

Transport of Acid Dye in Nylon and Concentration Dependence of the Diffusion Coefficient

EIZO SADA, HIDEHIRO KUMAZAWA, and SHINICHI MIZUTANI, *Department of Chemical Engineering, Kyoto University, Kyoto 606, Japan*, and TETSUO ANDO, *Tsuyakin Kogyo Co., Ltd., Bisai, Aichi 494, Japan*

Synopsis

The dyeing kinetics of an acid dye (C.I. Acid Blue 40) in a nylon 6 film were investigated using partition-cell and film-roll methods at 80°C and pHs 2.3 and 3.05. The concentration dependence of diffusion coefficient of the dye in the nylon substrate measured by both methods was interpreted in terms of parallel diffusion with bimodal sorption of the Nernst and Langmuir modes. As the concentration of dye increases, the transport of dye inside the nylon film becomes dominated by pore diffusion and surface diffusion of sorbed Nernst populations.

INTRODUCTION

The sorption and diffusion of dyes in nylon has been the subject of many studies mainly due to practical interest in dyeing processes. Specifically, the diffusion of an acid dye in nylon has been the intensive target of investigation. It has been reported that the diffusion coefficients of acid dyes in the nylon substrate depend strongly on the concentration of dyes in the substrate. To interpret the concentration dependence of the diffusion coefficients, several concepts have been proposed, but no single theory covering the entire period of the process has been yet available. Furthermore, the existing studies were confined to some part of the whole dyeing process, and, hence, the values of diffusion coefficients so derived were apt to depend upon the measuring procedure.

Recently, Kawana et al.¹ measured sorption and permeation of a tribasic dye in nylon 6 films, and measurements of sorption isotherm and concentration dependence of diffusion coefficient were successfully analyzed by the dual-mode sorption and mobility model consisting of Nernst-type sorption plus ion exchange. The dual-mode sorption and mobility approach seems to provide a useful concept to cover the entire period of the dyeing process.

The present work, following the previous work² on sorption and diffusion of an acid dye (C.I. Acid Blue 182, basicity = 1) in nylon, has been undertaken to establish the mechanism covering the whole process in the dyeing of nylon with an acid dye (C.I. Acid Blue 40, basicity = 1). The concentration dependences of the diffusion coefficients were measured by means of both steady-state permeation and non-steady-state dyeing methods, and the dyeing mechanism up to the full uptake could be discussed by comparing the information obtained from these two methods with each other.

THEORETICAL BACKGROUND

The theoretical background which can be applicable to analysis of experimental results on permeation of an acid dye in the nylon film has already been described in the previous article.²

The diffusion flux of an acid dye in a nylon film can be expressed as

$$J = -D_C(C) \frac{dC}{dx} \quad (1)$$

provided that the process of permeation of the dye in the film follows Fick's diffusion law. After integrating eq. (1) over C from C_l to C_h with J constant under the steady-state, one gets

$$Jd = \int_{C_l}^{C_h} D_C(C) dC = \bar{D}_C(C_h - C_l) \quad (2)$$

where \bar{D}_C denotes the integral diffusion coefficient defined by

$$\bar{D}_C = \frac{1}{C_h - C_l} \int_{C_l}^{C_h} D_C(C) dC \quad (3)$$

It is assumed that the process of permeation of acid dyes in the nylon film is governed by parallel transport comprising pore and surface diffusions with bimodal sorption of Langmuir and Nernst types.² The conceptual sketch for diffusion of acid dye in nylon was given in Figure 1, where the pore-like diffusion was conveniently invoked. It is assumed that an acid dye diffuses in the porelike region and the two sorbed populations, which are termed Nernst and Langmuir populations, can diffuse along the porelike region with different mobilities (dual mobility model). It is valid to assume that there are always local equilibria between dye species in the porelike region and sorbed on the Nernst sites and between dye species sorbed on the Nernst sites (or in the porelike region) and on the Langmuir sites. Thus, the diffusion coefficient in the nylon can be given by³

$$D_C = D_p + K_N D_N^0 + \frac{K_L S D_L^0}{1 + K_L C} \quad (4)$$

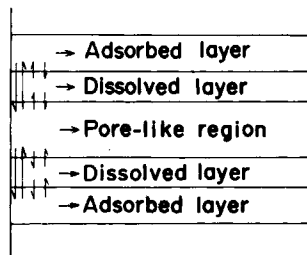


Fig. 1. Conceptual sketch for diffusion of acid dye in nylon.

