## 355. *Researches on Monolayers. Part VIII.*[1] *Reactions of Metal–Unsulphonated Ligand* (1 : 2) *Dyes with Protein and Similar Monolayers and their Relation to Dyeing Mechanisms.*

By C. H. Giles and T. H. MacEwan.

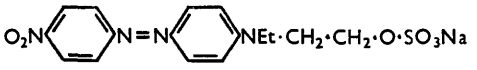
Dyes consisting of metal complexes with two unsulphonated azo-compounds as ligands have been applied to monolayers of edestin and methoxymethylnylon. The dyes are highly aggregated in the cold and their unusual effects on the films can be explained as due to adsorption as aggregates. The complexes have a dichelate structure. The aggregate, if ordered, must be a structure with " fins " of protruding aromatic nuclei, between which chain molecules in the film engage by non-polar, and in some cases polar, forces. A complex without pendant polar groups markedly increases film rigidity; proton-acceptor groups in a complex solubilise the films, and proton donor groups cross-link and stabilise them.

The mechanism of dyeing of nylon and protein fibres with these complexes is considered to be adsorption (probably of micelles), (*a*) in water-accessible regions by ion exchange, van der Waals forces, and, if suitable groups are available, hydrogen-bond donation by the dye to backbone –CO·NH– groups; and (*b*) in water-inaccessible regions, by van der Waals forces and by hydrogen bonding. Process (*b*) (" solid solution ") gives linear portions of adsorption isotherms.

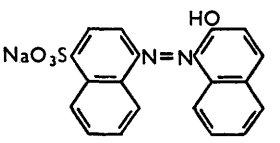
The 1 : 2-metal–ligand dyes, first introduced in 1949, are now important for colouring wool and synthetic fibres. They are anionic, being salts of strong acids, but they differ from the older 1 : 1-metal–ligand wool dyes in being unsulphonated and having their water-solubility conferred by non-ionic polar groups. They are distinguished by slow dyeing rate and very high fastness to wet treatments and to light, even in pale depths. A full account of their chemistry and development is given by Schetty.[2] Very little is known of their mechanism of dyeing; it must differ from that of most other wool dyes, which usually contain strongly ionic groups (generally $SO_3Na$). Schetty [2] considers that the dyeing process is similar to that of cellulose acetate with the non-ionic disperse dyes: the metal atom does not take part in the dye–fibre link, which is primarily due to van der Waals attraction. Zollinger [3] has obtained isotherms for two 1 : 2-complex dyes on several fibres and has interpreted them as evidence both of a " solid solution " mechanism, *i.e.*, similar to cellulose acetate dyeing, and of dye–fibre salt formation. Our results support the views of both these authors.

Part VII [1] described reactions of a protein (casein) in monolayers in presence of a variety of sulphonated dyes, etc. A similar technique was used here, with films of edestin and methoxymethylnylon and various solutes, including 1 : 2-complex dyes.

The following were used as models in studying the effect of the constitution of the solute upon the films: (I) D-glucose, (II) *meso*-inositol, (III) tannic acid, (IV) sodium



(VI)

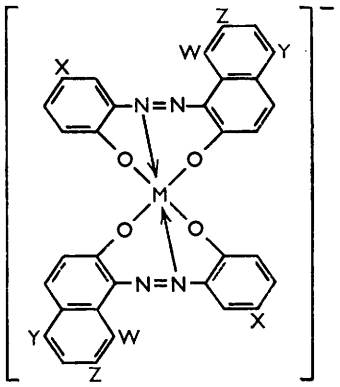


(VII)

1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone-3 : 7-disulphonate (Alizarine Cyanine; C.I. 58610), (V) tetradecyl sodium sulphate, (VI), and (VII) (C.I. 15620). Sodium salts of two

[1] Part VII, Cameron, Giles, and MacEwan, *J.*, 1958, 1224.
[2] Schetty, *J. Soc. Dyers Colourists*, 1955, **71**, 705.
[3] Zollinger, *Melliand Textilber.*, 1956, **37**, 1316; *Textil-Rundschau*, 1958, **13**, 217; cf. Back and Zollinger, *Helv. Chim. Acta*, 1958, **41**, 2242.

sulphonated azo-dye–chromium complexes (1 : 1) were included, *viz.*, (VIII) C.I. 13900, complex of 3-amino-2-hydroxy-5-nitrobenzenesulphonic acid→acetoacetanilide, and (IX) C.I. 18745, complex of 3-amino-2-hydroxy-5-nitrobenzenesulphonic acid→3-methyl-1-phenylpyrazol-5-one; and the sodium salts of the 1 : 2-metal–ligand dye anions (X)—(XV). Results are in Fig. 1.




