

The Tracer Diffusion of Dye Anions in Nylon 6 Film

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Synopsis

The tracer diffusion coefficients of three S-35-labeled dyes in nylon 6 film have been determined. The diffusion coefficients show marked concentration dependence, but this takes a form different from that shown by chloride ions in a related study. It is not possible to explain the data on the basis of electrostatic factors as in earlier work in which diffusion was accompanied by a free-energy change. A diffusional interaction between dye molecules is postulated which takes the form of a free-volume saturation effect leading to an upper limiting diffusion coefficient at adsorption levels which depend upon the polymer order and the characteristics of the diffusing ion.

INTRODUCTION

The study of the diffusion of dyes and dye ions in nylon films has been the subject of considerable attention, particularly by McGregor and Peters¹ who have made a detailed examination of the dependence of the diffusion coefficients of ions in nylon on the adsorbed dye concentration. Using microdensitometric methods, diffusion coefficients at various adsorbed dye concentrations have been calculated from diffusion profiles, and explanations which conform very closely with the experimental data have been advanced on the postulate that the chemical potential gradient in the system provides the driving force for diffusion. However, these conclusions are subject to criticism on the grounds that the separate points along a concentration-distance profile are not independent and that the calculation of the chemical potential gradient is itself based on arguable assumptions. Nevertheless, a useful insight and a predictive analysis of the diffusion process have been gained.

The present study has been based on the use of radioactively labeled dye ions so that the diffusion occurs with no net local free-energy change, i.e., in the absence of a chemical potential gradient in terms of the earlier analysis. This technique applied to chloride ions² has shown that even in the absence of any chemical potential gradient the diffusion coefficient in nylon film is concentration dependent and the relationship is the same as found to fit the data of McGregor and Peters. The investigation has now been extended to the study of dye ions in nylon film.

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EXPERIMENTAL METHODS AND RESULTS**Nylon 6 Film**

Nylon 6 film supplied by Laboratory Apparatus and Glassblowing Co. Ltd., Manchester (U.K.), under the description "autoclavable nylon film" was selected for the diffusion experiments because of its uniformity of thickness and freedom from striations. It contained a surface finish which was readily removed by extraction at 60°C for 6 hr with deionized water.

The amine and carboxyl endgroup contents of the film were determined by standard methods. In the case of amine endgroup determination, both conductimetric and potentiometric methods were employed.

