

Sorption and Permeation of Orange II Through Nitrocellulose-Poly (vinylamine) Blended Membranes

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니트로셀룰로오스-폴리비닐아민 혼합膜에 의한 Orange II의 收着과 透過

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Abstract—Nitrocellulose [NC]-Poly(vinylamine) [PVAm] blended membranes with the change of amino group contents were prepared. The sorption and permeation of a mono-sulfonic acid dye, Orange II, in the membranes were investigated by the steady-state permeation method at 50°C and pH 2.2. The results were discussed in the framework of dual sorption and diffusion theory. It was found that the sorption isotherms comprise a partition and two Langmuir type adsorption having similar binding constants. One of the latter sorption modes is due to unknown adsorption sites in NC and the other is due to the amino groups in PVAm. Apparent diffusion coefficients for collective P and L dye species, D_P and D_L , were obtained. Interpretation of D_P values leads to two modes of partitions; one is such that dye is immobilized in NC and the other is the dissolution of the dye into the internal water phase.

Introduction

In the acid dyeing of nylon, the binding of dye anions by amino groups in nylon takes place in an ion-exchange mechanism¹⁻³). Overdyeing is, however, often encountered in the dyeing of nylon at lower pH, i.e., the total uptake of dye sorbed exceeds the equivalent amino end group content in nylon^{1, 3-5}).

In the previous papers,^{6, 7}) the sorption and diffusion of three anionic dyes in nylon 6 have been discussed in the light of the dual mechanism from the results obtained by the film-roll method and the steady-state permeation method. The diffusivity of the adsorbed species, (L), on the charged amino group in nylon, was found to be of primary importance in determining the concentration dependence of the apparent diffusion coefficients.

This study is presented to obtain detailed infor-

mation about the dual mechanism of sorption and diffusion of acid dyes in the NC-PVAm blended membranes. NC is known to form a porous phase upon formation of a film, thereby the diffusion of salts and probably dye ions takes place through the tortuous water channels contained in it.

The concern of this study was focused on the elucidation of the effect of the charged amino sites in the membrane and on the extension of the dual sorption and diffusion concept to a membrane having certain configurational aspects that pores may play a predominant role for dye transport.

Experimental

Materials

NC used in this work was supplied by Daicel Co. (RS-120, N:11.85%) and was purified by reprecipitating from Methanol-Ether. Poly(vinyla-

mine) was obtained by the Hofmann decomposition from Poly(acrylamide) in a usual method^{8,9}. The acid dye used was Orange II (C.I. Acid Orange 7, Merck Co.) and purified by reprecipitation method.

Membrane preparation

The casting solutions were prepared by dissolving the requisite quantity of NC and PVAm in a mixture of Ether and Methanol (2:3 vol.). The content of PVAm in the membranes was controlled as $1.9\text{--}7.6 \times 10^{-5}$ eq amino group/g. These solutions were cast on the glass plate at 25°C, for 8 minutes, and the glass plate was immersed in deionized water for one hour. The membranes thus obtained were equilibrated in pH 2.2 aqueous Hydrochloric acid before use.

Sorption isotherm

Equilibrium sorption isotherms were determined by soaking the membranes in the dye baths containing HCl to maintain pH 2.2 at 50°C for 24 hr. The membranes removed from the dye baths after equilibration was weighed and the uptake of dye was determined spectrophotometrically by the initial and final concentrations of the dye bath.

Permeability coefficients

To determine the permeability coefficients of dye anions through the membrane, the steady-state permeation method was used. As shown in Fig. 1, the permeation cell is consisting of two compartments by connecting a large volume cell to the upstream side in order to maintain the constant concentration during the experiment. 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

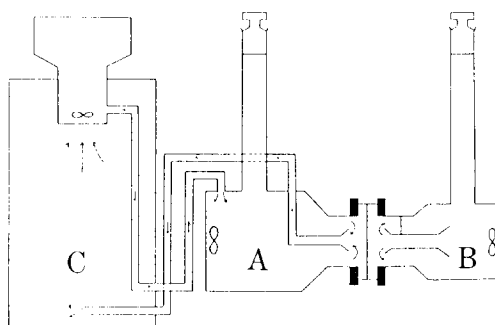


Fig. 1. Permeation cell.

to ensure infinite bath conditions in the case of dilute solutions (lower than ca. 10^{-5} mol/l). The agitation of the dye solutions was as efficient as possible to minimize the stagnant boundary solution layers on the surface of the membrane. In the steady state, the amount of the permeated dye through the membrane against time should give a linear relationship, which gives the permeability coefficient P . The results obtained are shown in Table 1.

