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# New Transport Phenomenon. Enhanced Transport into a Membrane Due to the Presence of Polyelectrolyte

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The transport of chromophore into a membrane in the presence of polyelectrolyte is enhanced much as it is in the presence of simple salt. The presence of polyelectrolyte with different kinds of counterions seem to modify this observed enhancement. The differences in enhanced transport into the cellulose membrane in the presence of polyelectrolyte may suggest a new model for reinterpretation of the transport phenomenon in a biological system.

In previous publications,[1,2] it has been shown by Donnan membrane equilibrium theory that the adsorption of chromophore on cotton increases with addition of polyelectrolyte in the bulk solution. Thus, the chromophore is accumulated in the internal solution of cellulose due to the presence of polyelectrolyte which is not able to enter into the pores of the cellulose. One might expect, therefore, to find progressively enhanced transport of chromophore into a cellulose membrane with addition of polyelectrolyte. We here report the effect of polyelectrolytes and their counterions on transport of chromophore into a cellulose. There have been no reports of studies concerned with the transport of simple ions and chromophores into a membrane in the presence of polyelectrolyte. Enhanced transport of chromophores into a membrane because of the presence of polyelectrolyte is similar to such enhancement in the presence of simple salt. The dependence of such transport on different kinds of counterion suggest a new type of transport phenomenon that may provide useful information for a model for transport into the cell membrane of biological systems. Specifically, the uptake of chromophore into a cellulose membrane in the presence of polyelectrolyte with different kinds of counterion on the polymer chain, when compared with the sodium salt, has been sizably enhanced to provide the basis for the above statement.

## Experimental

*Materials.* Chromophore(C.I. Direct Yellow 12, C.I. Direct Red 2 and, C.I. Direct Blue 15) was obtained and purified as described elesewhere.[2,3] Sodium alginate(NaAlg, MW: 10,000)(Kamogawa Kasei Co.), sodium polyacrylate(NaPA, MW: 37,000), sodium polymethacrylate(PMA, MW: 260,000), and sodium polystyrenesulfonate(NaPSS, MW: 69,000) (Polyscience Co.) were purified as described eleswhere[2] and converted to different kinds of counterion($NH_4^+$, $K^+$, and $Cs^+$) with the corresponding hydroxide or carbonate, respectively. The conversion of counterion was above 90% by the analysis of Hitachi 50A atomic absorption spectrophotometer. In our experiment conditions, alginate(Alg) which does not interact with chromophore or cellulose,[2] was used as the biological polyelectrolyte. Commercial cotton and cellulose membrane(cellophane film) were soaked in boiled deionized distilled water for 1 and 3 h, respectively. Then, cotton was treated with methanol and cellulose membrane was washed with deionized distilled water. Carboxyl group contents of cotton and cellulose membrane determined by iodometry were 4.00 and 62.5 meq/dg, respectively.[2,3] T. Vickerstaff indicated that the water content of cellulose and cellulose membrane were 0.22 and 0.33 l/kg, respectively, consisting with the volume term of substrate(V) (see, Eq. 4) theoretically determined.[5] The degree of dissociation constant ($\alpha$) of polyelectrolytes was measured by the method of selective ion sensitive electrodes of Orion Research 94-11.

*Uptake and Transport of Chromophore to Cellulose.* Uptake of chromophore for cotton and cellulose membrane was carried out at temperature of 90±0.5 °C for 6 h and 25±0.5 °C for 48 h, respectively.[2] The concentration of chromophore in solution ranged from $1.004\times10^{-5}$ to $2.164\times10^{-3}$ mol/l. The concentration of electrolyte and polyelectrolyte ranged from $1\times10^{-2}$ to $10\times10^{-2}$ mol/l. Accurately weighed uptaken samples were extracted with 25% aqueous pyridine. The concentration of chromophore extracted was determined using a Hitachi 124 spectrophotometer with 25% pyridine as reference. To prevent complications arising from cis-trans formation of C.I. Direct Yellow 12, bisazo derivative, the chromophore solution was illuminated for about 1 h just before measurement.[1,2] Transport of chromophore was measured in the apparatus of Amicon ultrafiltration cell as described elesewhere.[5] To obtain the interpolated degree of dissociation constant of polyelectrolyte, uptake of C.I. Direct Yellow 12 on cotton in the presence of polyelectrolytes containing the constant concentration of sodium chloride(0.01 M, 1 M=1 mol $dm^{-3}$) at 25 and 90 °C was done as described in the previous paper.[2] Interaction between polyelectrolytes and chromophore used in this system was neglegible as described with previous articles.[2,6]

