

Permeation of Solutes Through Chemically Modified Chitosan Membranes

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SYNOPSIS

Chemically and mechanically stable chitosan and *N*-acylchitosan were prepared. *N*-Octanoylchitosan gives the pronounced decrease of water content, whereas *N*-benzoylchitosan keeps a higher content of water. The equilibrium sorption of various sodium salts was determined and is explained by a dual mechanism, consisting of partition and Langmuir sorption. The characteristics of the membranes and the size of the salt anions clearly influence permeability as well as sorption. Permeation behavior was interpreted by the Teorell–Meyer–Sievers (TMS) theorem. The mobility of anions decreases with Stokes radius, decreasing in the order chitosan > *N*-benzoylchitosan > *N*-octanoylchitosan, indicating the effect of the polymer chain molecules, especially a steric obstruction effect on the ion transportation through the membranes. The introduction of the *N*-acylated hydrophobic group to the charged chitosan membranes appears to enhance permselectivity. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Some natural polymers are useful functional materials. One of them, chitin, is a polysaccharide formed by the linkage of $\beta(1 \rightarrow 4)$ of *N*-acetyl-D-glucosamine and used in medicine and biotechnology.^{1,2} Further, chitosan, a poly(amino-saccharide), obtained by the deacetylation of chitin, is useful in producing derivatives by chemical modification in dilute aqueous acid. The polymers so obtained are used as carriers in the gel permeation chromatography,³ and affinity chromatography,⁴ and as supporting materials for immobilized enzymes.⁵

We have already reported the interaction of various chemically modified chitosan with small molecules with a view to obtaining an insight into the process of molecular separation.^{6–9}

Natural materials are now widely used in membrane separation technology. For example, cellulose and its derivatives are used in the preparation of permselective membranes. Recently, chitin and chi-

tosan membranes were evaluated in ultrafiltration,^{10–12} reverse osmosis,¹³ and attempts at separation by pervaporation of a methanol–water mixture.^{14,15} Uragami et al. reported the upstream diffusion of halide ions through chitosan membranes,¹⁶ while Hirano et al. prepared *N*-acyl and *N*-benzylidene chitosan gel membranes and investigated the rate of water transport through them.¹⁷ The *N*-acylchitosan membranes are mechanically stable, as well as being stable to acid and alkali. As they have antithrombotic properties, they are expected to have medical uses.¹⁸ Recently, Miya et al. obtained a 100% substituted *N*-acetylated membrane by reaction with acetic anhydride in the solid phase.¹⁹

Sakurai et al. found variations in crystal and higher order structure of chitosan membranes prepared under different conditions²⁰ and examined the effect of these structural differences on the permeability of oxygen and carbon dioxide.²¹

During a review of the literature, we found much work on membranes prepared from chitosan and its derivatives. However, little fundamental and systematic work has been done to throw light on the design of membranes for molecular and ion separation.²²

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In view of this, we developed selective *N*-acylation by a solid–liquid phase reaction and found that selective permeation of D,L-amino acids was accelerated in the presence of the hydrophobic group in the membranes.²³

We accumulated data for salts permeating through membranes consisting of polyamide 6,²⁴ cationic poly(vinyl alcohol),²⁵ charged poly(allyl amine),²⁶ anionically charged cellulose,^{27,28} and anionically charged poly(vinyl alcohol)²⁹ membranes. To shed much more light on salt permeation in relation to the structure of the membranes, we prepared *N*-octanoyl and *N*-benzoyl membranes. The membranes were characterized and their permselectivity was determined.

EXPERIMENTAL

Materials

Chitosan (the same as used previously^{6–9}), was kindly donated by Katokichi Co. Ltd. Sodium chloride (NaCl, Special Grade, Nacalai Tesque Inc.), sodium benzene sulfonate (NaSO₃Ph, 1st Grade, Tokyo Kasei Co.), sodium 2-naphthalene-sulfonate (NaSO₃Nph, 1st Grade, Tokyo Kasei Co.), and sodium tetraphenyl borate (NaBPh₄, Special Grade, Nacalai Tesque Inc.) were used. Deionized water was used in all experiments.

Preparation and Characterization of Membranes

The pure chitosan membrane was obtained by neutralizing the chitosan-acetic acid salt membrane. The *N*-acylchitosan membranes were prepared by the reaction of the chitosan acetate membrane with carboxylic anhydrides as described previously (Fig. 1).²³ The thickness *d* (cm) of the membranes was measured with a precision micrometer.²³ The content of *N*-acyl groups in the membrane was determined using infrared (IR) spectroscopy and elemental analysis.^{7,23}

Permeability Measurements

The permeability coefficient *P* (cm²/s) was measured using a two-chambered glass cell at 25 ± 0.05°C as described in previous reports.^{23–26} The effective membrane area *A* was 88.6 × 10⁻² cm². The volume of the up- and downstream salt solution were 250 and 50 mL, respectively. The downstream concentration *C*₂ (mol/cm³) was monitored with an electronic conductometer (FU-22A, Toa Electronic Ltd.). The *P* values were determined by the following equations:

$$J_s = (1/A)(dS/dt) \quad (1)$$

$$P = J_s d / (C_1 - C_2) \quad (2)$$

where *C*₁ (mol/cm³) and *S* (mol) are, respectively, the upstream concentration and the amount permeated through the membrane. The salt flux *J* (mol/cm³ s) was estimated from the slope of the linear portion in the curves of *S* against *t* in the steady state.