Results and Discussion

The sorption and diffusion of anionic dye in nylon can be explained by considering the two thermodynamically distinct populations: "adsorbed" (L) and "dissolved" (P), i.e., a Langmuir type adsorption and a Nernst type partition. In the previous papers^{6,7}, it has been confirmed that the sorption and diffusion of acid dyes in nylon can be well explained by these mechanisms.

As can be seen in Fig. 2, all of the curves indicate the dual mode sorption. From this isothermal sorption curves, K_p , K_L , and S values were deter-

Table 1. Parameters and characteristics for Orange II in each membrane

Membranes	Amino group [eq/g]	K_p [l/g]	K_L [l/mol]	$S \times 10^5$ [eq/g]	Density	Water content [%]
C-0	0	0.13	1.0×10^5	2.80	1.48	25.9
C-2	1.9×10^{-5}	0.14	2.4×10^5	3.77	1.42	27.1
C-4	3.8×10^{-5}	0.28	2.8×10^5	6.15	1.49	39.4
C-8	7.6×10^{-5}	0.33	3.3×10^5	9.76	1.41	41.2

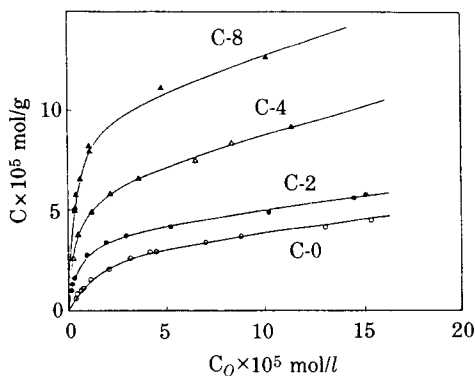


Fig. 2. Isothermal sorption of Orange II by NC-PVAm Membranes.

Table 2. Permeability coefficient against dye concentration in membranes

\$C_{oA}\$ [mol/l]	C-2 \$P \times 10^6\$ [cm\$^2\$/min]	C-4 \$P \times 10^5\$ [cm\$^2\$/min]	C-8 \$P \times 10^5\$ [cm\$^2\$/min]
\$1.00 \times 10^{-4}\$	0.81	0.68	1.81
\$8.00 \times 10^{-5}\$	0.85	0.84	2.14
\$6.00 \times 10^{-5}\$	1.05	1.00	2.37
\$4.00 \times 10^{-5}\$	1.20	1.32	2.91
\$2.00 \times 10^{-5}\$	1.68	1.89	4.69
\$1.00 \times 10^{-5}\$	2.33	2.75	6.66

mined by the least square method. The results are summarized in Table 2. It is known that the saturation values (S) of acid dyes in nylon is favorably in agreement with the amino group content. However this is not the case for NC-PVAm blended membranes, since the apparent S values exceed the stoichiometric amount in PVAm. It is worthwhile to mention that the sorption isotherm by NC reference membrane, C-O, has a same pattern of the curves. As shown in Fig. 2, the sorption of NC membrane contributes to that of NC-PVAm membranes, even though NC itself has been considered to be uncharged. As judged from the S values, C-O membrane may have a site for Langmuir type adsorption per ca.200 residues of the glucose unit. The nature of such site, however, was not specified in the present study. By subtracting the sorption by C-O from the sorption isotherms of C-2, C-4, and C-8 membranes, the resultant S values are

0.97, 3.35 and \$6.96 \times 10^{-5}\$ eq/g, respectively. These values make ca.51, 88, and 90% of the incorporated equivalency of PVAm. This increase of available site fraction accompanies the increase in the water content as 27.1, 39.4, and 41.2%.

\$K_p\$ and \$K_L\$ is increased with the increase of amino group content in the membrane. The comparison of \$K_p\$ with the water content in the membrane gives an idea for the nature of the partition type sorption. The observed \$K_p\$ of C-O membrane indicates that the dye dissolved in the internal water is adsorbed on the pore surface and/or dissolved in the NC phase. The exact partition should be

$$C_p = K_p C_o = (K_p^c + W) C_o = C_p^c + C_p^w \quad (1)$$

where W is the water content and \$K_p^c\$ is the partition coefficient between the internal water and NC phase including the pore surface, and \$C_p^c\$, \$C_p^w\$ are the dye concentrations in the NC and the internal water phases, respectively.