After substituting eq. (4) into eq. (3) and integrating the resultant equation over C from C_l to C_h , one gets

$$\bar{D}_C = D_p + K_N D_N^0 + \frac{D_L^0 S}{C_h - C_l} \ln \frac{1 + K_L C_h}{1 + K_L C_l} \quad (5)$$

which predicts a linear relationship between \bar{D}_C and $\ln[(1 + K_L C_h)/(1 + K_L C_l)]/(C_h - C_l)$.

When the driving force for diffusion is based on a gradient of the concentration of dye in the sorbed phase, the diffusive flux can be written by

$$J = -D_q \frac{dq}{dx} \quad (6)$$

The diffusion coefficient D_q appearing in this equation can be expressed as²

$$D_q = \frac{D_p + K_N D_N^0 + K_L S(1 - \theta) D_L^0}{K_N + K_L S(1 - \theta)^2} \quad (7)$$

in terms of the parallel diffusion mentioned above. Here θ denotes the coverage of Langmuirean sorption sites and is given by

$$\theta = \frac{K_L C}{1 + K_L C} \quad (8)$$

There exists an obvious relationship between D_C and D_q as

$$D_C = \frac{\partial q}{\partial C} D_q \quad (9)$$

The dual-mode sorption and mobility concept stated above is originally presented for sorption and transport of a gas in glassy polymers.^{4,5} The sorption isotherm can be written as a combination of Henry's law sorption and Langmuir-type trapping with preexisting microvoid,⁴ viz.,

$$q = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (10)$$

where k_D , C'_H , and b are adjustable parameters, which imply the Henry's law constant, the total sorption capacity of the polymer for a penetrant gas in the Langmuir mode, and the affinity constant of the gas for the Langmuir site. Both the sorbed populations can contribute to the total diffusion flux. This approach has been called dual-mode mobility concept.⁵ The diffusion flux via the dual-mode mobility model based on the gradients of chemical potential

has been given as⁵

$$J = - \left(k_D D_D + \frac{C'_H b D_H}{1 + bp} \right) \frac{\partial p}{\partial x} \quad (11)$$

where D_D and D_H refer to diffusion coefficients of Henry's law and Langmuir modes, respectively, in the polymer film.

After integrating eq. (11) over pressure p from upstream pressure p_h to downstream pressure p_l with J constant under the steady-state, one gets the permeability coefficient expression as

$$\bar{P} = k_D D_D + \frac{C'_H D_H}{p_h - p_l} \ln \frac{1 + bp_h}{1 + bp_l} \quad (12)$$

Equation (5) is a corresponding equation in permeation of an acid dye through nylon. It should be noted that (i) $C_L > C_N$ or $C_L \gg C_N$ in the acid dye-nylon system, whereas $C_H \sim C_D$ in the gas-glassy polymer system, and (ii) $D_N^0 \sim D_L^0$ in the acid dye-nylon system, whereas $D_H < D_D$ or $D_H \ll D_D$ in the gas-glassy polymer system.

EXPERIMENTAL

The acid dye used was Kayanol Blue N2G (C.I. Acid Blue 40, molecular weight = 0.473 kg/mol, basicity = 1), which was purified following the method of Robinson and Mills.⁶ The nylon 6 film was used as the substrate. The nylon film, which was the same one as used in the previous work,² was kindly supplied by Unichika Co., Ltd., Japan, and was biaxially draw of 41 μm (density = 1.14 g/cm³). The permeation cell with two identical compartments, which was also the same one as used in the previous work,² was employed for the steady-state diffusion runs. The permeation area was 17.3 cm², and each compartment of the permeation cell had ca. 1000 cm³ in volume. The unsteady-state dyeing runs were followed by the film-roll method developed by Sekido and Matsui.⁷ The volume of dyeing liquor was about 1000 cm³ to guarantee that the concentration of dyeing liquor can be regarded as being constant during the run.

The dyeing temperature was maintained at 353 K and pHs of the dyeing liquor were adjusted at 2.3 and 3.05 by adding concentrated H₂SO₄. The concentration of the dye in the permeated solution for the permeation runs was determined by UV spectrophotometry at 594 nm. The concentration of dye taken up by the nylon film roll was determined by UV spectrophotometry at 494 nm after dissolving the dyed nylon film in formic acid.