Equilibrium Sorption

Equilibrium sorption of the 0.005–0.10 mol/dm³ solution at 25 ± 0.05°C was attained in 3 days, when the membrane was removed from the solution, carefully wiped with a filter paper, and immersed in distilled water at the same temperature for one day. NaCl concentrations in solution, as well as in permeability experiments, were determined conductometrically. Absorbances of NaSO₃Ph, NaSO₃Nph, and NaBPh₄ at 210, 275, and 250 nm, respectively, were determined spectrophotometrically with a double-beam spectrophotometer (Hitachi 556).

Analysis of Permeation Data Using the TMS Theorem

The Teorell–Meyer–Sievers (TMS) theory^{30–32} was used, as previously^{25,26} in the interpretation of the results. In this case the ions are considered to per-

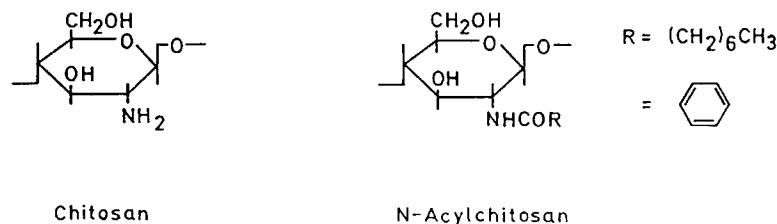


Figure 1 Structural formulas of chitosan and *N*-acylchitosan membranes.

Table I Characteristics of Chitosan and *N*-Acylchitosan Membranes

Membrane	DS ^a	Thickness (μm)	Solubility in ^b		Water Content (wt %)
			10% AcOH	LiCl/NMP/DMAc (1/1/10)	
Chitosan (amine 75%)	(0.75) ^c	6.48	s	i	55.1
Chitosan (amine 85%)	(0.85) ^c	4.77	s	i	43.5
<i>N</i> -Octanoylchitosan ^d	0.30	3.98	s	i	33.1
<i>N</i> -Benzoylchitosan ^e	0.43	4.81	sw	sw	51.2

^a Degree of substitution of acyl group.

^b i, insoluble; s, soluble, sw, swelling.

^c Degree of substitution of amino group.

^d Prepared from chitosan (amine 75%).

^e Prepared from chitosan (amine 85%).

meate through the upstream solution, the charged membrane matrix, and the downstream solution system. According to the TMS theory, the permeability coefficient P of a uni-univalent electrolyte can be expressed by Eq. (3) which is based on the Nernst-Planck equation, assuming that:

1. The total membrane potential is the sum of the Donnan potentials at the two membrane-solution interfaces and the diffusion potential in the membrane.
2. The fixed charges (NH_3^+) carried by the membrane matrix are assumed to be uniformly distributed, remaining constant irrespective of external electrolyte concentrations.
3. The fluxes of anions and cations are equal in any part of the membrane (electroneutrality condition).

$$P = \frac{\omega^+ \omega^- RTX}{(\omega^+ + \omega^-)(C_2 - C_1)} \left(\sqrt{1 + (2C_2/QX)^2} - \sqrt{1 + (2C_1/QX)^2} + W \ln \frac{\sqrt{1 + (2C_2/QX)^2} - W}{\sqrt{1 + (2C_1/QX)^2} - W} \right) \quad (3)$$

where $W = (\omega^+ - \omega^-)/(\omega^+ + \omega^-)$ and $Q^2 = \gamma^+ \gamma^- / k^+ k^-$; X is the effective concentration of fixed charges; γ^+ and γ^- are single-ion activity coefficients in the membrane phase, and are assumed to be unity; k^+ and k^- are the partition coefficients and both are assumed to be equal to K , giving $Q = 1/K$, where K is the partition coefficient obtained experimentally; Q reflects the sorptivity of salts on the membrane. ω^+ and ω^- are the ionic molar mobilities in the mem-

brane phase and ω^+/ω^- is assumed to be constant; thus W is indicative of the molar mobility difference between cation and anion.

Under the experimental conditions, electrolyte concentration C_2 of the downstream side cell can be assumed to be zero.

If we assume the tortuosity factor θ to be a parameter representing obstruction effect on the mobility of the cation in the membrane, the cation mobility ω^+ is expressed as

$$\omega^+ = \theta \omega_0^+ \quad (4)$$

in which ω_0^+ is the molar mobility in bulk water. Using Eq. (4) and W ,

$$\omega^- = (1 - W)\theta\omega_0^-/(1 + W) \quad (5)$$

By fitting the data to permeability and salt concentration C_1 in Eq. (3), and changing the values of X , W , and θ , the most suitable values of ω^+ and ω^- can be found. The diffusion coefficient of the solute, $D(\text{cm}^2/\text{s})$ is calculated neglecting the charge effect:

$$D = 2\omega^+ \omega^- RT/(\omega^+ + \omega^-) \quad (6)$$

Equation (6) is obtained when $X \rightarrow 0$ or $C_1 \rightarrow \infty$, and $2\omega^+ \omega^- / (\omega^+ + \omega^-)$ is the harmonic mean value of cation and anion mobility; this corresponds to the salt transport through the uncharged membrane.

