Diffusion of Dyes in Polymer Films

Part 4.—Benzopurine 4B and its Meta Isomer in Cellulose

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The diffusion of Benzopurpurine 4B and m-Benzopurpurine 4B into cellulose films from a well-stirred, infinite dyebath gives rate-of-dyeing curves which agree with simple diffusion theory. However, a microdensitometric analysis of the concentration distributions during dyeing shows great deviations from simple theory so that the diffusion coefficients to be obtained from the rate-of-dyeing curves are of little theoretical value.

. The anomalous diffusion behaviour is discussed and it is concluded that the results can best be explained on the basis that the diffusion is accompanied by internal sorption processes which occur at a rate comparable with that of the diffusion process itself. This conclusion is confirmed by numerical solutions which are presented for the problems of (a) diffusion in a medium containing dead-end pore volume and (b) diffusion accompanied by reversible chemical reaction. These two problems can be formulated in the same manner mathematically, but the experimental results are in best agreement with the parameter values required for an explanation in terms of diffusion accompanied by reversible chemical reaction.

The transfer of a direct dye (C.I. Direct Blue 1) from an aqueous dye-bath into cellulose films can be described in terms of the laws of diffusion using a diffusion coefficient which is dependent explicitly on concentration but neither on distance nor on time.[1, 2] Films of cellulose were dyed for different periods of time from a bath, the concentration and temperature of which were maintained constant. From these dyed films, cross-sections were cut and the dye concentration across the film determined with the aid of a microdensitometer. With this particular dye, the concentration at the surface of the film was found to be constant within the limits of experimental error.

However, since dyes vary widely in their affinities, it was thought desirable to examine one or two other dyes. Direct Blue 1 is of moderate affinity only and relatively soluble in water. Benzopurpurine 4B, on the other hand, is a dye of high affinity[3] being less soluble than the blue dye. It differs from the blue dye in carrying two sulphonic acid groups compared with the four of the latter and hence, since the molecules are of similar size, has a greater tendency to aggregate.[3] Moreover, since aggregation might modify the dyeing process, the meta isomer, a dye of much smaller tendency to aggregate has been examined for comparison. The work presented here is a study of the diffusion properties of Benzopurpurine 4B (C.I. Direct Red 2) and its meta isomer derived from m-tolidine.

EXPERIMENTAL

MATERIALS

The cellulose sheet was identical with that used previously.[2] The dyes were purified by the method of Robinson and Mills[4] until no impurities were detected by paper chromatography and the extinction coefficients of aqueous solutions of the dyes agreed with those of other workers.[5] The dyes retained moisture tenaciously and were therefore dried *in vacuo* over phosphorous pentoxide before satisfactory extinction ·coefficients could be

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achieved. The Benzopurpurine 4B in distilled water (0·110 g/l.) had a molar extinction coefficient of $4·97 \times 10^4$ at 500 mμ. The m-Benzopurpurine 4B in distilled water (0·0225 g/l.) had a molar extinction coefficient of $3·80 \times 10^{-4}$ at 475 mμ. In solution in 25 % aqueous pyridine, the maxima were 510 mμ and 484 mμ respectively, and the molar extinction coefficients were $5·94 \times 10^4$ and $4·04 \times 10^4$ respectively.

WORKING PROCEDURES

The dyeings were made using cellulose films fixed in stainless steel frames immersed in a vigorously stirred bath of dye solution. The dyeing and cross-sectioning techniques have been described elsewhere.[1, 2] For the determination of dye concentration in the cross-sections, the microdensitometer made by Joyce Loebl was used [1] with a suitable green filter in the optical beam, (Wratten no. 61) for Benzopurpurine 4B and a blue-green filter (Wratten no. 59) for the meta isomer. Corrections were made for the deviations from the Lambert-Beer law where necessary.

Dyeings were carried out at temperatures ranging from 21 to 90°C in concentrations of salt from zero to 10 g/l. with a dye concentration of 0·1 to 1·0 g/l. The quantity of liquor used was 1·0 l., sufficient to ensure that the concentration remained constant throughout.

All data given here have either been corrected for the thickness of the sections used or are based, for each time of dyeing, upon the examination of several sections so as to minimize the importance of random variations in section thickness. These variations were usually within ± 10 % but could, in extreme instances, be much greater.

RESULTS

The overall rate of absorption of the dyes was measured and the amount of dye M_t, relative to that taken up at equilibrium M_∞, plotted against the square root of time. On the basis of the simple diffusion equation, the graphs obtained should give straight lines through the origin which fall off at the higher concentrations. The curves given in fig. 1 confirm this behaviour.