*Non-polar complex*

(X) M = Cr; W, X, Y, Z = H

*Proton-accepting polar complexes*

(XI) M = Cr; X = $SO_2Me$; W, Y, Z = H
(XII) M = Co; X = $SO_2Me$; W, Y, Z = H

*Proton-donating polar complexes*

(XIII) M = Cr; W = NH·COMe; X = $SO_2Me$; Y, Z = H
(XIV) M = Cr; X = $SO_2Me$; Y = NH·COMe; W, Z = H
(XV) M = Cr; W, X, Y = H; Z = OH

## Experimental

Apparatus and experimental details were described previously.[1] The dyes were chromatographically pure and contained only a few % of inorganic salt, which exerts no influence under buffer conditions. Edestin was a commercial sample (B.D.H.) spread from a 0·1% solution in 0·5M-sodium hydroxide. Methoxymethylnylon (Imperial Chemical Industries Limited; 40% methoxymethyl substitution in amide group of nylon 66) was spread from a 0·01% solution in methanol. Qualitative viscosity tests to confirm rigidity were made by blowing on the films after covering them with talc.

According to Fosbinder and Lessig [4] edestin only spreads on substrates above or below pH 5·0—11·0. We used pH 2·3—4·7. In all cases the spreading was spontaneous and the films were quite stable.

Fading tests were made as follows: formaldehyde-hardened gelatin films [5] dyed with dyes (X), (XI), or (XIII) by placing them in $10^{-5}$M-solutions at 40° for *ca.* 2 hr. and then leaving overnight in the cooling solution, were rinsed, and then dried in air. They were then exposed 8 in. from a 400 w mercury-vapour lamp (cf. ref. 5). The optical density of each film was measured before and at intervals during exposure on a Unicam S.P. 600 spectrophotometer, in the waveband of maximum absorption (which was not sharp). Change in temperature and time of dyeing did not significantly alter fading characteristics.

