

Simultaneous Sorption and Diffusion of a 4-Aminoazobenzene Derivative and Its Conjugate Acid in Cellulose Membrane Carrying Sulfonic Acid Groups

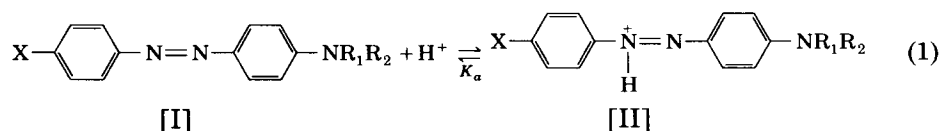
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Synopsis

An azo dye, 2-methyl-*N,N*-bis(2-hydroxyethyl)-4-aminoazobenzene (nonionic dye) and its conjugate acid (cationic dye) are simultaneously adsorbed by the cellulose membranes carrying sulfonic acid groups from a slightly acidic aqueous solution. Sorption equilibria of the nonionic and the cationic dye are described in terms of the Henry's partition and the ionic exchange mechanism, respectively; in the latter case, the ion exchange constants obtained for the membrane with sulfonic acid group content (SAG) = 261 meq/kg at 30°C are $K_{DH}^{Na} = 1.43 \times 10^{-5}$ and $K_{DH}^H = 0.542$, respectively, where Na, H, and DH refer to sodium, hydrogen, and cationic dye ions. The diffusion coefficients of the nonionic dye (D_N) and the cationic dye (D_C) in the membranes were estimated from the permeation data of the dyes through the membrane. Both D_N and D_C decrease with increasing SAG. The ratio D_N/D_C ranged in 2.2–10, the ratio increases with the SAG.

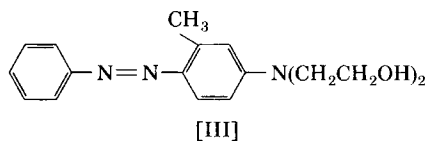
INTRODUCTION

Some of 4-aminoazobenzene derivatives dissolve in a slightly acidic aqueous solution in the form of two species, i.e., nonionic dyes [I] (nonionic species) and their conjugated acids [II] (cationic species) as described by eq. (1)¹; the latter species are characterized by the intense absorption peak in the range of 500–550 nm¹:



where X = H or NO₂, R₁ and R₂ = CH₂CH₃ or CH₂CH₂OH, and K_a = the dissociation constant of the conjugate acid. Both the nonionic and the cationic species are taken up from the solution by polymers carrying acidic groups capable of acting as dyeing sites for cationic dyes.

In this paper, the simultaneous sorption and diffusion of a 4-aminiazobenzene derivative, [III] (abbreviated as Dye III), in

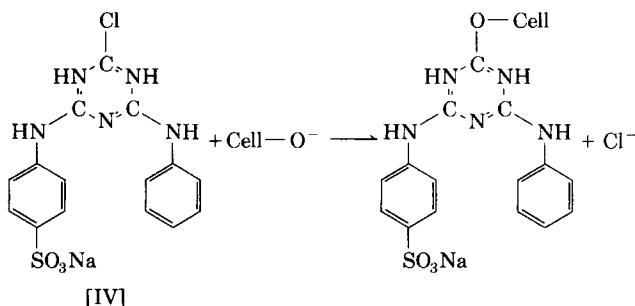


cellulose membranes carrying sulfonic acid groups from a slightly acidic solutions are studied. Thus the difference between the diffusion behavior of a nonionic and that of an ionic penetrant having a similar structure in the same polymer is revealed.

EXPERIMENTAL

Materials

Cellulose membrane carrying sulfonic acid group (abbreviated as modified membrane) was prepared by dyeing of ordinary cellulose sheets with a colorless reactive dye [IV]² as described below:



The dyeing was repeated several times according to the standard dyeing procedure for monochlorotriazine reactive dyes. Thus the modified membranes with sulfonic acid group content (abbreviated as SAG), 261 and 61.4 meq/kg of dry membrane, were prepared. The values of SAG of the dyed film was determined by means of the Methylene Blue method.³ The mean thickness of the modified membranes in the water swollen state was 4.2×10^{-3} cm.