The manner in which Benzopurpurine 4B and its meta isomer (fig. 2 and table 1) are distributed in the film during the dyeing process does not, on the other hand, follow the behaviour observed with Direct Blue 1.[2] With this last dye the surface

TABLE 1.—SUMMARY OF EXPERIMENTS

expt. no.	dyestuff	film	temp.	dye conc. g/l.	salt conc. g/l.	equilibrium sorption g/100 g	$t^{\frac{1}{2}}$ min	apparent diffusion coefficient $\bar{D}$ cm² sec⁻¹ × 10¹¹
1	m-Benz. 4B	P.T. 600	90°	1·00	10·00	3·40	4·16	1660
2	,,	,,	51·5°	2·17	5·00	4·90	100·0	69·2
3	,,	,,	25°C	0·50	5·00	5·09	900	7·7
4	Benz. 4B	,,	90°	0·25	5·00	3·91	32·0	216
5	,,	,,	50°	0·25	5·00	5·75	1508·0	4·6
6	,,	,,	50°	1·00	1·00	4·96	1225·0	5·7
7	,,	,,	25°	0·25	5·00 *	1·84	70·8	94·0
8	,,	,,	21°	0·25	5·00 *	—	159·0	42·0
9	,,	,, †	96°	0·50	2·00	—	—	—
10	,,	,, †	30°	0·50	2·50	—	558	30·0

* 100 ml/l. pyridine added to the dyebath.   † never-dried cellophane film used.

concentration was constant, i.e., independent of time and the diffusion process could be described by the normal laws of diffusion with a diffusion coefficient dependent on concentration only. The two dyes examined in this paper exhibited surface concentrations which increased with time.

The correctness of the results in fig. 2 is confirmed by the fact that graphical integration of the distributions to obtain values for the amount of dye sorbed at any given time gave quantities in good agreement with the direct estimations in fig. 1. Furthermore in expt. 5 (fig. 2 and table 1), the thickness of each section was determined by means of an interference microscope and the results have been corrected to allow for any variations in section thickness. These corrections did not amount to more than $\pm 10\%$ for the sections employed. The distribution curves shown
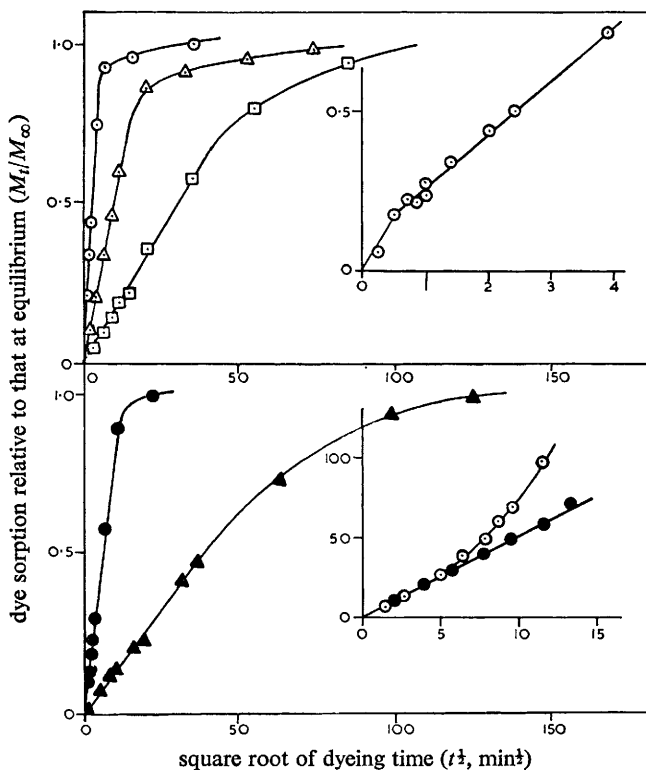

FIG. 1.—Rate of sorption measurements.

$\odot$, expt. 1 ; $\triangle$, expt. 2 ; $\square$, expt. 3 ; $\bullet$, expt. 4 ; $\blacktriangle$, expt. 5 ; cf. table 1.

Upper inset—expt. 1 ; cf. fig. 8 for $\eta = 0.01$.

*Lower inset**—1.0 g/l Benzopurpurine 4 B and 1.0 g/l salt at 50°C

$\bullet$, fresh dye solution ; $\odot$, old dye solution

* The ordinate here is: dye sorbed (arbitrary units)

(ordinate label: dye sorption relative to that at equilibrium (M_t/M_∞))

(abscissa label: square root of dyeing time ($t^{\frac{1}{2}}$, min$^{\frac{1}{2}}$))

elsewhere in fig. 2 are in each instance the mean of several repetitions. Only expt. 1, 9 and 10 (fig. 2) are based upon single measurements of the distribution for each time of dyeing : in expt. 1 there is direct confirmation from the sorption measurements and in all cases the observed rise in surface concentration with time far exceeds the experimental error which can arise from the use of single measurements on single sections.

The distributions also show unexpected behaviour when plotted as relative concentration against $x/t^{\frac{1}{2}}$, where x is the penetration distance of a given concentration at time t. In addition to a rising surface concentration, there is often a regular crossing or intersection of the curves (fig. 2). Similar results have been reported

by Pontius et al.[6] for the diffusion of acid dyes in gelatin films and we find that there is, in some instances, a similar intersection of their curves when we plot them as concentration C against $x/t^{\frac{1}{2}}$.

