Dyeing of Polyacrylonitrile Fibers: I. Rates of Diffusion with Malachite Green and Diffusion Model

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INTRODUCTION

When polyacrylonitrile fibers first began to be marketed, it was considered impossible to dye them satisfactorily.   These difficulties were attributed to a lack of specific sites on the fiber that could interact favorably with an entering dye molecule and to a hydrophobic character of the polymer which limits swelling in water.

The first feasible solution consisted of the deposition of cuprous ions[1] in the fiber which made it receptive to acid dyes.   This was done by the dyer. Subsequently, fiber manufacturers modified polymer composition with a view to providing dyeing sites, usually by copolymerizing the acrylonitrile with a limited amount of other monomers.   In Acrilan (1656) and Creslan, amino groups have been reported;[2] at a low enough pH, these should contribute sites for anionic dyes.   Zefran has been characterized as an alloy fiber[3] which for the purpose can be defined as one in which dye-binding groups are present in a distinct polymeric form, as a blend, block, or graft copolymer with the acrylonitrile.   Various classes of dyes are readily taken up, by mechanisms not to be discussed here.   The present paper is confined to fibers that can be dyed with cationic, or basic, dyes.   A range of these dyes was found[4] to have much better fastness properties on Orlon than on the nonsynthetic fibers on which basic dyes had acquired a reputation for poor fastness.   This resulted in a change in Orlon composition[5] to improve the uptake of these dyes and in the marketing by other producers of fibers for which basic dyeing is also recommended.

Dyeing processes in general have been reviewed by Vickerstaff.[6]   Regarding the present system, several papers have been published on the equilibria and rates of a number of dyes on Orlon, Dralon, and Acrilan.[7–10] With only minor modification, these provide the thermodynamic framework for the present paper.   The dyeing process is essentially governed by an ion exchange equilibrium described by a Langmuir isotherm.   The saturation uptake corresponds to a limited number of anionic or anionogenic groups which exchange their counterions for dye cations of higher affinity. In all, or almost all, of these fibers, the active sites are sulfonate (possibly some sulfate) groups deriving either from a persulfate-bisulfite type redox initiator system or from copolymerization with a sulfonate containing comonomer.

EXPERIMENTAL

Malachite Green

The carbinol was recrystallized from 1:1 heptane-ether. The dye was then formed by addition of acid and the solution buffered to pH 4.2 (sodium acetate-acetic acid, $0.07M$ in Na^+). The resulting solution was used, after heating near the boil for several hours and without intermediate isolation of the dye, dilutions of the stock solution also being made with $0.07M$ buffer. This procedure eliminated difficulties initially encountered due to changes in absorbance on heating.[11]

Fibers

All experimental fibers were wet spun by extruding a polymer solution in concentrated aqueous zinc chloride into a coagulation bath of more dilute $ZnCl_2$. Before the dyeing experiments, all fibers were heated overnight at 97° in a concentrated pH 4.2 sodium acetate-acetic acid buffer (5% in the former), then rinsed in very dilute buffer (0.005% sodium acetate).

Determination of Rates of Dyeing

The apparatus and basic procedures are described elsewhere.[11] Modified Erlenmeyer flasks containing 100 ml of dye solution (pH 4.2) were immersed in a constant temperature shaker, normally at 97.3°, containing tetraethylene glycol as the transfer fluid. Solution samples were analysed on a Beckman DK-2 spectrophotometer at appropriate time intervals, then returned to the dyebath. Unless otherwise stated, the dye in solution was made equal to the saturation uptake of 1.00 g. of fiber, predicted from the sulfur content. The sulfur was determined by elementary analysis. From the absorbance at time t, the weight of fiber, and initial amount and concentration of solution, the concentration of dye on fiber, and other rate and equilibrium results were calculated on a Bendix G-15 computer.

Fiber Surface Areas (A_w)

The outer fiber surface per unit weight was determined from large photomicrographs containing a sufficient number of fibers. A photomicrograph of a calibrated slide under the same conditions was used to obtain the magnification. The average area a of the fiber images was obtained by cutting them out and weighing them and a large rectangular area of dimensions known from measurement of the calibrated slide. The average perimeter p was obtained by rolling the images (using a needle inserted through the center) along a flexible tape for a known number of revolutions, then dividing the length per revolution by the magnification. A_w is then given by $A_w = (p/a\rho)$ cm.^{2}g.$^{-1}$, where ρ is the density. With round fibers, it is possible to measure the denier d with a vibroscope and $A_w = \sqrt{\dfrac{3.6\pi\rho}{d}} \times 10^3$ cm.^{2}g.$^{-1}$. Until certain vibroscope improvements were

made, however, the above method gave more reliable results, and it was used for all data reported here.   The perimeter could also be determined, with only a small decrease in accuracy, by tracing the fiber outlines on the photomicrographs with a map measure, then dividing by the magnification.

Densities

A heptane–carbon tetrachloride density gradient column was used for the determination of fiber densities.

Creep

Loads of 0.1 g./den. were applied on single fibers contained in blank dyebaths at the dyeing temperature and clamped between a lower fixed and an upper mobile clamp of a continuously recording linear displacement apparatus.   The unit is a simple continuous balance servo system utilizing a Statham force gage as the error detector and the position of the gage on a lead screw as the means of balancing.   The normal zero potentiometer is used to set the desired load.

Tensile Compliance and Break Extension

Measurements were again carried out in a blank dyebath, approximately at dyeing temperatures, on a model TTB Instron at one inch per minute rate of extension.

RESULTS AND DISCUSSION

Effect of Denier on Rate

In Figure 1, the concentration of dye on fiber (C_ϕ) is plotted as a function of time for experimental copolymer fibers of equal composition and stretch ratio, but differing greatly in denier.   The rate of dyeing is seen to increase with decreasing denier.   This could serve to illustrate one of the more obvious dangers in a fiber laboratory's use of a dyeing evaluation that does not attempt to understand the fundamental processes involved, and which would be likely to attribute the difference in the dyeing behavior here to a more open or permeable structure of the thinner fibers.   The opposite will be shown to be true, the faster rate of the thinner fibers being due simply to the greater surface area exposed to the solutions.