Dye III, chemicals, and water used were the same as those used in the previous paper.^{1,4}

Measurements

Sorption Equilibrium. The membrane was soaked in a corresponding blank bath for 1–2 h before use; then the small pieces of the soaked membrane (dry weight of ca. 15 mg) and 25 mL of the aqueous solution of Dye III were placed in test tubes (50 mL capacity) fitted with silicone rubber stoppers. The test tubes were immersed in an incubator regulated to $30 \pm 0.05^\circ\text{C}$ for 3 days with gentle agitation; it was enough to attain the sorption equilibria. After that, the membranes were removed from the solutions, blotted quickly with filter papers, dried over silica gel, and then weighted. The dye on the

membranes was extracted with 50% aqueous ethanol solution. The concentration of the dye in the extracts and in the solutions was determined on Simadzu UV-150-02 spectrophotometer. The value of pH of solutions was measured on a Hitachi-Horiba F-7ss glass rod pH meter.

Absorption Spectrum of Dye III on Membranes. A membrane come to a sorption equilibrium was removed from the solution, blotted quickly with filter paper, and then the absorption spectrum of the membrane in a wet state was recorded on a Shimadzu MPS-50L spectrophotometer. The flux of the dye through the membrane at a steady state was determined by means of standard technique as used in a previous paper.⁵ Calculations were made on an NEC-PC-9801-VMO personal computer.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of the modified membrane (SAG = 261 meq/kg) dyed with Dye III at 30°C and pH = ca. 7.5 in the presence of sodium acetate of 0.02M (---) and that of the dyed membrane treated in 0.01N HCl aqueous solution at 30°C for 48 h (—). The basicity of Dye III was determined to be $K_a = 4.24 \times 10^{-4}$ L/mol at 30°C and ionic strength of 0.01 by means of an optical method¹; therefore, the broken and the solid lines in Figure 1 may be regarded as the absorption spectrum of the nonionic species and that of the cationic one, respectively.

The absorption bands of organic compounds due to $\pi \rightarrow \pi^*$ transitions undergo to a blue shift with decreasing solvent polarity.⁶ The λ_{\max} of the nonionic species on the modified membrane was determined to be 432 nm, which is shorter than that of the same dye in water, 453 nm. Similar spectral changes have been found when 4-aminoazobenzene derivatives are included in the hydrophobic cavity of β -cyclodextrin.⁷ This means that the nonionic species adsorbed on the membrane locates in less polar environment than in water.

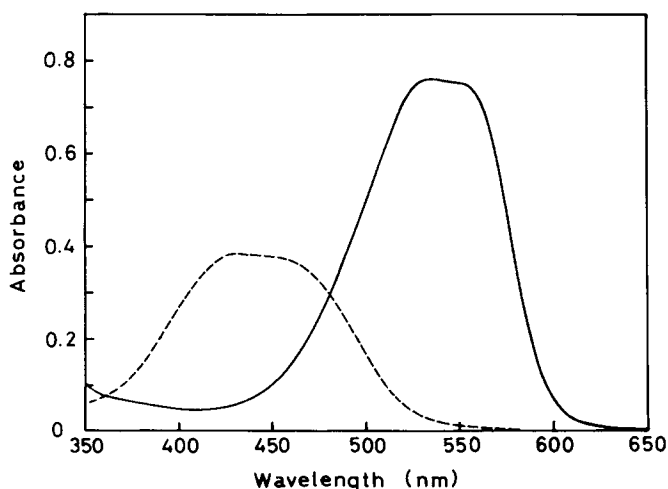


Fig. 1. Absorption spectra of Dye III and its conjugated acid on the modified cellulose membrane (SAG = 261 meq/kg) in a wet state: (---) Dye III (nonionic species); (—) conjugate acid of Dye III (cationic species).

It has been observed that the λ_{\max} of the cationic species shifts to longer wavelength on binding by a polymer carrying sulfonic acid groups in water.⁴ In general, the λ_{\max} of chromophors carrying electrical charges tends to a red shift on binding by polymers with charged groups act as the binding sites for the chromophors. For example, the λ_{\max} of acid dyes tend to red shift when the dyes are adsorbed on nylon 6 film from water.⁸ The λ_{\max} of the cationic species on the modified membrane was measured to be 535 nm, which is longer than that of the same species in water, 519 nm. This fact suggests that the cationic species bind to the charged groups in the modified membrane.

