Concentration Dependence in Dye Diffusion

SHLOMO ROSENBAUM* and F. L. GOODWIN, *Research Department,*
The Dow Chemical Company, Williamsburg, Virginia

Synopsis

The adherence of the diffusion of (cationic) dyes in polyacrylonitrile fibers to Fick's law with a constant diffusion coefficient is discussed at the hand of diverse experiments. More specifically, an attempt is made to account for apparently abnormal radial color intensity distributions.   There is no evidence for polymer plasticization by the dye. The (linear axial) thermal expansion, glass transition temperature, disorienting shrinkage temperature, and other properties are not appreciably affected by saturating the fiber with dye.   The evidence from both sorption and penetration measurements indicate concentration-independent diffusion from a limited number of specific (sulfonate) surface sites.   The behavior appears to be so simple that saturation values can be measured from the sorption curves.   It is shown that, for diluents with the molecular properties of dyes, a free volume model of dye diffusion predicts the absence of plasticization effects in dyeing systems in general.   Replacement of the concentration in the diffusion equation by an activity function, $\theta/(1-\theta)$, where θ is the fraction of sites occupied by dye, suggested for the analogous case of anionic dyes on nylon is considered and shown not to be justified on a thermodynamic basis.   A similar function can be derived on reasonable kinetic grounds, but is not borne out by the detailed results.

Since the diffusion behavior of small penetrants through films or fibers can yield important information on polymer structure, it is unfortunate that it is often complicated by a strong concentration dependence of the diffusion coefficients.[1]   This effect, usually related closely to changes in segmental relaxation times,[2] might be expected to be small or negligible in diffusion of moderate concentrations of compounds of the molecular structure of dyes.   Pending the more systematic discussion further on, mere inspection of the dyes in Table I will indicate the unlikelihood that they will act as effective plasticizers.

The experimental work in the study of which the present paper forms part has been concentrated on one system, that of cationic (basic) dyes and polyacrylonitrile fibers with sulfonate groups from either a comonomer or a bisulfite-containing initiator system.   The dyeing equilibrium is determined[3] by exchange of dye cations from solutions for the counter-cations orginally associated with the sulfonate.   A free volume model of dye diffusion[4] has been very useful in explaining and predicting kinetic results.   Confinement to one system has the disadvantage that the more

* Present address: Research Laboratory, The Dow Chemical Company, Walnut Creek, California.

general conclusions which often appear justified cannot be regarded with the confidence desired until confirmed by specific experiments. At least at the present stage, this should be outweighed by greater feasibility of thoroughness of characterization from various aspects, using different procedures and with reasonable confirmation of assumptions and results.

Neglect of concentration dependence in dye sorption studies has been held responsible[5] for inadequacies in present understanding of dyeing kinetics. An almost complete cessation of work, or at least publications, in this area appears to have resulted from repeated emphasis of the dangers inherent in sorption experiments.[6-8] While in the present work there was no indication that disregard of these led to any serious inconsistencies, they did lend added urgency to the considerations discussed here. Also, diffusion coefficients increasing strongly with increasing concentration were suggested by visual examination of cross sections of fibers dyed for short periods of time.[9] With increasing distance from the surface, the color intensity at first remains almost constant; this region is separated from the white interior by a narrow zone of sharply decreasing color intensity, closely resembling a moving boundary. Concentration dependence has been reported for a number of other dyeing systems.[5-8,10,11]

EXPERIMENTAL

Details pertaining to one experiment are tabulated along with the results. General experimental procedures are described elsewhere: sorption,[12] penetration,[9] preparation of fibers,[13] disorienting shrinkage,[14] linear thermal expansion,[15] tensile.[13] The infinite bath condition for penetration experiments was regarded as upheld if solution concentrations changed by not more than 2%. Sorption experiments were carred out from concentrations high enough to maintain a saturated surface.[13] Dyes will be designated throughout by the first letter of their color. The dyes used are described in Table I.
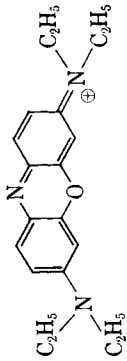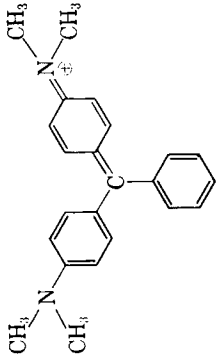
RESULTS AND DISCUSSION

Plasticization

Concentration dependence would appear to be predicted by a free volume model of dye diffusion in which holes formed above the glass transition temperature T_g allow the motion of segments of the polymer molecules as well as dye molecules and, hence, the transport of the latter to the fiber interior. If the dye is transferred by interchange between encountering sites, the volume fraction v_s of which is small, the diffusion coefficient $\mathfrak{D}$ is related to the relaxation time τ of a polymer segment of diameter δ by[4]