The behaviour shown in fig. 2 was in general unaffected by changes in the rate of stirring of the dyebath and was reproducible. The simplest comparison of the overall rates of dye sorption is obtained from the direct measurements of the time required $t_{\frac{1}{2}}$ to attain a dye sorption equal to one-half of that at equilibrium. These

penetration distance x (arbitrary units)
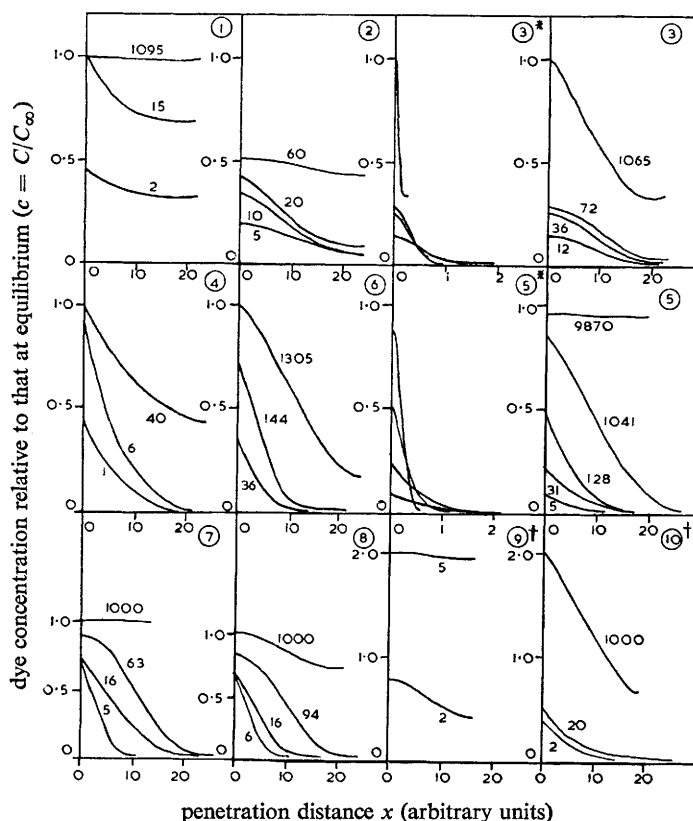
or * here the abscissae are values of $x/t^{\frac{1}{2}}$ (in arbitrary units) where t is the time of dyeing. The numbers on the curves are the times of dyeing t (min) and the numbers labelling each figure refer to the expt. no. in table 1.

The ordinates for the diagrams referring to expt. 9 and 10 are:

dye concentration (arbitrary units)

Fig. 2.—Concentration distributions during dyeing.

are given in table 1 together with the corresponding apparent diffusion coefficients [7] and the equilibrium dye sorptions. Solutions of Benzopurpurine 4B containing the rather high concentrations of salt employed here can exhibit behaviour which depends upon the age of the solution, particularly at lower temperatures. The freshly-prepared solutions give reproducible behaviour, but solutions which have been stored for some time give curves of dye sorbed against $t^{\frac{1}{2}}$ which are markedly convex to the $t^{\frac{1}{2}}$ axis and which lie above the curves for the freshly-prepared solution (fig. 1). There may be a deposition of dye on the surfaces of the films in addition to any aggregation of dye that may occur within the films.

DISCUSSION

The diffusion characteristics of both dyes show marked deviations from the behaviour of Direct Blue 1 in the same substrate.[2]   The apparent diffusion coefficients in table 1 can bear no simple relationship to the actual diffusion coefficients of the dyes in the cellulose because of these deviations from the mathematical model of diffusion from a constant surface concentration (fig. 2).   The diffusion coefficient of the m-isomer is much greater than that of Benzopurpurine 4B under comparable conditions; since these molecules are of the same size, it is apparent that the rate of absorption of dye is influenced by factors other than those governing a simple diffusion process.

Particularly remarkable is the observation that the surface concentration can continue to increase by as much as 100 % even after a comparatively uniform dye distribution is attained (expt. 1 and 2).   Both dyes can exhibit at least a ten-fold rise in surface concentration during dyeing, usually at the lower temperatures (expt. 3 and 5).   Pyridine was added in expt. 7 and 8 in order to reduce the aggregation of these dyes.   The presence of pyridine reduces the extent of the changes in surface concentration but at the same time also markedly reduces the equilibrium dye sorption.   It seems unlikely, therefore, that the reduction in the surface effects can be attributed entirely to the disaggregating effect of this solvent.   The behaviour shown in fig. 2 depends on the dyeing conditions and does not appear to be dependent on a fixed property of the substrate; similar behaviour is found both with normal P.T. 600 film and with the never-dried film.   It was normal procedure in these experiments to pre-treat the cellulose films at the dyeing temperature in a solution which was identical with the dyebath except that it contained no dye.   This pretreatment lasted for about 2 h and the cellulose films were therefore already swollen by water before dyeing began.   There were no detectable changes in the dimensions of the normal P.T. 600 film during dyeing and we have obtained satisfactory agreement with other dyes between diffusion experiments using cellulose films in the steady state and in the non-steady state.[8]   There is no evidence that direct cotton dyes cause swelling or modification of cellulose during dyeing and although changes in the structure of cellulose films may well occur on prolonged immersion in a hot aqueous dyebath, we do not think that the present results are attributable to such changes.