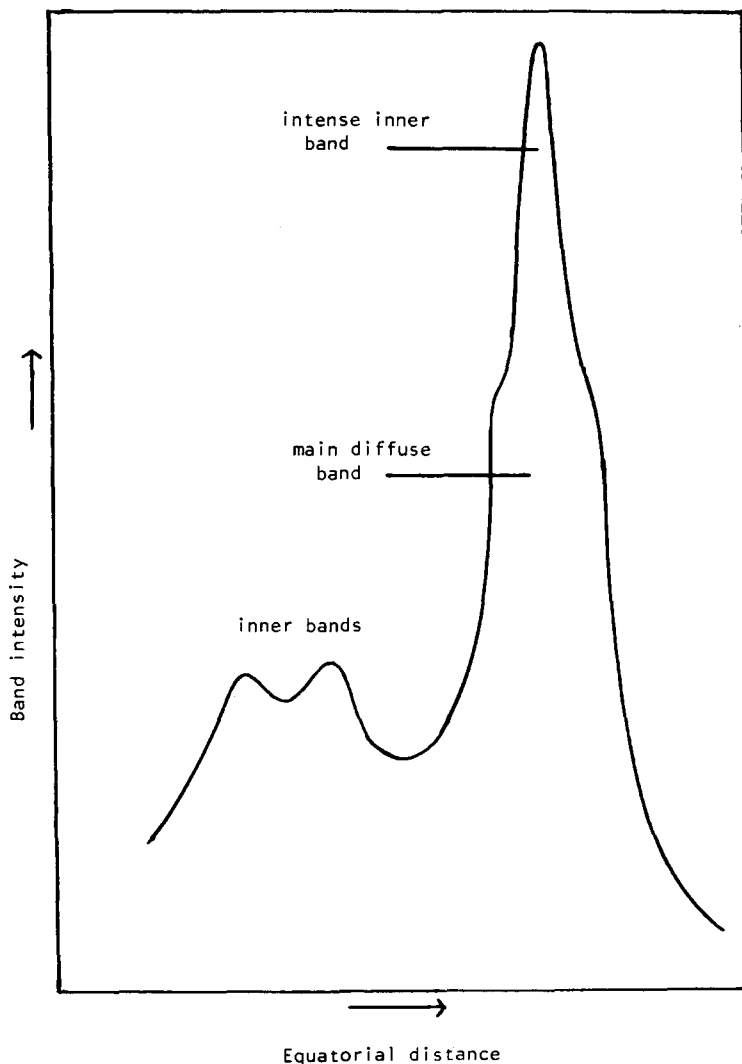


Fig. 1. Densitometric scan diagram of an x-ray diffraction photograph of the nylon 6 film.

TABLE I
Characteristics of The Nylon Film

Amine endgroup content	$2.23 (\pm 0.03) \times 10^{-2}$ eq./kg
Carboxyl endgroup content	$2.20 (\pm 0.05) \times 10^{-2}$ eq./kg
Density	1.27
Number-average molecular weight	45500
Water uptake value	
(i)	$6.7 (\pm 0.4) \times 10^{-2}$ l./kg
(ii)	$6.3 (\pm 0.4) \times 10^{-2}$ l./kg

The internal aqueous volume of the water-swollen nylon film was determined by two methods:

(i) **Aqueous Absorption.** Samples of the nylon film were immersed in deionized distilled water at 60°C in a closed vessel. Vacuum was applied, which removed air from the film. After 1 hr the film samples were removed, lightly blotted, and weighed. The samples were then dried to constant weight over P₂O₅ and reweighed. Water uptake values were calculated by difference.

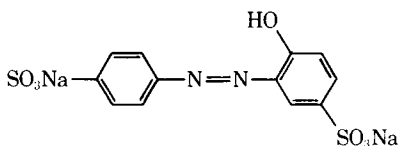
(ii) **Differential Density.** The density of water-swollen nylon film in water was determined. The sample was then dried over P₂O₅ to constant weight and the density redetermined in liquid paraffin. The water uptake value was calculated from the difference.

The characteristics of the film are tabulated in Table I.

The x-ray diffraction characteristics of the film were also determined. The photographs were characterized by an almost complete lack of orientation effects, and the intensities of the outer diffraction rings were almost uniform over their circumference. They were almost identical with published x-ray diffraction photographs of undrawn nylon apart from the presence within the main diffuse band of a very narrow intense but non-directional band discernible on close inspection. Figure 1 shows a densitometric scan diagram. The effect indicates that the film was unoriented but fairly highly crystalline. This conclusion is supported by the water uptake values which are consistent with 75–80% crystallinity on the basis of the work of Puffr and Sebenda³ and the unusually high density value.

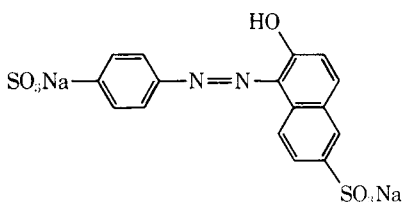
Preparation of Dyestuffs

Three dyes were selected for the diffusion experiments and had the following structures:



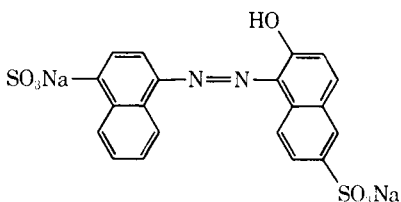
Length, 1.51 nm
 Width, 0.91 nm
 Height, 0.52 nm
 Area, 1.37 nm²
 Volume (1), 0.71 nm³
 Volume (2), 0.97 nm³
 Molecular weight, 342
 Extinction coefficient, 1.682 m²/mole at
 320 nm in water at 25°C