Concentration Dependence of Rate

Figure 2 shows the concentration of dye on fiber vs. time with four widely different initial dyebath concentrations on equal weights of the same fiber.   If we had to do with a homogeneous equilibrium of the type,

$$\phi SO_3^- M^+ + D_\sigma^+ \rightleftharpoons \phi SO_3^- D^+ + M_\sigma^+$$
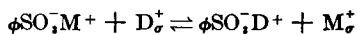
(M^+ — counterion; D^+ — dye cation; ϕ — fiber; σ — solution) we should expect the initial rate to be first order with respect to concentration of dye in
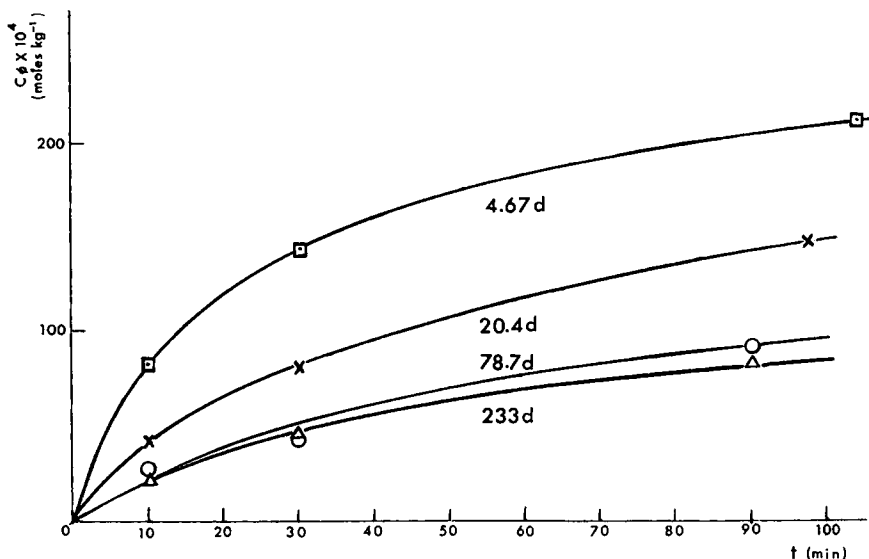
Fig. 1. Variation of concentration of dye on fiber with time for different deniers: □ 4.7d, X 20d, O 79d, △230d.

solution C_σ, and the initial slopes, then, to vary by factors of up to ten. In practice, the order was found to be zero, or very close to it, in all cases studied with Malachite Green. Regardless of concentration, all points follow the same initial slope and, further on, the same curve, almost up to the time when essentially all dye has been removed from solution and the curves branch off horizontally. This is readily understood in terms of a very fast saturation of the outer fiber surface, followed by slow diffusion within the fiber from that saturated surface layer. With an acid dye on protein fibers, such a saturated layer was postulated by Speakman and Smith[12] on the basis of similar and other findings. The data are especially clear-cut with the present fibers, due to the low diffusion rates coupled with high affinities per site.

Glenz and Beckmann[7] reported that the dyebath concentration was the most important factor, next to the temperature, in determining the dyeing rate on Dralon. This finding was probably largely caused by their practice of plotting the percent exhaustion rather than the concentration on the fiber. From a paper just published by Beckmann[9] it appears that when, following a suggestion by Vickerstaff, they plot the latter, curves similar to ours are often obtained.

Figure 2 is probably the most clear-cut we have obtained. Usually, the complete lack of concentration dependence holds only above a (rather low) limit, below which a fractional order in C_σ becomes apparent. Thus, Figures 3 and 4 are more representative. In the high concentration range in which the runs in the present paper were conducted, this is of no consequence, however.
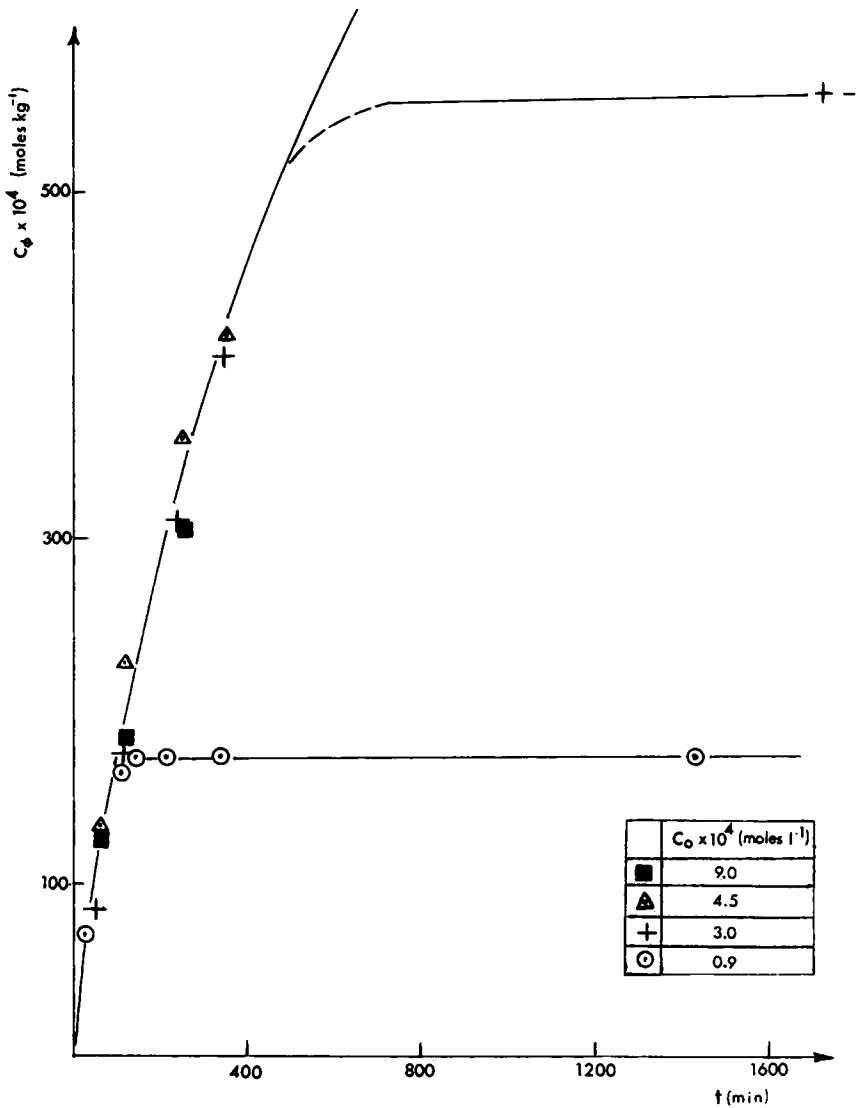
Fig. 2. Concentration dependence of rate: Experimental fiber A.