On the other hand, the diffusion of small organic molecules into polymers is often associated with strong interactions between the penetrant and the polymer which result in marked swelling of the polymer and complicated diffusion behaviour. Long and Richman [9] have measured the concentration distributions established during the diffusion of methyl iodide vapour into films of polyvinyl acetate and films of cellulose acetate at temperatures below the glass-transition temperatures of these polymer-penetrant systems.   Their results are similar to the present ones in that a markedly rising surface concentration is found, but this is associated with concentration distributions that suggest a large increase of diffusion coefficient with concentration, with rate-of-sorption curves which do not conform to simple theory (in contra-distinction to the results reported here) and with a distinctive two-stage behaviour of the sorption process.[9b]   The diffusion process above the glass transition temperature [9a] does not show this rising surface concentration and the two-stage mechanism is absent.   There is no question of the experiments carried out here with direct dyes being at a temperature below the glass transition temperature for the amorphous regions of water-swollen cellulose.   Long and Richman attribute their results to the occurrence of slow relaxation processes in the penetrant + polymer

system.   These processes must occur at all points in the system to which the methyl iodide has penetrated and therefore a theoretical treatment of the results of Long and Richman ought to include expressions for the time-dependent processes at any point in the substrate.   For this reason the treatment given by Long and Richman, which is based upon an anomalous time-dependent surface condition at the boundaries of the film alone,[9b] did not seem appropriate for the present work.

The abnormalities of the processes described in fig. 2 are not revealed by the rate of sorption measurements, so that unfortunately it is no longer possible to maintain [10] that, if a graph of dye sorbed from an infinite bath against $t^{\frac{1}{2}}$ is linear and passes through the origin, then the process is controlled by diffusion from a constant surface concentration with a diffusion coefficient dependent explicitly neither on x nor on t but only on C.   The results in fig. 1 generally satisfy this criterion, although when plotted on a large enough scale even the data from expt. 2, 3 and 5 show in the initial stages of diffusion a slight curvature convex to the $t^{\frac{1}{2}}$ axis and a very small intercept of the linear portion on this axis.   Such effects are only apparent on very careful examination and would seem insignificant in the absence of other information such as that in fig. 2.   In one experiment, an intercept on the concentration-axis was observed (fig. 1).

The values of the diffusion coefficients in table 1 bear no simple relationship to the actual diffusion coefficient of the dye within the substrate, even though on the evidence of fig. 1 alone one would have assumed the opposite.   If the behaviour shown here is common to other dyestuffs and substrates, the problem of developing a simple treatment of dyeing kinetics which has any real physical meaning will be formidable.

Of the factors to consider, the first is that the surface concentration rises with increasing time of dyeing because the dyebath is unable to supply dye to the film surfaces at an adequate rate.

Although the rate of sorption must theoretically be infinite when the film is immersed in the dye liquor the duration of this high rate is very short and unlikely to be detectable unless the diffusion coefficient in the film were unusually large and/or the surface concentration very high.   However, the values of the apparent diffusion coefficient $\overline{D}$ and the magnitudes of the equilibrium absorption are similar to those for Direct Blue 1,[2] a dye which gave constant values of the surface concentration. That the bath is able to supply dye to the surface at an adequate rate is confirmed by the lack of influence of the rate-of-stirring as well as the fact that the changes of surface concentration with time in general increase as the temperature decreases, which is the reverse of the expected behaviour if the dyebath depletion is controlling the rate.   Moreover, the activation energies for diffusion calculated from the $\overline{D}$ values in table 1 are 10-20 kcal/mole.   These are values larger than those expected for a process controlled by diffusion through the aqueous layer adjacent to the surface of the cellulose films.

If the dye in the aqueous solutions is predominantly aggregated, it may be that the aggregates break down so slowly that the supply of monomeric dye to the film surface is inadequate to maintain the diffusion process into the film.   This does not seem very probable because there is no evidence that disaggregation is a slow process and because old solutions which contained highly aggregated and possibly even micro-particulate dye gave rise to a greater rate of dye sorption than that from fresh solutions—though to what extent this was due to deposition of dye on the surface of the films is uncertain.