## Discussion

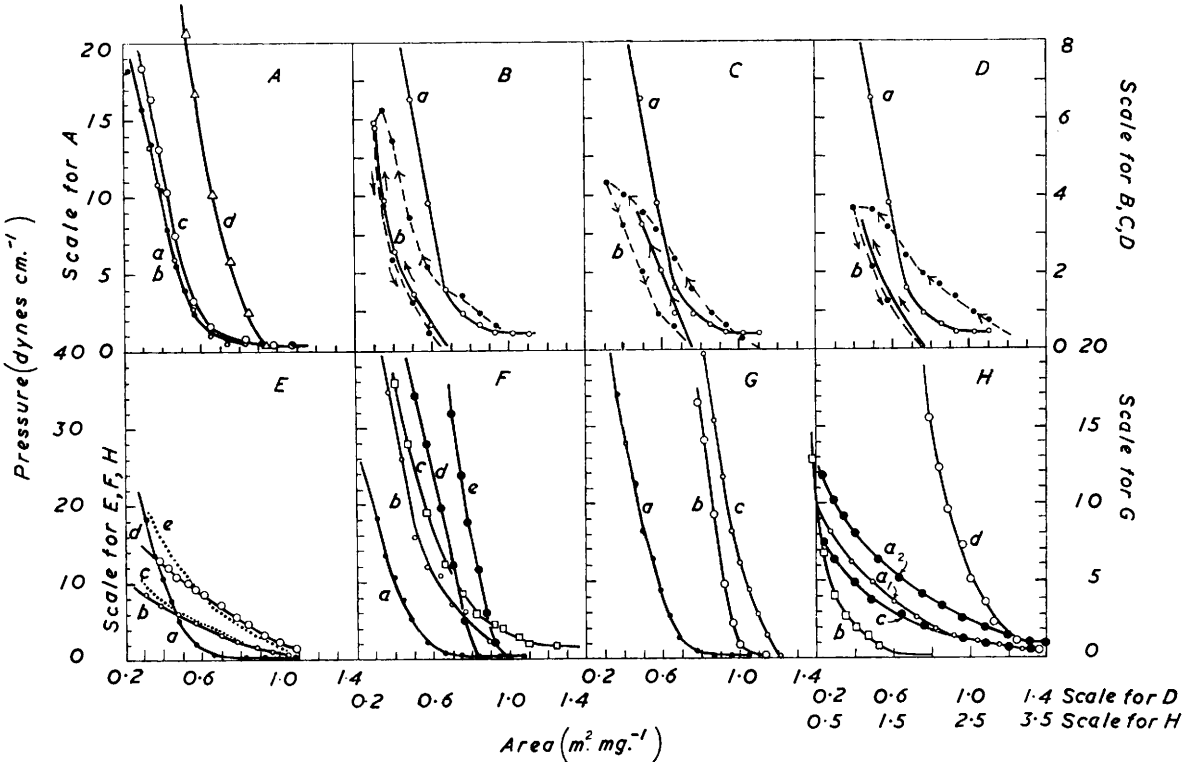
The previous results [1] were considered as evidence that (*a*) Monobasic compounds of weak hydrogen-bonding power at high film pressures tend to form a duplex layer or a layer of micelles beneath the film, which thus becomes more soluble (but see below); (*b*) Solutes with two sulphonate groups expand the film slightly through cross-linking by ion–ion attraction; (*c*) Bifunctional hydrogen-bond donating compounds cause film "condensation" (especially noticeable with Alizarine Cyanine). The present results are interpreted on the following basis; a fall in the slope of the curve shows that the film solubility increases; a rise in slope coupled with increase in rigidity of the film, demonstrated by the powder test, shows that cross-linking has occurred.

*Effects produced by Hydroxylic Solutes.*—Glucose appears not to form bonds with proteins in water, and has no effect on the film (Fig. 1*A*, *b*), but *meso*-inositol does form complexes (detected by refractometry) [6] and it also appears to have a small cross-linking

[4] Fosbinder and Lessig, *J. Franklin Inst.*, 1933, **215**, 579.
[5] Baxter, Giles, and Lewington, *J. Soc. Dyers Colourists*, 1957, **73**, 386.
[6] Bruce, Giles, and Jain, *J.*, 1958, 1610.

effect in the film (Fig. 1*A*, *c*). (The difference between these two solutes is attributable to differences in attraction for water, reflected in their solubilities [6].) Tannic acid makes the methoxymethylnylon film very rigid; so does, in less degree, Alizarine Cyanine (IV). In view of the conclusions to be discussed regarding the 1 : 2-complexes, it is possible that this dye may be adsorbed as a micelle; it is rather insoluble. These results are consistent with earlier observations on the effects of hydroxylic molecules. Thus Ellis and Pankhurst [7a] (cf. ref. 7*b*) observed that collagen films were not " condensed " by monomeric mono-, di-, and tri-hydric phenols, but only by polyhydric phenols of molecular weight higher than the catechin monomer; Clark, Holt, and Went [8] found that nylon or protein films are " condensed " by silicic acid only after the latter has polymerised. In both those cases the condensation takes place through film–solute hydrogen bonding.

FIG. 1. *Force–area curves for edestin films (A—G) and methoxymethylnylon films (H).*




*a*: Control curve in all cases.
*A*: *b* (coinciding with *a*), (I), $10^{-2}$M; *c*, (II), $10^{-2}$M; *d*, (IV), $5 \times 10^{-4}$M. All at pH 2·30.
*B*: *b*, (V), $5 \times 10^{-5}$M, showing first compression, expansion, and second compression (pH 2·30).
*C*: *b*, (VI), $10^{-4}$M, as *B*,*b* (pH 2·30).
*D*: *b*, (VII), $10^{-4}$M, as *B*,*b* (pH 2·30).
*E*: *b*, (XI), $10^{-5}$M; *c*, (VIII), $10^{-4}$M; *d*, (XII), $10^{-5}$M; *e*, (IX), $10^{-4}$M. All at pH 3·26.
*F*: *b*, (XIV), $10^{-5}$M; *c*, (XIII), $10^{-5}$M; *d*, (XV), $10^{-5}$M; *e*, (X), $10^{-5}$M. All at pH 3·26.
*G*: *b*, (XV), $10^{-5}$M; *c*, (X), $10^{-5}$M. Both at pH 4·70.
*H*: $a_1$, control at pH 3·26; $a_2$ control at pH 1·60; *b*, (III), 40 mg. l.$^{-1}$ at pH 1·60; *c*, (IV), $5 \times 10^{-4}$M at pH 1·60; *d*, (X), $10^{-4}$M at pH 3·26.