Diffusion Equation

A solution of Fick's equation for infinite cylinders has most often been used in dyeing studies, even for fibers that do not have a round cross section. We found it preferable, even for the round fibers, to use a solution for semi-infinite media, modified to: $C_\phi = (b \, C_{sat} \, A_w \, \sqrt{D}) \, \sqrt{t}$ where $t =$ time, $D =$ apparent diffusion coefficient, $A_w =$ outer fiber surface area per unit weight, $C_{sat} =$ saturation uptake by fiber, in same units as C_ϕ, $b = 2 \sqrt{\pi}$, $C_\phi =$ concentration of dye on fiber at time t. Normally the concen-
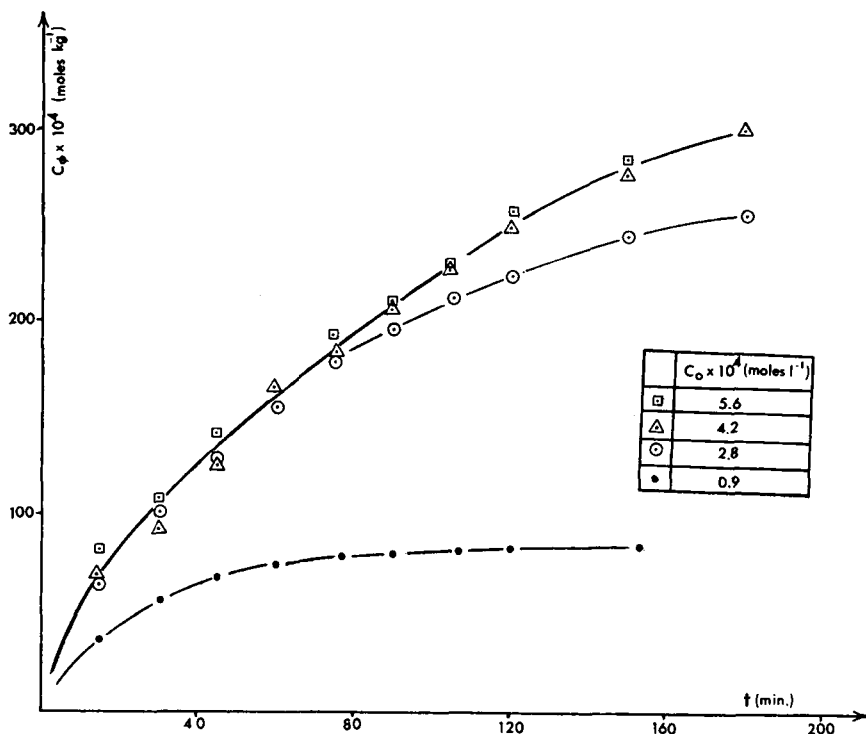
Fig. 3. Concentration dependence of rate: Dralon (Bayer).

tration of dye on fiber that would be in equilibrium with the solution concentration prevailing at time t would have to be used, rather than C_{sat}. This would entail the determination of the complete sorption isotherm for each fiber.   The use of C_{sat} is based on our finding of lack of concentration dependence, at least over the parts of the sorption-time curves where the semi-infinite conditions apply.   As long as diffusion proceeds from a saturated surface, substitution of C_{sat} should be justified.   If the initial dyebath concentration is high enough to saturate the fiber, the lack of concentration dependence should hold at least up to 50% exhaustion.   The relation for infinite media also should normally break down in the later stages of dyeing.   In practice, we usually obtain linear plots of C_ϕ vs. $\sqrt{t}$ up to about half of saturation uptake.   From examination of cross sections of thick fibers, it appears that the region where the plot levels off in the direction of the $\sqrt{t}$ axis corresponds approximately to the time when the concentration of dye near the center of the fiber becomes appreciable, but it was difficult to determine this more quantitatively, and it does not seem to hold in all cases.

The plots do not normally go through the origin.   Intercepts on the $\sqrt{t}$ axis are generally observed and have been interpreted in different ways. Medley and Andrews[13] cite previous references, and themselves attribute it to a surface barrier.   Pending the outcome of specific work designed to
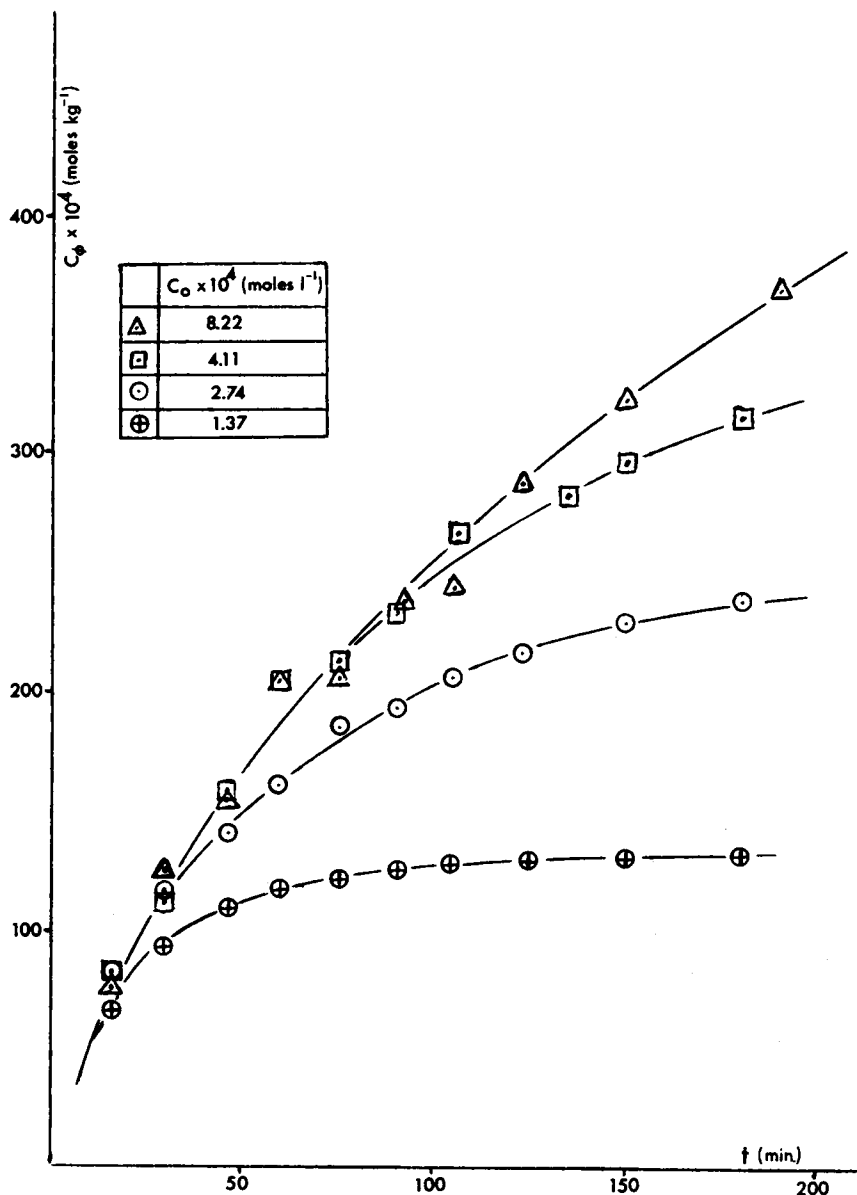
Fig. 4. Concentration dependence of rate: Experimental fiber B.

further clarify the very early part of the curve, the effect has been neglected here.