A solid line in Figure 2 shows the absorption spectrum of the modified membrane (SAG = 261 meq/kg) dyed with Dye III at 30°C and pH = 5.07 in the presence of an acetate buffer of 0.02M. This spectrum has a shoulder at about 430 nm and λ_{\max} at 534 nm, respectively; the spectrum can be considered as the superposition of two different spectrum, since it can be divided into the spectrum of the nonionic species and that of the cationic one as shown in Figure 2. This means that both the nonionic and the cationic species are simultaneously taken up by the modified membrane from the solution in spite of very low concentration of the cationic species in the solution; the concentration of the cationic species in the solution at pH = 5.07 is lower than that of the nonionic species by a factor of about 50.

It was observed that the absorbance of the dyed membrane at 534 nm, the λ_{\max} of the cationic species, decreases appreciably as the concentration of the buffer in the solution is increased. An ordinary cellulose film dyed with Dye III at 30°C and pH = 5.07 in the presence of the acetate buffer of 0.02M showed only a slight shoulder at about 535 nm, indicating that a little amount of the cationic species is taken up by the film. Therefore, it seems that the

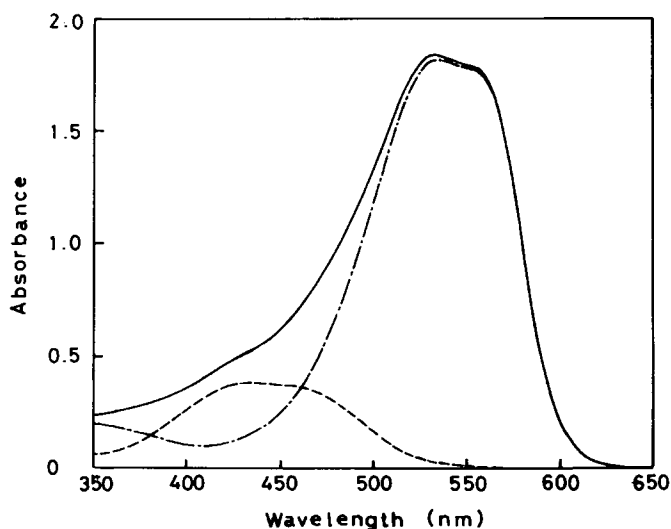


Fig. 2. Absorption spectrum of the modified cellulose membrane (SAG = 261 meq/kg) dyed with Dye III in the presence of acetate buffer of 0.02M (pH = 5.07) at 30°C: (—) absorption spectrum of the modified film dyed in aqueous solution of Dye III ($9.95 \times 10^{-5}M$) at 30°C and pH = 5.07 for 48 h; (---) absorption spectrum of the nonionic species; (- - -) absorption spectrum of the cationic species.

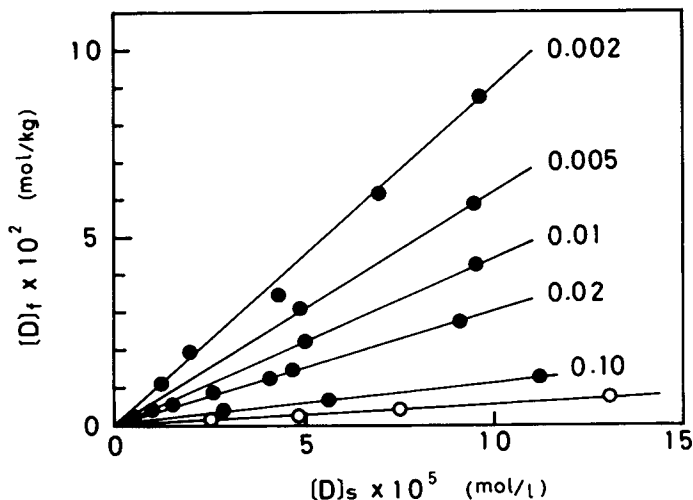


Fig. 3. Adsorption isotherms of Dye III on the modified cellulose membrane (SAG = 261 meq/kg) determined at 30°C in the presence of various concentration of acetate buffer (pH = ca. 5.07 and 7.5): (—●—) Determined in the presence of various concentration of acetate buffer (pH = ca. 5.07), the numerical values described near the lines indicate the concentration of the acetate buffer in mol/L; (—○—) determined in the presence of sodium acetate of 0.02M (pH = 7.5).

most of the cationic species bind to the sulfonic acid groups in the modified membrane and compete with the cations dissociated from the acetate buffer for binding sites, i.e., the sulfonic acid groups.