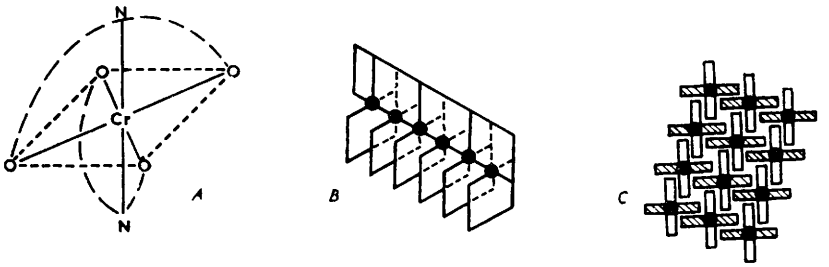
*Effects produced by Sulphate Esters and Monosulphonated Dyes.*—The effect of the surface-active dyes (VI)—(IX) on edestin films (Fig. 1*C*, 1*D*, 1*E*, *c* and *e*) resembles their effect on casein films [1] and a similar explanation may be offered, *viz.*, film penetration at

[7] (*a*) Ellis and Pankhurst, *Discuss. Faraday Soc.*, 1954, **16**, 170; (*b*) Lanham and Pankhurst, *Trans. Faraday Soc.*, 1956, **52**, 521.
[8] Clark, Holt, and Went, *Trans. Faraday Soc.*, 1957, **53**, 1500; Clark and Holt, *ibid.*, p. 1509.

low pressures, and at high pressures some adsorption of a duplex film or micelles below the surface (though there may also be some penetration to give a mixed monolayer). Decompression followed by recompression showed that edestin films on solutions of the surface-active compounds (V)—(IX) were unstable during first compression, apparently through slow dissolution (casein films do not behave thus; see Experimental section of ref. 1). They were stable when subsequently expanded and recompressed, provided they were allowed to stand for 30 min. between each reading during the recompression cycle (see Fig. 1*B*—1*D*, *b*). The recompression curves may represent some form of more stable duplex layers (cf. Fig. 11*a* of ref. 9, though it seems more likely that in the present films the top layer is protein).

*Effects produced by* 1 : 2-*Complex Dyes.*—Dye (X), which has no available polar groups, surprisingly causes an extreme increase in rigidity of the film (Fig. 1*F*, *e*), of a magnitude previously only observed with solutes with large, polymeric molecules containing powerfully proton-donating groups, *e.g.*, tannic acid (cf. ref. 7); the addition of such groups, as in (XIII)—(XV) (Fig. 1*F*, *b*, *c*, *d*), slightly *reduces* rigidity [at pH 3·26; at pH 4·7 (XV) slightly *increases* rigidity]. Further, dyes (XI) and (XII) (Fig. 1*E*, *b*, *d*) are even more effective than normal surface-active dyes (VI, VII, cf. XII of ref. 1) (Fig. 1*E*, *b*, *d*) in making the films compressible, yet they are not surface active. (None of these 1 : 2-complexes

FIG. 2. *Structure of* 1 : 2-*metal–ligand dye molecule and micelle.*




*A*. Arrangement of co-ordinating atoms (schematic). The four oxygen atoms are in one plane. The curved broken lines show the three chelating atoms of the respective azo-dye molecules.
*B*. Isometric projection (schematic) of one line of associated complex molecules in suggested micelle. (Azo-dye units are shown as plain rectangles for clarity.)
*C*. Plan (schematic) of one part of a layer of suggested micelle, showing interlocking of azo-dye units by planar association. Hatched rectangles show units below, and white rectangles show units above, the line of metal atoms. Dimensions of unit cross-sections and metal atoms approximately to scale. [Dye (X), close-packed micelle; dyes with bulky peripheral polar groups may have a less close-packed structure.]

gave any evidence of surface activity.) The most reasonable interpretation of these phenomena, consistent with other properties of the dyes, is that the adsorbed species is in all cases a dye micelle. This is best discussed with reference first to the geometry of these dye molecules.

