

Dual Permeation of Acid Dyes through Nylon 6 Membrane

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Synopsis

Permeation of acid dyes in nylon 6 membrane was measured and analyzed by the dual sorption and diffusion mechanism, comprising partition and Langmuir-type modes. The results were compared with our previous work on diffusion in the same system by the film roll method. Diffusion coefficients of both dye species were found to be similar in magnitude.

INTRODUCTION

It has been known that overdyeing is often encountered in the dyeing of nylon when the total uptake of anionic dye exceeds the equivalent amino end group content in nylon.¹⁻⁴ The authors^{5,6} have suggested that the sorption and diffusion of acid dyes in overdyeing systems might be quantitatively analyzed by the dual sorption and diffusion model, which is based on two distinct Langmuirean and Nernstean species.

In a previous report⁷ the sorption and diffusion of three anionic dyes in nylon 6 from the infinite dyebath were determined.

The relation between the diffusion coefficients and dye concentration was obtained from the diffusion profile by means of the film roll method. Both sorption and diffusion behavior were consistently discussed in the light of the dual mechanism. The transient diffusion profiles, i.e., the dye distribution curve in the polymer matrix at different penetration times, as determined by the film roll method are very informative for the kinetic analysis of this system. However, the method has its own problems, such as the limited number of layers in a film roll and the presence of water layers between the successive film layers. The need of a film of relatively large size is an additional drawback to compare with the steady-state permeation method. The latter approach is simple and does not need a special technique in the performance of the experiment.

In this study, an attempt has been made to obtain more detailed information about the dual mechanism by means of steady-state permeation measurements.

EXPERIMENTAL

Materials

Biaxially drawn nylon film used in this work was kindly supplied by Unitika Co. The film thickness, ca. 15 μm , was measured by means of a Tokyo Seimitsu thickness gauge with a precision of $\pm 1 \mu\text{m}$. The amino end group content was

4.02×10^{-5} equiv/g dry film. The pretreatment of this film was the same as before.⁷

The acid dyes used were Orange II (C.I. Acid Orange 7, Dye I), Sunset Yellow (C.I. Food Yellow 3, Dye II), and sulfanilic acid \rightarrow 2-naphthol-3,6-disulfonic acid (R acid) (Dye III). The preparation and the purification of these dyes were described previously.⁷

Determination of Aggregation Constants of Dyes in Solution

The spectral change of dye solution was measured at 25°C in the range 350–600 nm by means of a Hitachi double wavelength spectrophotometer 556.

Determination of Permeability Coefficients

To determine the permeability coefficients of dye anions through the nylon film, the steady-state method was used. The cell used was the same as in a previous work,⁸ consisting of two compartments, A and B, the volumes of which were 150 and 50 mL, respectively. The dye concentration in cell A was kept between 10^{-5} and 10^{-3} mol/L of a solution adjusted to pH 2.2 by adding hydrochloric acid. Cell B was filled with aqueous hydrochloric acid solution of pH 2.2. Nylon film was placed between the two compartments with Teflon seals, and the solutions in A and B were stirred as efficiently as possible.

During the experiment, the dye molecules in A diffuse into B through the membrane. Aliquots of dye solution were taken out of cell B at appropriate time intervals and the concentration of dye determined spectrophotometrically. Cell B was refilled each time with equal amounts of blank HCl solution. As the constancy of the concentration in cell A throughout the experiment is a fundamental necessity, the volume of solution A was designed to be sufficiently large to ensure infinite bath conditions in the case of dilute solutions (lower than ca. 5×10^{-5} mol/L). The permeation apparatus shown in Fig. 1 had a total upstream volume (A + C) of approximately 3500 ml and a downstream volume (B) of 50 mL. The agitation of the dye solutions was as efficient as possible to minimize the stagnant boundary solution layers on the surface of the membrane. Examples of the experimental results thus obtained are shown in Fig. 2.

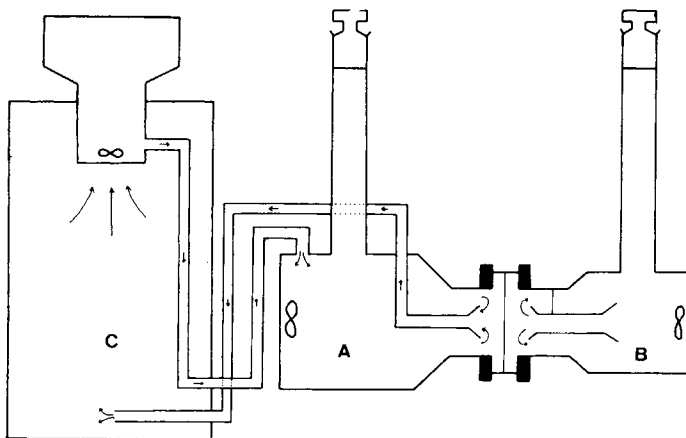


Fig. 1. Permeation cell.