## Results and Discussions

Figure 1 compares the uptake of C.I. Direct Yellow 12 in a cellulose membrane in the presence of the sodium salt of galacturonic acid (a model for pyranose unit in sodium alginate) with that in the presence of sodium alginate. It is obvious that the adsorption isotherm in the presence of NaAlg differs from that in the presence of galacturonic acid. Thus, the effect of NaAlg on the uptake by the cellulose membrane differs from that of small molecule electrolytes such as galacturonic acid or an inorganic salt which are able to enter into the cellulose membrane.

Figure 2 illustrates the transport of C.I. Direct Yellow 12 into a cellulose membrane in the presence of NaAlg at 25 °C. As is apparent in Fig. 2, enhanced transport of chromophore into a cellulose membrane with addition

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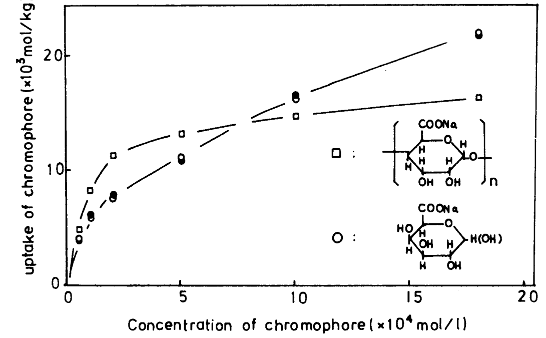

Fig. 1. Adsorption isotherm of C.I. Direct Yellow 12 into a cellulose membrane in the presence of either sodium alginate or the sodium salt of galacturonic acid at 25 °C.
□: sodium alginate ($2\times10^{-2}$ pyranose unit mol/l) ionization degree=0.4—0.5. ○: galacturonic acid sodium salt ($1\times10^{-2}$ mol/l). ●: sodium chloride ($1\times10^{-2}$ mol/l)

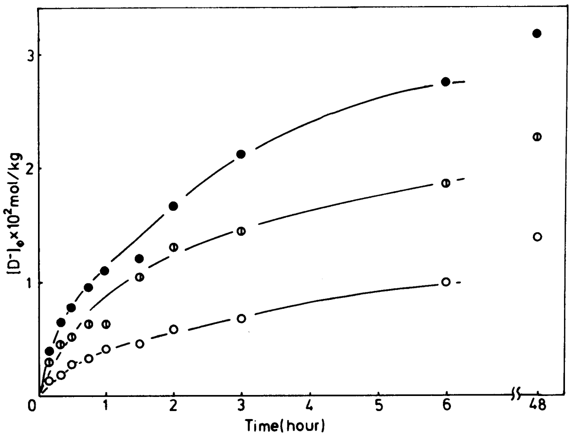

Fig. 2. Transport of C.I. Direct Yellow 12 into a cellulose membrane in the presence of sodium alginate at 25 °C.
○: 0.02 pyranose unit mol/l. ◑: 0.04 pyranose unit mol/l. ●: 0.06 pyranose unit mol/l.

of NaAlg was observed. Table 1 lists an example of transport of chromophore into a cellulose membrane. Transport increased progressively with addition of alginate, reaching a factor about 25 over that without NaAlg. This large enhancement may be due merely to the fact that a chromophore is accumulated inside the membrane film by a Donnan membrane-equilibrium effect.