Dye 1



Length, 1.69 nm
 Width, 1.00 nm
 Height, 0.52 nm
 Area, 1.69 nm²
 Volume (1), 0.88 nm³
 Volume (2), 1.32 nm³
 Molecular weight, 391
 Extinction coefficient, 2.472 m²/mole at
 480 nm in water at 25°C

Dye 2
 (C.I. Food Yellow 3)



Length, 1.69 nm
 Width, 1.00 nm
 Height, 0.52 nm
 Area, 1.69 nm²
 Volume (1), 0.88 nm³
 Volume (2), 1.32 nm³
 Molecular weight, 443
 Extinction coefficient, 2.352 m²/mole at
 502 nm in water at 25°C

Dye 3
 (C. I. Acid Red 13)

The molecular dimensions were estimated with the aid of Courtauld's models. Volume (1) is length \times width \times height; volume (2) is $\pi/4 \times$ (width)² \times length.

Samples of each dye were prepared in the normal and S-35-labeled form. Since efficient utilization of labeled compounds was essential in the interests of economy, the preparation of the S-35-labeled amine was carried out by a reverse Bucherer reaction since this gave a yield of virtually 100% with respect to labeled sulfuric acid. The dyes were then prepared by coupling to the appropriate phenol or naphthol sulfonic acid. Details of the preparations are omitted here in the interests of brevity but can be examined elsewhere.⁴ Purification of dye was carried out in each case by ion exchange.

Liquid Scintillation Counting

Because of the ability of the dye molecules in solution to absorb scintillation emissions, it was necessary to destroy the chromogen chemically in order to estimate radioactivity in solution. An earlier investigation by White⁵ had shown that with azo dyes sodium hypochlorite was suitable for the purpose under appropriate conditions. With all three dyes, good decolorization was obtained, and providing the procedure outlined below was followed, no by-products were formed which interfered with counting.

Samples of dye solution, 20 ml, were pipetted into a tube, 1.5 ml sodium hypochlorite solution (13% available chlorine) was added, and the mixture boiled under reflux for 10 min. Shorter treatments have decolorization, but the solutions were not spectroscopically stable. After decolorizing, the solutions were made up to 25 ml with distilled water, and 1 ml was added to

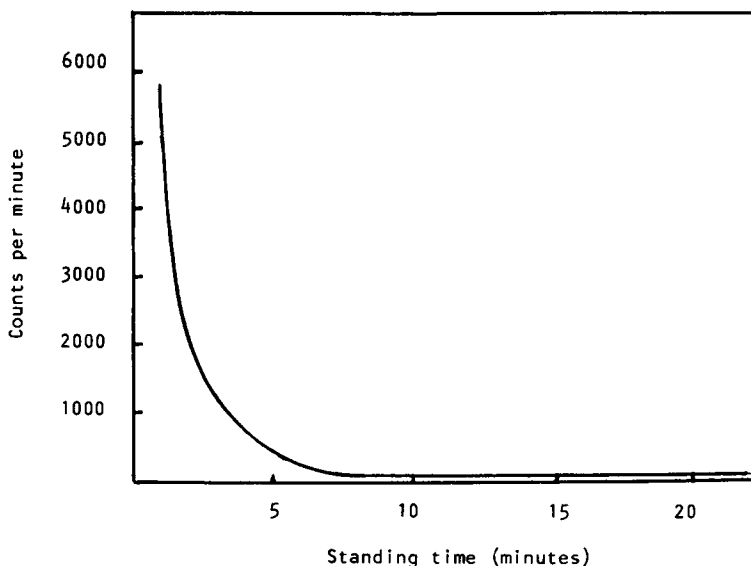


Fig. 2. Effect of standing time on the fluorescence of a bleached dye-scintillator mixture.

5 ml of scintillation solution for counting. Further side reactions occurred at this stage as counting rates were observed to fall rapidly over a period of 20 min, when they became stable. The presence of some short-lived fluorescent species in the solution was indicated. Since standing before commencing counting avoided difficulty, its nature was not investigated. The effect of standing is shown in Figure 2, which illustrates data produced with an unlabeled sample of dye 1. Counting was carried out therefore at least 15 min after mixing with scintillator.