Figure 3 shows the adsorption isotherms of Dye III on the modified membrane (SAG = 261 meq/kg) determined at 30°C and pH = ca. 7.5 in the presence of sodium acetate of 0.02M (—○—) and those determined at 30°C and pH = around 5.07 in the presence of various concentration of the acetate buffer (—●—). The amount of the dye taken up by the membrane, $[D]_f$, decreased with increasing concentration of the buffer at pH = ca. 5.07. The linear isotherm obtained at pH = ca. 7.5 can be assigned to that of the nonionic species, since only the nonionic species is taken up by the modified membrane at pH = ca. 7.5 as described before. The sorption of the nonionic species by the modified membrane is described by the partition mechanism similar to those of nonionic azo dyes by cellulose.^{9,10} On the other hand, the isotherms determined at pH = ca. 5.07 should be taken as the superposition of the isotherm of the nonionic species and that of the cationic one, since both the cationic and the nonionic species are taken up by the membrane at pH = ca. 5.07 as shown in Figure 2.

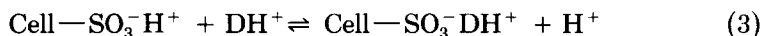
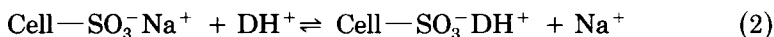
The effect of the concentration of the acetate buffer on the partition coefficient (K_p) of Dye III between water and ordinary cellulose was determined as given in Table I; the values of K_p seem to be independent of the buffer concentration in pH range, 5.04–7.5. The sorption of the nonionic species by the modified membrane may be also considered to be independent of the buffer concentration; therefore, the decrease in $[D]_f$ at around pH = 5.07 with an increase in the buffer concentration is ascribed to the decrease in $[DH^+]_f$. This finding also indicates that the cationic species compete with the cations from the buffer for the binding sites (sulfonic acid groups). In such

TABLE I
Effect of the Concentration of Acetate Buffer on the Partition Coefficient of Dye III

| Concentration of acetate buffer (mol/L) | pH (30°C) | Partition ^a coefficient (30°C) |
|-----------------------------------------|-----------|-------------------------------------------|
| 0 (Deionized water) | ca. 5.7 | 21.8 |
| 0.020 | 5.07 | 22.4 |
| 0.100 | 5.04 | 22.0 |
| 0.100 (Sodium acetate) | 7.5 | 21.4 |

^aDetermined by means of paper chromatography technique.¹⁰

cases, the sorption equilibrium is expressed as the ion-exchange equilibria^{11,12} as described below:



where $\text{Cell}-\text{SO}_3^-\text{H}^+$ and DH^+ refer to sulfonic acid group in the modified membrane and the conjugate acid (the cationic species).

The equilibria for eqs. (2) and (3) may be expressed in terms of the exchange constants given by eqs. (4) and (5), respectively:

$$K_{\text{Na}}^{\text{DH}} = \frac{[\text{DH}^+]_f [\text{Na}^+]_s}{[\text{Na}^+]_f [\text{DH}^+]_s} \quad (4)$$

$$K_{\text{H}}^{\text{DH}} = \frac{[\text{DH}^+]_f [\text{H}^+]_s}{[\text{H}^+]_f [\text{DH}^+]_s} \quad (5)$$

where $K_{\text{Na}}^{\text{DH}}$ and K_{H}^{DH} are ion-exchange constants, $[\text{DH}^+]_f$, $[\text{H}^+]_f$, and $[\text{Na}^+]_f$ refer to the quantities of the cationic species, hydrogen ions, and sodium ions in the membrane in mol/kg, and $[\text{DH}^+]_s$, $[\text{H}^+]_s$ and $[\text{Na}^+]_s$ are the corresponding concentration of each species in solution in mol/L, where, for the sake of convenience in numerical treatments, the value of the volume term of the membrane is assumed to be unity. With the electrical neutrality condition, we get

$$[\text{S}]_f = [\text{DH}^+]_f + [\text{Na}^+]_f + [\text{H}^+]_f \quad (6)$$

where $[\text{S}]_f$ refers to the total amount of the binding site in the membrane in mol/kg.

From eqs. (4)–(6), we get the following equations^{11,12}:

$$[\text{DH}^+]_f = \frac{K_L [\text{S}]_f [\text{DH}^+]_s}{1 + K_L [\text{DH}^+]_s} \quad (7)$$

$$\frac{1}{K_L} = K_{\text{DH}}^{\text{Na}} [\text{Na}^+]_s + K_{\text{DH}}^{\text{H}} [\text{H}^+]_s \quad (8)$$

where K_L is Langmuir equilibrium constant.

