NOTE

Permeability Properties of Chitosan–Transition Metal Complex Membranes

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INTRODUCTION

Chitosan is an aminopolysaccharide that is obtained by deacetylation of chitin, which is one of the most abundant natural polymers and available largely in the cuticle of the crustacea such as shrimps and crabs. Chitin and chitosan have potential uses as functional materials such as metal adsorbents, immobilization supports, drug carriers, and biomaterials.[1] The chemical structure of chitosan is similar to that of cellulose, but chitosan has one amino group in addition to the hydroxyl groups in the repeating unit. Accordingly, chitosan can strongly coordinate to metal ions through its amino group. It is known that chitosan does not retain alkali and alkaline earth metal ions, while it collects transition metal ions.[2] The chitosan–Cu complex is the most popular among chitosan–transition metal complexes. There are a number of reports on chitosan–transition metal complexes; most of them are applications to recover transition metal ions or complex ions,[3–5] whereas there are very few articles on membrane applications.[6,7] Chitosan has a good membrane-forming ability and chitosan membrane can permeate solutes of molecular weight smaller than 2900.[8] The author has already reported on the permeability of the membranes derived from chitosan.[9–11]

This article describes the preparation of chitosan–metal complex membranes containing first raw transition metals and the permeability properties of them, focusing on the degree of swelling and the complexing ability of the membranes. As reported, two coordination modes have been proposed for chitosan–transition metal complexes; the one is the bridge model[12–15] and the other is the pendant model.[2,15,16] Although these modes are under debate,[2] permeability of the chitosan–transition metal complex membranes is presented from the viewpoint that inter- and intramolecular coordination is formed in the membrane. This type of crosslinking in the PAA membrane is also suitable for reverse osmosis.[17] Moreover, the permeation of some dipeptides through the chitosan–Cu complex membranes is described as a preliminary experiment of ligand exchange or affinity membranes.

EXPERIMENTAL

Materials

Chitosan was purchased from Tokyo Kasei Kogyo Co. Ltd., Japan, and purified before use; chitosan was dissolved in 5% aqueous acetic acid, filtered with a sintered glass filter, precipitated with $1 \ mol/dm^3$ KOH, rinsed with deionized (DI) water until neutral, and dried. This purification procedure was repeated three times, then average molecular weight[18] was 1.6×10^6, and the degree of acetylation[19] was 15%. Glycylglycine (Gly-Gly), alanylalanine (Ala-Ala), and alanylhistidine (Ala-His) were reagent grade materials from Wako Pure Chemical Industries Ltd., Japan, Aldrich Chemical Co. Inc., USA, and Fluka Chemie AG, Switzerland, respectively. Acetone and methanol were distilled just before use. All other chemicals were of reagent grade and used without further purification.

Preparation of the Membranes

One gram of chitosan was dissolved in 5% aqueous acetic acid ($100 \ cm^3$) and $4 \ cm^3$ of the viscous solution was poured onto a PTFE plate that had a well of 6 cm diameter, dried at 40°C, treated with $1 \ mol/dm^3$ NaOH, and washed with DI water. The chitosan membrane obtained was immersed in each $1 \ mol/dm^3$ solution of the following transition metal salts for 24 h at room temperature: $MnSO_4$, $FeSO_4$, $CoSO_4$, $NiSO_4$, $CuSO_4$, and $ZnSO_4$, followed by washing with DI water. The thickness of the membranes was about 60–90 μm.
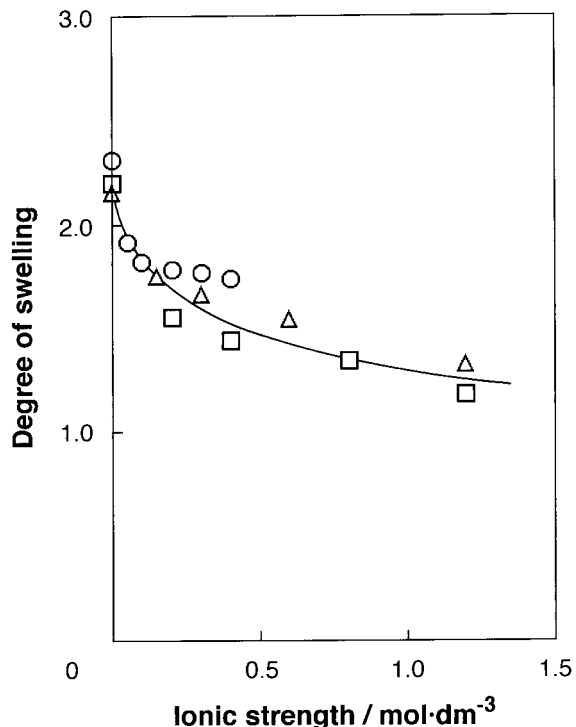
The chitosan solution on the PTFE plate was also