The scintillator solution employed consisted of: 2:5 diphenyl oxazole (10 g/l.); 2-*p*-phenylenebis(5-phenyloxazole) (0.5 g/l.); and naphthalene (50 g/l.) in Dioxan/Cellosolve (5:1). Counting was carried out using a Unilux II Liquid Scintillation Counter (Nuclear Chicago Corp.).

Study of Tracer Diffusion and Titration of Nylon Film with the Free Dye Acids

Samples of the nylon film were equilibrated with solutions of the unlabeled free dye acids of known concentration at 60°C. The method used was to replace the dye solution repeatedly until no further adsorption occurred. This avoided the build-up in the dyebath of decomposition products of the nylon due to hydrolytic and oxidative attack,⁶ as it had been previously shown that these are capable of distorting titration curves of this kind.² The dyed film was then placed in a diffusion cell represented schematically in Figure 3. The film (4) was placed between the two halves of the cell (3) and held in position by clamps between the annular ground-glass flanges (6). Dye solution was put into each half of the cell through the opening (1), and the solutions were stirred with ministirrers (2) supplied

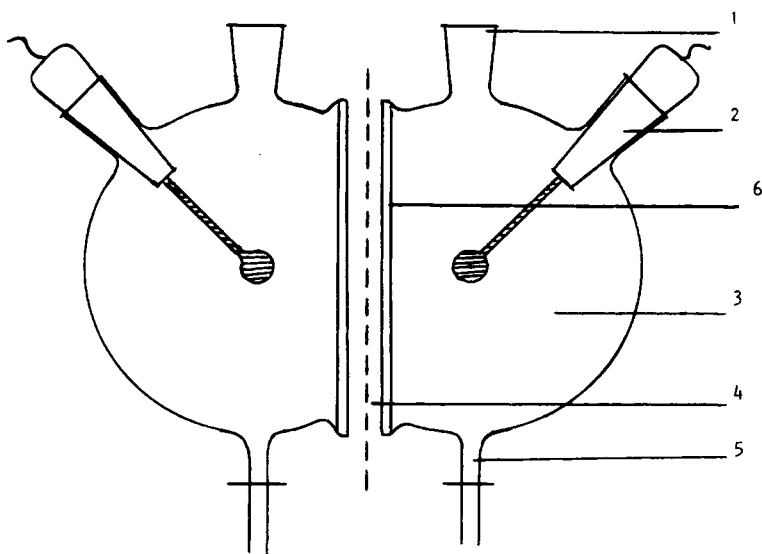


Fig. 3. The diffusion cell.

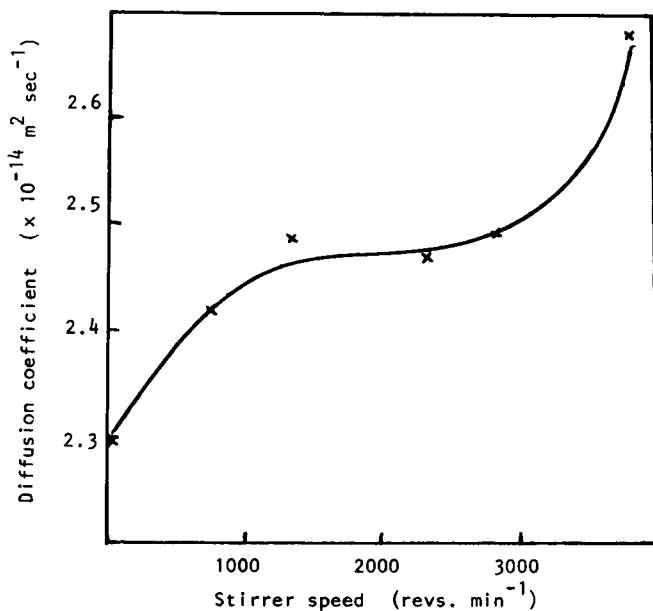


Fig. 4. Effect of stirring speed on the observed diffusion coefficient.

