The Cellulose–Dye Adsorption Process. A Study by the Monolayer Method

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The reactions of monolayers of cellulose, spread from Cadoxen solvent, with a variety of solutes in the aqueous phase have been studied by measurement of film expansion, compressibility, and viscosity, with a view to elucidating the mechanism of dye adsorption by cellulose. Refractometry measurements of bulk solutions have also been used.

Phenol has no effect on the film, but urea expands it. Cationic dyes, *e.g.*, Methylene Blue, associate weakly with the monolayer to give a mixed film of high compressibility. Anionic dyes slightly expand the film, without change in its compressibility or viscosity. This expansion is almost identical for monoazo-dyes with little affinity for cellulose in bulk, as it is for bisazo-dyes, with similar molecular width, but of high cellulose affinity. A direct dye with a wider molecule causes greater film expansion, approximately proportionate to this increased width. This evidence suggests face-to-face association of cellulose and anionic dye molecules parallel to the cellulose chain.

Refractometry, but not the other tests, reveals weak complexing, probably of an acid–base type, between cellulose and amino-groups in dyes. This is the only dye–cellulose force identified.

Dye adsorption by cellulose in bulk is explained by this and other recent work, *e.g.*, the known tendency of the dye to escape from aqueous solution, causes it to concentrate at the cellulose–water interface. There it becomes aligned parallel to the cellulose chains possibly by hydrophobic bonding with glucosidic >CH groups. It then associates to form multilayers or three-dimensional aggregates. This process occurs more readily with long narrow planar molecules and is assisted in technical practice by the presence of excess of neutral inorganic salt in the dye-bath.

CELLULOSE dyeing, quantitatively the most important dyeing process, has never been satisfactorily explained. The mechanism of formation of dye–cellulose covalent bonds in the fibre-reactive dyeing process † has been reasonably well established,[1] but none of the various mechanisms suggested to account for the adsorption of the many varieties of non-reactive dyes fully accounts for their affinity for the fibre. The reactive dyes also have affinity for the fibre, apart from their ability to form the covalent bonds, and this affinity has technical importance.

Required Conditions for Dyeing Cellulose.—The dye molecule requires to be planar and to have a long conjugate chain, and at least one ionic group, and it appears that substantivity is favoured if sulphonate groups are arranged on one side of the dye molecule and amino-groups on the other.[2]

A neutral electrolyte in large excess is also necessary in the dye-bath to produce maximum adsorption of dye by cellulose, sodium chloride or sulphate being used in practice. Tetrasulphonated direct dyes are not adsorbed at all in complete absence of a salt.[2] The explanation usually given is that repulsion of dye occurs