$$\mathfrak{D} = f(\delta^2/\tau)v_s \tag{1a}$$

When the requirements of a dye molecule for jumping into a hole it faces

TABLE I
Description of Dyes Used

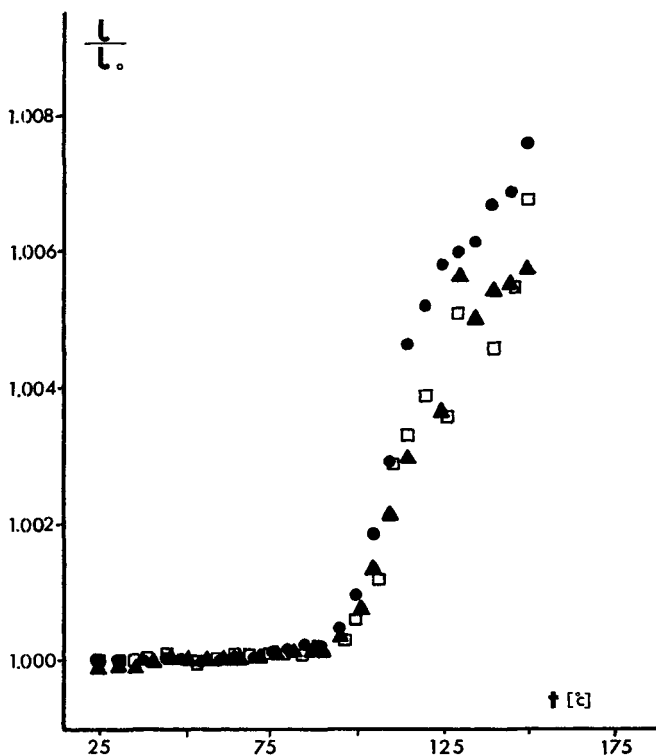| Letter	Color	Class	Name	Structure	Purification reference
B	Blue	Oxazine			3
G	Green	Triphenyl-methane	Malachite green		13
V	Violet	Monoazo	Calcozine acrylic violet 3R		

Fig. 1. Effect of dye on linear axial thermal expansion and glass transition temperature (dye G, site concentration 0.062 mole/kg.) at various dye concentrations: (●) 0.060 mole/kg. fiber; (▲) 0.030 mole/kg.; (□) 0.

(of diameter equal to that of a segment) are not much greater than those for a polymer segment, f is of the order of magnitude of unity.   In systems where the location of the dye is not restricted to a limited number of sites, e.g., if $v_s \rightarrow 1$, this simplifies to

$$\mathfrak{D} = f\delta^2/\tau \qquad (1b)$$

The free volume is increased, hence T_g and τ decrease, by addition of a nonpolymeric diluent or plasticizer.[16-18]   Since a dye must be regarded as a diluent, it should be expected from the relations shown that the diffusion coefficient will increase with increasing dye concentration.   By the same token, a large number of physical properties dependent upon the free volume should be affected.

The linear axial thermal expansion of an experimental acrylic fiber of relatively high sulfonate site concentration (0.062 mole/kg.) with about 97%, 49%, and none of the sites occupied by dye G is shown in Figure 1.   The fibers which were almost saturated with dye may have expanded somewhat more at high temperatures, but the effect was slight (the curve is based on an average of three runs, however).   There was no
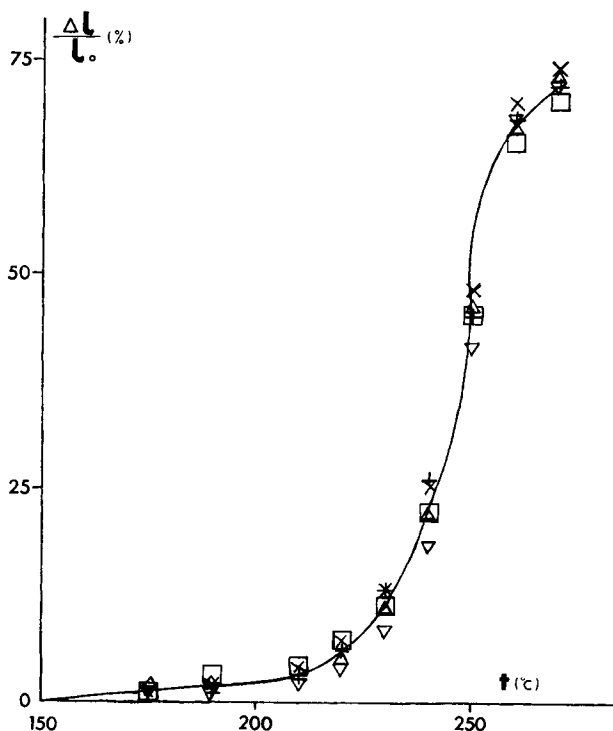
Fig. 2. Effect of dye on disorienting shrinkage at various dye concentrations on fiber: (△) dye G, 0.060 mole/kg.; (▽) dye G, 0.030 mole/kg.; (✕) dye B, 0.055 mole/kg.; (+) dye B, 0.27 mole/kg.; (□) no dye. Saturation value 0.062 mole/kg.

increase for the half-saturated fiber by comparison to the undyed, and no differences in the glass transition temperature, the point at which the curves begin to rise abruptly.[15] Load–elongation curves also showed no decrease in T_g on saturation of the sites (with malachite green) and no other plasticizing effects (there may, in fact, have been some stiffening in the resistance to elongation).

Oriented crystalline polymers undergo marked shrinkage at the crystalline melting point with complete structural disorientation.[19,20] With acrylic fibers, shrinkage is not followed by melting to a flowing liquid,[14] and it occurs considerably below reported melting points. The shrinkage temperature is decreased strongly by plasticizing liquids such as ethylene glycol. Figure 2 shows that dyes did not affect the shrinkage temperature appreciably.