by Electrothermal Equipment Co. The cell was placed in a thermostat at 60°C and left for 24 hr to ensure equilibration. The solution in one half of the cell was then removed through the exit (5) and replaced by a radioactively labeled solution at the same concentration. Careful matching of the concentrations was essential, and this was carried out by careful spectro-

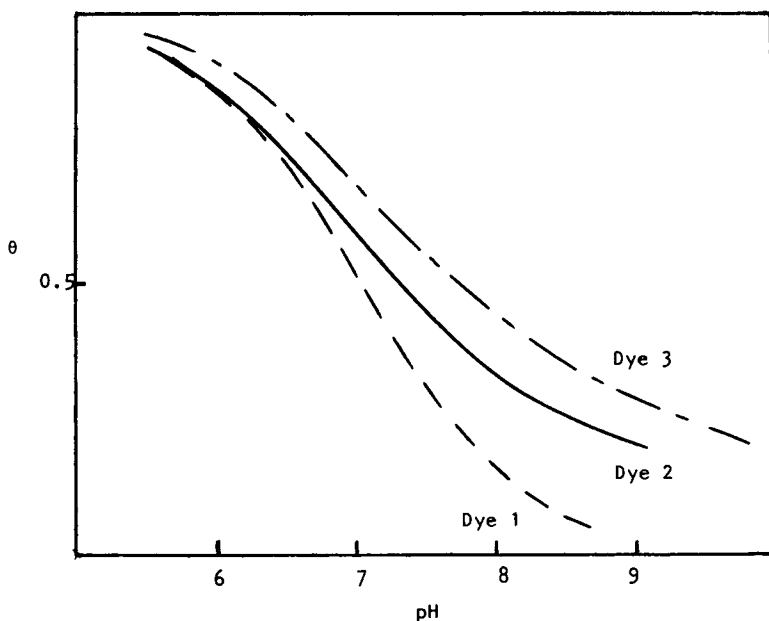


Fig. 5. Titration curves of the nylon 6 film with the free dye acids of dyes 1 to 3.

photometric and precision pH measurements using a Radiometer Digital pH Meter Type PHM52 with a combined electrode Type 9K230IC. The stated accuracy of the instrument was ± 0.002 pH units, and this was found to be correct.

Replacement of the unlabeled by a labeled solution initiated the isotopic diffusion process. This was followed by repeated removal and replacement of the two solutions at appropriate time intervals. The diffusion process was followed by liquid scintillation counting. At the end of the diffusion run, the film sample was removed, lightly rinsed, and dried. The dye content of the film was determined by spectrophotometric measurement of the extract solutions. The dye was completely removed from the film in each case by boiling 10% ammonia solution. The radioactive dye content of the extracts was also determined.

Preliminary experiments were required to determine the stirring conditions necessary for the production of reproducible data. The speed of rotation of the stirrers was determined by a stroboscopic method, and the diffusion coefficient of dye 3 was determined under a fixed set of conditions apart from varying stirring speed. The results are shown in Figure 4. The diffusion coefficient can be seen to rise with stirring speed to a steady value as expected and then to rise with increased rate of stirring. This last effect has been seen before⁷ and is likely to be due to turbulence. For the present work, a stirring speed giving results in the middle of the steady zone (2000 rpm) was selected.