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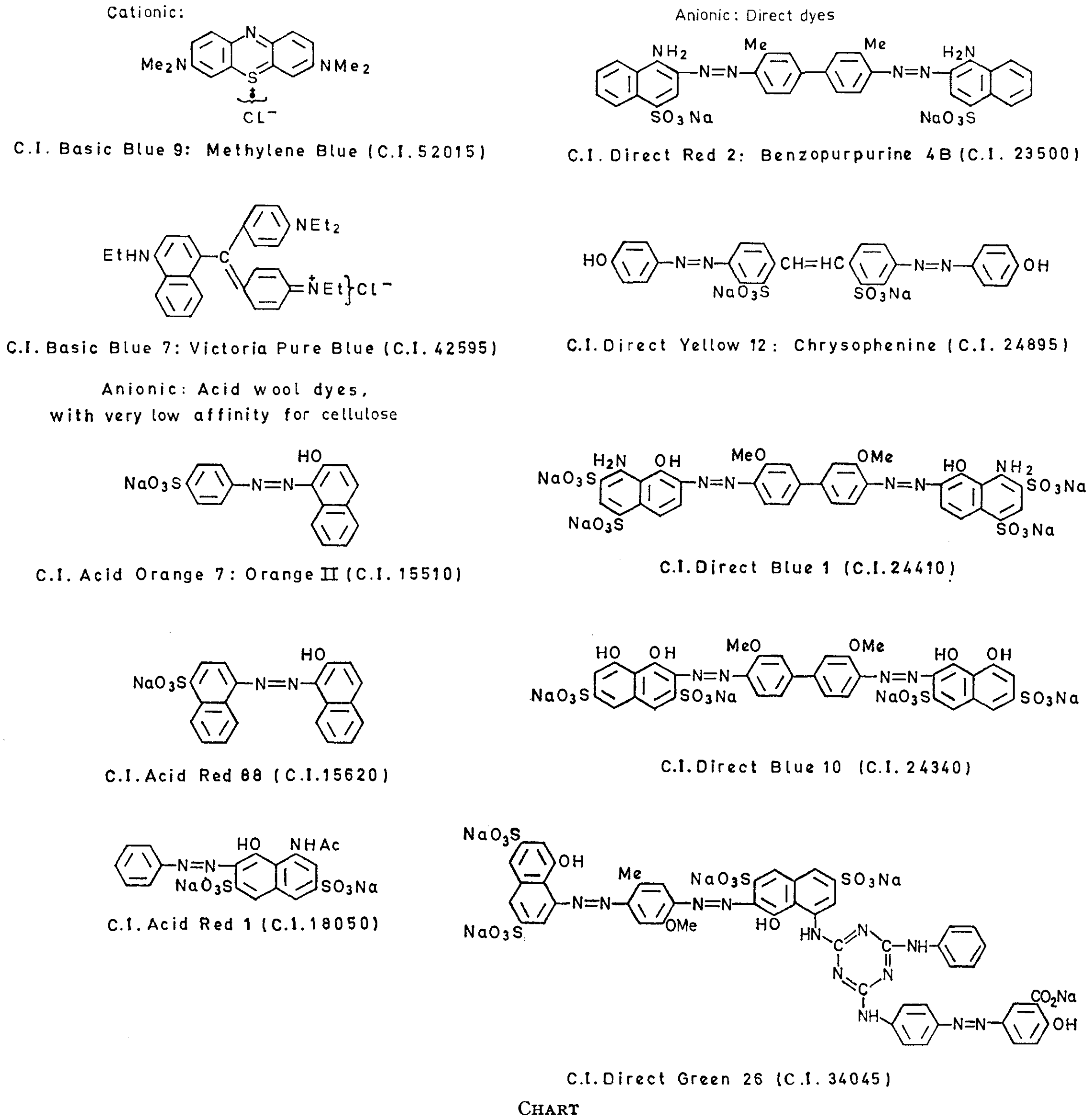
† Covalent bonds between dye and fibre are formed.

[1] F. W. Beech, 'Fibre-Reactive Dyes,' Logos Press, London, 1970.

[2] T. Vickerstaff, 'The Physical Chemistry of Dyeing,' Oliver and Boyd, London, 2nd edn., 1954.

as a result of the negative surface charge on the fibre, which arises from the small proportion of anionic groups (mainly CO_2H) in cellulose. It is known that added electrolyte neutralises this surface charge.[2]

There is no sharp demarcation line between dyes 'with' and 'without' affinity, which in fact can vary continuously over a wide range. A simple qualitative test of affinity is to observe the amount of dye taken up by cellulose from water under specified conditions similar to technical practice: 'substantive' dyes, *e.g.*, direct dyes, deeply colour the fibre, whereas non-substantive dyes, *e.g.*, sulphonated 'acid' wool dyes, merely stain it in a pale depth of shade.



Cationic:

C.I. Basic Blue 9: Methylene Blue (C.I. 52015)

C.I. Basic Blue 7: Victoria Pure Blue (C.I. 42595)

Anionic: Acid wool dyes, with very low affinity for cellulose

C.I. Acid Orange 7: Orange II (C.I. 15510)

C.I. Acid Red 88 (C.I. 15620)

C.I. Acid Red 1 (C.I. 18050)

Anionic: Direct dyes

C.I. Direct Red 2: Benzopurpurine 4B (C.I. 23500)

C.I. Direct Yellow 12: Chrysophenine (C.I. 24895)

C.I. Direct Blue 1 (C.I. 24410)

C.I. Direct Blue 10 (C.I. 24340)

C.I. Direct Green 26 (C.I. 34045)

CHART

Hypotheses of Cellulose Substantivity.—The hypotheses suggested to account for the affinity of dyes for cellulose include chemical [2-6] and physical [7] action.

(a) *Chemical.* (i) Hydrogen bonds,[2] (ii) ion–dipole forces,[3] (iii) π-bonds,[4] and (iv) non-polar van der Waals forces [5] have all been suggested. When the present work was commenced, (i) had been shown to be unlikely,[6] for (ii) there was little evidence, and (iii) and (iv) seemed possible. The subject is discussed below.