Equations (7) and (8) express that the value of $[\text{DH}^+]_f$ decreases with increasing $[\text{Na}^+]_s$ at a constant pH as the result of the decrease in K_L with the increasing $[\text{Na}^+]_s$. The adsorption isotherms of the cationic species on the modified membrane, which are required to characterize the sorption behavior of the dye, were made from Figure 3; the values of $[\text{DH}^+]_s$ and $[\text{DH}^+]_f$ were calculated by use of the following formulae:

$$[\text{DH}^+]_s = 10^{-\text{pH}}[\text{D}]_s / (10^{-\text{pH}} + K_a), \quad [\text{DH}^+]_f = [\text{D}]_f - [\text{DN}]_f,$$

$$[\text{DN}]_f = K_p[\text{DN}]_s, \quad \text{and} \quad [\text{DN}]_s = [\text{D}]_s - [\text{DH}^+]_s$$

where $[\text{D}]$ and $[\text{DN}]$ refer to the concentration of the total dye and that of the nonionic species, respectively, and subscripts f and s refer to the membrane and solution.

The adsorption isotherms of the cationic species on the modified membrane thus made seemed to be linear. However, the isotherms have been determined within the concentration range, $K_L \times [\text{DH}^+]_f \ll 1$; therefore, these isotherms may be regarded as the initial parts of the Langmuir's isotherms; the slopes of them give approximate values of $K_L \times [\text{S}]_f$. The values of K_L (experimental K_L 's) thus obtained for the modified membrane with SAG = 261 meq/kg are given in the fourth column of Table II, where SAG, 261 meq/kg, was used as $[\text{S}]_f$.

Equation 8 indicates that the value of K_{DH} can be obtained from the slope of the linear plot of $[\text{Na}^+]_s$ vs $1/K_L$ obtained at a constant pH. Unfortunately, the experimental K_L 's were determined at slightly different pH as given in the third column of Table II; the pH value of the acetate buffer used tends to increase slightly on dilution. Hence, the experimental K_L 's were corrected for these determined at pH = 5.07 as given in the last column of Table II. The corrections were made by means of an iterative procedure on the computer.

TABLE II
Effect of the Concentration of Sodium Ions on the Langmuir Equilibrium Constant for the Sorption of the Conjugate Acid of Dye III by the Cellulose Membrane Carrying Sulfonic Acid Groups (261 meq/kg) at 30°C

| Concentration of acetate buffer (mol/L) | $[\text{Na}^+]_s$ (g ion/L) | pH (30°C) | $K_L \times 10^{-4}$ (L/mol) | | K_p |
|-----------------------------------------|-----------------------------|-----------|------------------------------|--------------------------------------|-------|
| | | | Observed ^a | Corrected ^b for pH = 5.07 | |
| 0.002 | 0.00127 | 5.11 | 17.7 | 18.8 | 52.4 |
| 0.005 | 0.00317 | 5.09 | 11.4 | 11.7 | |
| 0.010 | 0.00635 | 5.08 | 7.75 | 7.80 | |
| 0.020 | 0.0127 | 5.07 | 4.48 | 4.48 | |
| 0.100 | 0.0637 | 5.04 | 1.06 | 1.05 | |

^a Determined at pH given in the third column in the presence of the buffer given in the first column.

^b Corrected for the value determined at pH = 5.07 in the presence of the buffer given in the first column by means of an iterative method.

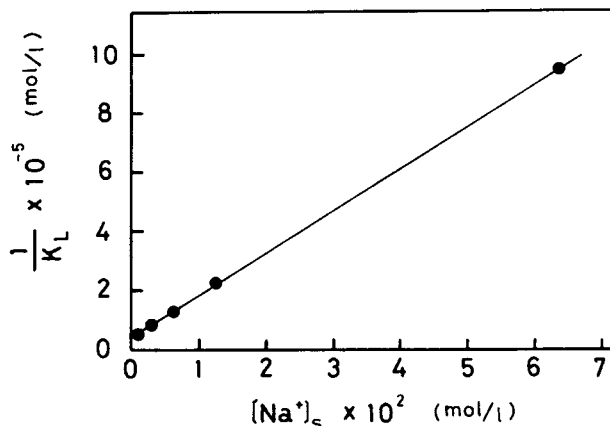


Fig. 4. Plot of eq. (8) for the conjugate acid of Dye III on the modified cellulose membrane (SAG = 261 meq/kg) at 30°C.