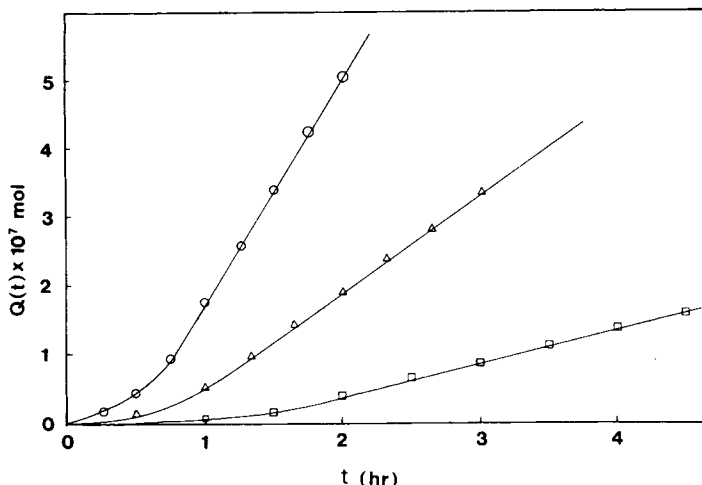


Fig. 2. Permeation of dyes through Nylon 6 membrane; C_0 1.0×10^{-4} mol/L, pH 2.2, 50°C. (○) Dye I, (Δ) dye II, (□) dye III.

RESULTS AND DISCUSSION

As described in the preceding communication,⁷ the sorption and diffusion of dye in nylon can be explained by considering the dual species, i.e., of Langmuir sorption and Nernst partition, each of the species denoted by the subscript L and P , respectively. The sorption and diffusion of dye in the acid dyeing of nylon is thus described by the following equations⁷:

$$C = C_p + C_L = K_p C_0 + \frac{K_L S C_0}{z(1 + K_L C_0)} \quad (1)$$

$$D(C) = \left\{ D_p^0 \frac{z}{\alpha(1 - \theta)^2 + z} + D_L^0 \frac{\alpha(1 - \theta)}{\alpha(1 - \theta)^2 + z} \right\} \quad (2)$$

where C is the dye concentration in nylon in equilibrium with the dye bath with concentration C_0 ; S is the saturation value; z is the basicity of dye anion; K_p and K_L are constant; $D(C)$ is the differential diffusion coefficient; D_p^0 and D_L^0 are the thermodynamic diffusion coefficients (assumed constant) of each species; $\alpha = K_L S / K_p$; and $\theta = z C_L / S$.

On the other hand, assuming that eq. (1) is justified for $z > 1$ on an empirical basis,⁷ we expect the following expression for the differential permeability coefficient⁹:

$$P(C) = K_p D_p^0 + \frac{K_L S D_L^0}{z(1 + K_L C_0)} \quad (3)$$

which leads to the following expression for the integral permeability coefficient:

$$P = K_p D_p^0 + \frac{D_L^0 S}{z(C_{0A} - C_{0B})} \ln \frac{1 + K_L C_{0A}}{1 + K_L C_{0B}} \quad (4)$$

where C_{0A} and C_{0B} are dye concentrations in the solutions on each side of the membrane, i.e., in half-cell A and B, respectively. According to eq. (4), a plot of \bar{P} against $[1/z(C_{0A} - C_{0B})] \ln [(1 + K_L C_{0A}) / (1 + K_L C_{0B})]$ should be a straight line with intercept $K_p D_p^0$ and slope SD_L^0/z .

It is known that water-soluble dyes often exist in solution not as monomers but as aggregates.¹ According to the widely held view that such aggregates cannot permeate through the polymer matrix, it is necessary to use the monomer concentration when considering permeation through the polymer membrane. From the measurement of the absorption spectra of D-I at 25°C, the equilibrium aggregation constant K between monomer and n -mer in solution was determined as $K = 1.15 \times 10^3$ with $n = 2$ in the concentration range up to 1×10^{-3} mol/L by the method of Hida et al.¹⁰ The value of K is compared with a reported value¹¹ of 707 in the concentration range of 4×10^{-6} to 1×10^{-3} mol/L.

By using a heat of aggregation of -10.5 kcal/mol,¹² an estimated value of 290 for the aggregation constant at 50°C was obtained and was used to calculate the corrected monomer concentration under our experimental condition for D-I. The more water-soluble dyes D-II and D-III showed no spectral evidence of aggregation in the concentration ranges employed in our experiments.