Remembering these multifold mechanism in P and L type sorptions, we can express the observed diffusion coefficient and the integral permeation coefficient by the following equations^{6, 10};

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

$$\bar{P}(C) = K_p D_p^A + \frac{D_L^A S}{z(C_{oA} - C_{oB})} \ln \frac{1 + K_L C_{oA}}{1 + K_L C_{oB}} \quad (3)$$

When \$C_{oA} \gg C_{oB}\$ and \$1 + K_L C_{oA} \gg 1 + K_L C_{oB}\$, eq. (3) is conveniently written by

$$\bar{P}(C) = K_p D_p^A + \frac{D_L^A S}{z C_{oA}} \ln(1 + K_L C_{oA}). \quad (4)$$

Here the superscript A means the apparency, S is the saturation value, z the basicity of dye anion, and \$K_p\$, \$K_L\$ are constant, \$D(C)\$ is the differential diffusion coefficient, and \$C_{oA}\$, \$C_{oB}\$ are dye concentrations in the solutions on each side of the membrane, i.e., in half-cell A and B, respectively.

In Fig. 3, linear plots of \$\bar{P}(C)\$ against \$1/C_{oA} \ln(1 + K_L C_{oA})\$ are shown as predicted by eq. (4). Table 3 summarizes \$D_p\$ and \$D_L\$ obtained from these plots. These values increase with the introduction of amino group in the membrane. Such effects should be primarily attributed to the increase of

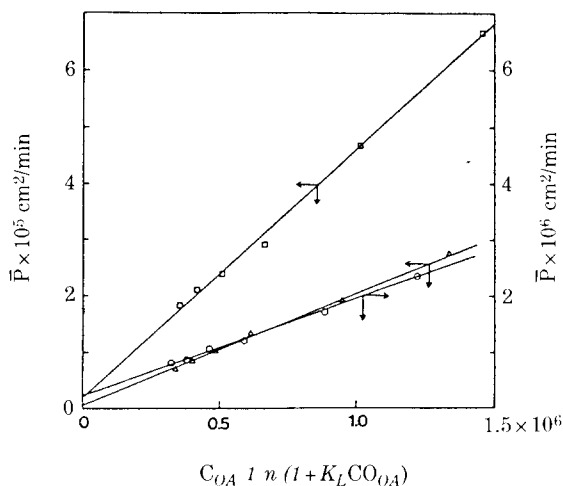


Fig. 3. Linear plots of integral permeability coefficient.

○: C-2, △: C-4, □: C-8 Membrane

water content in the membrane.

As discussed before, dyes sorbed by P mode comprise two species; one dissolved in the internal water and the other sorbed by NC. If the former is assumed to be the only species that can diffuse with a diffusion coefficient, D_p' , comparable to that in water and also if the latter is immobilized by NC, the flux J_p is written by

$$J_p = D_p^A \frac{\partial C_p}{\partial x} - D_p' \frac{\partial C_p^*}{\partial x}$$

hence $D_p' = D_p^A \frac{\partial C_p}{\partial C_p^*} - D_p^A K^c / W$ (15)

where C_p^* is the dye concentration in the internal water phase. D_p' are calculated as 0.59, 1.19, and 3.87×10^{-6} cm²/min for C-2, 4, and 8 membrane, respectively. Tortuosity factors,^{11,12} $[1 - \theta_p] / (1 + \theta_p)^2$, where θ_p is the polymer fraction in the membrane, are calculated as 0.0245, 0.0599, and 0.0671 for these membranes, respectively. The diffusion coefficients in the internal water are thus calculated to be 2.4, 2.0, and 5.8×10^{-5} cm²/min, which can be compared with the diffu-

sion coefficient of Orange II in water¹³). Therefore, the assumption made for P mode dyes for this discussion seems to be valid; those dyes dissolved in the internal water diffuse as in the external water and the other dyes taken up by NC is immobilized. Since the amount of the latter dyes is more than hundred times of the former, the diffusion coefficient for the later dyes should be less than 1/1000 of D_p' or ca. 1×10^{-9} cm²/min.

D_L values also show a steep increase with PVAm content. In definition, D_L is the diffusion coefficient of the dye that is under close interaction with the positively charged amino groups of PVAm. The increase in D_L implies that the microscopic states of PVAm molecules, e.g., the extent of hydration and the juxtaposition, should greatly influence the value. Between C-4 and C-8 membranes, the water content increases slightly while D_L is doubled. Therefore a possible explanation for the increase in D_L is that PVAm molecules gather to form a phase in the membrane, where the hydration is rather restricted but the delivery of the dye anions is rather facilitated.