All the 'chemical' hypotheses require the formation, at least initially, of a monolayer of dye molecules (or

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[3] J. Wegmann, *Amer. Dyestuff Reporter*, 1962, **51**, P276.

[4] (*a*) C. H. Bamford, *Discuss. Faraday Soc.*, **1954**, **16**, 229; (*b*) C. Robinson, *ibid.*, p. 125; (*c*) W. L. Lead, *J. Soc. Dyers and Colourists*, 1957, **73**, 464; (*d*) Z. I. Yoshida, E. Ōsawa, and R. Ada, *J. Phys. Chem.*, 1964, **68**, 2895.

[5] (*a*) A. N. Derbyshire and R. H. Peters, *J. Soc. Dyers and Colourists*, 1955, **71**, 530; (*b*) A. S. A. Hassan and C. H. Giles, *ibid.*, 1958, **74**, 846.

[6] F. M. Arshid, C. H. Giles, and S. K. Jain, *J. Chem. Soc.*, 1956, 559.

[7] H. Bach, E. Pfeil, W. Philipar, and M. Reich, *Angew. Chem.*, 1963, **75**, 407.

anions) over the internal surface of the cellulose, and are consistent with the observed dichroism of dyed cellulose, since the dye molecules would be aligned parallel to the cellulose molecules. In polarised light the dyed fibre behaves as if the dye molecules are thus oriented.[2,8] Also, the long-wave (X-band) absorption of a direct cotton dye, attributed to its monomeric form, shows a red shift when the dye is adsorbed on cellulose,[9] suggesting a head-to-tail self-association of dye.[10] Peters and Vickerstaff,[11] on the basis of an original treatment of Rideal and Gilbert,[12] developed a thermodynamic treatment for determining the affinity of a dye for cellulose, assuming that the dye is adsorbed as a monolayer.

(b) *Physical.* The most recent hypothesis is that of Pfeil *et al.*;[7] this revives earlier ideas that there is a connection between substantivity and colloidal properties of cotton dyes. These authors measured spectral absorption curves of various direct cotton dyes and related non-substantive dyes, (i) dissolved in water alone, in aqueous sodium chloride, in various simple alcohols, or in pyridine respectively; (ii) adsorbed in films of regenerated cellulose or poly(vinyl alcohol); (iii) compressed in solid potassium bromide. They interpreted the data as evidence of aggregation of dye in the cellulose, and suggested that the dye has no specific attraction for the cellulose molecule. Once having penetrated the pores between the micellar structure of the cellulose, the dye loses its associated water and thereupon forms aggregates which are thus trapped in the cellulose polymeric structure and are unable to diffuse outwards. The importance of molecular planarity is then that it enables the dye more readily to penetrate the cellulose structure and to aggregate. This 'physical' hypothesis bears obvious similarities to the very early ones mentioned.

Present Work.—It was considered that a satisfactory evaluation of the relative applicability of the 'chemical' and the 'physical' theories outlined above could only be obtained if dye–cellulose reactions could be studied under conditions where fibre structure can play no part, *e.g.*, in a monolayer on water. Hitherto, monolayers of cellulose had not been obtained and indeed some authors have considered that cellulose is too crystalline to be spread. Films of cellulose were however successfully spread here,[13a] by use of Cadoxen solvent (Figure 1),[13b] and it was therefore decided to use such films in studies of reactions with various dyes. Measurements of pressure–area and of area–viscosity relations were made. When dissolved, or as a monolayer on water, cellulose cannot act as suggested in the 'aggregation hypothesis' since there are no intermolecular pores in which dye can aggregate and any chemical attraction for dyes should be clearly revealed. Monolayers on aqueous solutions are particularly useful means of studying dye–fibre reactions with model systems.[14a,15,16]

EXPERIMENTAL

Materials.—Stearic acid and octadecyl alcohol were 'specially pure' biochemical reagents (B.D.H.). Cadoxen solution [13b] was prepared as follows. Freshly distilled ethylenediamine (b.p. 117 °C) (70 ml) was diluted to 200 ml with distilled water and sodium hydroxide (2·8 g) was added and the mixture cooled below 0 °C in ice and salt mixture; meanwhile cadmium oxide (16 g) was slowly added with vigorous stirring during 4 h and stirring was continued a further 2 h. The solution was then stored for 6 h at room temperature, to allow precipitation of cadmium hydroxide; it was then filtered through a G4 sintered glass filter and stored in a refrigerator. The solution is colourless, completely transparent, and stable.