Figure 1 Dependence of the swelling degree of the chitosan membrane on the ionic strength of salt solutions: ($\bigcirc$) NaCl; ($\triangle$) CaCl$_2$; ($\square$) CuSO$_4$.

immersed in [Cu(NH$_3$)$_4$]$^{2+}$ complex solution (25 cm^3 of 2 mol/dm^3 CuSO$_4$ and 25 cm^3 of aqueous ammonia) overnight, and washed with DI water.

Furthermore, the chitosan solution on the PTFE plate was immersed in 2 mol/dm^3 NaOH solution, then chitosan was gelled quickly. The chitosan gel membrane obtained was washed with DI water.

Measurement of the Degree of Swelling

Chitosan and chitosan gel membranes were immersed in 0, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 mol/dm^3 NaCl, CaCl$_2$, and CuSO$_4$ solutions for 24 h. The membranes were weighed after blotting the surface water, and dried in a thermostat controlled at 40°C until the constant weights were obtained. The degree of swelling of each membrane was calculated by the weights of the swollen and dried membranes.

Permeation Experiment

Materials to be permeated were KCl, sucrose, and dipeptides. The measurement of the permeability was carried out with a diaphragm-type cell that had effective permeation area of 4.0 cm^2. Into the left-hand chamber of the cell, 25 cm^3 of pure water was intro-

duced, and 25 cm^3 of 0.05 mol/dm^3 KCl or sucrose was introduced into the right-hand chamber of the cell. The cell was then placed in a thermostat controlled at 30°C, and 0.1 cm^3 of samples were withdrawn from both sides of the membrane every 2 h. KCl was determined by measuring K$^+$ ion concentration with a Hitachi Z-8100 atomic absorption spectrophotometer and sucrose was determined with a Hitachi U-2000 spectrophotometer by the phenol-sulfuric acid method. Each dipeptide was dissolved in water of pH 10 (0.05 mol/dm^3) and the solution was poured into the right-hand chamber of the cell and water of pH 10 was poured into the left-hand chamber of the cell. Dipeptides were assayed by the ninhydrin method using a spectrophotometer.

Metal ions in the membranes were determined with an atomic absorption spectrophotometer, after dissolving by means of wet ashing with H$_2$SO$_4$.

RESULTS AND DISCUSSION

It was reported that the adsorption of metal ion on chitosan, including film diffusion and pore diffusion, required 1 day to attain equilibrium in a batch experiment with chitosan beads.[3] Thus, to examine the degree of swelling, chitosan membranes were immersed in different salt solutions for 24 h. Figure 1 shows the dependence of the swelling degree of chitosan membranes on the ionic strength of the salt solutions. The degree of
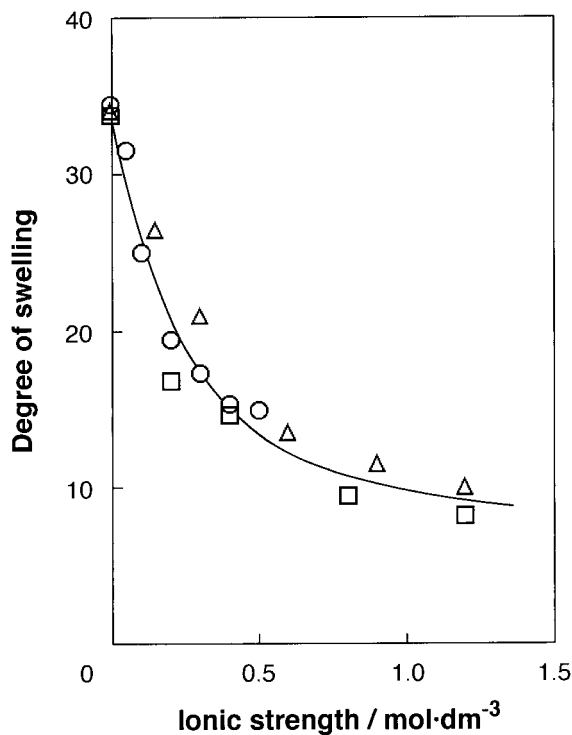