RESULTS AND DISCUSSION

Sorption Isotherm

The concentration of dye inside the polymer, which can be determined experimentally, comprises the concentrations of dye in the porelike region and the sorbed phase. When the sorption equilibrium is established, the amount of

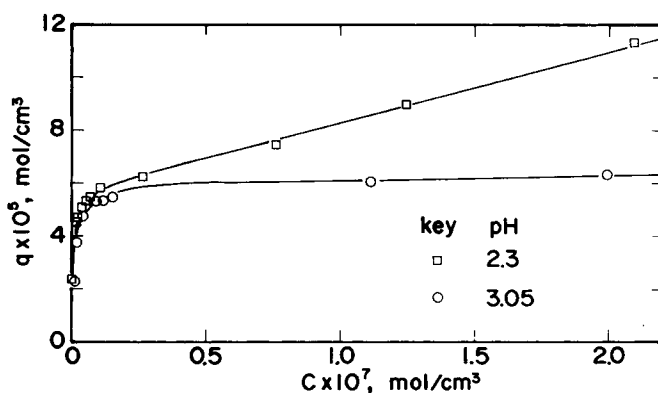


Fig. 2. Sorption isotherm of C.I. Acid Blue 40 in nylon 6 film.

dye lying in the porelike region is negligibly little compared with that of sorbed dye (less than 0.3% judging from the observed sorption equilibria depicted in Fig. 2). Therefore, the total uptake of dye at the sorption equilibrium can be regarded as the total amount of sorbed dye.

The observed sorption equilibria at pHs 2.3 and 3.05 were shown in Figure 2. The sorption isotherm at both pHs can be expressed by the sum of Langmuir-type adsorption and Nernst-type sorption, that is, dual-mode sorption of Langmuir and Nernst types,

$$q = C_N + C_L = K_N C + \frac{K_L S C}{1 + K_L C} \quad (13)$$

The optimum values of dual-mode sorption parameters (say K_N , K_L , and S) were determined by the simplex method. Table I shows the parameters determined in this way using the data in Figure 2. The solid curves in this figure were calculated via eq. (13) using the parameters given in Table I, and it is evident that they describe the experimental data well. The amount of Nernst population is found to increase with a decrease in pH.

Intrapolymer Diffusion

In all permeation runs, the total amount of dye permeated through the nylon film was linear to the permeation time over the whole period except initially as illustrated in Figure 3. This implies that the present experiment was undoubtedly operated under the steady-state conditions, and, accordingly, an integral diffusion coefficient of dye in the film can be derived by eq.

TABLE I
Dual-Sorption Parameters

pH	K_N	$K_L \times 10^{-8}$ (cm^3/mol)	$S \times 10^5$ (mol/cm^3)
2.30	272	2.41	5.59
3.05	5.31	0.834	5.71

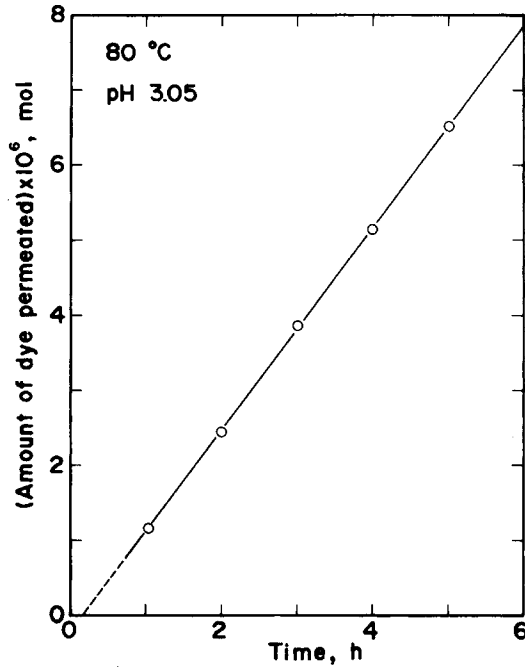


Fig. 3. Relationship between total amount of dye permeated through the nylon film and permeation time.