RESULTS AND DISCUSSION

Membrane Characteristics

In Table I, the characteristics of chitosan and *N*-acylchitosan membranes used in this work

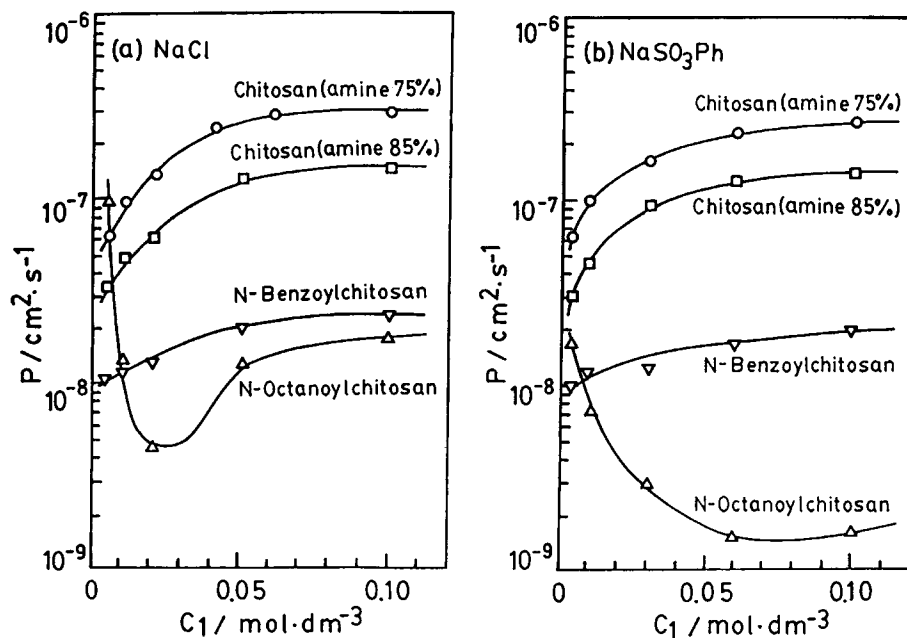


Figure 2 Permeability of (a) NaCl and (b) NaSO₃Ph through chitosan and *N*-acylated chitosan membranes.

are shown. The thickness of membranes were 3.9 ~ 6.5 μm .

In IR spectra the 3455, 3370, 3315, 1090, 665, 610, and 560 cm^{-1} bands, assigned to crystal bands of chitosan,^{19,33} are clearer and sharper in chitosan (85% amine) than in chitosan (75% amine). These results could be reasonably attributed to the higher contents of crystalline regions of the former, which contains fewer acetyl groups. On the other hand, *N*-octanoylchitosan shows a trace of crystalline bands, and *N*-benzoylchitosan practically loses these bands, but gives 700, 660, and 590 cm^{-1} bands, which are probably shift bands.

The solubility of the membranes was discussed in our previous report.^{7,9} Table I gives the water content, and it is interesting to note that the introduction of phenyl groups increases the water content.

The following can be deduced from these results and IR determinations described above: In the case of the unmodified chitosan membranes, the higher contents of amino groups give a highly crystallized (> 40%)¹⁹ and compact structure of a density greater than 1.4,³⁴ which results in a decrease in water content, because —OH groups involved in intra- and intermolecular hydrogen bonding lose bound water. The introduction of acyl long-chain groups increases hydrophobicity and leads to strong interaction between the chains, producing a compact assembled

structure,⁷ resulting in a decrease of water contents. In the case of *N*-benzoylated membrane, the bulky phenyl group perturbs crystalline structure,⁷ and the same level of the water content as in the chitosan membranes can be reasonably assumed.

Permeation of Sodium Salts

Figures 2 and 3 gives the concentration (C_1) dependence of permeability through chitosan and its acylated membranes. In both chitosan membranes the permeability of NaCl and NaSO₃Ph increases with increase in C_1 until saturation is reached. This is the same type of behavior as in permeation of NaCl through cationically charged poly(vinyl alcohol) (PVA-N) membranes²⁵ and charged poly(allyl amine) (PAA) membranes,²⁶ and suggested Donnan exclusion due to the fixed charges of the membrane in the low concentration range. The Donnan exclusion effect reduces gradually with increasing C_1 . In contrast to this type, NaSO₃Nph and NaBPh₄ give maxima in permeability. This was also observed in the PVA-N/NaSO₃Ph system,²⁵ which suggested that the larger the size of the anion, the greater are the differences in the mobility of the small sodium ion.

In *N*-benzoylchitosan the saturation-type behavior for NaCl and NaSO₃Ph, and the maximum type for NaSO₃Nph which is similar to that of chitosan.