*Nature of the* 1 : 2-*Complex Dye Micelle.*—These dyes are not generally very soluble in water and are highly aggregated in the cold [2] [some of the present examples slowly flocculated and (X) was particularly insoluble (*ca.* $10^{-5}$M in acid solutions)]. In attempting to interpret their adsorption behaviour we must consider the probable structure of the dye aggregates. As far as we know, micelles of dichelate compounds have not been studied, but those of long paraffin-chain ions in water have received considerable attention. In these there is an equilibrium between the short-range van der Waals forces, which bring the hydrocarbon chains into contact, thus expelling them from the water, and the long-range coulombic forces which cause mutual repulsion of the ionic groups.[10] In micelles of large planar anionic azo-dye molecules in water [11] and in monolayers of planar azo-dyes on

[9] Matalon and Schulman, *Discuss. Faraday Soc.*, 1949, **6**, 27.
[10] Tartar, *J. Phys. Chem.*, 1955, **59**, 1195.
[11] Morton, *J. Soc. Dyers Colourists*, 1946, **62**, 272.

water [12] the aromatic nuclei appear to be stacked side-by-side; thus there is the closest contact of the hydrocarbon portions. In the present case we assume (*a*) that the micelles have an ordered structure and (*b*) that this structure is determined by the tendency of the short-range forces to promote the closest possible contact between the planar dye units of adjacent molecules. On these assumptions, molecular models show that the aggregate must have an unusual structure. The model shows that the four oxygen atoms of the *o*-hydroxy-groups in the complex lie in one plane, with the respective co-ordinated nitrogen atoms of the two azo-groups arranged perpendicularly to this plane and equidistant from all the oxygen atoms. The two azo-dye units in the complex are planar and lie at right-angles to each other (cf. ref. 13) (see Fig. 2*A*), giving a dichelate-type of molecule. The principal aggregating force is assumed to be the tendency of the hydrophobic portions of

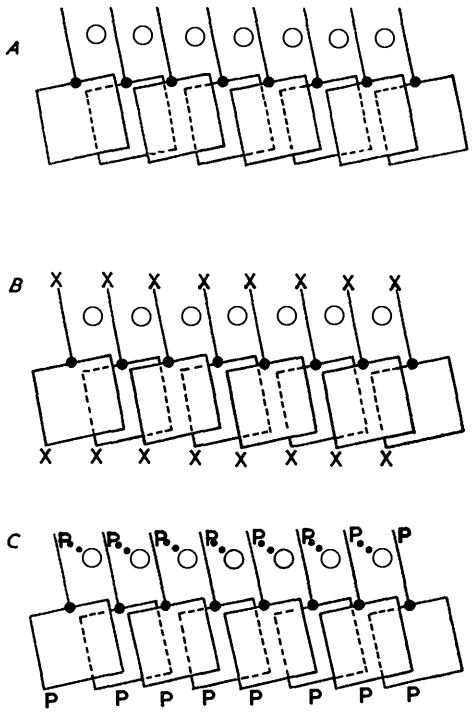



FIG. 3. *Schematic representation of possible mode of film–dye micelle association. Film chain molecules* (○) *orientated perpendicular to the paper. For clarity, dye units are shown as rectangles (face-on) and lines (edge-on), and tilted.*

*A*. Adsorption of non-polar dye (X).
*B*. Adsorption of dyes (XI) and (XII) at high film pressures. Proton-acceptor groups X beneath the micelle confer high solubility.
*C*. Adsorption of dyes (XIII)—(XV). Proton-donor groups *P* bond with film chains above micelle, and with water below.

these planar units to escape from the water and achieve closest side-by-side contact with neighbouring units. Models show that apparently the only way in which this can occur is in the form of structure illustrated in Fig. 2*B*, 2*C*, which is the most closely-packed possible arrangement. This structure can clearly be elaborated in three dimensions. The gegenions (usually sodium) may be accommodated partly in the gaps inside the structure and partly in the surrounding solution. Stability is enhanced by the wide separation of the ionic centres.