'Cellophane' regenerated film, previously boiled in water for 1 h (1 g) was dissolved in Cadoxen solution (1 l) by allowing the mixture to stand overnight in the refrigerator.

Solutes, etc.—The dyes used are shown in the Chart. Cationic dyes were purified by leaching diluent-free materials (Methylene Blue BP as received and Victoria Pure Blue as a 'batch' * sample) with 10% (v/v) dilute hydrochloric acid, filtering hot, and allowing the dye to crystallise from the filtrate. The process was carried out twice. The products were dried at 40—50 °C overnight and stored over P_2O_5.

The anionic dyes Orange II, C.I. 15620, C.I. 18050, and C.I. 34045 were purified by recrystallisation from 1 : 1 (v/v) ethanol–water and checked for freedom from coloured impurities by paper chromatography in mixed solvent (benzyl alcohol–dimethylformamide–water; 2 : 1 : 1, v/v). Elementary analysis showed that purified C.I. 34045 contained 10 mol water and 1 mol NaCl.

Benzopurpurine 4B, Chrysophenine, and C.I. 24410 were purified by the Robinson and Mills method [2] (Found for C.I. 24410: C, 40·85; H, 2·2; N, 8·4. Calc. for $C_{34}H_{24}N_6Na_4O_{16}S_4$: C, 41·1; H, 2·4; N, 8·5%). C.I. 24340 was purified by extracting the commercial product with 3 : 2 (v/v) ethanol–water and drying at 80 °C. Benzenesulphonic acid was a laboratory reagent (B.D.H.).

Foaming Treatment.—While the present work was in progress it was found [17] that anionic dyes, including C.I. 24410, reduce the surface tension (γ) of water and are thus surface-active. Moreover 'foaming' of the solution by aeration and removal of foam raises γ and removes a minimum in the γ–concentration curve. It was however found that if the C.I. 24410 sub-solution used beneath a cellulose monolayer was 'foamed' to constant γ before spreading the monolayer, the π–A curve was identical with that obtained by use of unfoamed solution.

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* *I.e.*, manufacturer's product without added diluent.

[8] T. H. Morton, *J. Soc. Dyers and Colourists*, 1946, **62**, 272.

[9] C. H. Giles, S. M. K. Rahman, and D. Smith, *J. Chem. Soc.*, 1961, 1209.

[10] S. F. Mason, *J. Soc. Dyers and Colourists*, 1968, **84**, 604.

[11] R. H. Peters and T. Vickerstaff, *Proc. Roy. Soc.*, 1948, *A*, **192**, 292.

[12] G. A. Gilbert and E. K. Rideal, *Proc. Roy. Soc.*, 1944, *A*, **182**, 335.

[13] (*a*) C. H. Giles and V. G. Agnihotri, *Chem. and Ind.*, 1967, 1874; (*b*) for a review of preparation, properties, and uses of Cadoxen, see *e.g.*, W. Brown, *Svensk Papperstidn.*, 1967, **70**, 458.

[14] (*a*) See, *e.g.*, C. H. Giles and T. H. MacEwan, *J. Chem. Soc.*, 1959, 1791; (*b*) A. B. Meggy, *J. Soc. Dyers and Colourists*, 1950, **66**, 510; (*c*) H. Zollinger, *ibid.*, 1965, **81**, 345.

[15] A. Cameron, C. H. Giles, and T. H. MacEwan, *J. Chem. Soc.*, 1958, 1224.

[16] For a review: C. H. Giles, *Proc. Symp. Contributions Chem. Synth. Dyes and Mechanism of Dyeing*, University of Bombay, 1968, 14.

[17] C. H. Giles and A. H. Soutar, *J. Soc. Dyers and Colourists*, 1971, **87**, 301.

Non-ionic Solutes. Phenol and urea were pure (B.D.H.) laboratory reagents.

Water.—This was doubly-distilled over $KMnO_4$ in a Quickfit all-glass still.