Figure 3 illustrates the uptake of C.I. Direct Yellow 12 into a cellulose membrane in the presence of various polyelectrolytes at 90 °C. Table 1 lists an example of uptake of chromophore into a cellulose. As is apparent in Fig. 3 and in Table 1, the increase in the uptake of chromophore to cellulose for polyelectrolytes follows the order, NaAlg>NaPSS$\gtrsim$NaPMA$\gtrsim$NaPA, indicating the analogous order to the sequence of increase in the degree of dissociation constant for polyelectrolytes as described in Table 2. Figure 4 illustrates the adsorption isotherms of C.I. Direct Yellow 12 on cellulose

TABLE 1. UPTAKE OF CHROMOPHORE[a)] INTO CELLULOSE IN THE PRESENCE OF POLYELECTROLYTE AT 25 AND 90 °C

| Polyelectrolyte × 10² unit mol/l | Uptake of chromophore (× 10⁴ mol/kg cellulose) 90 °C cellulose membrane | 90 °C cotton | 25 °C cellulose membrane | 25 °C cotton |
|---|---|---|---|---|
| NaAlg (2) | 42.5 | 24.2 | 133 | 55.7 |
| (4) | 68.2 | | 226 | |
| (6) | | | 318 | |
| (10) | 169 | | | |
| NaPSS (2) | 25.7 | 20.8 | | 47.5 |
| (4) | | 25.7 | | |
| NAPMA (2) | 20.8 | 15.3 | | 42.4 |
| NAPA (2) | 16.8 | 13.6 | | 39.5 |
| (4) | | 21.5 | | |
| (10) | | 39.4 | | |
| None | 6.81 | 7.69 | 34.5 | 24.9 |

a) C.I. Direct Yellow (sodium salt) $1\times10^{-3}$ mol/l. These results are consistent with the chromophore concentration used in this article($1-20\times10^{-4}$ mol/l).

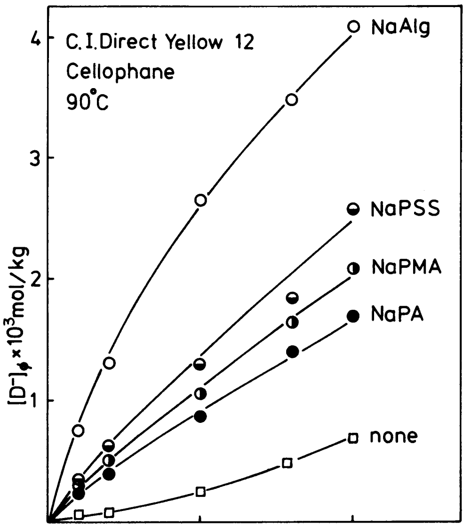

Fig. 3. Adsorption isotherm of C.I. Direct Yellow 12 into a cellulose membrane in aqueous solution of polyelectrolyte(0.02 unit mol/l) at 90 °C.
NaAlg: sodium alginate, NaPSS: sodium polystyrenesulfonate, NaPMA: sodium polymethacrylate, NaPA: sodium polyacrylate.

membrane in aqueous solutions of polyelectrolytes under conditions where sodium ion concentration is kept constant with corrected sodium ion concentration by using their measured value of dissociation constant for polyelectrolyte(see, $\alpha^*$ in Table 2). As is apparent in Fig. 4, the differences in the uptake of chromophore into cellulose membrane were largely reduced in comparison to those in Fig. 3. Thus, the differences in the uptake of chromophore into a cellulose membrane in aqueous solutions of various polyelectrolytes may be

Table 2. Interpolated degree of dissociation constant ($\alpha$) of polyelectrolyte

| Polyelectrolyte | Dissociation constant | | | |
|---|---|---|---|---|
| | $\alpha$ at 25 °C | $\alpha$ at 90 °C | $\alpha$* at 25 °C | Ref(No.) at 25 °C |
| NaAlg | 0.35± 0.05 | 0.40± 0.05 | 0.38± 0.02 | 0.50(2)<br>0.45(9)<br>0.33(10) |
| NaPSS | 0.15± 0.05 | 0.20± 0.05 | 0.29± 0.02 | 0.35(11)<br>0.38(12)<br>0.40(6) |
| NaPA | 0.15± 0.05 | 0.15± 0.05 | 0.23± 0.02 | 0.25(13)<br>0.28(14) |
| NaPMA | | | 0.18± 0.02 | |

* Values measured by the method of selective ion sensitive electrode.