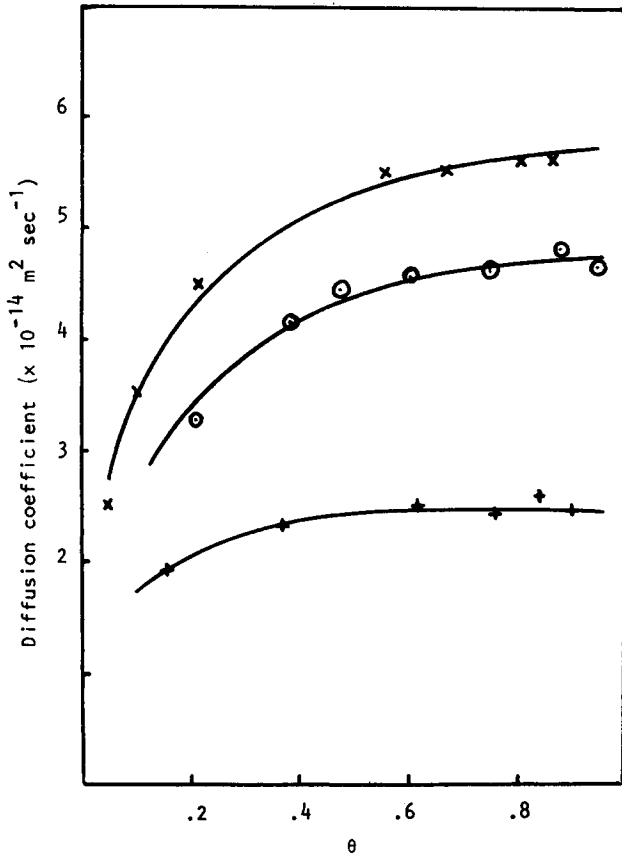


Fig. 6. Concentration dependence of the diffusion coefficients: (X) dye 1; (O) dye 2; (+) dye 3.

From the data relating to the dye content of the film samples, titration curves for the three free dye acids were obtained, and these are shown in Figure 5. The dye content of the film samples calculated from the radioactivity values was in each case exactly one half of that obtained by extraction and spectrophotometric measurement. This indicated the existence of a linear isotope concentration gradient in the film during the diffusional steady state as expected.

Diffusion coefficients were in each case calculated using the Daynes time lag equation

$$L = l^2/6D$$

in which L is the time lag in sec, l is the film thickness in meters, and D is the diffusion coefficient in meters²/sec. Time lag values of $(7-22) \times 10^3$ sec were obtained, in each case with high probability. Calculated diffusion coefficients are shown in Figure 6 as a function of the fractional electrostatic saturation value θ .

DISCUSSION OF RESULTS

The results show that the concentration dependence of the tracer diffusion coefficients of dyes 1-3 on the nylon 6 film is quite different from that observed either in regular kinetic diffusion studies on nylon film^{1,8} or in tracer diffusion studies of the chloride ion in the same film as in the present case.² In these quite independent investigations, a rectilinear reciprocal relationship was demonstrated between the diffusion coefficient and θ , the electrostatic saturation of the polymer. The dye used in the kinetic diffusion studies⁸ was C.I. Acid Red 18 which is very similar to dye 3, bearing an additional sulfonic acid group on the 8-position of the naphthol sulfonic acid coupling component.

The explanations advanced to explain the kinetic diffusional behavior of C.I. Acid Red 18 and the tracer diffusional behavior of the chloride ion contradicted one another to some extent, but both were based on an analysis of the influence of fixed charge centers in the polymer on the diffusional process. It can be seen that such a basis for an explanation will