Figure 4 shows the plot of eq. (8) made from the corrected K_L 's, from which the ion exchange constants, $K_{\text{DH}}^{\text{Na}} = 1.43 \times 10^{-3}$ and $K_{\text{DH}}^{\text{H}} = 0.452$ were obtained. The fairly large value of the latter constant obtained is indicative of the fact that the sulfonic acid groups in the modified membrane (SAG = 261 meq/kg) dissociates partly at pH = 5.07. The partial dissociation of sulfonic acid groups in polymer matrixes has been already observed as shown in Table III, the values of K_{DH}^{H} obtained here are similar to those for the binding of the cationic species by β -naphthalenesulfonic acid and formaldehyde condensates.⁴

The diffusion coefficient of dyes in membranes is often assessed from the permeation data of the dyes, time lag (Θ_L), and flux of the dye through the membrane at a steady state (J), and concentration profiles of the dyes in the membranes.

Figure 5 shows the concentration profile of Dye III in the modified membrane (SAG = 261 meq/kg) determined by means of the film roll method at 30°C and pH = 5.07 (0.02M acetate buffer). The profile seems to indicate that the diffusion is described as a simple Fickian since the curve calculated by eq. (9) using $D = 2.84 \times 10^{-9} \text{ cm}^2/\text{s}$ gives good fit to the experimental points; the value of D was obtained by means of the curve fitting by use of

$$[\text{D}]_t = \text{erfc} \frac{x}{2(Dt)^{1/2}} \quad (9)$$

where x and t refer to the distance from the membrane surface and time of diffusion, respectively.

However, the value of D obtained above should be taken as a mean value of the diffusion coefficient of the nonionic species and that of the cationic species, since both species are taken up by the modified membrane under the operating condition of the profile measurement (30°C, pH = 5.07).

The values of diffusion coefficient of Dye III in the modified membrane determined from the permeation data by use of eqs. (10) and (11) are given in

TABLE III
Ion-Exchange Constant for Various Dye-Polymer Systems

| Dye | Polymer | Temp (°C) | pH | $K_{D^{\text{Na}}}$ (or $K_{D^{\text{Na}}}$) | $K_{D^{\text{H}}}$ (or $K_{D^{\text{H}}}$) | Reference |
|---------------------------------|-----------------------------------------------------------------------|--------------|-----------|--------------------------------------------------|------------------------------------------------|-----------|
| Dye III | Cellulose membrane carrying sulfonic acid groups ^a | 30.0 | 5.07 | 1.43×10^{-3} | 0.452 | This work |
| | β -Naphthalene sulfonic acid and formaldehyde condensates | 20.0 25.0 | 5.01-5.51 | 7.3×10^{-6} 6.5×10^{-6} | 0.59 0.60 | 4 |
| Monooxadine dye (C.I. 51000) | Polyacrylonitrile fibers | 98.9 | 4.2 | $5.4-9.1 \times 10^{-4}$ | 0.078-0.12 | 11 |
| C.I. Basic Blue 22 | Film of a copolymer | 99.8 | | | 8.70×10^{-3} | 12 |
| C.I. Basic Red 14 | (acrylonitrile, ca. 93%, | 99.1 | 3.4 | | 1.01×10^{-3} | |
| C.I. Basic Red 24 | vinyl acetate ca. 7%) | 94.6 | | | 1.93×10^{-3} | |
| C.I. Basic Violet 19 | | 99.3 | | | 7.62×10^{-3} | |

^aSAG = 261 meq/kg.

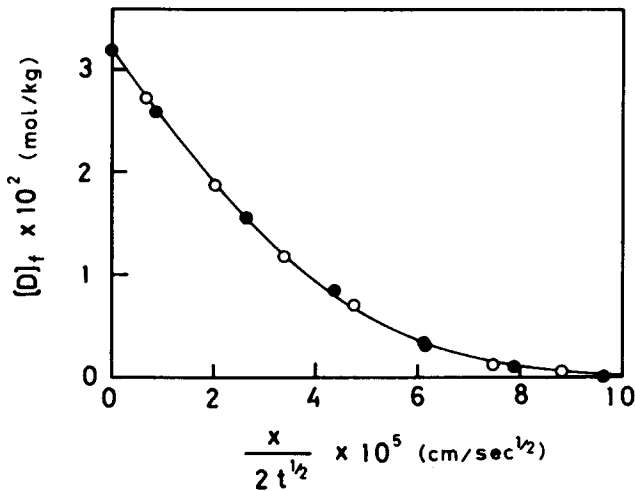


Fig. 5. Concentration profile of Dye III in the modified cellulose membrane (SAG = 261 meq/kg) determined means of the film roll method. The film rolls were dyed in aqueous solution of Dye III ($1.1 \times 10^{-4}M$) in the presence of acetate buffer of 0.02M at 30°C and pH = 5.07: (●) dyed for 240 min; (○) dyed for 400 min.