Wherever the main purpose of the work is the direct description of the dyeing rate, the more empirical relation $C_\phi = C_\phi{}^\circ + m\sqrt{t}$ is preferred, Table I shows the values of slope m and intercept $C_\phi{}^\circ$ for different commercial polyacrylonitrile fibers based on the data plotted in Figure 5.

TABLE I
Rate of Dyeing of Commercial Fibers

		$C_\phi{}^\circ \times 10^4$ (m. kg.$^{-1}$)	$m \times 10^4$ (m. kg.$^{-1}$ min.$^{-1/2}$)
▽ Acrilan 16 (Chemstrand)	3d[a], b[b]	0	33.33
○ Cashmilon (Asahi, Japan)	3d, sd[c]	− 9	31.25
✕ Courtelle (Courtaulds, U.K.)	3d, b	− 4	8.52
⊕ Crylor (Soc. Crylor, France)	3d, sd	− 7	11.11
+ Dralon (Bayer, Germany)	3d, sd	− 48	27.27
△ Orlon 42 (du Pont)	3d, b	− 42	28.08
☐ Orlon 72 (du Pont)	1.5d, sd	− 28	28.16
⊙ Orlon Sayelle (du Pont)	3d, sd	−162	147.1
● Tacryl (Stockholms Superfosfat, Sweden)	3d, b	− 92	74.07

[a] d = denier.
[b] b = bright.
[c] sd = semidull.

Variation of D with Denier

Figure 1 showed that an increase in denier results in a decrease in dyeing rate. A plot of the apparent diffusion coefficient D against denier (Fig. 6) for the same fibers indicates that the effect of denier on the diffusion velocity was in the opposite direction, i.e., making the fiber thicker resulted in a structure more amenable to dye uptake. The difference in the preparation of these fibers was in the size of the spinnerette holes, all other factors being held constant.

Diffusion Model

The common way of describing the diffusion process in dyeing involves apparently static capillaries, or pores, running through amorphous parts of the fiber.[6,14] The pores are filled with dye solution from which adsorption onto a fiber molecule or crystallite surface takes place. To move toward the center of the fiber, the dye molecule has to be desorbed into the water in the capillary, followed by sorption at a site further on. The activation energy of dyeing is identified with the energy required to return the dye from the site to the capillary. This model, in which the fiber plays a completely passive role, has had only limited success in the past, and it is especially unlikely in fibers such as those under consideration here, where
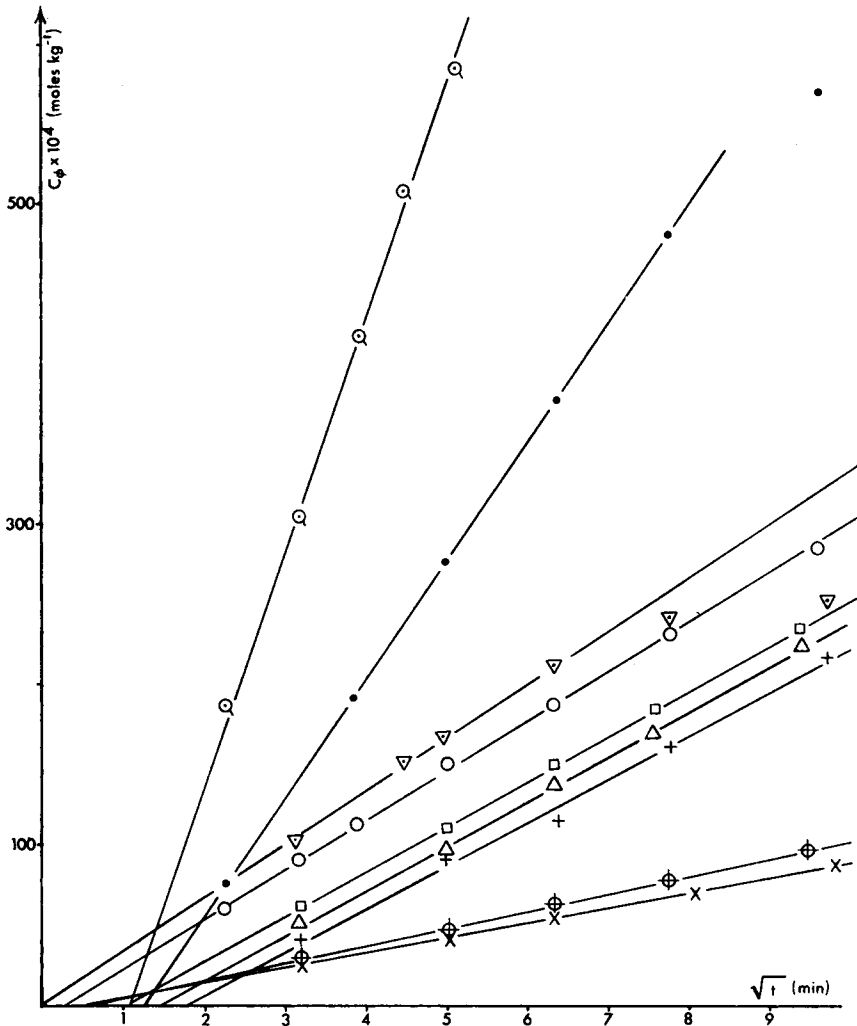
Fig. 5. Rate of dyeing of commercial fibers: ∇ Acrilan 16;   O Cashmilon;   X, Courtelle;   ⊕ Crylor;   + Dralon;   △ Orlon 42;   □ Orlon 72;   ⊙ Orlon Sayelle;   • Tacryl.