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

[12] Giles and Neustädter, *J.*, 1952, 3806; Cameron and Giles, *J.*, 1957, 3140.
[13] Race, Rowe, and Speakman, *J. Soc. Dyers Colourists*, 1946, **62**, 372.

protein or nylon backbones in these channels, the whole forming a rigid two-dimensional network. Thus this structure can account for the observed rigidity produced by dye (X), which has no available polar groups and if monodisperse would not be expected to have any such effect. In the structure actually shown in Fig. 2*C*, adsorbed protein backbone chains would be nearly twice as far apart as when close-packed alone on the surface. The actual increase in area observed with (X) is about 80%. The micelle structure also accounts for the effects of the other 1 : 2-complexes as follows.

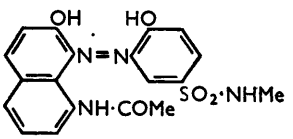
(i) The micelles of (XI) and (XII) have an exterior surface exposing strongly polar, water-attracting proton-accepting groups ($SO_2Me$) (Fig. 3*B*). Models show that the micelle can tilt to give an upper hydrophobic and a lower hydrophilic surface. If adsorbed that way the under-surface of the film–dye micelle assembly would be water-soluble, which would explain why the whole film shows the force–area curve characteristic of normal surface-active dye–protein films, with very high compressibility. (Proton-accepting groups do not form strong bonds with proteins.[1,14,15])

(ii) The films with dyes (XIII)—(XV) also have strongly water-attracting under-surfaces. Their effect in increasing the film solubility (Fig. 1*F*, 1*G*) is however masked by the competitive action of the polar groups in the upper surfaces of the micelles. These groups are strongly proton-donating and form stable hydrogen-bond cross-links with the protein chains. The result is that these dyes do increase the rigidity of the film considerably, but a little less so than does the non-polar dye (X), and they increase the film area less than (X) does, probably because of their stronger cross-linking action.

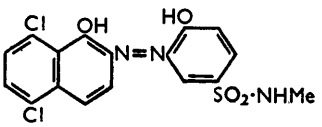
Change in pH from 3·26 to 4·7 has no effect on the increase in edestin film area produced by the proton-donor dye (XV), but it slightly reduces (by *ca.* 5%) the increase given by the non-polar dye (X).

*Effect of Chelation in Complex.*—The acetamido-group in (XIII) is chelated with the azo-group.[2] The dye is thus not normally a proton-donor. This explains its marked expansive and solubilising effect on edestin films below 10 dynes $cm.^{-1}$ (Fig. 1*F*, 1*C*). At higher pressures however the dye causes marked film rigidity and so must then be acting as a proton-donor [cf. (XIV), (XV), Fig. 1*F*, *b*, *d*]; when the complex molecules are forced close to the protein the chelate ring presumably breaks and a dye–protein hydrogen bond forms preferentially. This is consistent with the known weakness of a second hydrogen bond to an azo-group.[12]

*Nature of Film–Dye Hydrogen Bonds.*—The proton-donor dye (IV) has much less effect on the compressibility of methoxymethyl nylon films (Fig. 1*H*, *c*) than on edestin (Fig. 1*A*, *d*); the hydrogen-bond acceptor centres in the films are therefore probably the backbone –CO·NH– groups. In contrast, the non-polar dye (X) has a similar effect on both films (Fig. 1*F*, *e* and 1*H*, *d*), confirming non-hydrogen-bond adsorption. Earlier adsorption tests[14,15] showed that some proton-donors are much more strongly adsorbed than proton-acceptors by protein or nylon fibres, from solutions or as vapours. The solutes used now and previously show the same effect. In ability to bind with proteins or nylon, groups fall roughly thus: ArOH > Ar·NH·COMe > $Ar{\cdot}NH_2$, Ar·NHR, Alk–OH > proton-acceptor groups.