Finally, the parameters of sorption and diffusion of Orange II in NC-PVAm membrane are discussed in reference to those in nylon. D_p and D_L values for NC-PVAm membrane are in the same order with each other, which agrees fortuitously with the nylon case. The absolute values of D_p can not be compared with the nylon because D_p contains two equilibrium constants as discussed above. D_L values for NC-PVAm membrane, $0.3\text{--}4.8 \times 10^{-9}$ cm²/min, are also comparable with that for nylon, 9.5×10^{-9} cm²/min. In nylon, charged amino sites are ca. 25 Å apart from each other. This being taken account, the smaller D_L for C-2 membrane seems to advocate the aforementioned interpretation that PVAm molecules which convey charged sites of ca. 3 Å apart, are dispersed

Table 3. Diffusion coefficient for Orange II in each membrane

Membrane	D_L [cm ² /min]	D_p [cm ² /min]	D_L [cm ² /min]	α^*
C-2	3.33×10^{-10}	1.15	0.32	65
C-4	2.14×10^{-10}	1.68	2.15	62
C-8	4.76×10^{-9}	4.83	4.76	98

* $\alpha = (K_L/K_p)S$

separately in the bulk NC phase. The proximity of D_L for NC-PVAm membranes and D_L for nylon seems to be a consequence of the significant hydration of the amino groups in both NC-PVAm and nylon membranes: the rate determining step of the diffusion of L mode dye is the escape from the electrostatic restraint given by the positively charged site. K_P and K_L values of NC-PVAm membranes, are also apparent values. The K_L values, $1-3 \times 10^5$ (1/mol) are somewhat smaller than that for nylon, 6.4×10^5 . Two reasons for this reduction may be cited: one is the inclusion of NC's binding sites which have a smaller binding constant, and the other is the arrangement of PVAm charges in a linear array. The former gives rise former gives rise to an lowering of K_L according to NC content of the membrane. In fact, K_L approaches, with PVAm content, ca. 4×10^5 , which may be taken as the intrinsic K_L of PVAm for the dye. The latter reason is discussed based on the well known fact that polyvinylc electrolytes attract counter-ions having smaller intrinsic diameter more strongly. Thus a charged site on PVAm molecule interact with chloride anion more strongly than an isolated site in nylon. This entails the dye anion certain difficulty in replacing the chloride and hence K_L value becomes smaller. In terms of the dual diffusion concept, another characteristic of NC-PVAm membrane is the small $\alpha (=K_L/K_P S)$ value. The predicted variation of the (differential) diffusion coefficient in C-2 membrane is depicted in Fig. 4 by using $\alpha = 65$ and D_P and D_L value. (see Table 3).

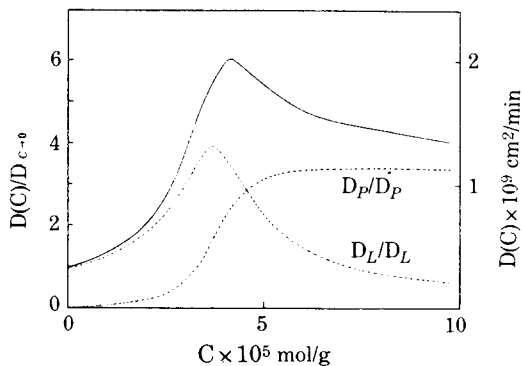


Fig. 4. Concentration dependence of diffusion coefficient of C-2 Membrane.

The abscissa is the dye concentration in C-2 membrane, the right-hand ordinate is the diffusion coefficient, $D(C)$, and the left-hand ordinate represents the relative diffusion coefficients, $D(C)/D_{C=0}$, where $D_{C=0}$ is the diffusion coefficient at zero concentration. The broken lines give the relative diffusion coefficients of the respective species. The solid line is the sum of the D_P and D_L contributions. The maximum diffusion coefficient is given above the saturation value. The gradual decrease of the diffusion coefficients after that is caused by the fact that $D_P > D_L$.

From the above results, it is quite clear that the diffusivities of D_P contribute to the overall apparent diffusion coefficients. In the case of nylon, the diffusivity of the adsorbed species, L , is the primarily important factor in determining the concentration dependence of the diffusion coefficients but, in the case of small α value, D_P exerts a great effect upon the overall diffusion coefficient beyond saturation value, in particular.

Summarizing these discussions, we can conclude that sorption and diffusion of Orange II in NC-PVAm membrane are multi-modal. The P mode sorption comprises partitions of the dye into the internal water and NC phases. The L mode sorption also comprises two modes with comparable energies for adsorption. However, the frame of the dual sorption and diffusion concept can be applied to the overall sorption and permeation data.

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