Plots of the experimental data according to eq. (4) are shown in Fig. 3. For large values of K_L , the term $\ln [(1 + K_L C_{OA}) / (1 + K_L C_{OB})]$ is sensitive to changes in C_{OB} . The experiments were performed with C_{OB} as constant as possible. Nevertheless, due to the change of C_{OB} during each experimental run, the abscissa values are subject to a maximum error of $\pm 10\%$, as illustrated by means of bars for D-II in Fig. 3. From the straight lines in Fig. 3, D_p^0 and D_L^0 were determined using eq. (4) together with the values of K_p , K_L , and S obtained in the previous work.⁷ The results are summarized in Table I.

Our previous data by the film roll method had been obtained in the form of

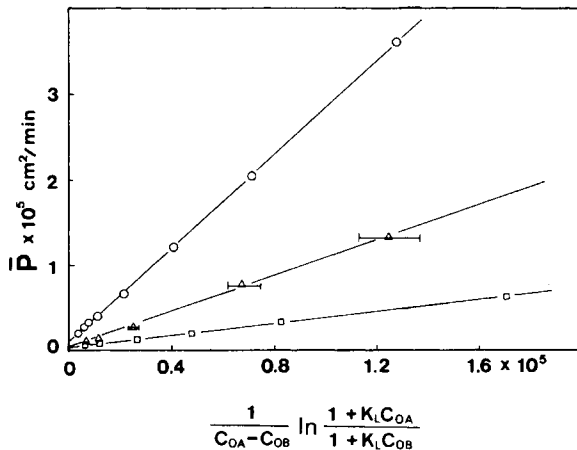


Fig. 3. Linear plots of integral permeability coefficient according to eq. (4). (O) dye I, (Δ) dye II, (\square) dye III.

TABLE I
Parameters for Polybasic Acid Dye Diffusion in Nylon 6

z	K_p , ^a L/g	K_L , ^a L/mol	$S \times 10^5$, ^a equiv/g	$D_p^0 \times 10^9$, cm ² /min		$D_L^0 \times 10^9$, cm ² /min	
				Eq. (4)	Eq. (3)	Eq. (4)	Eq. (3)
1	0.160	6.4×10^5	3.72	6	<5	6.0	9.3
2	0.024	1.1×10^6	3.61	4	<3	4.7	8.8
3	0.013	2.0×10^6	3.71	4	<3	2.4	3.8

^a From Ref. 7.

the diffusion coefficient $D(C)$, as shown in Figs. 4-6. For direct comparison with the present results, these data can be transformed to the corresponding differential permeability values $P(C_0)$ by means of the relation

$$P(C_0) = D(C) \frac{dC}{dC_0} = D(C) \left[K_p + \frac{SK_L}{z(1 + K_L C_0)^2} \right] \quad (5)$$

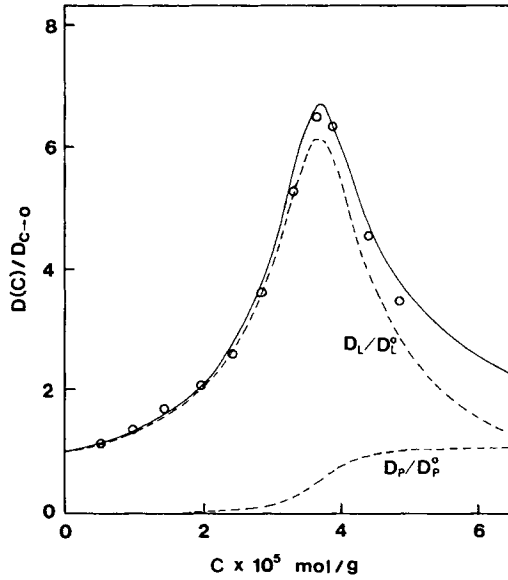


Fig. 4. Concentration dependence of diffusion coefficient of D-I determined by film roll method. Full lines refer to calculated D values which are made up of D_L and D_p contributions (shown separately by broken lines).

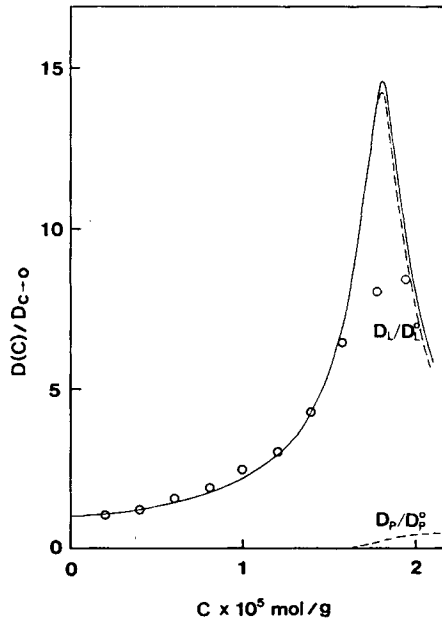


Fig. 5. Concentration dependence of diffusion coefficient of D-II determined by film roll method. Meaning of lines as in Fig. 4.