Concentration Dependence

In diffusion from a saturated surface with a total site concentration S equal to that of the bulk of the fiber, the apparent (initial[2]) diffusion coefficient $\bar{\mathfrak{D}}_a$ through a fiber that contained no dye before the experiment can be obtained from the relation[18]
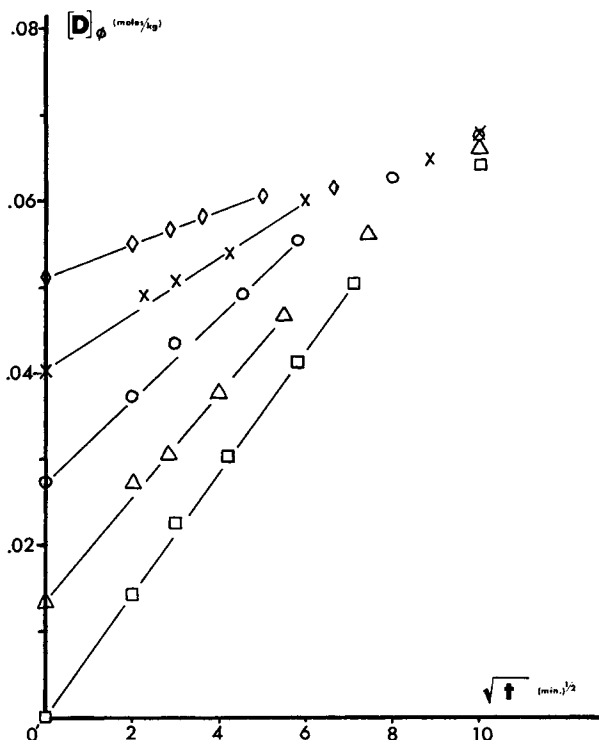
Fig. 3. Effect of initial uniform concentration C_1 of dye on rate of sorption. Dye G; concentration of dye in solution 12.2×10^{-4} moles/l.; $S = 0.070$ mole/kg.; pH 4.0; [NaAc] $0.05M$; 91.1°C.

$$C_t = 2A_w(\mathfrak{D}_a/\pi)^{1/2}t^{1/2}S \tag{2}$$

C_t is the concentration of dye taken up by fiber during time t and A_w is the outer surface area. An increase in S increases the number of dye molecules taken up by the surface layers from which diffusion into the interior takes place. This has been treated earlier.[21] It should also be possible to decrease the uptake by having part of the sites occupied by dye before the experiment. With an initial concentration C_1 uniformly distributed throughout the fiber (including the surface), the relation becomes

$$C_t = 2A_w(\mathfrak{D}_a/\pi)^{1/2}t^{1/2}(S - C_1) \tag{3}$$

which reduces to eq. (2) at $C_1 = 0$. Figure 3 shows sorption curves obtained on fibers which had previously been dyed in baths containing different amounts of dye G for one day at 91.8°C.; the fibers with $C_1 = 0$ had been similarly treated in a blank bath. The concentration C plotted is the sum of C_1 and of concentration C_t taken up during time t from solutions of initial concentration 0.00122 mole/l. This was almost 1.75 times the amount required to saturate all undyed sulfonate sites in the fibers with $C_1 = 0$ and more than six times for those with the highest
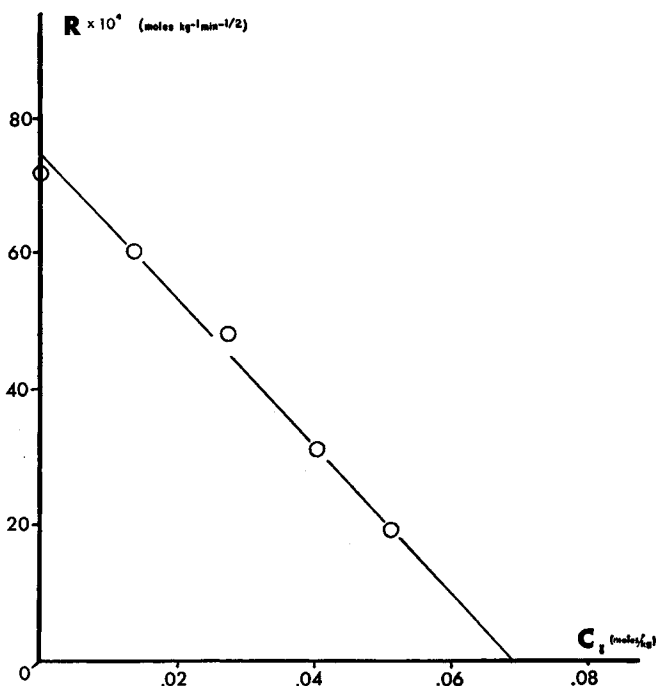
Fig. 4. Variation of slope R of sorption curve with C_1.   Dye G.   Data of Figure 3.

C_1 (0.512 mole/kg.).   As expected, the rate of dye uptake decreased with decreasing number of sites not occupied previously.

The slopes R of the sorption curves in Figure 3 varied with C_1 as shown in Figure 4.   Similar plots for dyes B and V are given in Figure 5.   For both G and B, especially the latter, the diffusion coefficient was found clearly to be independent of concentration (the small early decrease with G is within experimental error).   Detailed assumptions are also further confirmed, such as limitation of dye transfer from solution to the unoccupied specific sites.   The lines extrapolate to zero dyeing rate at $C_1 = 0.069$ mole/kg., in very good agreement with the sulfonate site content from sulfur analysis (0.070 mole/kg.).   This is true even for dye G which after prolonged dyeing times with excess dye has given superstoichiometric decreases in solution concentration.   Such plots may, in fact, provide a new method for the determination of saturation values without the difficulties[3] of extrapolation from equilibrium isotherms.