The rise of surface concentration with time is shown in fig. 3 ; in several experiments the surface concentration rises to a first approximation linearly with $t^{\frac{1}{2}}$.   Crank[7]

has given the following solution of the problem of diffusion into a plane slab, from a surface concentration varying as $C_{x=0} = kt^{\frac{1}{2}}$, with a constant diffusion coefficient D:

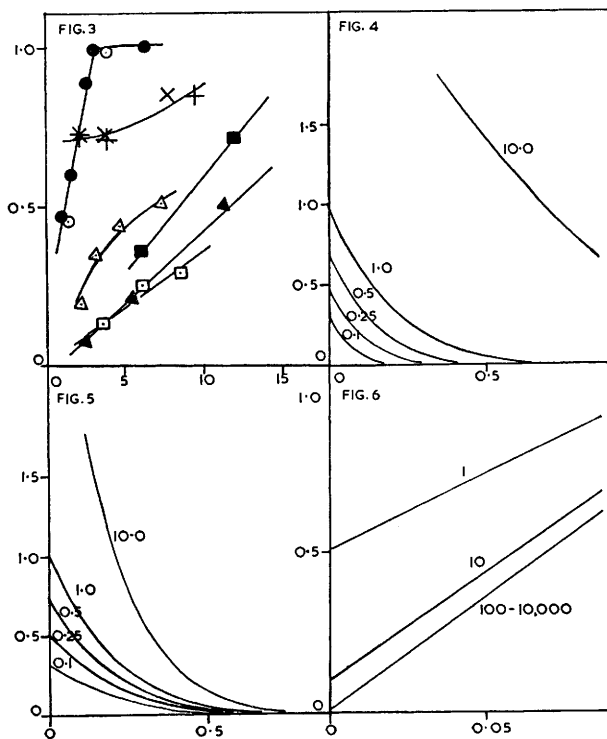$$C_x = k\sqrt{\pi t} \ \text{ierfc} \ x/2\sqrt{Dt}. \tag{1}$$

FIG. 3–6.

FIG. 3.—Variation of dye concentration at the film surface with time.
abscissa: square root of time of dyeing ($t^{\frac{1}{2}}$, min$^{\frac{1}{2}}$)
ordinate: dye concentration relative to that at equilibrium $(c)_{x=0}$
The symbols on the curves correspond to those used in fig. 1; with the additions: ■, expt. 6; X, expt. 7; +, expt. 8.

FIG. 4.—Theoretical concentration distributions for diffusion from a surface concentration rising linearly with $t^{\frac{1}{2}}$.
ordinate: concentration, C abscissa: penetration distance, x
the numbers on the curves are values of the time t.

FIG. 5.—Theoretical concentration distributions for diffusion from a surface concentration rising linearly with $t^{\frac{1}{2}}$.
ordinate: concentration C abscissa: composite variable $x/t^{\frac{1}{2}}$
the numbers on the curves are values of the time t

FIG. 6.—Theoretical variation of surface concentration with time when $\eta R = 100$.
ordinate: dye concentration relative to that at equilibrium $(c)_{x=0}$
abscissa: time variable ($\tau^{\frac{1}{2}}$)   the numbers on the curves are values of R

In fig. 4, the theoretical concentration distributions are given for different times for $k = 1$, $D = 0.04$, values which are appropriate to the behaviour of the dyes. Although the profiles are similar in shape to the observed ones, they do not intersect when plotted against $x/\sqrt{t}$ (fig. 5). It also appears that the employment of a

monotonically increasing surface concentration as a boundary condition at $x = 0$ in these mathematical solutions will often give a theoretical sorption behaviour which, when plotted as in fig. 1, will exhibit a convexity to the $t^{\frac{1}{2}}$ axis, and this convexity can be marked.[7] Also the concentration distributions will be more concave than expected from Fick's law.

Alternatively, it may be postulated that there is a barrier to diffusion at the surface of the film. It is not clear why this should be so in the present experiments [11, 12] and furthermore Crank [7] has given solutions for a problem of this type which show (Crank, *loc. cit.*, fig. 3.4, p. 35) again that the concentration distribution curves do not intersect when plotted as C against $x/(4Dt)^{\frac{1}{2}}$. Moreover with a surface barrier, the surface concentration does not rise linearly with $t^{\frac{1}{2}}$ as has been found in the present work.

The possibility has been suggested [13] that the intersection of the curves (fig. 2) may be an experimental artefact arising from the use of too large a slit width in the microdensitometer but this is considered unlikely because the present experimental arrangement [1] did not reveal such behaviour when Direct Blue 1 [2] was examined even though the instrument parameters were identical and the penetration distances involved were very similar. In addition, this kind of intersection can be predicted on theoretical grounds as a possible consequence of two well-defined physical situations.

The dyestuffs used in this work aggregate in solution [3, 3a] and are likely also to aggregate within the fibre so that the contribution of aggregation phenomena to the observed results is difficult to assess. It may be that more than one species diffuses within the substrate and that, in some experiments, multilayer formation of dye occurs within the films.