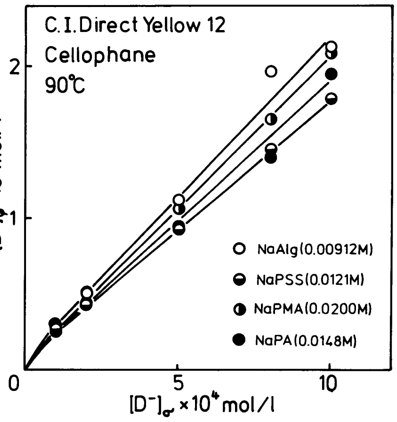

Fig. 4. Adsorption isotherm of C.I. Direct Yellow 12 into a cellulose membrane in aqueous solution of polyelectrolyte under condition of corrected sodium ion concentration (parenthesis) at 90 °C.

due to the fact that the differences in the degree of dissociation constant for polyelectrolytes has a crucial role on the differences in the uptake of chromophore into a cellulose membrane.

For the quantitative interpretation of the degree of dissociation constant of polyelectrolyte in the bulk solution on equilibrium uptake of chromophore, the following theoretical treatment was applied to the present results as described in the previous article.[2,5] As envisaged in the adsorption model on cellulose in Fig. 5, chromophore is assumed to be adsorbed in the internal solution of cellulose(*i* phase). Bulk phase($\sigma$) is assumed to penetrate into the pore of cellulose membrane and this portion of it is designated as $\gamma$. It is assumed that polyanion($P_{\bar{n}}$) is present only in the $\sigma$ phase. According to Donnan membrane-equilibrium between the two phase and maintaining electrical neutrality in each phase, the standard free energy ($-\Delta\mu°$) can be calculated as described in the previous article.[2,7]

According to Donnan membrane-equilibrium between two phases, the ionic concentrations are related as follows;

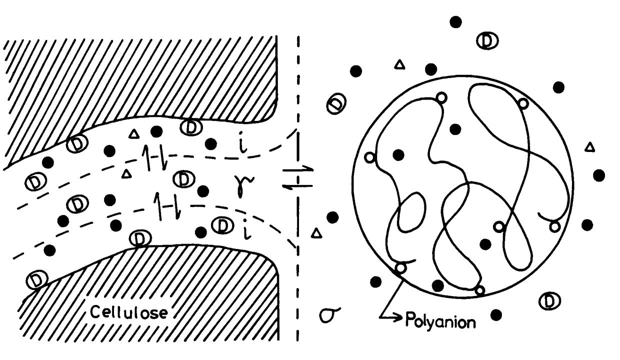

Fig. 5. Adsorption model on cellulose.
Alginate ion(polyion, $P_{\bar{n}}$) is present only in the bulk phase($\sigma$). D, chromophore anion; ●, sodium ion (counterion of chromophore or polyelectrolyte); $P_{\bar{n}}$, alginate ion shown with pyranose unit mol; *i*, internal solution of cellulose; $\sigma$, bulk phase; $\gamma$, bulk phase assumed to penetrate into the pores of cellulose.

$$[\mathrm{Na^+}]_\sigma^z[\mathrm{D^-}]_\sigma = [\mathrm{Na^+}]_\gamma^z[\mathrm{D^-}]_\gamma = [\mathrm{Na^+}]_i^z[\mathrm{D^-}]_i \tag{1}$$

where $z$ is the basicity of the dye(chromophore) anion and $D^-$ is chromophore anion. For maintaining electrical neutrality in each phase,

$$\sigma \text{ phase: } [\mathrm{Na^+}]_\sigma = z[\mathrm{D^-}]_\sigma + \alpha[\mathrm{P^-}]_\sigma + [\mathrm{Cl}]_\sigma \tag{2}$$

where $\alpha[P^-]$ represents the concentration of polyanion shown with unit mol $\alpha$ represents the degree of ionization of polyelectrolyte to be calculated and $[Cl^-]$ represents the ionic concentration of chloride used as sodium chloride.