The results with dye V (Fig. 5, upper and right scale) appear to detract from the simplicity.   While the variation was linear, the C_1 intercept was far below the saturation value predicted by elementary sulfur analysis, raising the possibility of a diffusion coefficient decreasing with increasing concentration.   Such negative concentration dependence could be regarded as evidence for a porous solid model of dye diffusion since dye already in the fiber could clog the pores for dye trying to enter.   This is considered extremely unlikely for a number of reasons.   It would be in contrast to
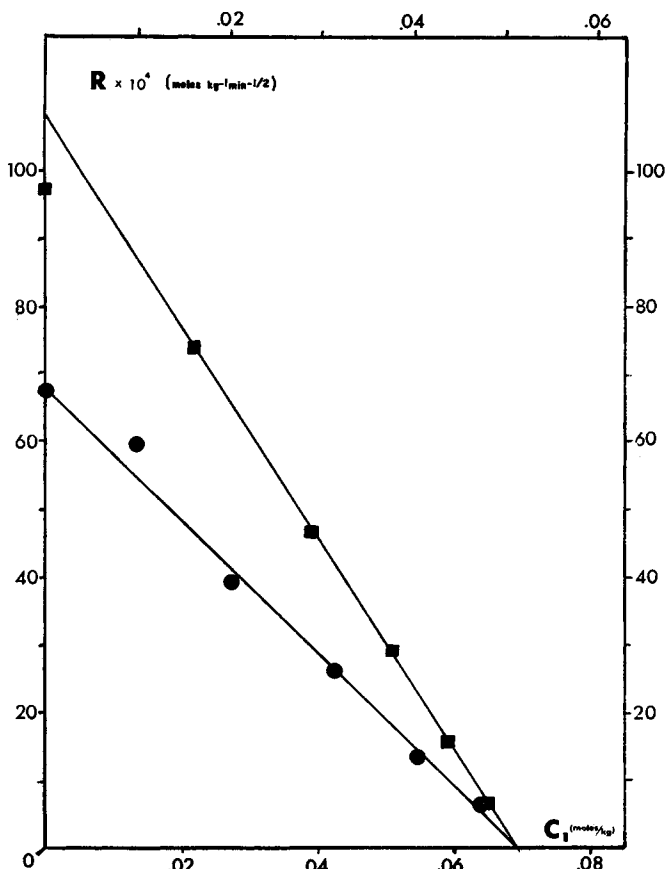
Fig. 5. Variation of R with C_1 for (●) dye B (left and bottom scales); (■) dye V (right and top scales). All conditions same as for Fig. 3.

all other evidence[4,13,15,21] which can be treated successfully by a free volume model and not at all by postulating pores in the fiber. In the present system, dye aggregation in the fiber appears equally remote.[3] Concentration dependence of this type has not, apparently, been claimed for any dyeing system. The same dye certainly did not show such a concentration dependence in the penetration experiments (see below). We, therefore, prefer to look for the explanation elsewhere. Very little has been revealed about this dye. The main reasons for using it were good stability and relatively little deviation from ideal equilibrium behavior. For the two dyes which showed the simple behavior, the structure and molecular weight has either long been well established (G) or confirmed (B) after several recrystallizations through elementary analysis and agreement of equilibrium saturation values with sulfur analysis for sites. It would be possible to account for the low intercept of V by assuming either a lower molecular weight, cationic impurities of lower molecular weight, or saturation by one dye molecule of more than one site. Generalizing these by

assuming an "average equivalent weight" of cations smaller by a factor of $0.051/0.069$ than the molecular weight used (i.e., reading the left and bottom scales on Figure 5 rather than the top and right ones), the simplicity would be extended to this dye, too. The linearity of the plot which makes this possible could be regarded as internal support for the underlying assumption.

Since it was indicated earlier that a free volume model predicts plasticization with addition of diluent, failure to find a concentration dependence in the diffusion coefficient might appear to exclude that model for dye diffusion. On closer examination of quantitative treatments supported by results on systems with pronounced concentration dependence, the apparent discrepancy disappears. Regardless of the specific treatment, it is obvious that an upper limit to the concentration will decrease the importance of the dependence. With a saturation value of 0.07 mole/kg. (higher than that in most fibers currently available) and dyes of molecular weight of 300–400, the maximum concentration of dye is below 3% by weight. A further factor is the large size of (hence, low free volume associated with) a dye molecule.[17] Fujita and Kishimoto[16] describe the concentration dependence of the free volume by

$$f(T,C) = f(T,0) + \beta C \qquad (4)$$

where the term on the left is the fractional free volume at temperature T and diluent concentration C, the first term on the right is the same for the undiluted polymer. The parameter β decreases sharply with increasing molecular size of diluent. The effect of strong fiber–dye interaction may be less certain,[22,23] but Kokes and Long[24] report a uniform decrease in concentration dependence with decrease in the Flory interaction parameter χ_1. Lastly, plasticizing effectiveness has been shown[25,26] to be increased by linear (aliphatic) character and high internal mobility of the diluent molecule; nothing could be further from these criteria than the stiff, aromatic dye molecules. From all this, it can be concluded that not only is there no discrepancy, but the free volume model will, in fact, predict the lack of measurable concentration dependence. It should also be possible to extend that prediction to dyeing systems in general, since they are all similar in these respects; future finding of plasticization by dye is thought unlikely, unless very unusual conditions obtain (e.g., extremely high concentrations, dyeing very close to T_g).

Most of the points made in the previous paragraph are supported even more clearly by a recent paper of DiMarzio and Gibbs[27] in which the decrease in plasticizer efficiency with stiffness in the plasticizer molecule is a natural result of the underlying lattice treatment.