Additions of pyridine and rises of temperature cause disaggregation of the dye: the rate of build up of the surface concentration is now much faster and the system now behaves more like that observed for Direct Blue 1.[2]

Nevertheless, since these intersections are manifest within the substrate, it is natural to seek for their origin within this region, and one possibility is that the adsorption equilibrium at any point within the substrate is not attained sufficiently rapidly by comparison with the rate of transport of matter through the substrate (cf. particularly expt. 1, 2 and 9).

This increase in dye adsorption in excess of that expected from Fick's law could arise from the presence in the polymer of " dead-end " pores, i.e., pores which do not contribute to the transport of dye through the solid but act as a sink for the dye.[14] Dye diffuses into these pores but can go no farther. An alternative way to obtain a build-up of dye is for the adsorption of dye by the cellulose at any point in the fibre to be slow relative to the movement of the dye forward: the situation is identical formally with that which exists when diffusion is accompanied by reversible chemical reaction.[15] This case mathematically could also include the situation where the dye forms aggregates in the cellulose film, and is not completely irrelevant to the problem discussed by Long and Richman.[9b]

The alternative analysis in terms of reversible reaction, which has been given for more general boundary conditions,[15] assumes that the diffusing species may be adsorbed and immobilized.

Crank's analysis,[7, 15] will be outlined first, the relationships of his parameters to those of Goodright *et al.*[14] will be mentioned and then numerical solutions presented. Crank [7, 15] discussed diffusion into a plane sheet occupying the space $-a \leqslant x \leqslant a$, from a restricted amount of solution occupying the space $-l-a \leqslant x \leqslant -a$, $a \leqslant x \leqslant l+a$. The concentration of solute in the solution is uniform at all times and is initially C_0, the sheet being free from solute at the start of diffusion; C is

the concentration of solute free to diffuse within the sheet and S is that of the immobilized solute, each being expressed as amount per unit volume of sheet. The diffusion is governed by the equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t}, \tag{2}$$

and the simultaneous adsorption is of the type

$$\partial S/\partial t = \lambda C - \mu S \tag{3}$$

where D is the diffusion coefficient and λ and μ are the rate constants for the adsorption and desorption processes respectively. Solutions of (2) and (3) are obtained [15] for the initial condition

$$S = C = 0, \qquad -a < x < +a, \qquad t = 0, \tag{4}$$

and with the further conditions that there be no accumulation of solute at the surfaces of the film,

$$l\partial C/\partial t = \mp D\partial C/\partial x, \qquad x = \pm a, t > 0, \tag{5}$$

and that the concentration of solute free to diffuse just within the surface of the sheet is the same as that in the solution. This latter is shown not to be a necessary restriction. In the present work, it is appropriate to use only the solutions for an infinite dyebath ($l = \infty$).

If the total amount of dye sorbed is

$$C_T = S + C \tag{6}$$

and if $R = \lambda/\mu$, then for l infinite,

$$c = \frac{C_T}{(R+1)C_0} = 1 - \frac{2}{(R+1)}\sum_{n=1}^{n=\infty} \frac{D^2 k_n^3 (p_n/\mu + 1)^2 \exp(p_n t) \cos k_n x}{p_n^2 a\{(p_n/\mu + 1)^2 + R\} \sin k_n a}, \tag{7}$$

where

$$k_n^2 = -\frac{p_n}{D}\frac{p_n + \lambda + \mu}{p_n + \mu}; \tag{8}$$

and where the k_n are the non-zero, positive roots of

$$\cos k_n a = 0 \tag{9}$$

Numerical solutions have now been obtained of eqn. (7), which gives the total concentration C_T at any point at any time, relative to that at equilibrium. The solutions were obtained using a Mercury Autocode programme on the Atlas computer. The graphical integration of selected examples of the theoretical concentration distribution curves, to obtain the amount of dye sorbed at any time, gave results in good agreement with the computations of Crank.[7, 15]

A selection of results is given in fig. 6-11, fig. 8 being a copy of a graph obtained by Crank,[7, 15] The solutions are most conveniently discussed in terms of the following parameters:

$$R^1 = (R+1) = (\lambda + \mu/\mu) = \text{the partition coefficient for the equilibrium distribution of solute between the solution and the substrate,} \tag{10}$$

$$\eta = \mu a^2/D, \tag{11}$$

$$\tau = Dt/(R+1)a^2, \tag{12}$$

$$X = x/\tau^{\frac{1}{2}}. \tag{13}$$

In the treatment used by Goodknight [14] et al., the dead-end pores are supposed to be connected to the main flow channels by restricting necks in which a quasi-