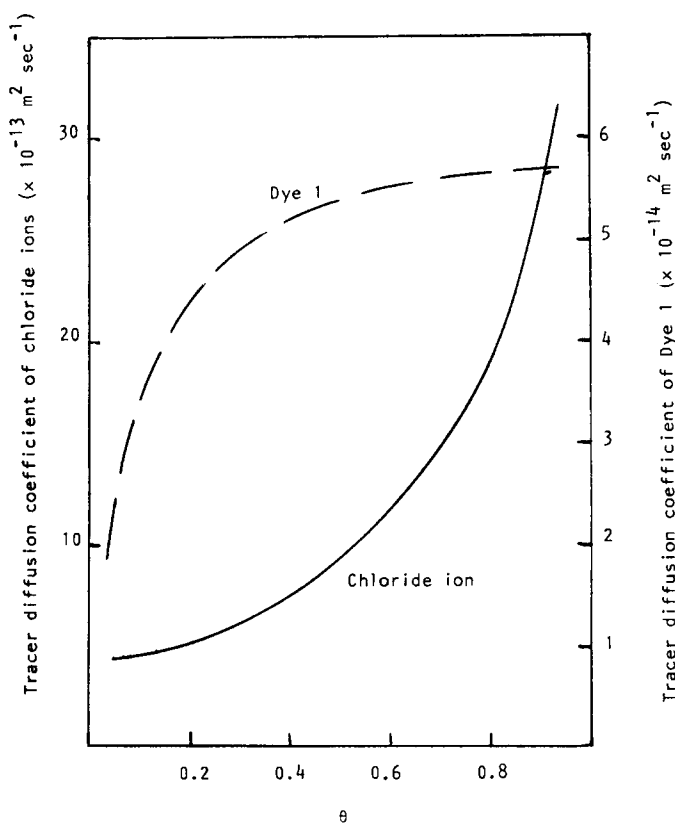


Fig. 7. Comparison of the concentration dependence of diffusion coefficients (dye 1 and Cl^-).

not work in the present case since the tracer diffusional behavior of dyes 1-3 is in a sense opposite to that of the chloride ion, as shown in Figure 7, which combines present data with earlier results obtained by the authors.² Clearly, the increase in diffusion rate which should occur with increasing electrostatic saturation is curtailed with the larger ions in the film.

It is a characteristic assumption of the diffusional model of McGregor et al.⁸ and that used by the authors to account for the diffusional behavior of the chloride ion² that the free volume available for diffusion in the polymer is sufficient at any value of θ for all the concentration dependence of the diffusion coefficient to be attributable to the concentration of free fixed countercharges. It is the validity of this assumption that is questioned by the present data.

Both diffusional models are versions of the pore or free-volume models of the diffusional process. These postulate the existence of void spaces in the polymer in which diffusing molecules or ions exist. The voidages are treated as permanent in the pore model and transitory in the free-volume model. In both cases, when applied to dye diffusion, the magnitude of the void volume is regarded as a property of the polymer; and the more the latter becomes ordered, the less will be the gross void volume. However, the treatments of diffusion in nylon both assume implicitly that the freedom of a dye molecule or ion to move in a void is constant, irrespective of the polymer order. Thus, the magnitude of the diffusion coefficient is determined according to this concept by the proportion of the polymer volume in which the voids can exist and the concentration dependence of the diffusion coefficient is independent of polymer orientation.

However, it has been shown in kinetic diffusion studies on nylon yarns of varying orientation using fairly large dye ions that polymer orientation has a significant effect on the diffusion-concentration relationship.⁹ With large molecules in relatively highly ordered polymers, the diffusion coefficient has been shown to be much less dependent on dye concentration than with dyes such as C.I. Acid Reds 13 or 18 in relatively unoriented nylon polymer.⁸ The tentative explanation of this effect was based on the possibility of occupying the diffusional free volume totally at high adsorbed dye concentrations, particularly with large molecules in highly oriented fibers.

This explanation is supported by the present data. The film used was fairly highly crystalline, and the diffusional behavior suggests an increasing ease of free-volume saturation as molecular size increases. With dye 1, the diffusion coefficient approaches a constant value at $\theta = 0.9$ (Fig. 6), while with dyes 2 and 3 the effect is seen at $\theta = 0.8$ and 0.5 , respectively.

These differences are not reflected in the molecular characteristics of the dyes but do correspond with the affinity differences between the dyes (Fig. 5). There is also a correspondence between the upper limiting diffusion coefficients and the values which may be calculated for the standard partial molal affinities for the three dyes from the titration curves. This is shown in Figure 8. It would be of value to determine the relative influence of enthalpic and entropic factors contributing to the diffusion coefficients, and