Equilibrium Consideration of the Adsorption Function $\theta/(1 - \theta)$

McGregor, Peters, and Petropoulos[28] measured concentration distributions with acid (anionic) dyes on nylon of apparently the same type as the color intensity distributions described earlier for the present system. They

provide the first attempt to account for peculiarities observed in dye diffusion by the postulate that the flux Q is proportional to the distance gradient of activity a, which cannot be replaced by concentration as in the usual form of Fick's first law.   It is shown that if in

$$Q = -\mathfrak{D}_T(\partial a/\partial x) \tag{5}$$

the diffusion coefficient D_T is a constant independent of a (or C) and the activity is given by $\theta/(1 - \theta)$, where θ is the fraction C/S of sites occupied, then the Fick's law coefficient is

$$\mathfrak{D}(C) = \mathfrak{D}_T/(1 - \theta)^2 \tag{6}$$

and concentration–distance curves of the type measured are predicted. This is not merely an empirical device to account for their diffusion data, since Atherton, Downey, and Peters had shown much earlier[29] that constant equilibrium affinities of anionic dyes for the amino endgroups of nylon can be calculated by the use of that function; it had originally been introduced for dye acids on wool by Gilbert and Rideal.[30,31]   As in our system, the acid dyeing of nylon involves charged dyes and a limited number of oppositely charged sites.   In view of the close analogy of the two systems, the feasibility of using the same function was examined.

It was shown earlier[3] that the equilibrium between cationic dyes and the sulfonate groups SO_3^- present in a limited concentration S in most acrylic fibers is governed by ion exchange between the dye cations D^+ and the original countercations.   The thermodynamic exchange constant is

$$K = \frac{a(D)_\phi a(M)_\sigma}{a(M)_\phi a(D)_\sigma} \tag{7}$$

where $a(D)_\phi$ and $a(M)_\phi$ are the activities on the fiber of dye and a single other counterion M^+, respectively, and $a(D)_\sigma$, $a(M)_\sigma$ the same in solution (the detailed treatment is for any number of cationic species).   With activities replaced by concentrations and conventional assumptions, this leads to

$$([D]_\phi/[D]_\sigma)[M]_\sigma = KS - K[D]_\phi \tag{8}$$

If activities on the fiber are to be replaced by $\theta/(1 - \theta)$, this must evidently be done for all species, since Fowler's[32,33] statistical thermodynamic derivation on which the treatments for wool and nylon were based is general and cannot be taken arbitrarily to apply to dye only (it should make little difference in any case).   Such replacement leads to impossible results, regardless of whether the denominator in a given activity term is taken to be the fraction not occupied at all or the fraction not occupied by that particular species.

The first alternative is the only one justified by the original derivation. To the extent that the principle of electroneutrality is obeyed, however, all sites are occupied by a cation, and the activity of any species $\theta_i/(1 - \Sigma\theta_i)$ approaches infinity at all times.   If this is disregarded, formal treat-

ment results in cancellation of the denominator, hence to eq. (8), so that no harm (or good) is done.

The second alternative might be illustrated by the extreme case of exchange of one isotope, say normal H^+, by deuterium ions. In consecutive small exchanges, the total hydrogen ion activity

$$a(H)_\phi = \frac{\theta_{H^1}}{1 - \theta_{H^1}} + \frac{\theta_{H^2}}{1 - \theta_{H^2}}$$

would decrease from extremely high at the beginning to a minimum of 2 at half exchange, then to another high at total exchange. Nonetheless, in early efforts to account for deviations of equilibrium results from eq. (8) and in view of the success reported on similar systems, the approach was tried to check whether it would serve at least for empirical description of the data or even point to invalidity of our basic equilibrium mechanism. Replacing in eq. (7) only activities in solution by concentrations and rearranging yields

$$[D]_\phi[D]_\sigma^{-1/2}[M]_\sigma^{1/2} = KS - K[D]_\phi \tag{9}$$

Results obtained by variation of total dye concentration and sodium ion concentrations ($[M]_\sigma$) are plotted according to eq. (8) and according to eq. (9) in Figure 6. While in neither do all points fall on one straight line extrapolating to S_s, as required, the deviations were much less serious for eq. (8) than for eq. (9). Both here and in another such plot tried, eq. (9) leads to negative equilibrium constants. The deviations from eq. (8) could be accounted for by interactions between the sites.[3]

While the function can be discarded here only for cationic dyes on acrylic fibers with anionic sites, doubt is also cast on the analogous systems —with reversal of the respective charges—of anionic dyes on fibers with ammonium sites (wool, nylon). This appears to correspond with the considerations of Alexander and Kitchener.[34]

Kinetic Consideration

Even though no thermodynamic justification can be established for use of the function, the insight of Peters and co-workers could be utilized if it can be derived on kinetic grounds. The simplest way is based on the consideration that the driving force for the diffusion is provided not only by the concentration (or activity) gradient of dye D but also by the opposite gradient of counterions M diffusing out of the fibers at the same time. If it is postulated then that

$$Q = -\tilde{\mathfrak{D}} \frac{\partial [D]/[M]}{\partial x} \tag{10}$$

instead of Fick's postulate
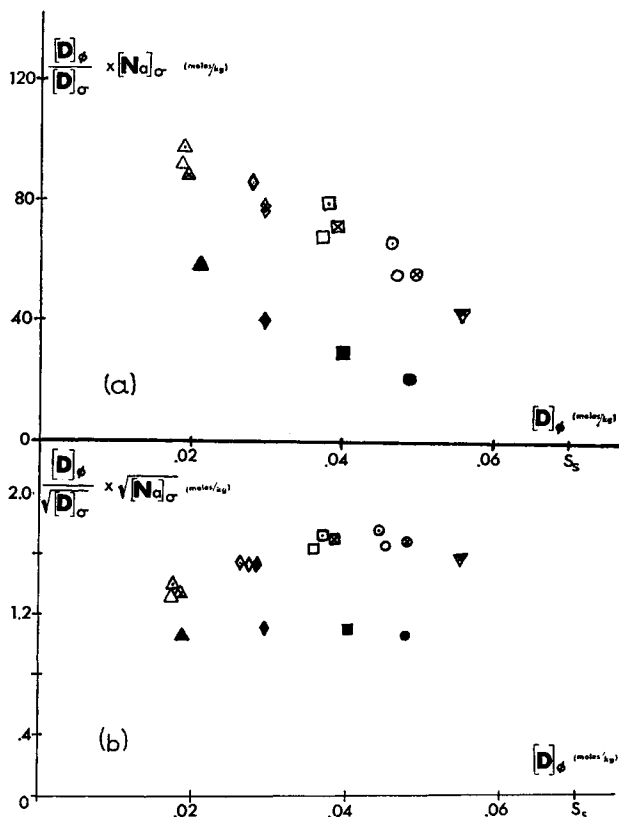
$$Q = -\tilde{\mathfrak{D}}\partial [D]/\partial x \tag{11}$$