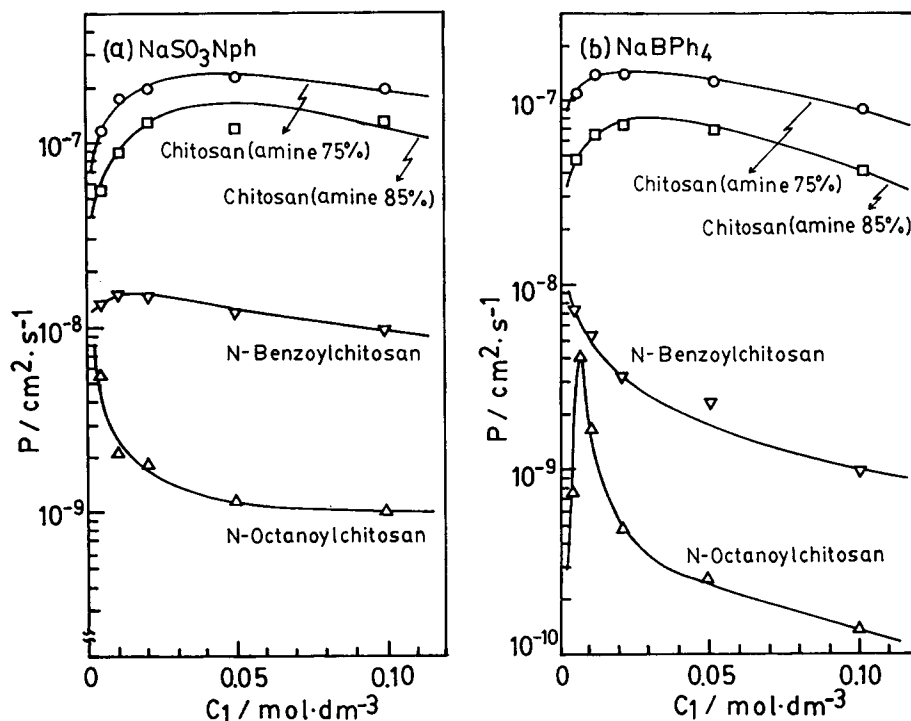


Figure 3 Permeability of (a) NaSO_3Nph and (b) NaBPh_4 through chitosan and *N*-acylated chitosan membranes.

On the other hand, NaBPh_4 , the most bulky of the salts, shows monotonous decrease of P with increase in C_1 .

N-Octanoylchitosan gives a monotonous decrease and NaCl gives a minimum, as shown in Figure 2. This type of pattern was observed in PVA-N/NaBPh_4 ²⁵ and PAA/NaBPh_4 ,²⁶ while the change in P values is larger in this case. These observations, in addition to differences in mobilities of both cation and anion, clearly indicate an obstruction to the movement of ions by the hydrophobic substituents in the membrane.

Selective Permeation through Membranes

In Figure 2 *N*-octanoylchitosan show peculiar behavior at concentrations (C_1) below 0.02 mol/dm^3 . However, at higher concentrations, the values of permeability follow the order chitosan (amine 75%) > chitosan (amine 85%) > *N*-benzoylchitosan > *N*-octanoylchitosan. And for all the membranes, in the higher concentration range, salt permeability decreases in the order $\text{NaCl} > \text{NaSO}_3\text{Ph} > \text{NaSO}_3\text{Nph} > \text{NaBPh}_4$. The relationships between P and the molecular weight (M_w) or Stokes's radius of the permeants at $C_1 = 0.10 \text{ mol/dm}^3$ is given in Figure 4.

In the case of chitosan membranes, a slight decrease in P on increasing the M_w or Stokes's radius is observed.

In the case of *N*-benzoylated and *N*-octanoylated membranes, a decrease is observed on increasing the M_w or Stokes's radius, which suggests that the introduction of benzoyl or octanoyl groups in the membrane causes significant obstruction even when the increase in the size of the permeant is minute. The fact that P of chitosan (amine 85%) is smaller than that of chitosan (amine 75%) is ascribed to the influence of crystallinity. Due to the lower acetyl content, the former has a higher crystallinity than the latter.

It is worth noting that the octanoyl membrane has a lower water content than the original chitosan and benzoylated membranes, pointing to a more compact structure due to the long acyl group. The compact structure gives the smallest value for permeability.

The permeability ratio $P_{\text{NaCl}}/P_{\text{NaBPh}_4}$ follows the sequence chitosan (amine 75%) (3.3) \leq chitosan (amine 85%) (3.5) < *N*-benzoylchitosan (23.3) \ll *N*-octanoylchitosan (159).

It is of interest that the introduction of hydrophobic groups in chitosan membranes yields high permselectivity.

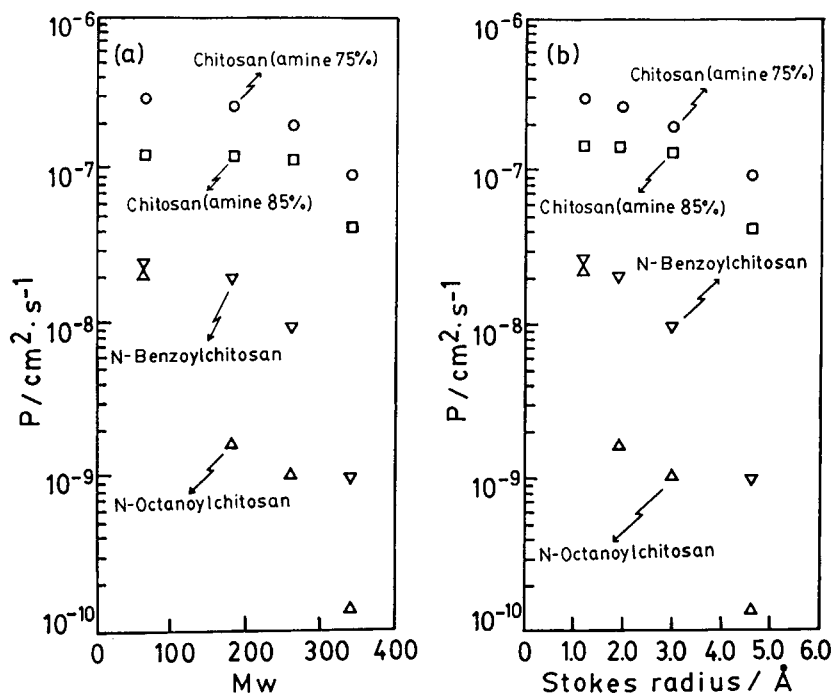


Figure 4 Relationship between (a) M_w and (b) Stokes's radius of anions of Na^+ salts and permeability.