steady-state flow occurs. Y is a constant parameter which describes the ease of flow into the dead-end pores, V_2 is the total volume of dead-end pores, V_1 is the total volume (excluding dead-end pores) of the main flow channel. If C_M is the concentration of solute in the main flow channels and if C_S is the concentration of
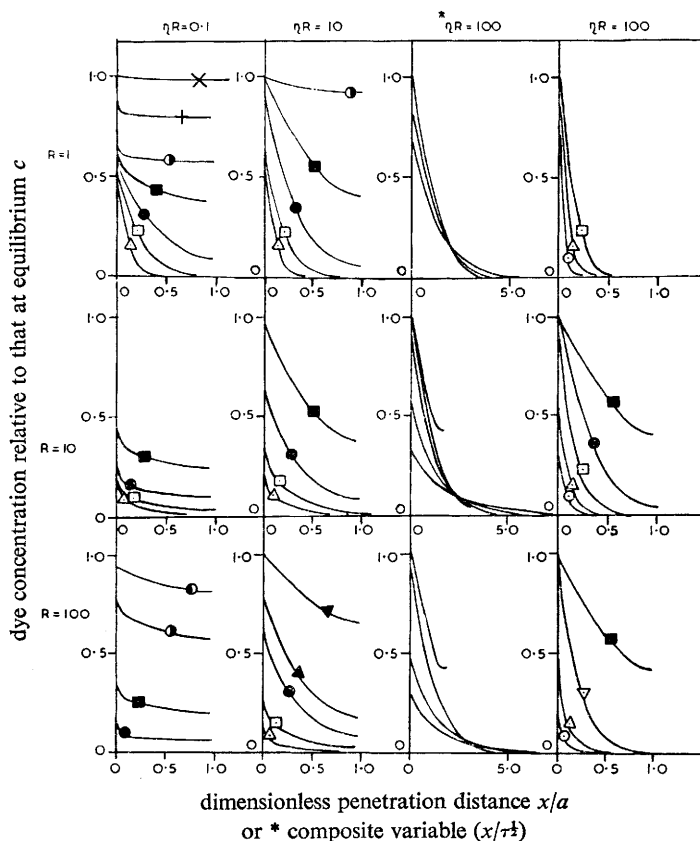

dimensionless penetration distance x/a
or * composite variable $(x/\tau^{\frac{1}{2}})$

FIG. 7.—Theoretical concentration distributions during dyeing.

Graphs for a given value of the product ηR are arranged vertically. The graphs in the top row are for $R = 1$, in the middle row for $R = 10$, and in the bottom row for $R = 100$.

The symbols on the curves refer to the following values of τ: $\bigcirc, 0.00125$; $\triangle, 0.005$; $\square, 0.020$; $\triangledown, 0.040$; $\bullet, 0.080$; $\blacktriangle, 0.160$; $\blacksquare, 0.320$; $\blacktriangledown, 0.640$; ◑, 1.280; ◐, 2.560; $+, 5.120$; $\times, 20.48$.

solute in the dead-end pores or sinks, then we have the following relationships between the two treatments:

$$C \equiv C_M; \qquad S \equiv V_2 C_S/V_1; \qquad \text{and} \qquad D \equiv D^*/\theta^2, \qquad (14)$$

where D^* is the diffusion coefficient in the solution filling the pores (assumed constant) and where θ is a tortuosity factor. Also

$$\lambda \equiv V_2 Y/V_1; \qquad \mu \equiv Y; \qquad R \equiv V_2/V_1. \qquad (15)$$

Eqn. (7) is also the solution of a problem of diffusion in a medium containing dead-end pore volume,[14] but the parameters assume a different significance. The quantity C_T is related to C_M and C_S through the equation,

$$C_T = C + S = C_M + (V_2 C_S/V_1), \qquad (16)$$

and therefore C_T is now the apparent concentration of dye in the main flow channels. The apparent concentration in terms of the unit volume of the *porous solid* is given by

$$C_T^1 = C_T V_1 / V_T, \tag{17}$$

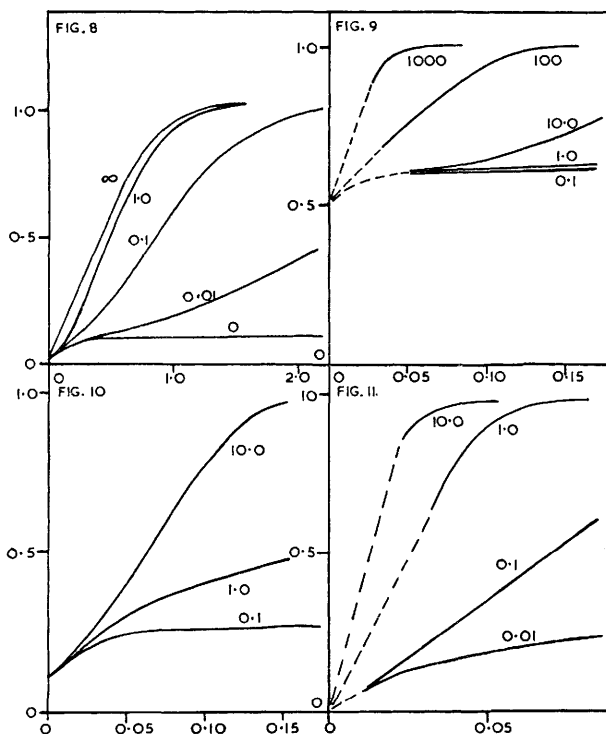where V_T is the total external volume of the porous solid having a main channel pore volume V_1.