Figure 2 Dependence of the swelling degree of the chitosan gel membrane on the ionic strength of salt solutions: ($\bigcirc$) NaCl; ($\triangle$) CaCl$_2$; ($\square$) CuSO$_4$.
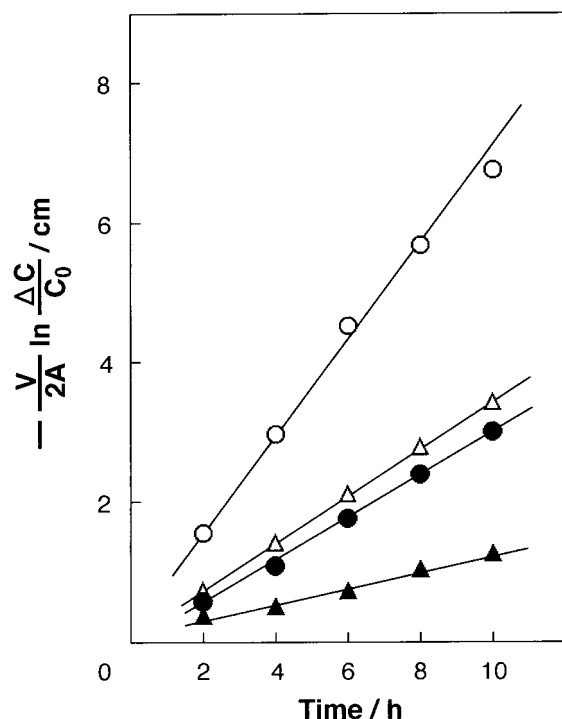
Figure 3 Permeability of the chitosan and chitosan–Cu complex membranes for KCl and sucrose: (○) KCl through the chitosan membrane; (●) KCl through the chitosan–Cu complex membrane; (△) sucrose through the chitosan membrane; (▲) sucrose through the chitosan–Cu complex membrane.

swelling decreases with increasing the ionic strength, because the osmotic pressure in the membrane decreases with increasing the ionic strength. Changes in the swelling degree are almost the same for NaCl, $CaCl_2$, and $CuSO_4$. Similarly, Figure 2 depicts the swelling degree of chitosan gel membranes. Decreases in the swelling degree of gel membranes are larger than those of the chitosan membranes mentioned above, and occur over the wide region of the ionic strength. The

reason for this is the loose membrane texture or polymer packing in the gel form. In the $CuSO_4$ solution, additionally, inter- and intramolecular crosslinking through Cu^{2+} ions seems to be formed.[12–15]

All the transition metals used in the permeation experiment were sulfate form, because Mochizuki et al. suggested that the crosslinking could be formed through the multivalent anions such as SO_4^{2-}, while the crosslinking was not formed through monovalent anions such as Cl^-.[7] Permeability of the membrane was estimated by the following equation described previously[10]:

$$\text{Permeability in cm/s} = -\frac{V}{2At} \ln \frac{\Delta C}{C_0},$$

where V is the volume of each chamber, A is the membrane area, t is the time, ΔC is the concentration difference between both solutions, and C_0 is the initial concentration of solutes. Figure 3 illustrates typical results of the permeation experiment using the chitosan–Cu membrane. The slope of each straight line represents the permeability. The permeabilities of the chitosan–Cu complex membrane are smaller than those of the chitosan membrane both for KCl and for sucrose. From the permeability and membrane thickness, δ, permeability coefficient, P, was calculated as follows[10]:

$$P \text{ in cm}^2\text{s} = (\text{Permeability}) \times \delta.$$

Table I compiles the permeability coefficients, along with some membrane properties. Chitosan membranes containing transition metal ions became very rigid and sturdy. This is attributable to a crosslinking effect of transition metal ions, which in turn, makes the membrane less permeable. In the case of the chitosan–Ni, chitosan–Cu, and chitosan–Zn membranes, the permeability coefficients are lower than that of the chitosan membrane. This find is interpreted in terms of the contraction of "hole" produced by the thermal motion of polymer chains, due to the formation of complexes with