(XVI)



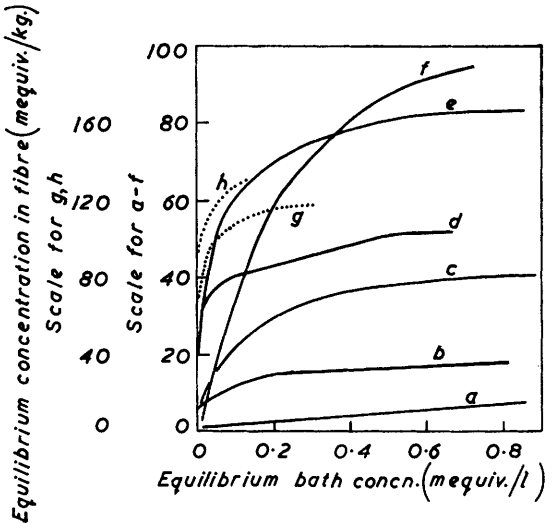

(XVII)

*Isotherms for Adsorption by Fibres.*—Zollinger [3] postulated salt-formation and solid solution of the free acid form to account for the isotherms he obtained, shown in Fig. 4, for

[14] Chipalkatti, Giles, and Vallance, *J.*, 1954, 4375.
[15] Chipalkatti (H. R.), Chipalkatti (V. B.), and Giles, *J. Soc. Dyers Colourists*, 1955, **71**, 652.

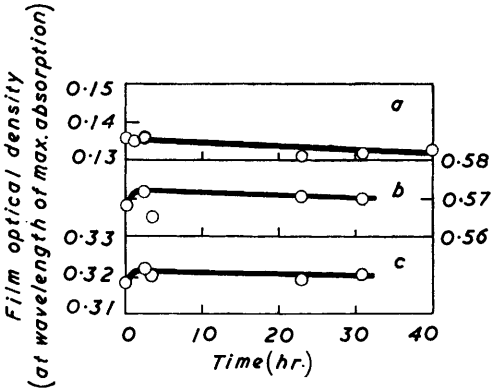
2 : 1 ligand–chromium complexes of (XVI) and (XVII). This interpretation is now confirmed, and may be extended in the light of present and other work (*e.g.*, refs.[1,7,8,16,17]) as follows. Normal (L type [16]) curves for silk (Fig. 4, *c*) and wool (*f*) represent mainly ion-exchange adsorption in *water-accessible* regions of the fibres. Linear portions of curves, for acetylated wool (*a*), acetylated nylon (*b*, very low slope), and stretched nylon (*d*) represent mainly hydrogen-bond adsorption in *water-inaccessible* regions.[16] [Acetylation removes the ion-exchange centres ($^+NH_3$ groups) in the fibre.] All the curves for nylon (*b*, *d*, *e*, *g*, *h*), unlike those for silk and wool, have " high affinity "[16] character, *i.e.*, initially they coincide with the *y*-axis. There is therefore a source of high affinity in nylon which

FIG. 4. *Adsorption isotherms of* 1 : 2*-metal–ligand dyes* (*after Zollinger* [3]).




Dye (XVI): *a*, Acetylated wool; *b*, acetylated nylon 66; *c*, silk; *d*, stretched nylon 66; *e*, unstretched nylon 66; *f*, wool.
Dye (XVII): *g*, acetylated nylon 66; *h*, stretched nylon 66.

FIG. 5. *Rates of photo-degradation of unsulphonated dye–metal complexes adsorbed in gelatin films.*




*a*, (X), measured at 5600 Å; *b*,* (XI), 4700 Å; *c*,* (XIII), 6200 Å.

* Slight increases in optical density in initial stages of irradiation, as shown here, have been observed in other cases with particulate colouring matters, and are attributed to breakdown of some particles into smaller units in the heat of the lamp (see ref. 5).

is not present in the proteins; this source must be van der Waals attraction by the hydrocarbon portions of the nylon chains; very possibly this high affinity arises from the engagement of the chains with the dye micelle [cf. Fig. 3*A* and the strong adsorption of (X) to the films]. Other work shows that " high-affinity " curves are almost always due to micellar adsorption.