$$\gamma \text{ phase: } [\mathrm{Na^+}]_\gamma = z[\mathrm{D^-}]_\gamma + [\mathrm{Cl^-}]_\gamma \tag{3}$$

$$i \text{ phase: } [\mathrm{Na^+}]_i = \frac{z[\mathrm{D^-}]_\phi}{V} + [\mathrm{Cl^-}]_i \tag{4}$$

where $V$ represents the volume term of *i* phase(cellulose membrane: 0.33 l kg$^{-1}$, cotton: 0.22 l kg$^{-1}$)[5] and $[D^-]_\phi$ is the concentration of dye (chromophore) anion adsorbed into a cellulose membrane in mol kg$^{-1}$ dry membrane.

Combination of Eqs. 1 and 3, $[Na^+]_i$ is obtained, where $[Na^+]_\phi = V[Na^+]_i$ and $[Na^+]_\phi$ is the concentration of sodium ion adsorbed in the cellulose membrane in mol kg$^{-1}$ dry membrane.

The following equation was used to calculate the standard free energy of this uptake($\Delta\mu°$).[5]

$$-\Delta\mu° = RT\ln[\mathrm{Na^+}]_\phi^z[\mathrm{D^-}]_\phi/V^{z+1}[\mathrm{Na^+}]_\gamma^z[\mathrm{D^-}]_\gamma \tag{5}$$

$$= RT\ln[\mathrm{Na^+}]_\phi^z[\mathrm{D^-}]_\phi/V^{z+1}[\mathrm{Na^+}]_\sigma^z[\mathrm{D^-}]_\sigma \tag{6}$$

Thus, according to the computer simulation so that the standard free energy may has nearly constant value with various changes in the experimental conditions, the interpolated degree of dissociation constant($\alpha$) of polyelectrolyte can be obtained. Table 2 lists the interpolated degree of dissociation constant of polyelectrolyte with that measured by the method of sodium ion sensitive electrode. In addition, Table 3 lists an example of the standard free energy which has nearly constant value in these systems.

As is apparent in Table 2, the degree of dissociation constant corrected by computer simulation has fairly good agreement with that measured value by an ion electrode, indicating that the differences in the degree of dissociation for polyelectrolytes with different kinds of ionizable groups induced the differences in the uptake of chromophore in aqueous solutions of various polyelectrolytes as described above in Fig. 1 and Table 1.

Further interesting trends of enhancement are seen in the transport of chromophore in the presence of polyelectrolytes with different kinds of counterions at 25° and 90 °C. Figure 6 illustrates the uptake of C.I. Direct Yellow 12 into a cellulose membrane in the presence of alginate with different kinds of counterions at 25 °C. Table 4 lists an example of the uptake of chromophores to cellulose in the presence of polyelectrolytes with different kinds of counterions at 25° and 90 °C. Thus, the uptake is substantially greater with the salt of potassium, cesium, and ammonium than the sodium salt. This enhanced uptake of chromophores may be due to the fact that the sodium salt of the chromophores is ion-exchanged with different kinds of counterion on the polymer chain in the bulk solution ($\sigma$) designated as in Fig. 5. The uptake by the cellulose of chromophore with different kinds of counterion in the absence of polyelectrolyte at both 25° and 90 °C is greater with the other counterion ($K^+$, $Cs^+$, and $NH_4^+$) than with $Na^+$ (Table 4).[8] Furthermore, the fact that the uptake of chromophore with different kinds of counterion in the presence of $NH_4Alg$ at 90 °C is the same is consistent with the assumption of ion-exchange described above.

In addition, this different enhancement with different kinds of counterion in the uptake of chromophore may depend on the differences in the degree of dissociation constant of polyelectrolytes with different kinds of counterion as well as the differences in the uptake described in both Fig. 3 and Table 1.