Equilibrium Sorption of Sodium Salts

Figures 5 and 6 show the sorption isotherms of the salts, C (mol/dm^3 of water in the membrane) against the concentration in the bath, C (mol/dm^3). The shape of the isotherms is the same as shown in our previous work^{6,7} on the sorption of azo dyes by hydrophobic chitosan gels, and was explained by a dual mechanism consisting of the partition and Langmuir sorption.

$$C = C_P + C_L = K_P C + \frac{SK_L C}{1 + K_L C} \quad (7)$$

where K_P is the (dimensionless) partition coefficient, K_L the Langmuir constant (dm^3/mol), and S the saturation value of Langmuir sorption (mol/dm^3). The values of these parameters were determined from sorption data by the least-squares method, and are listed in Table II.

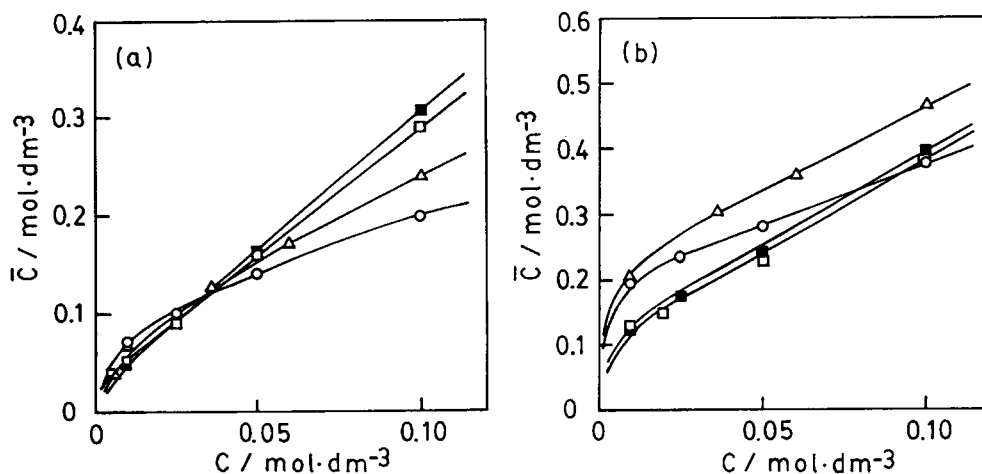


Figure 5 Equilibrium sorption of sodium salts by chitosan membranes: (a) Chitosan (amine 0.75); (b) Chitosan (amine 0.85). (○) NaCl ; (Δ) NaSO_3Ph ; (\square) NaSO_3Nph ; and (\blacksquare) NaBPh_4 .

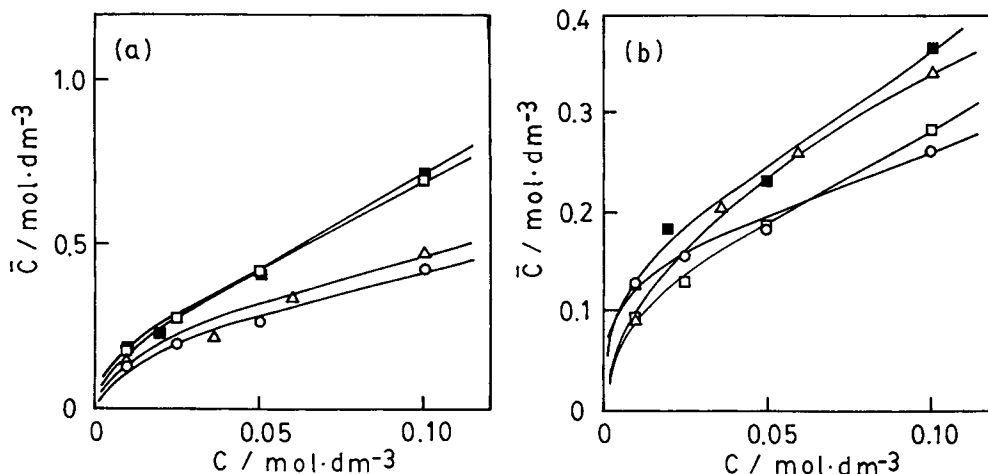


Figure 6 Equilibrium sorption of sodium salts by *N*-acylated chitosan membranes: (a) *N*-Octanoylchitosan (D.S. 0.30); (b) *N*-benzoylchitosan (D.S. 0.43). (○) NaCl; (△) NaSO₃Ph; (□) NaSO₃Nph; and (■) NaBPh₄.

K_P values follow the sequence NaCl < NaSO₃Ph < NaSO₃Nph < NaBPh₄ for every membrane, and chitosan (amine 75%) \approx *N*-benzoylchitosan < chitosan (amine 85%) < *N*-octanoylchitosan for each of the salts. In combination with the water content data (Table I), the higher fraction of lipophilic glucosamine residue in the membrane phase is estimated to have a stronger interaction with solutes. The smaller values of K_P of *N*-benzoylated membranes for NaSO₃Nph and NaBPh₄ are attributed to the bulkiness of these permeants.

The saturation value S of the Langmuir sorption is within 0.08 and 0.19 mol/dm³. The amino contents in chitosan and its acylated membranes are 1.9–6.6 mol/dm³. Bearing in mind that the pK_a values of the amino group in chitosan is ca. 6,¹ the effective charged sites are estimated to be between $\frac{1}{6}$ and $\frac{1}{20}$ of the amino contents.

As regards K_L values, chitosan (amine 85%) has the largest and that of chitosan (amine 75%) follows, which suggests that the sorption in this mode is enhanced by amino groups. Here again, the bulky phenyl and long acyl groups hinder sorption.