there is no indication of a major amount of swelling.   A more fruitful approach ought to be to take into account the motions in the polymer molecules[15,16] at the high temperatures required to dye polyacrylonitrile fibers in a reasonable time.   This is most readily visualized by attributing the diffusion of dye directly to the self-diffusion of the polymer segments.   In the most simplified form, a passive role could now be assigned to the dye, and its progress in the fiber treated in terms of an interchange between an occupied sulfonate group and a free one further inside the fiber.   The main parts of the apparent activation energy would then be contributed by the energy required for a segmental jump and especially by the energy necessary
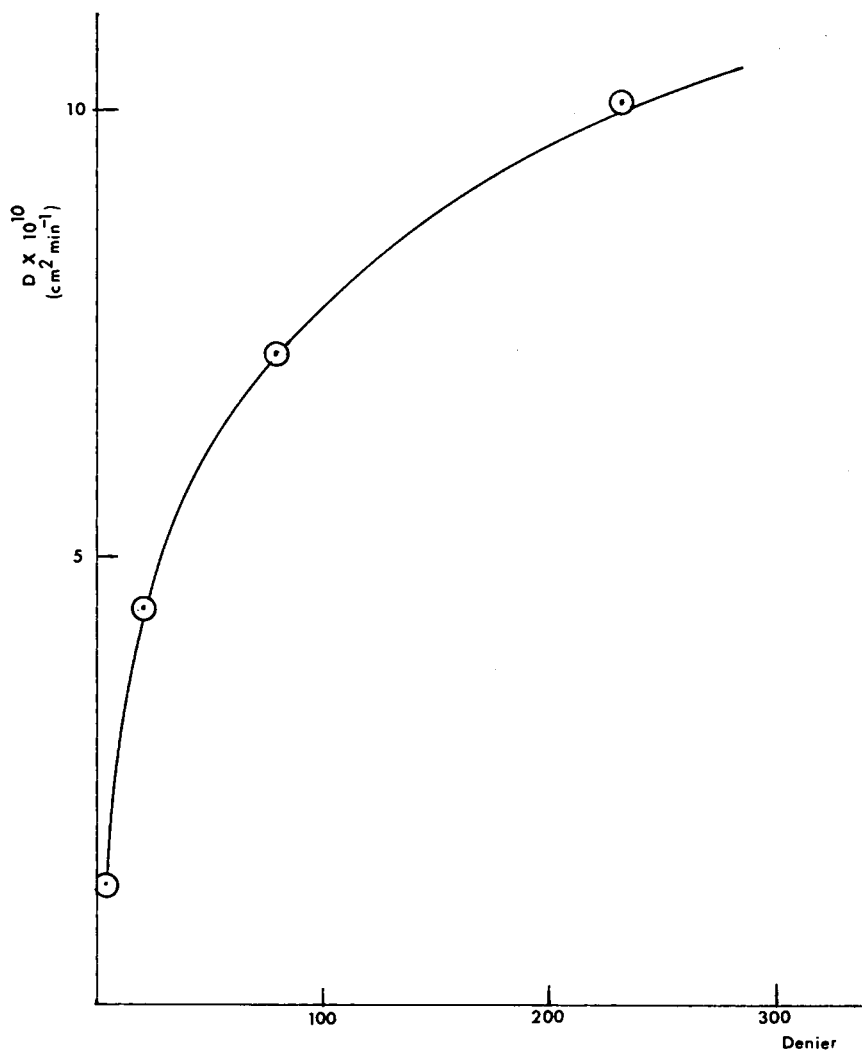
Fig. 6. Variation of diffusion coefficient D with denier.

to create a large enough "hole" (sufficient "free volume") into which the segment can move, which in turn should be a function of cohesive energy density.[17] An additional term may come from the energy required to overcome the forces between dye and site; this term should be less important, if interchange is indeed the major mechanism. To the extent that the dye plays a more active role in its diffusion toward the interior, it should still be treated by considering the motions of the holes, the dye molecule itself behaving qualitatively like a polymer segment.

While there may be a formal resemblance, the free volume cannot be regarded as equivalent to the pores mentioned. It is not regarded as having such a well defined physical existence at all, but simply to serve as a con-

venient means for numerical description of the irregularities in the vicinity of a molecule (or segment) in the liquid (or rubbery) state. Even if not stated explicitly, a model of this general type is really used in such controversies as whether carriers in dyeing have a plasticizing effect or not. To increase the rate of dye uptake in the polyacrylonitrile fibers under discussion, the static pore model might lead to recommendations of comonomers such as styrenes with bulky p and α substituents; in commercial practice, small esters (e.g., vinyl acetate, methyl acrylate) are used.

Dependence of D on Fiber Composition

Plots of C_ϕ vs. $\sqrt{t}$ for fibers of different composition are shown in Figure 7, and data on their composition in Table II. As would be expected

TABLE II

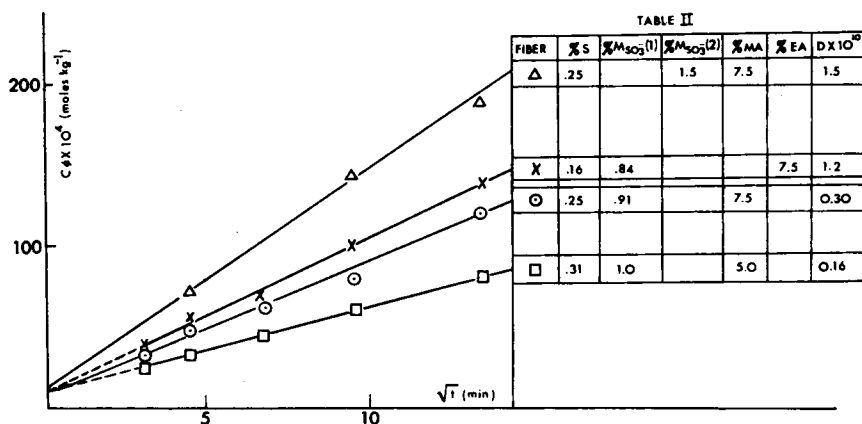| FIBER	%S	%M_{SO_3}(1)	%M_{SO_3}(2)	%MA	%EA	DX10^{10}
△	.25		1.5	7.5		1.5
X	.16	.84			7.5	1.2
⊙	.25	.91		7.5		0.30
□	.31	1.0		5.0		0.16

Fig. 7. Variation of rate of diffusion with composition.

from the diffusion mechanism discussed, substantial increases in D are obtained by increasing methyl acrylate (MA) content or by changing from MA to ethyl acrylate (EA). In monomer M_{SO_3} -2 the sulfonate group itself is more mobile than that in M_{SO_3} -1, as though it were mounted on a very flexible swivel. Data showing an increase of D with increasing sulfonate content will be reported at a later date.