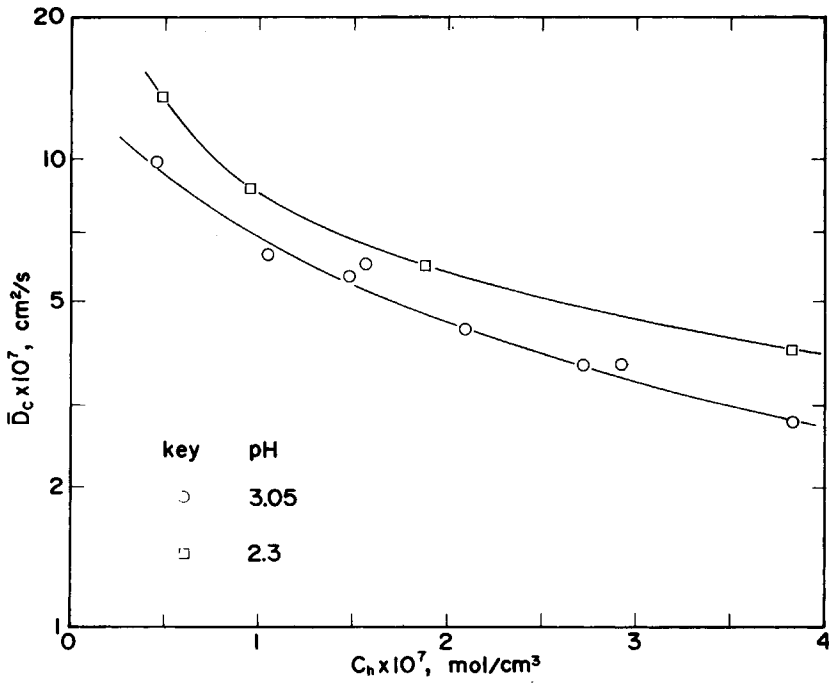


Fig. 4. Concentration dependence of integral diffusion coefficient of dye in nylon film.

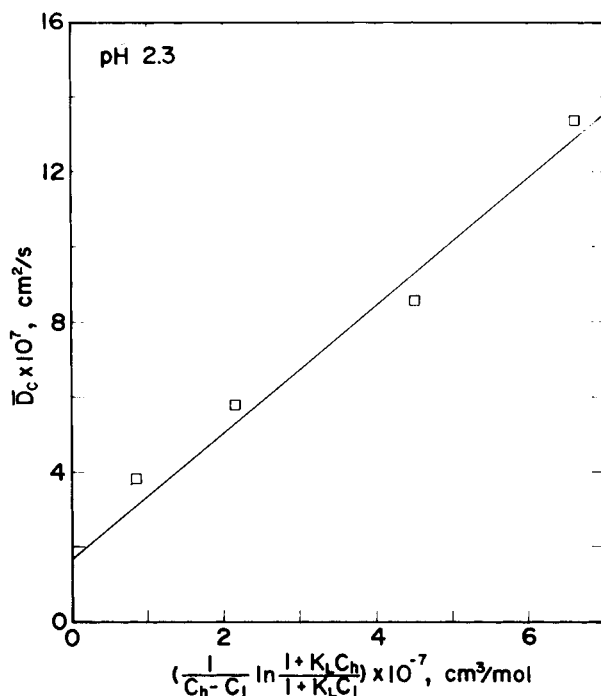


Fig. 5. Integral diffusion coefficients at pH 2.3: test of eq. (5).

(2) using the flux calculated from the slope of the relationship between amount of dye permeated and time. The integral diffusion coefficients calculated thus was plotted against C_h in Figure 4, where they can be seen to depend strongly on the concentration of dye. The values of the integral diffusion coefficient were plotted against $[1/C_h - C_i] \ln[(1 + K_L C_i)/(1 + K_L C_h)]$ on the basis of eq. (5) as shown in Figures 5 and 6. The plots in both figures give an approximately straight line. The slope of the straight line yields D_L^0 as the second column in Table II. The intercept of the line gives $D_p + K_N D_N^0$ as the third column. There seems to be a large contribution of pore diffusion because the magnitude of D_N^0 should be comparable to that of D_L^0 . After assuming that $D_N^0 = D_L^0$, the value of pore diffusion coefficient can be calculated as the fourth column in Table II. The contribution of pore diffusion is found to increase at lower pH.

As the local (point) values of diffusion coefficient of dye in the nylon substrate can be directly derived from the film-roll runs, the integral diffusion coefficients here were converted to D_C by

$$D_C = \bar{D}_C + C \frac{d\bar{D}_C}{dC} \quad (14)$$

The values of D_C calculated thus were plotted against C in Figure 7.