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

Dye (XVII) has higher non-polar attraction than (XVI) for nylon; this follows from these considerations: (i) adsorption of (XVII) is higher on both forms of nylon (Fig. 4, *g*, *b*, *h*, *d*); (ii) a lower proportion of the total adsorption of (XVII) than of that of (XVI) is due to ion-exchange, since acetylation reduces adsorption of (XVII) much less than (XVI) (Fig. 4, *h*, *g*; *d*, *b*); (iii) the non-linear isotherms indicate adsorption in water-accessible regions, in which (XVII), not being a proton-donor, has low hydrogen-bond affinity.

[16] Giles and MacEwan, *Proc. 2nd Internat. Congr. Surface Activity*, 1957, **3**, 457.
[17] Cameron, Giles, and MacEwan, *J.*, 1957, 4304.

Therefore, the main affinity of (XVII) must be non-polar (probably van der Waals attraction between the planar dye molecules and the hydrocarbon portions of the nylon molecular chain).

Models give evidence of a possible reason for the affinity difference between (XVI) and (XVII). Thus: (*a*) the longest molecular axis parallel with the micelle surface (*i.e.*, length of " fin ") is longer in (XVII) (*ca.* 14·5 Å) than in (XVI) (*ca.* 12 Å). (*b*) The NH·COMe substituent in (XVI) may interfere sterically with penetration of the nylon chain between the " fins." Both effects (*a*) and (*b*) will tend to reduce the area of direct contact of dye and fibre molecule, and thus will reduce their mutual van der Waals attraction.

*Micellar Adsorption.*—The properties of these dyes in fibres are consistent with their presence as large micelles of fairly uniform size. Dyeing is normally carried out at the b. p., and under these conditions the dyes have low degrees of aggregation.[2] Dye molecules entering the fibre may therefore be nearly monodisperse. Aggregates must then build up on the internal fibre surfaces, probably during dyeing, but possibly during subsequent cooling or drying.

*Light Fastness of* 1 : 2-*Metal–Ligand Dyes.*—Schetty [2] reports that a noticeable difference between the (Irgalan) 1 : 2-metal complex dyes and ordinary acid wool dyes " is that the former show within narrow limits constant light fastness when applied to the most diverse substances, such as silk, wool, nylon, Perlon, acetate rayon, and lacquers." Large aggregates of dye fade much more slowly than monodisperse dye molecules.[18] The micellar structure of these dyes postulated here would be expected to persist in all media (aqueous or non-aqueous) because of the high mutual attraction of the planar aromatic nuclei; and if it does, the consistently high resistance to light of these substances is explained.

Experiment has shown that dyes in monodisperse form fade approximately at a first-order rate, *i.e.*, exponentially, but when they are entirely in aggregates, *e.g.*, insoluble pigments, they fade at a steady rate (zero order), indicative of fading at the outer surface only of particles.[5] Most normal soluble dyes in transparent substrates, *e.g.*, gelatin, at first fade exponentially, and then, after a small proportion (*ca.* 10%) has been destroyed, the rate becomes steady.[18] This behaviour indicates the presence of a little monodisperse dye, which fades first, and some associated dye, which fades more slowly. Thus a fading-rate test can give useful information of the physical state of adsorbed dye. Fading tests were therefore made in this investigation as a check on the hypothesis that the 1 : 2-complex dyes are adsorbed mainly as micelles. The results are shown in Fig. 5. There is no evidence of an initial rapid loss in optical density, and this is consistent with a very large proportion of the adsorbed dye being in micellar form.

*Mechanism of Dyeing.*—All the facts suggest the following tentative picture of the dyeing mechanism on nylon and protein fibres. The dye builds up in the fibre during dyeing (probably) or subsequently, as " network " micelles (Fig. 2*B*, 2*C*). The adsorption mechanisms are: (a) *in water-accessible* regions of the fibre: (i) ion-exchange of the dye sodium salt with cationic amino-groups in both types of fibre, (ii) van der Waals attraction between the hydrocarbon parts of the nylon (and perhaps the protein) chain and (probably) the aromatic residues at the surface of the dye micelles, (iii) hydrogen-bond donation by the dye (if suitable groups are present) with backbone –CO·NH– groups in the fibre; (b) in *water-inaccessible* regions the free acid may be adsorbed preferentially by both mechanism (ii) and (iii) and also by hydrogen-bond acceptance by the dye.

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[18] Giles, *J. Soc. Dyers Colourists*, 1957, **73**, 127.