the 10th and 11th columns of Table IV. The values of D thus determined are somewhat smaller than those determined from the profile under the same conditions; however, the values of D determined from the permeation data are also the mean values of the nonionic and the cationic species:

$$-J = D \frac{dC}{dx} \approx \frac{\Delta[D]_f}{l} \quad (10)$$

$$D = \frac{l}{6\Theta_L} \quad (11)$$

where dC/dx , $\Delta[D]_f$, and l refer to the concentration gradient of the dye in the membrane at the steady state, the difference in the concentration of the dye in the membrane at each surface, and the thickness of the membrane in the swollen state, respectively.

In order to obtain the diffusion coefficient of the nonionic species (D_N) and that of the cationic species (D_C) in the modified membranes separately, the data given in Table IV were analyzed as follows.

The total flux J is given by eq. (12) when the coupling between the diffusion of nonionic species and that of cationic one can be neglected:

$$-J = D_N \frac{\partial [DN]_f}{\partial x} + D_C \frac{\partial [DH^+]_f}{\partial x} \quad (12)$$

where $\partial [DN]_f / \partial x$ and $\partial [DH^+]_f / \partial x$ refer to the concentration gradient of each species in the membrane at the steady state.

TABLE IV
Permeation Data for Dye III through the Cellulose Membrane Carrying Sulfonic Acid Groups and the Ordinary Cellulose Membrane at 30°C

| Sulfonic acid group content (meq/kg) | Concentration of acetate buffer (mol/L) | pH (30°C) | $\Delta[D]_s \times 10^5$ (mol/L) | $\Delta[DN]_f \times 10^3$ (mol/kg) | $\Delta[DH^+]_f \times 10^3$ (mol/kg) | $J \times 10^{11}$ (mol/cm ² s) | $\Theta_L \times 10^2$ (s) | Dapp $\times 10^9$ (cm ² /s) | |
|--------------------------------------|-----------------------------------------|-----------|-----------------------------------|-------------------------------------|---------------------------------------|--------------------------------------------|----------------------------|-----------------------------------------|------|
| | | | | | | | | Time lag | Flux |
| 261.4 | 0.002 | 5.11 | 9.56 | 5.11 | 82.3 | 2.71 | 18.34 | 1.60 | 1.30 |
| | 0.005 | 5.09 | 9.37 | 5.05 | 53.8 | 2.11 | 16.77 | 1.75 | 1.51 |
| | 0.010 | 5.08 | 9.49 | 5.08 | 37.7 | 1.73 | 14.19 | 2.07 | 1.70 |
| 64.1 | 0.020 | 5.07 | 9.15 | 4.90 | 23.7 | 1.49 | 12.61 | 2.33 | 2.19 |
| | 0.100 | 5.04 | 9.77 | 5.23 | 9.58 | 1.22 | 7.01 | 4.19 | 4.32 |
| | 0.002 | 5.11 | 9.61 | 2.64 | 4.53 | 1.76 | 2.65 | 11.1 | 10.1 |
| 0 ^a | 0.005 | 5.09 | 9.32 | 2.56 | 3.60 | 1.65 | 1.62 | 18.1 | 11.3 |
| | 0.020 | 5.07 | 9.14 | 2.51 | 1.37 | 1.18 | 2.17 | 13.5 | 12.8 |
| | 0.020 | 5.07 | 9.47 | 1.87 | 0 | 1.22 | 1.16 | 25.3 | 27.4 |

^a Ordinary cellulose membrane.