Table I Permeability Coefficients, Degree of Swelling, and Metal/Glucosamine Ratio of Chitosan and Chitosan–Transition Metal Complex Membranes

Salt	$P_{KCl} \times 10^7$ (cm²/s)	$P_{sucrose} \times 10^7$ (cm²/s)	Degree of Swelling[a]	Metal/Glucosamine Ratio[b]
—	15	4.2	3.95	—
$MnSO_4$	15	6.0	2.71	1 : 48
$FeSO_4$	13	5.0	2.13	1 : 36
$CoSO_4$	16	5.9	2.09	1 : 22
$NiSO_4$	6.9	2.1	1.80	1 : 19
$CuSO_4$	6.4	1.1	1.22	1 : 8
$ZnSO_4$	6.4	2.8	2.33	1 : 64

[a] Estimated by weight.
[b] Metal ion was determined by atomic absorption spectrophotometry after permeation experiment.

Table II Permeability Coefficients of Chitosan–Cu Complex Membranes for Dipeptides

Membrane	$P_{\text{Gly-Gly}} \times 10^7$ (cm²/s)	$P_{\text{Ala-Ala}} \times 10^7$ (cm²/s)	$P_{\text{Ala-His}} \times 10^7$ (cm²/s)
Chitosan–CuSO$_4$	1.3	1.1	1.1
Chitosan–Cu(NH$_3$)$_4$	1.3	1.1	1.1

transition metal ions.[7] In the case of the chitosan–Mn, chitosan–Fe, and chitosan–Co membranes, however, the permeability coefficients are a little larger than that of the chitosan membrane. Desorption of metal ions appears to occur during the permeation experiment, which in turn, leads to an increase of the swelling degree and the permeation area of the membrane. These results indicate that the stability constants of the complexes are not so large as to maintain the crosslinking of chitosan chain for a long time in the solutions, including no transition metal ions.

The order of the stability constants of these transition metal complexes is Mn < Fe < Co < Ni < Cu > Zn, which is known as the Irving–Williams order.[20] The permeability coefficients in this study are roughly in accord with their series. Thus, the difference in the stability constant of complexes may cause the difference in the swelling degree of the complex membranes. The swelling degrees of chitosan membranes in the transition metal salt solutions are listed in Table I. As can be seen, the order of the swelling degree is as follows: MnSO$_4$ > FeSO$_4$ > CoSO$_4$ > NiSO$_4$ > CuSO$_4$ < ZnSO$_4$. The mol ratios of transition metal ion to glucosamine unit of chitosan, calculated from the content of transition metal ions, are also listed in Table I. Again, they are in the same order as the degree of swelling.

On the other hand, the permeability coefficients of the gel membrane including the Cu^{2+} ion were one order larger than those of the chitosan membrane mentioned above, but there was no difference in the permeability coefficient between the chitosan–Cu gel membrane and the chitosan gel membrane. It seems that "hole" of the gel membrane is too large to affect the permeation of low molecular weight solutes. The higher molecular weight solutes would be controlled.

Table II displays the permeability coefficients of the chitosan–CuSO$_4$ and chitosan–Cu(NH$_3$)$_4$ membranes for dipeptides, Gly-Gly, Ala-Ala, and Ala-His. They are low, although the molecular weights of dipeptides are lower than that of sucrose, probably due to the interaction with the Cu^{2+} ion. However, the Cu^{2+} ion on the chitosan membrane was washed out with Gly-Gly solution. The complexing ability of chitosan to the Cu^{2+} ion appears lower than that of dipeptides. Some chelating groups, such as iminodiacetate, should be introduced to strongly retain the Cu^{2+} ion.

As was mentioned before, chitosan–transition metal complex membranes were prepared, and permeabilities of the membranes were measured for KCl and sucrose.

The permeability decreased significantly by complexing with Ni^{2+}, Cu^{2+}, and Zn^{2+} ions, due to the formation of compact chitosan–metal complexes. The permeabilities of the chitosan–Cu complex membranes for dipeptides were low. Dipeptides, however, caused the complexing with Cu^{2+} ion and made the membrane loose.

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