Film Balance.—This is modified from Allan and Alexander's design,[18] in which the float and head pivot on an agate knife-edge and plane, rather than on a spring or a torsion wire. The float is of Teflon, and the head of brass. The sensitivity is reduced to 0·1 dyn cm^{-1} by use of a heavier float than in the original design. The float ends are sealed to the trough by fine polyethylene filament (0·005 in, Courlene X3, Courtaulds Ltd.). The trough (10 × 25 cm internal dimensions) is cut from a single block of polyethylene, bolted to a brass plate for rigidity, and the movable barrier is also similarly made. All surfaces in contact with water, except the Teflon float, are coated with paraffin wax. The whole instrument is screened by a glass-fronted case, the barrier being mechanically controlled from outside. All measurements were made at room temperature (24 ± 0·5 °C).

The surface-active materials were injected below the surface by an Agla micrometer syringe (Burroughs, Wellcome and Co. Ltd.).

The cationic dyes were spread from ethanol solution (1 mg/1 ml) and the cellulose from Cadoxen solution (1 mg cellulose/1 ml Cadoxen), 30 min being allowed for equilibration before pressure measurement.*

Surface Viscometer.—This was constructed from the design of Davies [19] as modified by Davies and Mayers,[20] and uses the surface traction principle. Essentially the apparatus consists of two concentric platinum wire rings which are held just at the surface of the liquid. The bulk liquid is contained in a dish which is rotated at constant speed (37 s per revolution, obtained by a 1/30 h.p. Klaxon universal motor with Berco speed control and c.v. transformer) and the speed of rotation of the surface film lying in the annular canal between the rings is measured by timing a particle of talc floating on the surface. The viscous drag exerted by the canal walls on the film is measured as a retardation time. The apparatus was calibrated by measuring the retardation times of stearic acid and octadecyl alcohol at various surface concentrations, and plotting the times against the surface viscosity data given by Davies.[19] Means of measurements on 5—10 revolutions were calculated. Results are in ref. 21.

Refractometer.—The Pulfrich (Bellingham and Stanley model) instrument was used, with temperature controlled to 19 ± 0·5 °C by circulation of mains water.

Molecular Models.—These were of Catalin (Stuart type).

RESULTS AND DISCUSSION

The results are illustrated by Figures 1—5.

Effect of Non-ionic Solutes on Cellulose.—Urea expands the cellulose film; phenol has no effect (Figure 1). Correspondingly, urea in water swells cellulose but phenol in water is unadsorbed.[6] The refractive index tests reveals a 1 : 1 (1 : 2?) cellulose–urea complex. We suggest that this may be partly a weak acid–base ionic complex, and partly a hydrogen-bond complex. The cellulose–water bond must be weaker than the glucose–water bond, because no urea–glucose complex in water was detected in earlier tests.[6]

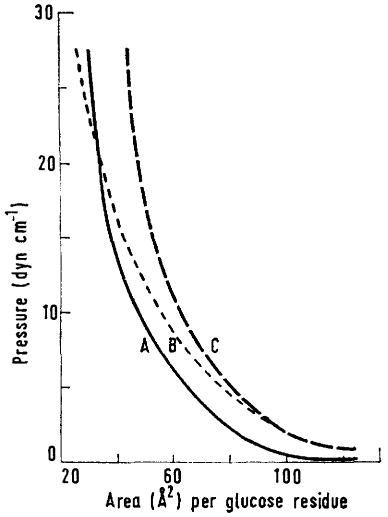

FIGURE 1 Pressure–area curves for cellulose monolayers on aqueous solutions of A, control (water) or 0·1M-phenol; B, 2 × 10^{-4}M-Methylene Blue or Victoria Pure Blue; and C, 4·5M-urea

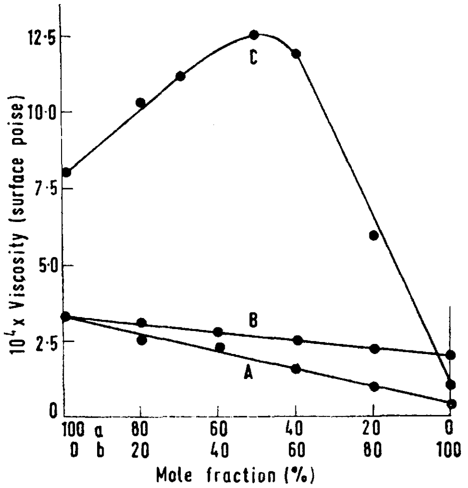

FIGURE 2 Surface viscosity, by method of continuous variations, of monolayers of cellulose and cellulose triacetate with dyes, at various molar ratios, illustrating the difference between mixed film formation (A, B) and complex formation (C). a, polymer; b, dye; A, cellulose–Methylene Blue on water; B, cellulose + C.I. 24410 on 0·01M-NaCl throughout; C, mixed film of cellulose triacetate + a non-ionic (disperse) dye on water (ref. 21).