The values of diffusion coefficient in the nylon substrate were calculated from the observed concentration profiles in the film roll by Matano's method.⁸

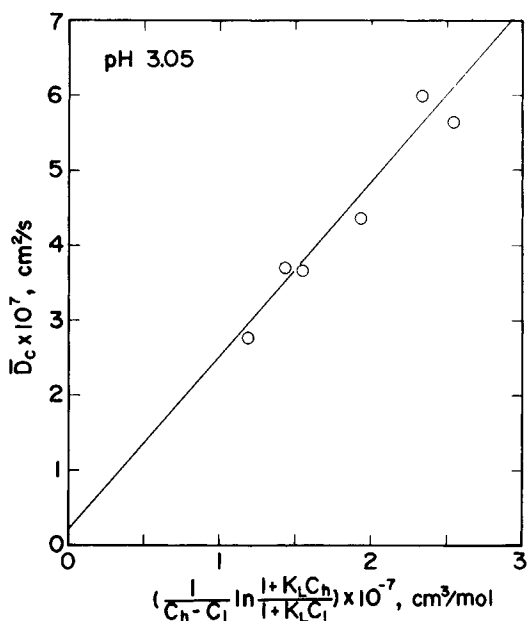


Fig. 6. Integral diffusion coefficients at pH 3.05: test of eq. (5).

The concentration of dye inside the film comprises the concentrations of dye in the porelike region and the sorbed phase, where the sorption equilibria prevail everywhere in the film. But the amount of dye in the porelike region is very little as compared with that in the sorbed phase as stated above (less than 0.3%). Thus, the diffusion coefficient by that method means D_q , which is defined by eq. (6), viz.,

$$D_q = -2 \frac{d\eta}{dx} \int_0^q \eta dq \quad (15)$$

where $\eta = x/2\sqrt{t}$.

The concentration profiles of dye inside the nylon film-roll were illustrated in Figures 8 and 9. Here, the concentration of dye inside the film, which can be determined experimentally, is replaced with that of the sorbed dye. The relation of q vs. $x/2\sqrt{t}$ at pH 2.3 is found to be somewhat dependent on time $q > 5.6 \times 10^{-5}$ mol/cm³ ($C > 10^{-8}$ mol/cm³), and a true equilibrium of sorption is not established yet in such a high concentration region. The fact which deviates a bit from Fickian diffusion for $q > 5.6 \times 10^{-5}$ mol/cm³,

TABLE II
Diffusion Parameters

pH	$D_L^0 \times 10^{10}$ (cm ² /s)	$(D_p + K_N D_N^0) \times 10^8$ (cm ² /s)	$D_p \times 10^{8a}$ (cm ² /s)
2.30	2.98	18.5	10.4
3.05	4.06	2.00	1.78

^aAssumed that $D_N^0 = D_L^0$.

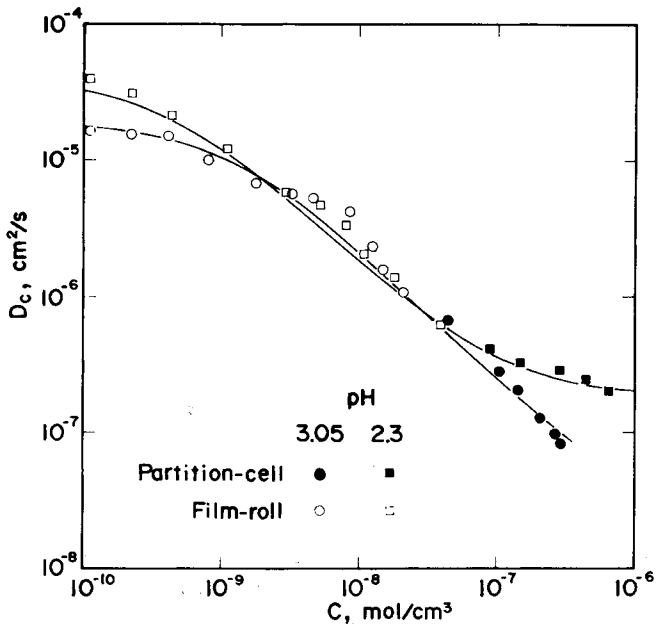


Fig. 7. Concentration dependence of diffusion coefficient of acid dye in nylon derived from partition-cell and film-roll runs.

however, was neglected during evaluation of diffusion coefficients via Matano's method. The values of D_q calculated thus were further converted to D_C by

$$D_C = \frac{\partial q}{\partial C} D_q = \left[K_N + \frac{K_L S}{(1 + K_L C)^2} \right] D_q \quad (16)$$

and plotted against C in Figure 7. The diffusion coefficients derived from both film-roll and partition-cell runs were found to be linked together. The diffusion coefficients at pHs 2.3 and 3.05 in the range of $2 \times 10^{-9} < C < 5 \times 10^{-8}$