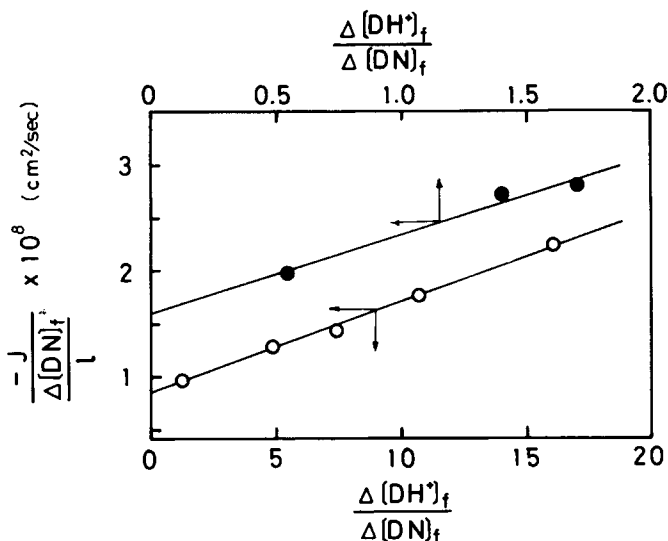


Fig. 6. Plot of eq. (13) for the permeation of Dye III through the modified cellulose membranes at 30°C: (—○—) the modified membrane (SAG = 261 meq/kg); (—●—) the modified membrane (SAG = 64.1 meq/kg).

Assuming $\partial[\text{DN}]_f/\partial x = \Delta[\text{DN}]_f/l$ and $\partial[\text{DH}^+]_f/\partial x = \Delta[\text{DH}^+]_f/l$, we get

$$\frac{-J}{\Delta[\text{DN}]_f/l} = \frac{\Delta[\text{DH}^+]_f}{\Delta[\text{DN}]_f} D_C + D_N \quad (13)$$

where $\Delta[\text{DN}]_f$ and $\Delta[\text{DH}^+]_f$ refer to the difference in the concentration of the nonionic species at each surface of the membrane and that of the cationic species at a steady state, respectively.

Figure 6 shows the plot of eq. (13), $\Delta[\text{DH}^+]_f/\Delta[\text{DN}]_f$ vs. $-J/\Delta[\text{DN}]_f/l$, for the permeation of Dye III through the modified membrane. From the slope and the intercept of the regression lines, the values of D_C and D_N were obtained are given in Table V. The value of D_C is far smaller than that of D_N and the ratio of D_C/D_N decreases with an increase in sulfonic acid group content in the modified membrane.

TABLE V
Diffusion Coefficients of the Nonionic and the Cationic Species in the Modified Membrane Carrying Sulfonic Acid Groups

| Sulfonic acid group content (meq/kg) | $D_C \times 10^{10}$ (cm ² /s) | $D_N \times 10^{10}$ (cm ² /s) | D_N/D_C |
|--------------------------------------|-------------------------------------------|-------------------------------------------|-----------|
| 261 | 8.5 | 85 | 10 |
| 64.1 | 73 | 160 | 2.0 |
| 0 | | 274 ^a | |

^a Determined from the flux using eq. (10).

The diffusion behavior of acid dyes in polyamide has been successfully described in terms of the dual sorption mechanism,¹³⁻¹⁶ the same dye taken up by the polymer by two different ways, Langmuir's type adsorption and Henry's low dissolution; a dye moves in polyamide as the two different species, i.e. adsorbed and dissolved species with diffusion coefficients D_L and D_P , respectively. It was deduced that the ratio of D_P^0/D_L^0 is not likely greater than unity for the diffusion of acid dyes in nylon 6,¹³ where superscript 0 denotes the limiting value for $[D]_f = 0$. For example, the value of $D_P^0/D_L^0 = 0.7$ was found for the diffusion behavior of C.I. Acid Orange 7 in nylon 6 at 50°C, pH = 2.2¹⁵; it is far smaller than the values of D_N/D_C obtained here. However, these D_P^0/D_L^0 values were estimated for the diffusion of dyes at very low pH at which the over dyeing can occur¹⁷; under this condition, the dissolved species are also attracted by the charged amido groups in the polymer as the adsorbed species are attracted by the charged amino end groups. On the other hand, the nonionic species are adsorbed on the modified membrane by non-electrostatic forces. When a trisulfonic acid dye, sulfanilic acid → R acid, is adsorbed by nylon 6 at 50°C and pH = 3.6, at which the overdyeing can occur only very slightly,¹⁷ the ratio $D_P^0/D_L^0 = 3.5$ has been estimated,¹⁶ which is in accord with the value of D_N/D_C obtained in this study.

The results shown in Table V seem to indicate that the diffusion coefficient of an ionic dye in the polymer carrying opposite charged groups is far smaller than that of a nonionic dye in the same polymer when the structure of the ionic dye is similar to that of the nonionic dye.

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Received May 31, 1988

Accepted July 13, 1988