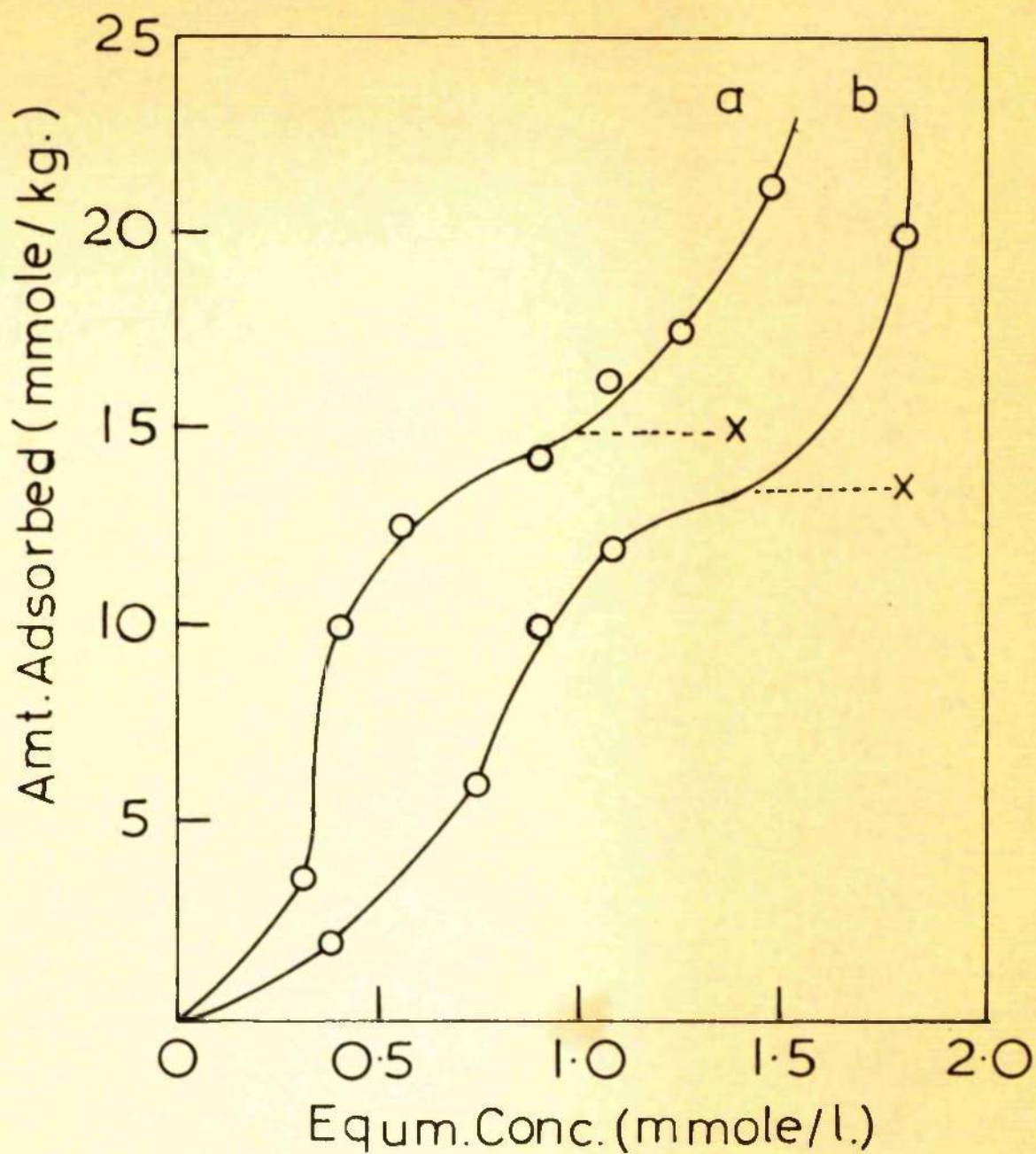
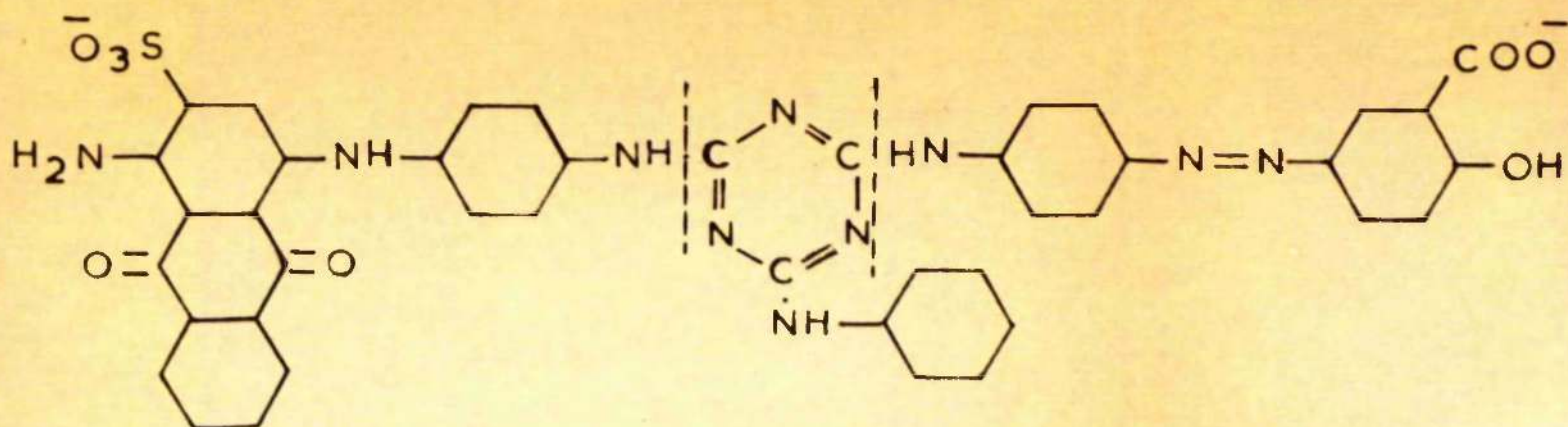