Relation of D to Mobility from Mechanical Measurements

Figure 8 shows the compliance C (or reciprocal of the initial modulus) against D for the fibers of different denier shown previously (Fig. 6). The relation appears linear, but we have no simple model by which C can be related quantitatively to the frequency of segmental jumps. Qualitatively, it is evident, however, that in a nonequilibrium experiment, ease of relaxation will result in a high compliance.

For quantitative interpretation, creep measurements were considered more suitable. These are still in a stage of development and only early

results are quoted here.   In view of experimental difficulties encountered, these should be interpreted with reserve.

A load of 0.1 g./den. was applied for ten minutes, recovery allowed for ten minutes, then the same load applied again for another ten minutes. The last curve was used if the slope was constant over a reasonable range, so that a Maxwell model could be used for the evaluation.   By Newton's law, the slope should be proportional to the fluidity $1/\eta$ (reciprocal of viscosity).   Figure 9 shows $1/\eta$ vs. D for all but two of the fibers evaluated. (These two would be far off the chart.)   Taking the data at their face value, the linear variation of $1/\eta$ (or the rate of displacement of the polymer
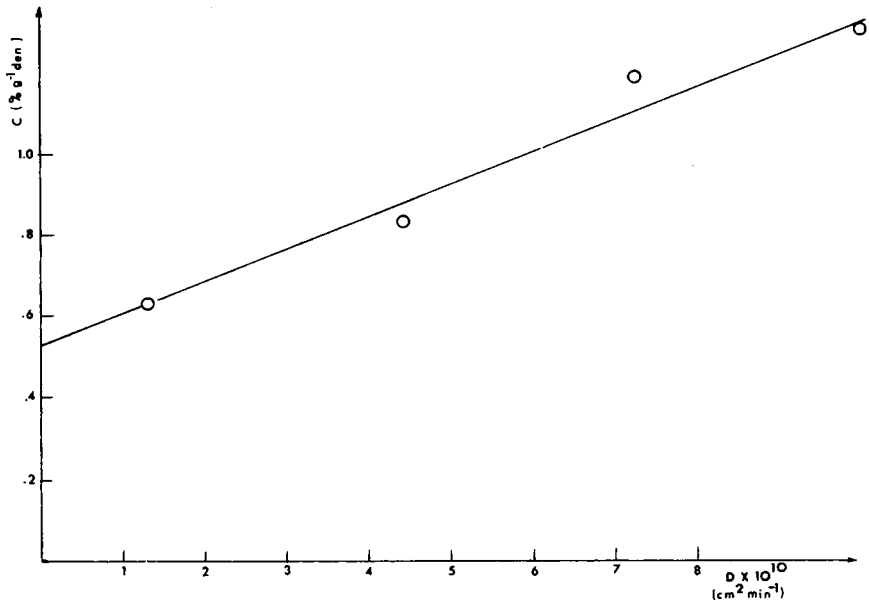

Fig. 8. Relation of D to tensile compliance.

molecules under stress) with the diffusion constant D of dye appears confirmed.   If D accurately reflected the coefficient of self-diffusion of the polymer segments (and disregarding anisotropy and distribution of relaxation mechanisms), a straight line through the origin would be expected theoretically[18,19] for the variation of diffusion constant with fluidity at constant temperature.   No attempt will be made at this stage to interpret the apparent intercept.

Sprague and Singleton[20] found on cellulose acetates that the per cent stress relaxed over a fixed period of time increases in a series of fibers with increasing diffusion coefficient for a disperse dye.   It will be shown[11] that stress relaxation data should also be amenable to quantitative treatment on the model outlined.

Temperature Dependence

The temperature dependence has been under intensive study, and will be reported separately. At this stage it will be discussed only by relation to the diffusion model. To the extent that diffusion of dye is determined by polymer mobility, it should decrease abruptly, or cease altogether, below
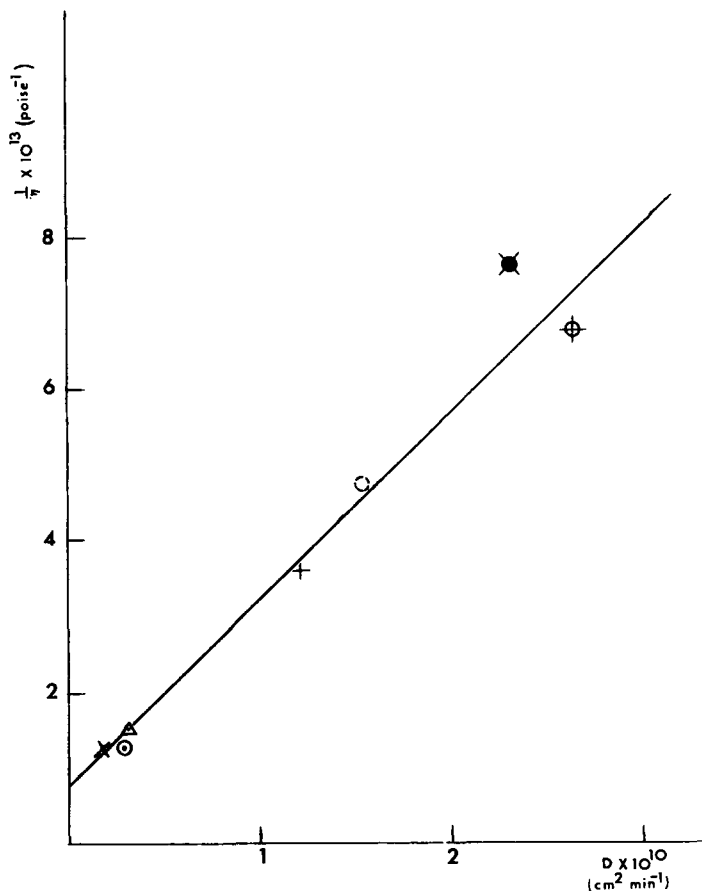

Fig. 9. Relation of D to fiber fluidity.

the glass transition temperature Tg. If that were so, it was considered ideal to have a Tg not lower than the normal textile washing temperatures which normally go up to 70°, so that the rate of dye uptake at normal dyeing temperatures (near the boil) may be high enough, but that the diffusion process is stopped or greatly lowered during the washing step.