Effect of Ionic Solutes on Cellulose.—*Cationic dyes.* The two dyes used are both surface-active and form stable monolayers on water alone. The dyes expand

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* On standing for several hours before compression, the area occupied by the cellulose molecules approximately doubled. We attribute this to development of carboxylate ions (probably by an oxidation in alkaline conditions). Attraction of bulky Cadoxen cations thereto separates the cellulose chains.

[18] A. J. G. Allan and A. E. Alexander, *Trans. Faraday Soc.*, 1954, **50**, 863.

[19] J. T. Davies, *Proc. 2nd Internat. Congress Surface Activity*, 1957, **1**, 241.

[20] J. T. Davies and G. R. A. Mayers, *Trans. Faraday Soc.*, 1960, **56**, 690.

[21] C. H. Giles, V. G. Agnihotri, and A. S. Trivedi, *J. Soc. Dyers and Colourists*, 1970, **85**, 451.

cellulose films considerably (Figure 1), but no dye–cellulose complex is formed, only a mixed film. This is clear from the increase in compressibility (*i.e.*, lowered slope of the π–A curve), and it is confirmed by two methods. (i) Schulman's test:[22] when the cellulose film is held at a given pressure and the dye injected beneath, no increase in pressure is observed. (ii) By film viscosity measurements by use of the method of continuous variations, already used for detecting complex-formation in monolayers of aliphatic substances by Enever and Pilpel,[23] and in dye–cellulose triacetate monolayers here[21] (Figure 2). Complex formation is clearly revealed in the cellulose triacetate films, but Methylene Blue–cellulose shows no evidence of a complex (Victoria Pure Blue was not tested in this way). Presumably the cationic dyes form a weak ion–ion association with the hydroxy-groups in the cellulose film; the hydrophobic portion of each dye molecule stands vertically at the surface, between the cellulose chains, and its cationic group, immersed in the water, is adjacent to a cellulose hydroxy-group.

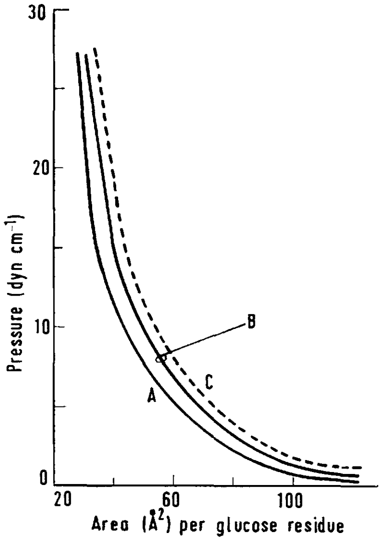

FIGURE 3 Pressure–area curves for cellulose monolayers on salt and non-substantive anionic solute solutions. A, control (water) or 0·1M-benzenesulphonic acid; B, 2 × 10^{-4}M-Orange II or C.I. 15620; and C, as B, with 0·035M-NaCl. The curve for 2 × 10^{-2}M-C.I. 18050 sub-phase is similar to B.

Anionic solutes. Benzenesulphonic acid has no effect on the cellulose film; it is not surface-active owing to its very high water solubility and forms no bonds with cellulose. All the anionic dyes however slighly expand the cellulose film and all except C.I. 34045 to a similar but slight extent, whether they are dyes suitable for cellulose or not. The expansion is increased in the presence of sodium chloride (Figures 3 and 4).

The Schulman test and the test by viscometry, however, give no evidence of a strong complex between cellulose and anionic dyes (Figure 2), though the refractive index test which can detect quite weak complexes reveals a 1 : 1-complex between C.I.24410 and cellulose, which is presumably a weak one (Figure 5).