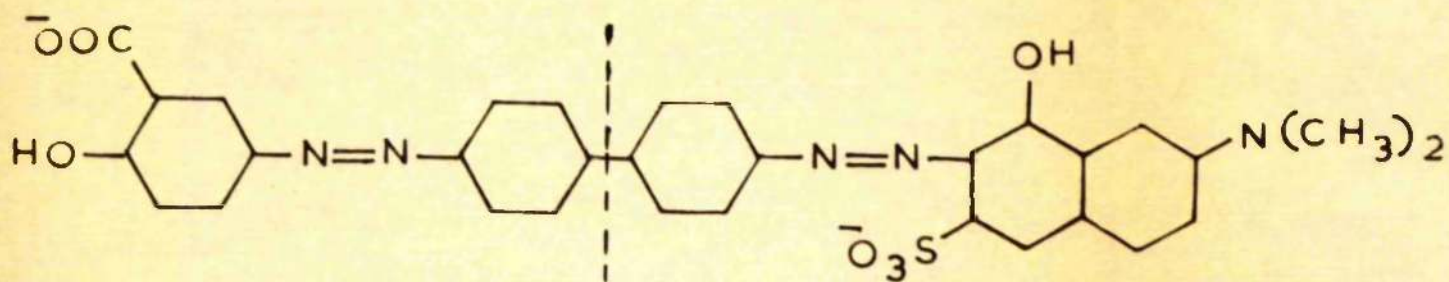
Fig.17. Adsorption isotherms of Solway Ultra Blue B (C.I.62055) on titanium dioxide.

(A) Sample R-SM.

(B) Sample 10863.

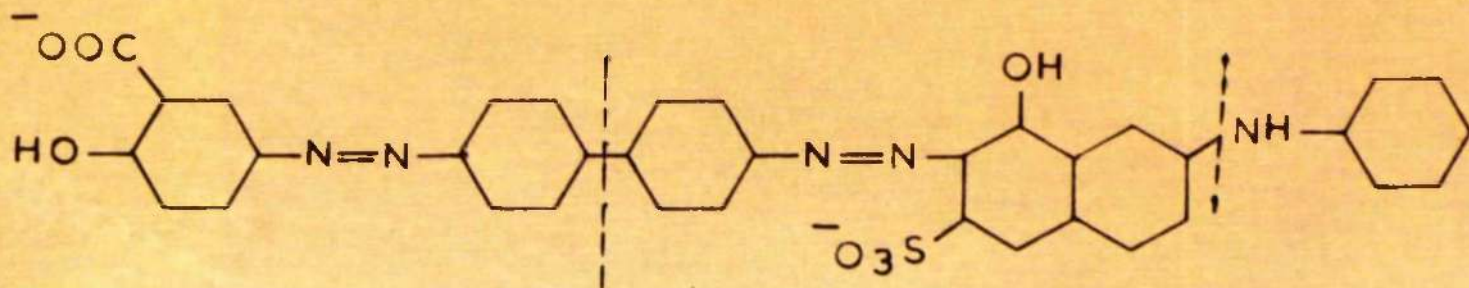


SOLOPHENYL BRILLIANT GREEN 5GL

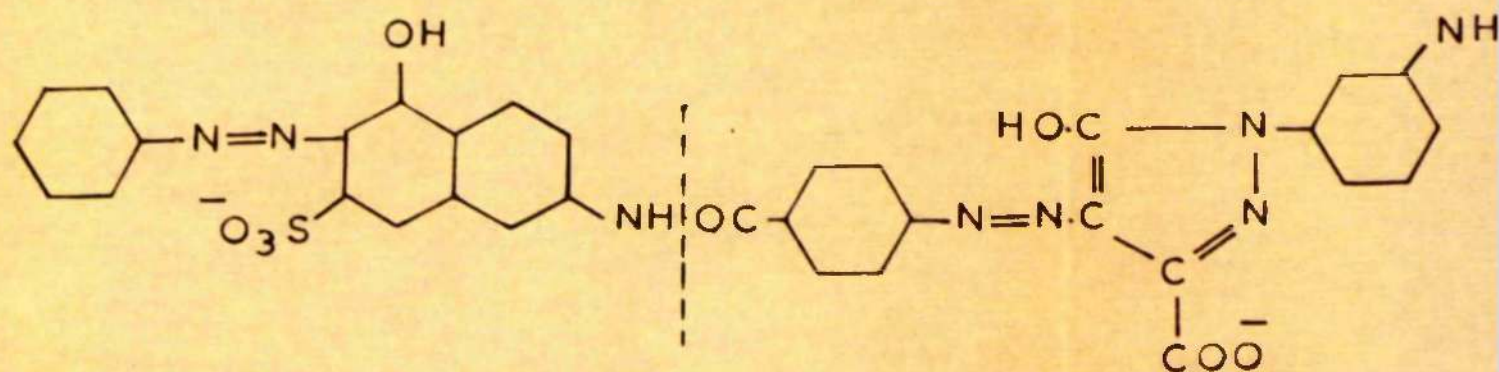


DIRECT BROWN BBN

Fig.18A. Constitutions of imperfectly conjugated dye molecules.



CHLORAZOL BROWN BS.



BENZAMIN BRILLIANT ORANGE GRN.

Fig.18B. Constitutions of imperfectly conjugated dye molecules.

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