A relation of rate of dye uptake to the difference between the dyeing temperature and Tg was shown earlier[21] for block copolymers of polyethylene terephthalate. The results were interpreted in terms of static
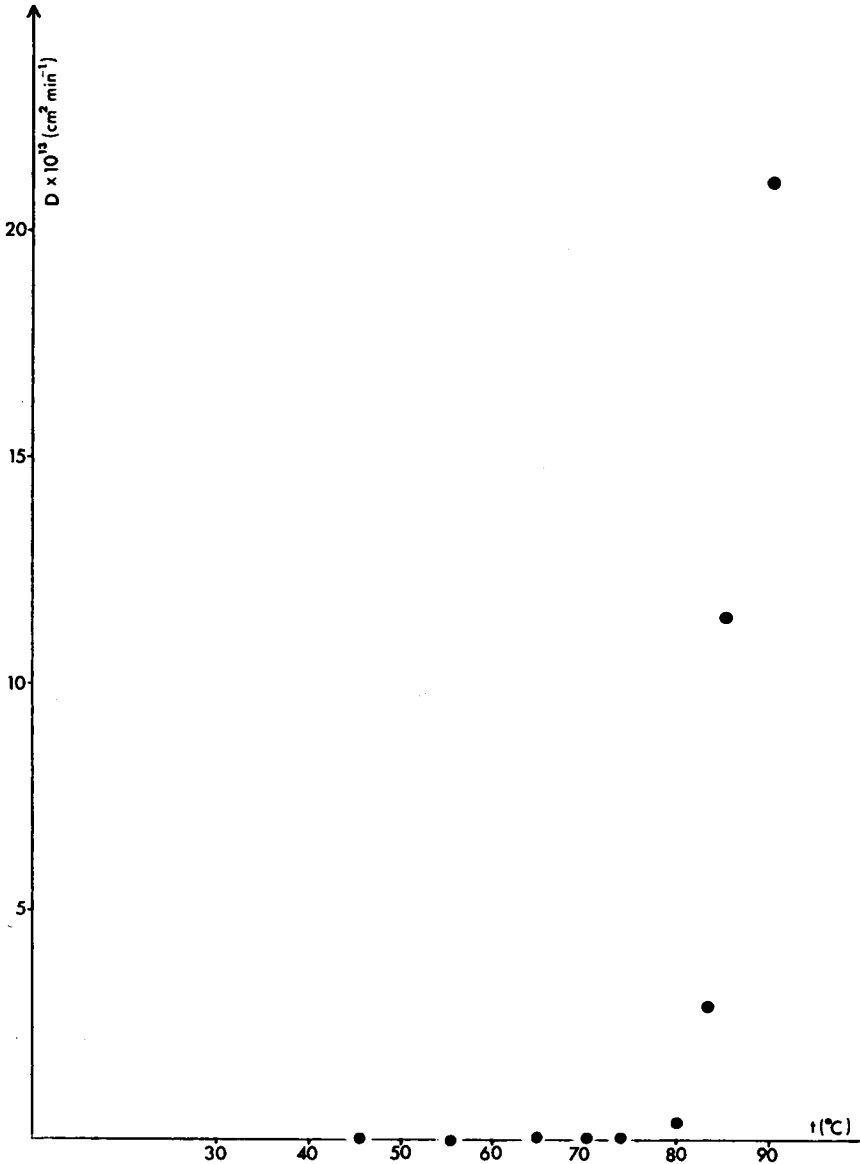
Fig. 10. Variation of D with temperature, Orlon 42.

spacings and temporary ones provided by segmental motions, their relative importance depending on the nature of the blocks.   Breaks in curves of dyeing rates vs. temperature at Tg have meanwhile been shown by other authors[20,21] with other fibers.   On the fibers presently under discussion the effect is so pronounced that glass transition temperatures can readily be measured from dyeing experiments.

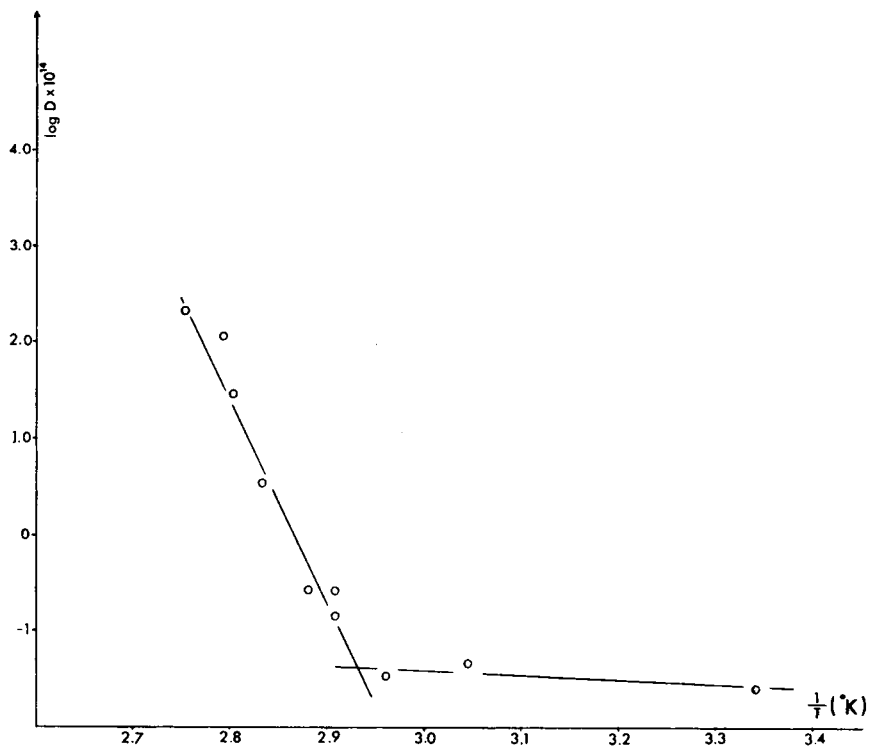The variation of D with T for Orlon 42 is shown in Figure 10, of log D

