

Chitosan 막의 물과 알코올에 대한 수착과 확산

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Sorption and Diffusion of Water and Alcohols in Chitosan Complex Membranes

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요약 : 계접질로부터 키틴을 단리시켜 수산화나트륨 수용액으로 탈아세틸화하여 키토산을 제조하였으며 제조된 키토산을 초산 수용액과 반응시켜 키토산-초산 복합체 막을 제조하였다. 합성된 복합체 막을 수산화나트륨 수용액으로 처리시킨 시간에 따라 분류하여 물 및 메탄올, 에탄올, 이소프로판올, 프로판올과 같은 저급 알코올과의 팽윤도를 측정하였으며 나타난 수착현상은 질량증가를 분석하는 방법으로 조사하였다. 시간의 함수에 대한 수착도로 부터 이들 용질들의 키토산 막내의 확산계수와 물에 대한 선택도를 구하였다. 나아가 Mg^{++} , Cu^{++} , Ni^{++} , Al^{+++} , Co^{++} , Fe^{++} , Ba^{++} 등의 금속염을 첨가시킨 키토산 막을 통하여 수착 및 확산계수를 구하고 선택도를 검토하였다. 키토산-초산 복합체 막의 경우 알칼리 처리시간이 증가할수록 막내의 결정성의 증가로 인해 평형수착도가 감소하였으며, 용액은 저급알코올의 경우 메탄올, 에탄올, 이소프로판올, 프로판올의 순으로 평형수착량이 감소하고 확산이 저하되는 것으로 나타났으며, 온도에 대한 영향은 거의 받지 않음을 알 수 있었다. 또한, 키토산 막에 금속염을 첨가시킴으로 알코올 수용액중 물의 선택도를 증가시킬 수 있는 것을 알았다.

Abstract : The present study investigates the sorption and diffusion of water and alcohols in chitosan-acetic acid complex membranes and chitosan-metal ion complex membranes. Chitosan was prepared from chitin abstracted from the crab shell and subsequently deacetylated with NaOH solution. Chitosan was dissolved in an aqueous acetic acid solution and cast into a membrane to form a chitosan-acetic acid complex membrane with varying NaOH treatment time. For these membranes we measured absorption of water, methanol, ethanol, isopropanol and propanol in the complex membrane. From the plots of absorption of solvents as a function of square root of time, diffusion coefficients were calculated. As an alkali treating time is prolonged, membrane becomes more crystalline and thus an equilibrium sorption value decreases. We observed the decreased equilibrium sorption and diffusion coefficient of lower alcohols in the order of methanol, ethanol, isopropanol and propanol resulting from their increased molar volume and decreased heat of vaporization. Sorption and diffusion beha-

vior in chitosan with inserted metal ions such as Mg^{++} , Cu^{++} , Ni^{++} , Co^{++} , Fe^{++} , Ba^{++} and Al^{+++} was investigated. Results of this study conclude that the water selectivity in alcohol-water mixture could be enhanced by metal ion implantation in chitosan membranes.

INTRODUCTION

Chitin is one of the most abundant organic materials which can be easily obtained in the nature. The natural sources of chitin are the shells of crustaceans (lobsters, shrimps, etc.) or the broth from industrial fungal processes (e.g., citric acid). That is, the natural sources of chitin would be the waste product of other industrial processes. Since waste disposal is becoming an acute problem, this seems a very desirable source of raw material. Several crystalline structures of chitin are known. Most researches concerning chitin are mainly focused on the acetylated amino groups of the main chain. Chitin is similar in its chemical structure to cellulose but its uses and applications have not yet been realized much as those of cellulosic materials.^{1~3}

Chitosan is the deacetylated product of chitin. While chitin is insoluble in most solvents, chitosan is readily soluble in acidic solutions and more available for industrial applications. In recent years, a basic and applied research on the effective use of chitin and chitosan derivatives has been actively conducted. Examples would be the adsorption of heavy metal ions,⁴ artificial skin substitutes,⁵ chitosan fibers,⁶ membranes^{7~13} etc.