In any event it is clear that the addition of polyelectrolytes leads to marked enhancement of uptake and ion transport into a cellulose membrane.

Ion transport into the cellulose membrane in the presence of polyelectrolytes provides an interesting model for transport in a biological system.

TABLE 3. STANDARD FREE ENERGY CHANGE($-\Delta\mu^\circ$) OF CHROMOPHORE INTO A CELLULOSE[a)] IN AQUEOUS POLYELECTROLYTE SOLUTIONS CONTAINING A CONSTANT CONCENTRATION OF SODIUM CHLORIDE AT 25 AND 90 °C[b)]

| Polyelectrolyte × $10^2$ mol/l | | kcal $mol^{-1}$ 25 °C | kcal $mol^{-1}$ 90 °C |
|---|---|---|---|
| NaAlg | (0) | 4.32 | 3.29 |
| | (2) | 4.29 | 3.11 |
| | (4) | 4.32 | 3.22 |
| | (6) | 4.36 | 3.63 |
| NaPSS | (0) | 4.38 | 3.19 |
| | (2) | 4.33 | 3.14 |
| | (4) | 4.38 | 3.17 |
| | (6) | 4.35 | 3.21 |
| NaPA | (0) | 4.31 | 3.14 |
| | (2) | 4.30 | 3.12 |
| | (4) | 4.15 | 2.97 |
| | (6) | 4.40 | 3.28 |

a) Cotton. b) Concentration of chromophore; $1\times10^{-4}$ mol/l, concentration of sodium chloride; $1\times10^{-2}$ mol/l. the dissociation constant of polyelectrolyte in this system is correspond to the value ($\alpha^*$) as described in Table 2.

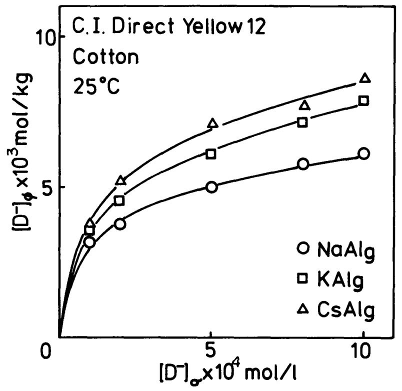

Fig. 6. Adsorption isotherm of C.I. Direct Yellow 12 on cotton in aqueous solution of alginate with different kinds of counterions(0.02 pyranose unit mol/l) at 25 °C.

TABLE 4. UPTAKE OF CHROMOPHORE INTO CELLULOSE IN THE PRESENCE OF ALGINIC ACID WITH DIFFERENT KINDS OF COUNTERIONS AT 25 AND 90 °C

| | | Uptake of chromophore/× $10^4$ mol/kg cellulose[a)] | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Polyelectrolyte[b)] | $Na^+$ | C.I. Direct Yellow 12 | | | | | | | C.I. Direct Blue 15 | | | C.I. Direct Red 2 |
| | | 90 °C | | | 25 °C | | | | 90 °C | 25 °C | | 90 °C |
| | | $NH_4^+$ | $K^+$ | $Cs^+$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Cs^+$ | $Na^+$ | $Na^+$ | $K^+$ | $Na^+$ |
| NaAlg | 43(24) | | | | 133(61) | | | | (27) | | | 41(84) |
| $NH_4Alg$ | 48(26) | 48 | | 49 | 172(67) | | | | (26) | | | 48 |
| KAlg | (26) | | | | 164 | | | | (26) | | | |
| CsAlg | 46(31) | | | | 181(77) | | | | (30) | | | (95) |
| None | 6.8(7.7) | 9.7 | 9.0 | 9.0 | 35(25) | 43 | 41 | 44 | (5.5) | 43 | 55 | (30) |

a) Parenthesis; values on cotton, concentration of chromophore used; $1\times10^{-3}$ mol/l, these results are cosistent with the chromophore concentration used in this article($1$—$20\times10^{-4}$ mol/l). b) 0.02 pyranose unit mol.

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