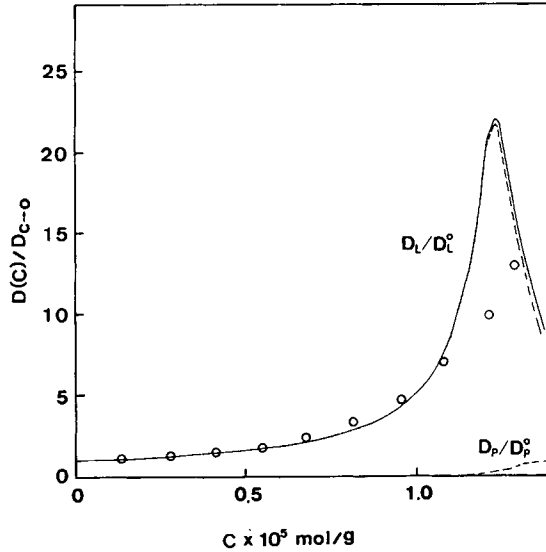


Fig. 6. Concentration dependence of diffusion coefficient D -III determined by film roll method. Meaning of lines as in Fig. 4.

where dC/dC_0 is given by eq. (1). By plotting $P(C_0)$ thus calculated vs. $1/(1 + K_L C_0)$, nearly straight lines were obtained (see Fig. 7) from the intercept and slope of which D_p^0 and D_L^0 could be deduced on the basis of eq. (3). These values are given in Table I and are found to be of the same order as the corresponding values deduced from the present permeation experiments. Precise comparison

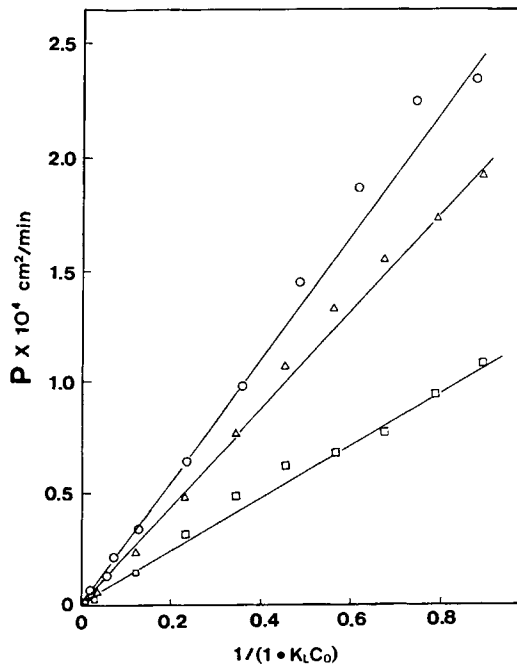


Fig. 7. Linear plots of differential permeability coefficient, deduced from $D(C)$, according to eq. (3). (O) dye I, (Δ) dye II, (\square) dye III.

of the D_p^0 values is not very meaningful because of their uncertainties. In the case of the D_L^0 values, some discrepancy may be noted, which could arise from the periodic accumulation of penetrant on the downstream side of the membrane (required to permit measurement of the concentration of penetrant with some precision during the permeation experiment). We may, therefore, conclude that the steady-state permeation results obtained here are reasonably consistent with the non-steady state diffusion data of Ref. 7.

The values of D_p^0 and D_L^0 determined by the application of eq. (3) as described above have been used to calculate the lines shown in Figs. 4–6. These figures show that the diffusion coefficient increases up to near saturation of the amino groups. In the case of the monobasic dye, a clear maximum is observed at this point. The overall D is largely determined by D_L , i.e., by the contribution of the L species, as shown by the appropriate broken line in Fig. 4. The solid line, which is the superposition of the D_p and D_L contributions, agrees very well with the experimental points. In the cases of D-II and D-III, the contribution of D_p is not significant. Some discrepancy between calculated and experimental results at the higher values of C may also be noted.

Comparison of the D_L^0 values for different dyes in Table I shows that the diffusion of anionic dyes in nylon becomes slower with the introduction of sulfonic acid groups. This effect may be (1) steric and (2) electrostatic. Thus, the additional sulphonic acid group may hinder the translation of the dye in the polymer matrix because of (1) its bulkiness and (2) its attraction to the positively charged sites ($-\text{NH}_3^+$) in the polymer. On the other hand, the fact that (within the uncertainty of the data) D_L^0 and D_p^0 appear to be of the same order would imply that the electrical barriers between charged sites are relatively flat. It is interesting to compare this situation with the corresponding finding in gas-glassy polymer systems¹³ where $D_p^0 \gg D_L^0$.

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