Fig. 6. Equilibrium data plotted according to (top) eq. (8) and (bottom) eq. (9): at various initial $[D]_\sigma$: (∇) 6.4×10^{-4} mole/l., (O) 5.4×10^{-4} mole/l., ($\square$) 4.20×10^{-4} mole/l., ($\square$) 3.1×10^{-4} mole/l., ($\triangle$) 2.1×10^{-4} mole/l.; and various $[Na]_\sigma$: ($\bullet$) 0.01 mole/l., (O) 0.05 mole/l., ($\otimes$) 0.07 mole/l., ($\odot$) 0.10 mole/l. S: $\backsim0.233\%$; pH 4.2. 98.9°C.

the desired relation is obtained immediately, since

$$[D]/[M] = [D]/(S - [D]) = \theta/(1 - \theta)$$

If successful, the postulate might be justified, even if it is arbitrary. It should be stated, however, that in a derivation of the diffusion equation from the kinetics of interchange between occupied and unoccupied sites[4] the effect of the equal and opposite counterion gradient forms a natural part of the treatment, and the result is of the form of Fick's law.

It is also possible to derive a relation of the form of eq. (6) on the basis of reasonable kinetic assumptions. An electrolyte M^+A^- is normally added to the dyebath in basic (or acid) dyeing and was provided in our experiments by the buffer system. If the dye cation cannot diffuse while it is on the fixed sulfonate sites, but only in association with a nonpolymeric anion A^- derived from interaction of the dyed site D^+S^- with an
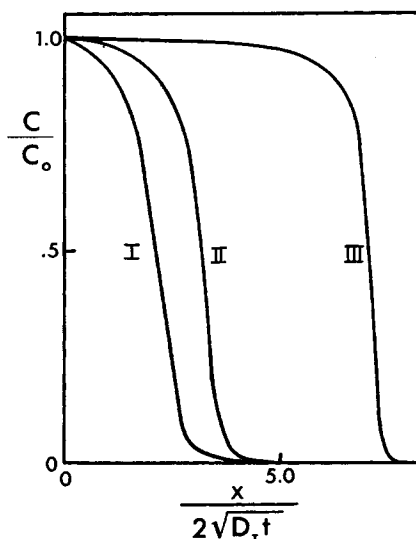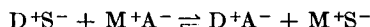
Fig. 7. Relative concentration–distance curves calculated by Atherton, McGregor, and Peters[28] for eq. (6) and θ_0 of (I) 0.90, (II) 0.95, (III) 0.99.

electrolyte of constant, uniform concentration $[M^+A^-]$ in the fiber, then local equilibrium

$$D^+S^- + M^+A^- \rightleftharpoons D^+A^- + M^+S^-$$

within any very thin layer normal to the direction of diffusion leads to a concentration C^* of diffusing species given by[4]

$$C^* = [DA] = K_E[MA][DS]/[MS] = K'\theta/(1 - \theta)$$

By Fick's law

$$Q = \mathfrak{D}\partial C^*/\partial x = \mathfrak{D}'\partial C/\partial x = K'\mathfrak{D}\partial[\theta/(1 - \theta)]/\partial x$$

Differentiation and substitution shows that

$$\mathfrak{D}' = (K_E[MA]/S)\mathfrak{D}/(1 - \theta)^2 \qquad (12)$$

so that even with a constant diffusion coefficient for the diffusing species, we should obtain concentration–distance curves equivalent to those calculated by Atherton, McGregor, and Peters[28] and shown in Figure 7. While the assumptions made were not considered unreasonable, the predictions of eq. (12) are not borne out by experiment.

The observed dependence of the rate of penetration on the fraction θ_0 of surface sites occupied in an infinite dyebath is shown in Tables II and III. In view of the tendency to surface saturation, so convenient for the sorption measurements, it was necessary to resort to very dilute solutions here in order to change the surface concentration. The difficulty of obtaining an infinite bath with the extremely dilute solutions that would have been necessary for G deterred us from doing the work with that dye. The

TABLE II

Dependence of Penetration λ_x on Surface Concentration C_0
for Dye B; pH 4.0; 0.05M NaAc

[D]$_\sigma$ $\times$ 10^4, mole/l.	C_0, mole/kg.	θ_0	λ_x at various times, div.[a]					
			5 min.	10 min.	15 min.	30 min.	60 min.	1200 min.
0.054	0.0160	0.230	1	2	3	4	5	7
0.202	0.0360	0.515	2	3	3–4	4	5	7
6.43	0.0659	0.941	1	2	3	4	5	7
9.46	0.0665	0.950	1	2	3	4	5	7

[a] Here 1 div. = 1.3 μ.