Interpretation of Permeation Data by the TMS Theory

Salt Permeation through Charged Membranes

Salt permeation has been interpreted by the TMS theory^{30,32} [cf. Experimental section, Eq. (3)]. Alkali metal salts permeating charged cellulosic membranes,^{27,28} sodium salts permeating PVA-N,²⁵ and PAA²⁶ membranes can be quoted as examples.

Assuming that only the partition species in the above model permeates, the permeability coefficient P becomes P_1 . The K in Eq. (3) is replaced by K_P , obtained from sorption experiments (Table II) and the following equation is obtained:

$$P = P_1 = \frac{\omega^+ \omega^- RTX}{(\omega^+ + \omega^-) C_1} \times \left(\sqrt{1 + 4\xi_1^2} + W \ln \frac{\sqrt{1 + 4\xi_1^2} - W}{1 - W} \right) \quad (8)$$

where

$$\xi_1 = C_1 K_P / X (C_2 \approx 0) \quad (9)$$

and putting

$$W = (\omega^+ - \omega^-) / (\omega^+ + \omega^-)$$

Using Eq. (8) and putting the values of K_P , W , and tortuosity factor θ , the concentration dependence of C_1 on P can be drawn (Fig. 7). Three typical patterns of permeation behavior of sodium salts found in this work are reproduced by these curves, except for *N*-octanoylchitosan/NaCl system. The permeation parameters are given in Table III. The effective charge X is 0.05–0.10 mol/dm³, which corresponds to 3–8% of the total charge of amino group. Similar phenomena were reported previously in respect to PVA-N²⁵ and PAA²⁶ membranes. This is attributable to the deactivation of the charge in the polymer matrix, and neglecting activity coefficients in the membranes.

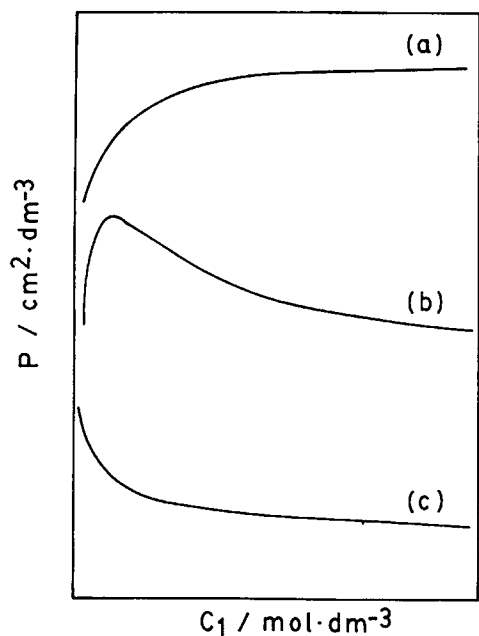


Figure 7 P against C_1 calculated from Eqs. (8) and (4): $K_p = 1$; $X = 0.05$; and $\theta = 0.05$. (a) $W = 0.5$; (b) $W = 0.9$; (c) $W = 0.99$.

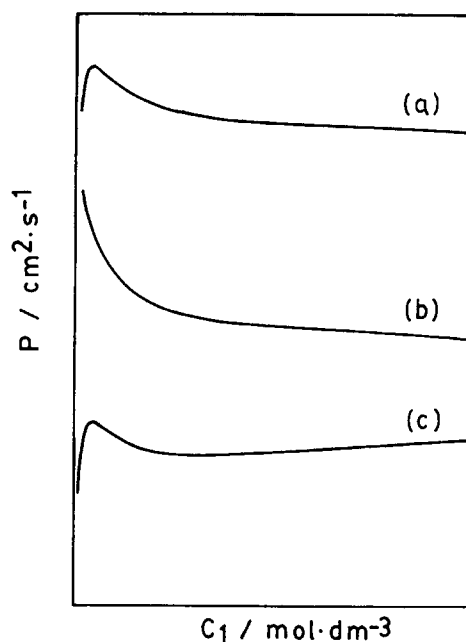


Figure 8 P against C_1 calculated from Eqs. (8), (11), and (4): $K_p = 2$; $K_L = 500$; $X = S = 0.1$; $\theta = 0.05$. (a) $W = 0.9$; (b) $W = 0.7$; (c) $W = -0.5$.

The values of W follow the sequence in the membranes: NaCl ($W = 0.2-0.9$) < NaSO₃Ph ($W = 0.3-0.9$) < NaSO₃Nph ($W = 0.8-0.9$) < NaBPh₄ ($W > 0.9$).

The values of W obtained from molar mobilities in aqueous solution at infinite dilution²⁵ are NaCl (-0.21) < NaSO₃Ph (0.025) < NaSO₃Nph (0.24) < NaBPh₄ (0.43).

This sequence suggests that the larger the size of the anion, the larger is the difference in the mobility of the sodium ion, especially in membrane transport, where steric hindrance is affected by the larger anion.