FIG. 8.—Theoretical rates of dye sorption for $R = 10$.
ordinate: dye sorption relative to that at equilibrium M_t/M_∞
abscissa: time variable $\tau^{\frac{1}{2}}$
the numbers on the curves are values of η.

FIG. 9, 10 and 11.—Theoretical variation of surface concentration with time.
ordinates: surface concentration $(c)_{x=0}$　　　abscissae: time variable $\tau^{\frac{1}{2}}$
The numbers on the curves are values of η.　Fig. 9, $R = 1.0$; fig. 10, $R = 10.0$; fig. 11, $R = 1000$.

It is possible to use the relative concentrations c without defining clearly the units in which any one concentration is expressed. The present diffusion-with-adsorption [15] model is also artificial in that it is compatible only with a constant diffusion coefficient and with a linear adsorption isotherm. This is unlikely to be true and therefore it would be unjustified to expect too great an agreement between the theoretical concentration distributions (fig. 7) and those found experimentally (fig. 2). Nevertheless, an intersection of the theoretical curves can be found when they are plotted as c against X (fig. 7); $c_{x=0}$ can theoretically be a linear function of $\tau^{\frac{1}{2}}$ (fig. 6). Most of the types of behaviour found in practice (fig. 1, 2, 3) can be predicted at least qualitatively (fig. 6-11). Indeed, the intersection of the profiles was found to occur for all solutions in which the value of the product ηR was of the order of

100, for values of R from 1 to 10^4. For small values of η combined with small values of R, it would require extreme care to distinguish the situation from one in which the surface concentration remained constant as diffusion proceeded, even employing a microdensitometric technique [1, 2, 9] (cf. fig. 7 for $R = 1$, $\eta = 0\cdot1$). It is possible that polymeric substrates contain regions which are less accessible to the solute than the bulk of the polymer and which may therefore produce behaviour of this kind by acting as dead-end pores. This possibility cannot even be excluded in the investigations with Direct Blue 1,[2] although it is unlikely on experimental grounds that more than about 10 % of the dye sorbed could be retained in this manner. This situation could also provide an explanation of the results of expt. 9 and 10, and possibly even of expt. 1 and 2 (fig. 2), but it is not so plausible an explanation of the remaining experiments because of the required magnitude of $R = V_2/V_1$.

It is clear from fig. 8 that substantially linear graphs of $M_t/M\infty$ against $t^{\frac{1}{2}}$ may be obtained even when the parameter η is small and, since an unambiguous interpretation of these measurements requires an independent estimate of D and of R in order to locate the observed behaviour on a graph of the type of fig. 8 by estimating the corresponding values of $\tau^{\frac{1}{2}}$, rate-of-sorption measurements alone are not likely to be very informative. A similar objection applies to a detailed comparison of the results in fig. 2 with those in fig. 7, but it is a far less weighty objection because the pattern of behaviour is here a more markedly varying function of η.

If R is identified instead with the ratio of the rate parameters for internal adsorption and desorption, then R^1 should correspond approximately to the observed value of the partition coefficient of solute between dyebath and substrate. If Donnan membrane phenomena are taken into account [16] the values of R^1 may exceed 10^3 and, certainly for such values of R^1, it is possible to reproduce theoretically most of the features of the experimental results. If we define as ideal behaviour diffusion from a constant surface concentration with a diffusion coefficient dependent on concentration c but dependent explicitly neither on x nor on t, then experimentally this condition would appear to be satisfied, either for small values of η combined with small values of R, or for large values of η. The former situation corresponds perhaps to the dead-end pore model and the latter to either model. Although a combination of the two simplified models may represent a closer approximation to reality, it would contain many adjustable parameters.

CONCLUSIONS

Although conventional rate-of-dyeing measurements suggest that the diffusion of the dyes used in this work conforms to simple theory, the application of a microdensitometric technique has revealed large deviations from the expected, ideal behaviour. The results can best be interpreted in terms of diffusion accompanied by a reversible internal adsorption process which immobilizes a proportion of the diffusing molecules, and the anomalies are considered to arise because the rates of the adsorption processes are comparable with that of the diffusion process itself. It is not possible to exclude an interpretation of some aspects of the results in terms of dead-end pore volume within the substrate, because the mathematical formulation of these possibilities can be made identical with that of the diffusion-with adsorption-model. But the values then required for the parameters of the system do not seem probable. The influence of changes in the state of aggregation of the dyes is difficult to assess because these changes are also associated with changes in sorption behaviour; there was evidence, however, that the age of the dye solutions had some influence on the dyeing behaviour of Benzopurpurine 4B.

DIFFUSION IN CELLULOSE

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