TABLE III

Dependence of Penetration λ_x on Surface Concentration C_0
for Dye V; pH 4.0; 0.05M NaAc

[D]$_\sigma$ $\times$ 10^4, mole/l.	C_0, mole/kg.	θ_0	λ_x at various times, div.[a]				
			5 min.	10 min.	15 min.	30 min.	60 min.
0.292	0.0200	0.286	2	3–4	4–5	6–7	7
1.06	0.0400	0.571	3	4	5	6–7	7
2.26	0.0500	0.714	3	4	5	6–7	7
8.70	0.0600	0.857	3	4–5	5–6	6–7	7

[a] Here, 1 div. = 1.3 μ.

other two dyes, of lower affinity, presented no experimental problems. From the equilibrium isotherms and the assumptions of equilibrium between surface and bath, the solution concentrations C_σ required to provide different surface concentrations C_0 were calculated. Pronounced differences in shade for different C_σ, readily visible under the microscope, confirmed obedience to the experimental requirements. Thanks to the variation of color intensity with distance described earlier, it is easy to measure visually the distance λ_x of penetration of the maximum in the gradient. While we considered a number of dangers in such measurements pending complete clarification of the origin of the distribution, none of these could detract from the point to be made here. Further, the close conformation of other penetration experiments[9] to the results from sorption experiments and to the expectations from theory is regarded as contributing support for their validity.

The results with the violet dye in Table III did not show that there was no dependence of penetration at all on θ_0. With this dye, however, the intensity gradient was not as sharp, so that an increase in intensity at any point with increasing θ_0 would lead to the appearance of faster penetration. Luck's optical considerations[36] may be pertinent for explaining the lack of sharpness of gradient. We believe that there really was no dependence of penetration speed on θ_0, but cannot claim to have established

it here. Nonetheless, the discrepancy between this appearance of minor dependence and the very strong dependence in Figure 7 militates against acceptance of eq. (12). The results with the blue dye (Table II) showed no dependence of penetration on θ_0 at all. Considerations such as those leading to eq. (12), or any others leading to relations of the same form, cannot therefore be responsible for the sharpness of the gradient with this dye.

Relation (12) further claims that the rate of penetration increases with decreasing site concentration S and increasing salt concentration. It is shown elsewhere[9] that, in line with thorough results from sorption experiments,[4] it increases with increasing S and is independent of salt concentration. This latter might conceivably be explained by non-linearity of variation of salt concentration [MA] on the fiber with that in solution, but it should be noted that dye readily diffuses when the $\sim 10^{-7}$ mole/l. of $OH^{\ominus}$ in deionized water are the only anions allowed.

It would appear that experiments in which the surface concentration of acid dyes on nylon is varied intentionally would indicate how far these remarks apply to that system. Tentative indications have been obtained to show that they do. Also, the saturation value S shown in the denominator of eq. (12) may have been overlooked in arriving at eq. (6). In that case, an increase in the amino group content in nylon should result in a decrease in the rate of penetration at constant surface concentration. Even though no conclusive data are available, there is some indication[4] in the results of Palmer[35] that this will not be substantiated.

It will be necessary to seek elsewhere for an explanation of the color intensity distribution. It is possible that some other activity function can be found, possibly based on the interaction between the sites.[3] Luck[36] has attributed the distribution in nylon to the increasing insensitivity of vision to increments in dye concentration and derived color intensity curves of the type observed from error curve concentration-distance plots. Although radial heterogeneities are not uncommon in fibers, an increase of diffusion coefficient with distance appears remote, judging by miscellaneous evidence. Deviations from Beer's law have been observed after prolonged dyeing times, but these cannot account for the distribution found in normal rate experiments. The additional efforts of an instrumental method, such as that of Peters and co-workers,[7] may be called for here. It is hoped that the findings of the foregoing discussion will contribute to a solution. The indications point strongly to a problem in our understanding of color distributions, possibly along lines such as those advanced by Luck, and that the course of the diffusion process itself is at least not seriously involved. Whatever the explanation advanced, it appears that it cannot be based on strong dependence of the diffusion coefficient on concentration.

The finding of lack of concentration dependence lends strong further validity to the conclusions of the previous papers on other aspects of this system. Additional confirmation was also obtained for the role of the specific sulfonate sites in the transfer of dye from solution to fiber. The

apparent simplicity of dye diffusion by comparison to that of most other penetrants recommends it for wider use in the study of polymer structure and kinetic behavior.