As shown in Figure 7, with increase in W , the "saturation type (a)" (≤ 0.5) becomes the "maximum type (b)" (0.8–0.9) and further the "monotonous de-

Table II Sorption Parameters

Membrane	Salt	K_p	$S \times 10$ (mol/dm ³)	$k_L \times 10^{-3}$ (dm ³ /mol)
Chitosan (amine 75%)	NaCl	1.10	0.92	0.20
	NaSO ₃ Ph	1.55	0.92	0.11
	NaSO ₃ Nph	2.58	0.28	1.94
	NaBPh ₄	2.79	0.27	1.30
Chitosan (amine 85%)	NaCl	1.88	1.91	2.53
	NaSO ₃ Ph	2.59	1.40	1.51
	NaSO ₃ Nph	2.79	1.03	1.02
	NaBPh ₄	3.00	0.94	2.63
<i>N</i> -Octanoylchitosan	NaCl	2.90	1.44	0.31
	NaSO ₃ Ph	3.25	1.43	0.45
	NaSO ₃ Nph	5.42	1.53	0.34
	NaBPh ₄	5.99	1.25	0.90
<i>N</i> -Benzoylchitosan	NaCl	1.41	1.26	0.46
	NaSO ₃ Ph	1.78	1.67	0.16
	NaSO ₃ Nph	2.07	0.78	0.51
	NaBPh ₄	2.33	1.35	0.45

Table III Permeation Parameters^a

Membrane ^b	W	Θ	X^d	$\omega^+ \times 10^{12e}$	$\omega^- \times 10^{12}$	$D \times 10^{9f}$
NaCl						
CS-75	0.2	0.03	0.06	167	111	33.1
CS-85	0.2	0.008	0.08	44.1	29.4	87.5
Ben-CS	0.4	0.002	0.07	11.0	4.73	16.4
Oct-CS	0.999 (0.8) ^c	0.07 (0.0005)	0.07 (0.08)	377 (2.69)	0.188 (0.299)	0.932 (1.33)
NaSO ₃ Ph						
CS-75	0.3	0.02	0.06	102	55.1	177
CS-85	0.3	0.007	0.08	35.5	19.1	61.8
Ben-CS	0.5	0.002	0.05	8.07	2.69	10.0
Oct-CS	0.9999 (0.9)	0.14 (0.0002)	0.09 (0.09)	753 (0.969)	0.038 (0.051)	0.188 (0.240)
NaSO ₃ Nph						
CS-75	0.8	0.023	0.08	124	13.8	61.6
CS-85	0.8	0.013	0.08	67.3	7.47	33.3
Ben-CS	0.9	0.003	0.05	15.6	0.821	3.87
Oct-CS	0.9999 (0.9)	0.07 (0.0001)	0.07 (0.07)	377 (0.404)	0.019 (0.021)	0.094 (0.10)
NaBPh ₄						
CS-75	0.9	0.021	0.06	113	5.95	28.0
CS-85	0.9	0.01	0.10	51.1	2.69	12.7
Ben-CS	0.999 (0.9)	0.02 (0.0002)	0.06 (0.10)	102 (0.807)	0.051 (0.042)	0.253 (0.20)
Oct-CS	0.99999 (0.9)	0.2 (0.00005)	0.08 (0.10)	807 (0.269)	0.004 (0.014)	0.020 (0.07)

^a Determined using Eqs. (8) and (4).

^b CS-75, Chitosan (amine 75%); CS-85; Chitosan (amine 85%); Ben-CS, *N*-benzoylchitosan; Oct-CS, *N*-octanoylchitosan.

^c The values in parentheses are determined using Eqs. (8), (11), and (4).

^d Equiv/dm³ of imbibed water.

^e cm²/mol J s.

^f cm²/s [determined by Eq. (6)].

crease type (c)" (> 0.9). All the results for the permeation of sodium salts are classified as follows:

- A. Saturation type: Chitosan (amine 75%, 85%), *N*-benzoylchitosan/NaCl, NaSO₃Ph systems.
- B. Maximum type: Chitosan (amine 75%, 85%)/NaSO₃Nph, NaBPh₄ systems and *N*-benzoylchitosan/NaSO₃Nph system.
- C. Monotonous decrease type: *N*-benzoylchitosan/NaBPh₄ system and *N*-octanoylchitosan/Na salt systems (except NaCl).

The Donnan exclusion effect by the fixed charges ($-\text{NH}_3^+$) in the membrane is clearly shown by the

A type, and the large decrease in mobility of the larger size anion compared with that of the sodium cation is given by the B type.

In type C the difference in mobilities of anions and cation is thought to be influenced by the steric effect of the substituent groups in the membranes; the tortuosity factors estimated for Oct-CS/Na salts and Ben-CS/NaBPh₄, however, are large (Table III). These anomalies present open questions.

Bimodal Permeation Model Based on the TMS Theory

In this model we assumed simultaneous permeation paths of partition and Langmuir species which are

independent of each other. The total permeability of the salts is given by

$$P = P_1 + P_2 \quad (10)$$

P_1 is obtained using Eqs. (8) and (9). P_2 is obtained from Eq. (11), using K_L of the sorption coefficient in the Langmuir mode of dual sorption:

$$P = P_2 = \frac{\omega^+ \omega^- RTX}{(\omega^+ + \omega^-) C_1} \times \left(\sqrt{1 + 4\xi_2^2} + W \ln \frac{\sqrt{1 + 4\xi_2^2} - W}{1 - W} \right) \quad (11)$$

where $\xi_2 = C_1 K_L / (1 + K_L C_1)$, ($C_2 \approx 0$).

Here we have assumed that $X \approx S$. A further assumption is that the molar mobilities of the individual anions and cations are equal in both respective permeation paths. The typical permeation curves, calculated using Eq. (11) are given in Figure 8, which shows that the maximum type B, the monotonous decrease type C, and minimum type D. The parameters obtained are shown in brackets in Table III, and the values of θ , ω^+ , and ω^- for the type C described above are thought to be reasonable. In addition, it was found that the bimodal permeation model can explain even a minimum type of the P vs. C_1 for N -octanoylchitosan/NaCl system.

Structure of Solutes and Membranes in Relation to Permeability

The interpretation of the results based on the TMS theory as described above can be summarized as two cases:

Case 1. Permeation giving saturation (A type) and a maximum (B type) has only partition species.