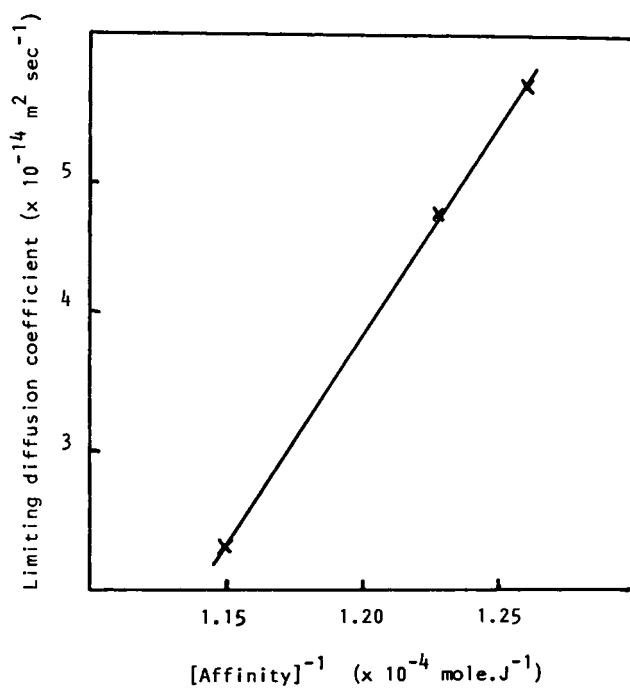


Fig. 8. Relationship between limiting diffusion coefficients and standard affinity.

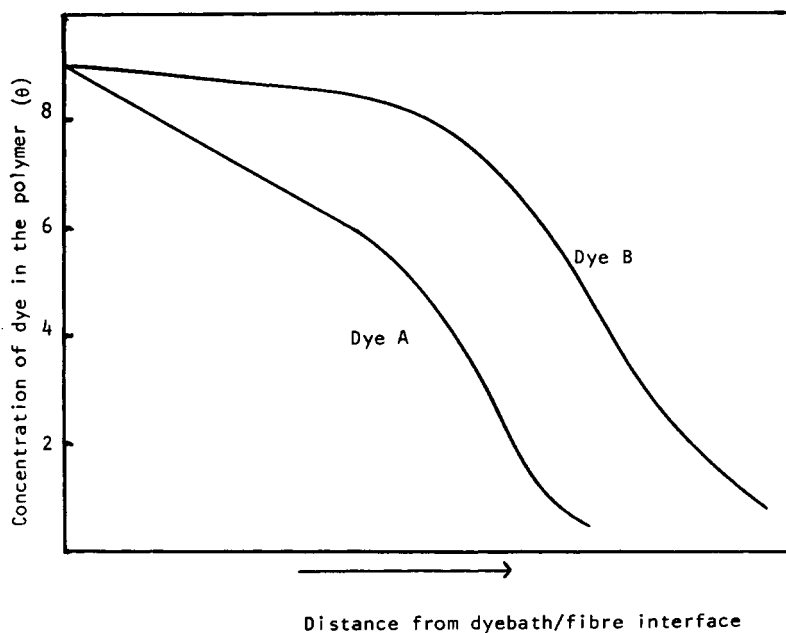


Fig. 9. Predicted concentration distance profiles.

this will be the subject of further studies as well as the examination of the behavior of a single dye on nylon polymers of different orientation.

It is of interest to postulate the effect of the particular kind of concentration dependence of diffusion coefficients shown in Figure 7 on expected concentration profiles in kinetic diffusion. Two examples are shown in Figure 9. For the hypothetical dye A with a limiting diffusion coefficient at $\theta = 0.6$, the diffusion coefficient will be constant over the concentration range $\theta = 1-0.6$, giving a linear profile with distance. When the concentration falls below the limiting value, the diffusion coefficient falls to give a concave relationship as shown. If the limiting θ value is higher than 0.6 and the limiting diffusion coefficient applies, then a curve such as is shown for hypothetical dye B is obtained. The similarity between these profiles and those of McGregor et al.⁸ is quite clear although no electrostatic factors have been invoked. It is clearly of importance to establish in future studies the level at which polymer orientation in conjunction with the characteristics of the diffusing ion is able to cooperate with or even displace electrostatic factors in determining the concentration dependence of the diffusion coefficients of ions in charged polymers.

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