References

1. Crank, J., *The Mathematics of Diffusion*, Clarendon, Oxford, 1957.
2. Fujita, H., *Fortschr. Hochpolymer-Forsch.*, **3**, 1 (1961).
3. Rosenbaum, S., *Textile Res. J.*, **33,**, 899 (1963).
4. Rosenbaum, S., *Textile Res. J.*, **34**, 291 (1964).
5. Vickerstaff, T., *The Physical Chemistry of Dyeing*, Interscience, New York, 1954.
6. Atherton, E. and R. H. Peters, *Textile Res. J.*, **26**, 497 (1956).
7. Peters, R. H., and J. H. Petropoulos, *Bull. Inst. Text. France*, **84**, 49 (1959).
8. McGregor, R., R. H. Peters, and J. H. Petropoulos, *Trans. Faraday Soc.*, **58**, 771 (1962).
9. Goodwin, F. L., and S. Rosenbaum, to be published.
10. Crank, J., *J. Soc. Dyers Colourists*, **64**, 386 (1948).
11. Garvie, W. M., and S. M. Neale, *Trans. Faraday Soc.*, **34**, 335 (1938).
12. Rosenbaum, S., *Textile Res. J.*, **34**, 52 (1964).
13. Rosenbaum, S., *J. Appl. Polymer Sci.*, **7**, 1225 (1963).
14. Goodwin, F. L., to be published.
15. Rosenbaum, S., to be published.
16. Fujita, H., and H. Kishimoto, *J. Polymer Sci.*, **28**, 547 (1948).
17. Ferry, J. D., and R. A. Stratton, *Kolloid-Z.*, **171**, 107 (1960).
18. Kelley, F. N., and F. Bueche, *J. Polymer Sci.*, **50**, 549 (1961).
19. Mandelkern, L., D. E. Roberts, A. F. Diorio, and A. S. Posner, *J. Am. Chem. Soc.*, **81**, 4184 (1959).
20. Prevorsek, D. E., A. B. Coe, and A. B. Tobolski, *Textile Res. J.*, **32**, 960 (1962).
21. Rosenbaum, S., *Textile Res. J.*, **34**, 159 (1964).
22. Zhurkov, S. N., *Compt. Rend. Acad. Sci. U.S.S.R.*, **47**, 475 (1945).
23. Boyer, R. F., and R. S. Spencer, *J. Polymer Sci.*, **2**, 157 (1947).
24. Kokes, R. J. and F. A. Long, *J. Am. Chem. Soc.*, **75**, 6142 (1953).
25. Jenckel, E., in *Die Physik Der Hochpolymeren*, H. A. Stuart, Ed., Vol. III, Springer, Berlin, 1955.
26. Aiken, W., T. Alfrey, A. Janssen, and H. Mark, *J. Polymer Sci.*, **2**, 178 (1947).
27. DiMarzio, E. A. and J. H. Gibbs, *J. Polymer Sci.*, **A1**, 1417 (1963).
28. McGregor, R., R. H. Peters, and J. H. Petropoulos, *Trans. Faraday Soc.*, **58**, 1054 (1962).
29. Atherton, E., D. A. Downey, and R. H. Peters, *Textile Res. J.*, **25**, 977 (1955).
30. Gilbert, G. A., and E. K. Rideal, *Proc. Royal Soc. (London)*, **A182**, 335 (1943).
31. Gilbert, G. A., *Proc. Roy. Soc. (London)*, **A183**, 167 (1944).
32. Fowler, R. H., *Proc. Cambridge Phil. Soc.*, **31**, 260 (1935).
33. Fowler, R., and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge, 1960.
34. Alexander, P., and J. A. Kitchener, *Textile Res. J.*, **20**, 203 (1950).
35. Palmer, H. J., *J. Soc. Dyers Colourists*, **67**, 609 (1951).
36. Luck, W., *Melliand Textilber.*, **36**, 927 (1955).

Résumé

Sur la base de diverses expériences, on discute la corrélation avec la loi de Fick de la diffusion des colorants (cationiques) dans les fibres de polyacrylonitrile avec un coefficient constant de diffusion. Plus spécialement on s'efforce de rendre compte des distributions radiales d'intensité de couleur apparemment anormales. Il n'y a pas de preuve de plastification du polymère par le colorant. L'expansion thermique (axiale linéaire), la température de transition vitreuse, la température de retrécissement non orienté, et les autres propriétés ne sont pas affectées d'une manière appréciable lorsqu'on sature la fibre par le colorant. La preuve provenant des mesurés de sorption et de pénétration indique une diffusion indépendante de la concentration à partir d'un nombre limité de sites en surface spécifiques (sulfonates). Le comportement semble être si simple que les valeurs de saturation peuvent être mesurées à partir des courbes de sorption. On montre que, pour des diluants possédant des propriétés moléculaires des colorants, un modèle à volume libre de diffusion de colorants prévoit l'absence d'effets plastifiants dans les systèmes colorants en général. Le remplacement de la concentration dans l'equation de diffusion par une fonction d'activité $\theta/(1 - \theta)$, où θ est la fraction de sites occupés par le colorant, qui a été suggérée, par les cas analogues des colorants anioniques sur le nylon, ne peut être considéré comme justifié sur des bases thermodynamiques. Une fonction similaire peut être déduite sur des bases cinétiques raisonables, mais n'est pas prouvé par des résultats détaillés.

Zusammenfassung

Die Befolgung des Fick'schen Gesetzes mit einem konstanten Diffusionskoeffizienten durch die Diffusion von (kationischen) Farbstoffen in Polyacrylnitrilfasern wird anhand verschiedener Experimente diskutiert. Genauer gesagt wird ein Versuch gemacht die, scheinbar abnorme radiale Farbintensitätsverteilung zu erklären. Es bestehen keine Hinweise auf eine Weichmachung des Polymeren durch den Farbstoff. Die (linear axiale) thermische Ausdehnung, die Glasumwandlungstemperatur, die Temperatur der verzerrenden Schrumpfung sowie andere Eigenschaften werden durch Sättigung der Faser mit Farbstoff nicht merklich beeinfusst. Die Ergebnisse der Sorptions-und Penetrationsmessungen lassen eine konzentrationsunabhängige Diffusion von einer begrenzten Zahl spezifischer (Sulfonat-) Oberflächenplätzen erkennen. Das Verhalten scheint so einfach zu sein, dass Sättigungswerte aus den Sorptionskurven bestimmt werden können. Es wird gezeigt, dass bei Verdünnungsmitteln mit den Moleküleigenschaften von Farbstoffen ein Freivolumsmodell der Farbstoffdiffusion die Abwesenheit von Weichmachereffekten an Farbsystemen im allgemeinen ausschliesst. Ersatz der Konzentration in der Diffusionsgleichung durch eine Aktivitätsfunktion $\theta/(1 - \theta)$, wo θ der Bruch teil der durch Farbstoff besetzten Stelle ist, wie es für den analogen Fall von anionischen Farbstoffen an Nylon vorgeschlagen wurde, wird in Betracht gezogen, aber auf Grund thermodynamischer Überlegungen verworfen. Eine ähnliche Funktion kann auf einer plausiblen kinetischen Grundlage abgeleitet werden, wird aber durch die Ergebnisse im einzelnen nicht gerechtfertigt.