Case 2. Permeation giving monotonous decrease (C type) and a minimum (D type) has Langmuir species in addition to partition species.

N -Octanoylchitosan/sodium salts and chitosan (amine 85%)/NaBPh₄ are case 2 systems. These systems contain a large contribution of steric hindrance in the membranes. By contrast, chitosan, N -benzoylchitosan/NaCl, NaSO₃Ph, and NaSO₃Nph systems belong to case 1, where the steric effect is smaller. In case 1 the transport of Langmuir species is hindered more than of partition species as a results of strong electrostatic interaction with fixed charged group in the membranes, which practically immobilizes the species. On the other hand, in case 2 permeation, in which the hindrance effect is large,

transport of the partition species is strongly suppressed to the level of Langmuir species.

Inspection of Table III, for all solutes the molar mobility of sodium ions and all anions gives the sequence chitosan (amine 75%) > chitosan (amine 85%) > N -benzoylchitosan > N -octanoylchitosan. The diffusion coefficients D of the salts, neglecting the charge effect, show similar behavior. The values D clearly correspond to the P values for $C = 0.1$ mol/dm³ for every membrane. This indicates that the structure and composition of membranes determine the permeation of the salts.

Figure 9 shows the decrease in mobility with increase of the hydration radius. This tendency is similar to that of the order of anionic permeability as shown in Figure 4.

The values of ω_0^+ (Na⁺) of the aqueous solution at infinite dilution are $5.38 \times A$ and of ω_0^- , for Cl⁻ ($8.20 \times A$) > SO₃Ph⁻ ($5.12 \times A$) > SO₃Nph⁻ ($3.29 \times A$) > BPh₄⁻ ($2.13 \times A$)²⁵ where ($A = 10^{-9}$ cm²/mol J s).

It can be seen that there is only a fourfold variation in mobility. By contrast, anionic mobility in both chitosan is smaller than in aqueous solution. In N -benzoylated membrane ω^- is 10^{-11} – 10^{-13} cm²/mol J s. It decreases linealy with increase in the Stokes's radius of the ions. In N -octanoylated membrane the decrease is clear, even for the small permeant ionic species, being 10^{-13} cm²/mol J s, which indicates the large effect of steric hindrance on mobility in the membranes.

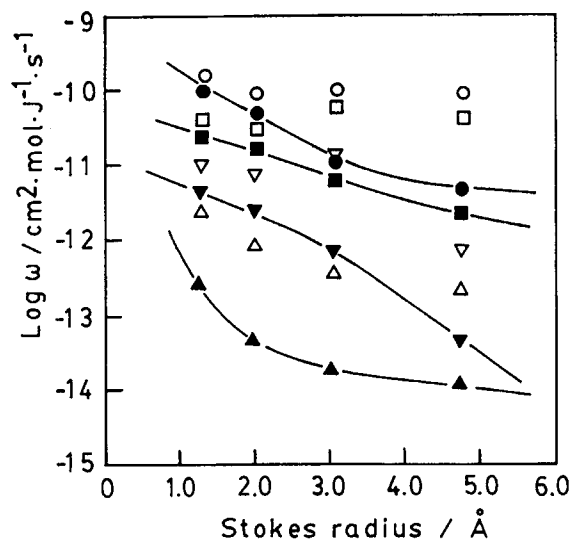


Figure 9 Relationship between Stokes's radius of anions of Na⁺ salts and ionic molar mobilities (ω^+ , ω^-). Open symbols: cation; filled symbols: anion. (○) Chitosan (amine 75%); (□) chitosan (amine 85%); (▽) N -octanoylchitosan; (△) N -benzoylchitosan.

The greater mobility of every sodium salt in chitosan (amine 75%) than in chitosan (amine 85%) is attributed to the higher degree of crystallinity in the latter owing to their greater amino group content. Concerning the *N*-acylated membranes, the anion mobility in *N*-octanoylchitosan is smaller than in *N*-benzoylchitosan by more than one order. This is explained by the partial destruction of the crystalline structure in the latter membrane by the bulky phenyl group, producing one with a high water content. As a result, steric hindrance by substituent groups increases gradually with increasing ionic size of the permeant. In the octanoylated membrane steric hindrance and compact structure due to the long acyl group hinder diffusion of even small anions. Increase in Stokes's radius drastically decreases mobility.

It is clear from the above discussion that the introduction of hydrophobic groups in charged chitosan membranes affects the higher order of their structure, thereby affecting ion mobility in the membrane. As a result, an improvement in selective separation of the solute can be achieved.

CONCLUSION

1. Chitosan and its *N*-acylated membranes were prepared by a solid-liquid phase reaction, and their structures were confirmed by IR spectra. The water content in *N*-octanoylated membrane was smaller than in *N*-benzoylated membrane in which they were relatively high.
2. The equilibrium sorption can be explained by a dual mechanism of partition and Langmuir modes. The partition coefficients in *N*-octanoylated membrane were large and increased with increasing hydrophobicity of the solute.
3. Studies of permeation of salts through the above membranes revealed four types, which are believed to be due to effects of Donnan exclusion producing mobility differences between anions and cations. The TMS theory was used for the systematic interpretation of results as relating to membrane structure.
4. The mobility of anions decreases with increase in the Stokes radius in the sequence of chitosan > *N*-benzoylchitosan > *N*-octanoylchitosan. The difference between anionic and cationic mobility increases with anionic

size. As a result of chemical modification, the difference is greatest in *N*-octanoylated membrane and smallest in chitosan membranes.

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