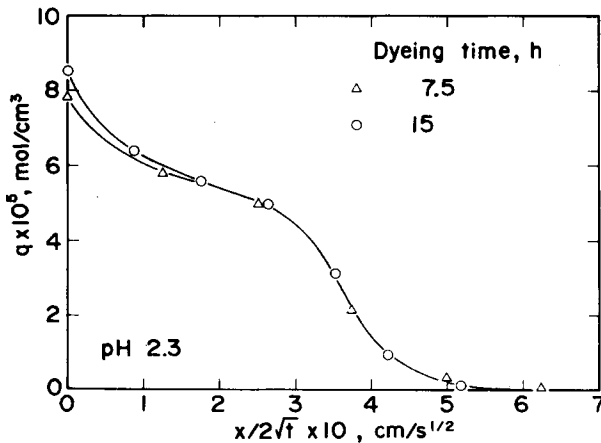


Fig. 8. Concentration profiles of dye in a rolled film of nylon at pH 2.3.

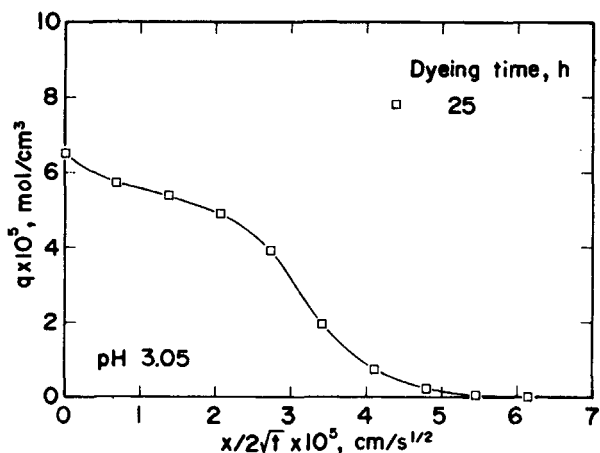


Fig. 9. Concentration profiles of dye in a rolled film of nylon at pH 3.05.

mol/cm³ were close to each other. The solid curves in this figure represent the theoretical predictions calculated by eq. (4) with the sorption parameters listed in Table I and the diffusion parameters derived from the steady-state permeation runs listed in Table II. The trend of the theoretical curve is close to the experimental data. The theoretical curves at pHs 2.3 and 3.05 are also close to each other in the range of $2 \times 10^{-9} < C < 5 \times 10^{-8}$ mol/cm³, being similar to the trend of experimental data. As the concentration of dye increases, the transport of dye inside the nylon substrate is dominated by pore diffusion as well as surface diffusion of sorbed Nernst populations.

CONCLUSION

The dyeing kinetics of an acid dye (C.I. Acid Blue 40) in a nylon 6 film at pHs 2.3 and 3.05 were investigated using partition-cell and film-roll methods. The concentration dependence of diffusion coefficient of the dye in the nylon substrate derived from both methods was interpreted in terms of parallel diffusion with bimodal sorption of Nernst and Langmuir types. The amount of Nernst population of sorbed dye was found to increase with a decrease in pH. As the concentration of dye increases, the transport of dye within the nylon substrate was dominated by pore diffusion as well as surface diffusion of sorbed Nernst population. The contribution of pore diffusion and surface diffusion of Nernst population increases at lower pH.

APPENDIX: NOMENCLATURE

- C concentration of dye in porelike region or dyebath
- C_h concentration of dye in upstream of partition cell
- C_l concentration of dye in downstream of partition cell
- C_L concentration of dye adsorbed on Langmuir site
- C_N concentration of dye sorbed in Nernst site
- d thickness of polymer film
- D_C diffusion coefficient of dye in polymer film defined by eq. (1)
- \bar{D}_C integral diffusion coefficient of dye in polymer film defined by eq. (3)

D_p	diffusion coefficient of dye in porelike region
D_q	diffusion coefficient of dye in polymer film defined by eq. (9)
D_L^0	surface diffusion coefficient of dye adsorbed on Langmuir site at the initial stage of adsorption
D_N^0	surface diffusion coefficient of dye sorbed in Nernst site
J	diffusion flux in polymer film
K_L	Langmuir-type adsorption constant
K_N	Nernst-type adsorption constant
p	pressure of penetrant gas
\bar{P}	permeability coefficient
q	concentration of sorbed dye
S	saturated concentration of adsorbed dye on Langmuir site
t	time
X	distance coordinate in polymer film
θ	fractional site saturation of dye given by eq. (8)
η	$= x/2\sqrt{t}$

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Received June 28, 1985

Accepted April 16, 1986