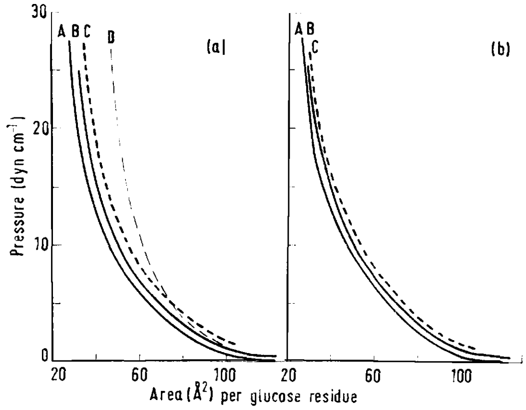

FIGURE 4 Pressure–area curves for cellulose monolayers on anionic direct dye solutions: (a) A, control (water); B, 5 × 10^{-5}M-C.I. 24410 or Benzopurpurpurine 4B solution; C, as B +0·1M-NaCl; D, 10^{-4}M-C.I. 34045; (b) A, control (water); B, 5 × 10^{-5}M-Chrysophenine solution; C, as B +0·1M-NaCl

The same test shows no evidence of a complex between cellulose and C.I. 24340 (Figure 5); C.I. 34045 was not tested thus.

Dye–Cellulose Bonding.—Further, the effect of these anionic solutes on the π–A curves illuminates the nature of the dye–cellulose reaction. The curves in the upper region are in each case parallel to the control, *i.e.*, compressibility is unchanged. By analogy with dye–protein monolayer reactions[14a] this behaviour can be interpreted as evidence of a face-to-face orientation of dye and cellulose molecules, parallel to and in the plane of the water surface. The fact that there is film expansion indicates some form of mutual dye–cellulose association; the dye molecules are a little wider than the cellulose, and if no association occurred, pressure would cause the cellulose chains to ride over the dye molecules and no change in film area would be observed.

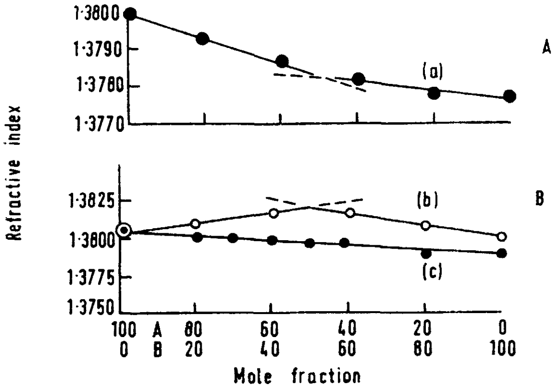

FIGURE 5 Refractive index of 0·1M-cellulose binary solutions at various molar ratios. A, cellulose; B, (a), urea; (b), C.I. 24410; (c), C.I. 24340

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[22] J. H. Schulman and A. H. Hughes, *Biochem. J.*, 1935, **29**, 1242.

[23] R. P. Enever and N. Pilpel, *Trans. Faraday Soc.*, 1967, **63**, 781, 1559.

This hypothesis is illustrated by a comparison of the results with the direct blue and the direct green dyes, and their correlation with measurements taken from the illustrations of Courtauld molecular models given by Robinson (Figures 4d and 5b in ref. 4*b*). Thus if the dye molecules are fully extended, oriented face-to-face and parallel with the cellulose chain, and if adjacent chains are slightly staggered to give closest side-by-side packing of the dye molecules, then the repeat separation of the axes of adjacent cellulose chains is *ca.* 8·5—9 and 11·5—12 Å when they are associated with the blue dye and the green dye respectively. The repeat separation of close-packed cellulose chains alone is *ca.* 8 Å, and therefore association of the two dyes in the suggested manner would increase the separation of the cellulose chains by between 6 and 11% for the blue, and between 44 and 50% for the green dye. The expansions found are 10 and 40% [see Figures 4(a) B and D].