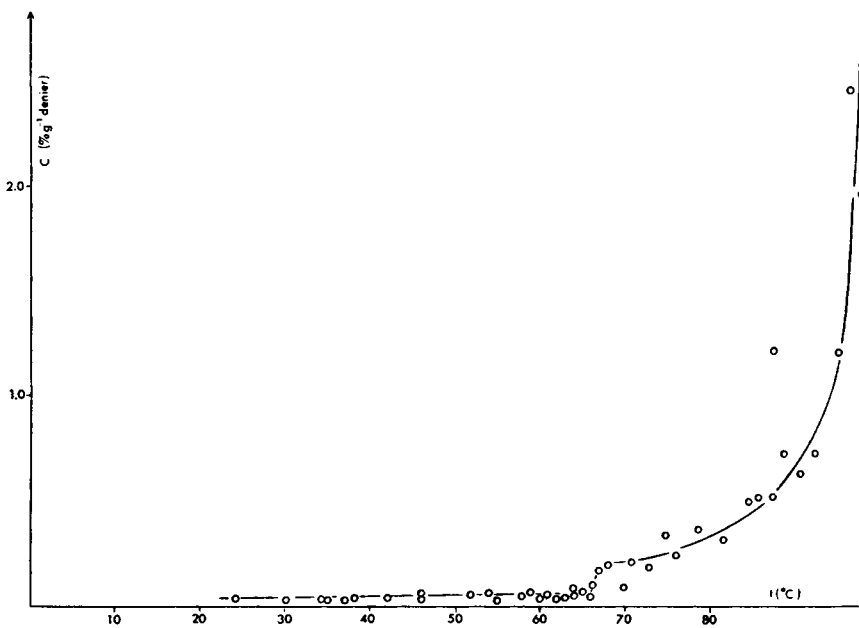Fig. 11. Variation of log D with reciprocal temperature, Orlon 42.

Fig. 12. Variation of tensile compliance with temperature, Orlon 42.
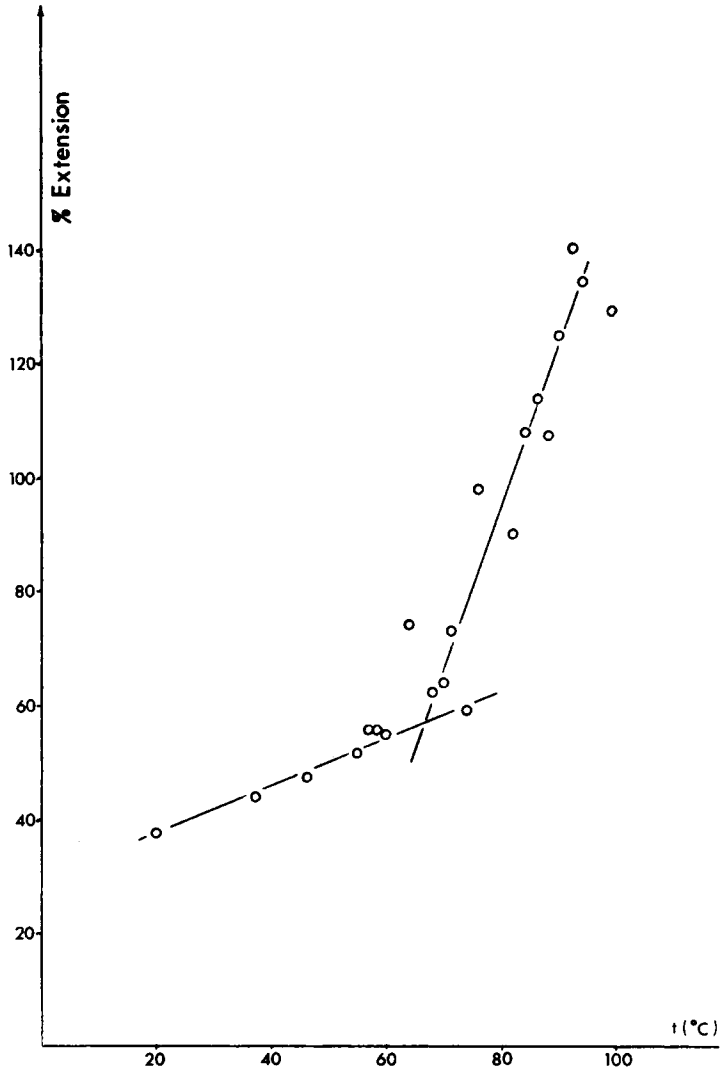
Fig. 13. Variation of break extension with temperature, Orlon 42.

vs. $1/T$ in Figure 11. The change in slope occurs very close to the temperature where initial modulus or compliance (Fig. 12) and break elongations (Fig. 13) in a blank dyebath change abruptly with temperature. It is possible that for the very small dyeing rates below Tg, which show little temperature dependence, the passive pore model would provide an adequate description.

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Synopsis

Diffusion of the cationic (basic) dye, Malachite Green, into polyacrylonitrile fibers is shown to take place from a saturated surface layer even with relatively low solution concentrations. This makes possible a simple determination of the integral diffusion coefficient from one sorption-time curve. In place of the commonly accepted model of dye diffusion, in which the fiber elements play a passive role, it is proposed that the motion in the polymer molecules constituting the fiber is the main factor governing the diffusion process at normal dyeing temperatures. In support, data are shown on the temperature dependence of the diffusion coefficient and its relation to fiber composition and mechanical behavior.

Résumé

On a démontré que la diffusion du colorant basique, le vert de malachite, dans les fibres de polyacrylonitrile prend place à partir d'une couche de surface saturée, même avec des solutions peu concentrée. Ainsi, on peut déterminer d'une manière simple le coefficient intégral de diffusion à partir d'une courbe sorption-temps. A la place du modèle habituel de la diffusion des colorants, dans lequel les éléments de fibres jouent un rôle passif, on a proposé que le mouvement dans les molécules du polymère, qui composent le fibre, soit le facteur déterminant du processus de diffusion aux températures normales de teintures. Comme preuve, on a donné des résultats sur la dépendance du coefficient de diffusion et sa relation avec la composition de la fibre et son comportement mécanique.

Zusammenfassung

Die Diffusion des kationischen (basischen) Farbstoffs Malachitgrün in Polyacryl-
nitrilfasern hinein geht auch bei verhältnismässig niedriger Lösungskonzentration von
einer gesättigten Oberflächenschichte aus. Dieser Umstand ermöglicht eine einfache
Bestimmung des integralen Diffusionskoeffizienten aus einer Kurve für die Zeitab-
hängigkeit der Sorption. An Stelle des gewöhnlcih verwendeten Modells für die Farb-
stoffdiffusion, bei welchem die Faserbausteine eine passive Rolle spielen, wird angenom-
men, dass die Bewegung in den die Faser aufbauenden Polymermolekülen den Haupt-
faktor für den Diffusionsprozess bei normalen Färbetemperaturen bildet. Als Beleg
dafür werden Daten für den Temperaturkoeffizienten des Diffusionskoeffizienten und
seine Beziehung zur Zusammensetzung und zum mechanischen Verhalten der Faser
angegeben.