In view of the uncertainty regarding the exact mode of packing of the cellulose–dye complexes, the agreement is as good as can be expected. We suggest that the aromatic nuclei of the dye, in attempting to escape from the water, are forced close to the $\geqslant$CH groups in the cellulose rings. This action will be assisted by the tendency of the water to concentrate around the polar (OH) groups of the cellulose and the polar and ionic groups of the dye molecule. Examination of the Courtauld molecular models (see Figure 2b in ref. 4*b*) reveals that when the present dye molecules are oriented face-to-face with a cellulose chain, the aromatic nuclei of the dye are virtually in contact with the $\geqslant$CH groups in the cellulose.* van der Waals dispersion forces can thus operate (*cf.* ref. 5*a*), to hold the molecules parallel and in contact, and cellulose dyeing could be considered a manifestation of hydrophobic bonding, comparable therefore with wool dyeing.[14b,c] [This is consistent with an observation by Mel'nikov *et al.*,[26] who found that addition of $>\mathrm{CH}_2$ groups to bis-(4-hydroxyphenyl)-alkanes increases their affinity for cellulose.]

This suggestion of face-to-face association agrees with the dichroic behaviour of dyed cellulose, already mentioned, and also with the high negative entropy of dyeing. Thus from published data for affinity[2] and heat of dyeing[25] of C.I. 24410 at high temperatures, the entropy is calculated as >60 cal mol^{-1} K^{-1}.

Multilayer Formation.—Once the first monolayer has been laid down on the cellulose, and water displaced, further molecules of dye are free to associate by deposition on those in the adsorbed layer. Calculations based on accessibility of cellulose internal surface and measurements by a new method using adsorption[27] suggest that only when many multilayers (probably >10) are formed is sufficient dye present to give acceptably deep shades. This occurs only with dyes having long planar molecules.

Effect of Salt.—The slight increase in film expansion caused by addition of sodium chloride to all the anionic dye solutions of the sub-phase can be attributed to increased mutual repulsion when ionic micelles of dye instead of single molecules associate with the cellulose chains.

Hydrogen Bonds.—Detailed refractive index and adsorption tests, as mentioned, showed that hydrogen bonds do not operate between cellulose and many solutes in water. The present tests however suggest that some form of bond may be effective in binding basic groups as in urea and the $-\mathrm{NH}_2$ groups in C.I. 24410 to cellulose.

Nevertheless the bond does not appear to be a normal hydrogen bond, because it has no effect on film viscosity, whereas the bond between cellulose acetate and polar groups in non-ionic dyes causes a very pronounced rise in this viscosity (Figure 2). A *weak* acid–base or ion–dipole association between the cellulosic hydroxy-groups and the amino-groups of the dye seems to be indicated. There is however no clear evidence that *strongly ionised* cationic groups, as in the cationic dyes, have any significant effect in promoting dye–cellulose affinity. Nor does the absence of ionic groups seem to disfavour adsorption: haemotoxylin, a polyhydric phenol with no ionic group, is readily adsorbed by cellulose from water.[28]

π-Bonds.—Yoshida,[4c] using the refractometric method of complex-detection, found that several aromatic sulphonates (as sodium salts), form 1 : 1 complexes with glucose, sucrose, or cellobiose. An aliphatic sulphonate (sodium butane-1-sulphonate) showed no complex formation with any of these proton donors. Experiments here[29] confirm Yoshida's observations, but also show that azo-dyes do not form such complexes.[29,30] π-Bonds do not therefore appear to be important in dye–cellulose adsorption

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* We assume throughout that the cellulose chains lie flat on the water surface. An alternative suggestion[24] is that they are arranged edge-on. If so, the anionic dye molecules between them would presumably also have this orientation, but we believe this would cause a change in film compressibility.

[24] J. O. Warwicker, personal communication.

[25] E. H. Daruwalla and A. P. D'Silva, *Textile Res. J.*, 1963, **33**, 40.

[26] B. N. Mel'nikov, I. B. Blinicheva, S. A. Zabrodin, *Izv. Vyssh. Vchab. Zaved., Tekhnol. Teskt. Prom.*, 1968 (ii), 99 (*Chem. Abs.*, 1968, **69**, 3470).

[27] C. H. Giles, R. Haslam, A. R. Hill, and A. S. Trivedi, *J. Appl. Chem. Biotechnol.*, 1971, **21**, 5.

[28] F. M. Arshid, J. N. Desai, D. J. Duff, C. H. Giles, S. K. Jain, and I. R. Macneal, *J. Soc. Dyers and Colourists*, 1954, **70**, 392.

[29] A. McIntosh, unpublished work.

[30] D. S. E. Campbell, D. Cathcart, and C. H. Giles, *J. Soc. Dyers and Colourists*, 1957, **73**, 546.