Much interest has been focused on the sorption phenomena after the discussion made at the Faraday Society meeting in 1946 on the liquid absorbing capacity.¹⁴ After Muzzarelli et al.³ reported the use of chemically modified chitin and chitosan membranes, they are used in various fields such as in metal ion separation,⁷ gas separation,^{8,9} reverse osmosis,¹⁰ ultrafiltration, evaporation¹¹ and pervaporation.^{11~13}

Samuels first reported the solid state structure of the chitosan films prepared from formic acid so-

lution, and the films cast from formic acid solution followed by washing with NaOH solution.¹⁵ He proposed the former (cast film) as form I crystal and the latter (washed film) as form II crystal type. Sakurai et al. later extended his study about crystal structures¹⁶ and used these films for gas separation¹⁷ and water vapour sorption study.¹⁸ It is assumed that the complex formation, i. e., the incorporation of fatty acid in the chitosan crystal should give crystal structure, crystallinity and crystallization behaviour differing from those of chitosan itself. However, no other studies using chitosan complex membranes for sorption behavior and for pervaporation have been examined so far.

The present study investigates the sorption and diffusion of chitosan-acetic acid complex membranes and chitosan-metal ion complex membranes. Effect of alkali treatment of chitosan-acetic acid complex membrane on the sorption of liquid water and various alcohols was examined on the basis of molecular features. Various metal ion complex membranes were also studied to help understand the sorption of chitosan films. This study will later be used for the basis of predicting the permeation characteristics of these membranes for alcohol-water separation using pervaporation technique.

EXPERIMENTAL

Materials

Chitin was obtained from crab shell by modified Hackman method.¹⁹ Chitin was subsequently deacetylated with NaOH solution to obtain chitosan. A detailed manufacturing method for chitin and chitosan is described elsewhere.⁴ Acetic acid, sodium hydroxide, methanol, ethanol, isopropanol and propanol are from Duksan Pharmaceutical Co. Metal sulfates ($Al_2(SO_4)_3$, $BaSO_4$, $NiSO_4$, $CuSO_4$, $CoSO_4$, $MgSO_4$, $FeSO_4$) are from Chameleon Co.

Characterization

For structure determination, infrared spectrophotometer (FTIR Nicolet Model 5-DX) and X-ray diffractometer (Rigaku Denki Model RAD-C) were used. The X-ray source was $\text{CuK}\alpha$ radiation (30kV, 20mA) using monochromator. Densities of samples were measured by density gradient column method.

Preparation of Chitosan Complex Membrane

2 g of chitosan was added to 200 ml of 2 wt% aqueous acetic acid solution at room temperature with stirring. Polymer solution (pH=3.5) was filtered to remove dirt and undissolved chitosan, and then cast onto a glass plate to manufacture the chitosan membrane. After drying the solvent at room temperature for more than 12 hours, membranes were treated with 1 N aqueous sodium hydroxide solution. Depending upon the alkali treating time, cast membranes are either in chitosan type (cast membrane) or in chitosan complex type membrane (washed membrane) as depicted in

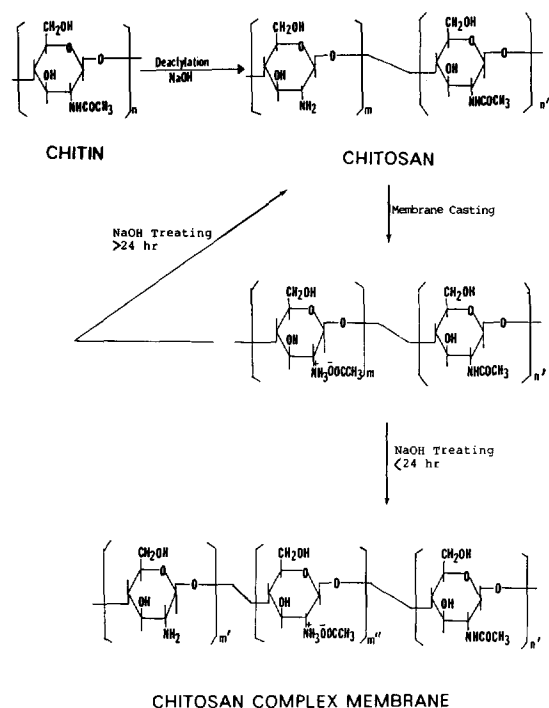


Fig. 1. Manufacture of chitosan complex membranes.

Fig. 1. Alkali treating time was controlled to be 30 min, 1, 3, 6, 9, 12 and 24 hours. Non-alkali treated sample was used as a control (cast membrane).

Chitosan-metal ion complex membranes were made by mixing 100 ml of 2% aqueous acetic acid solution with 1.5 g of chitosan powder, and 0.1939×10^{-3} mole of metal salts were dissolved in the chitosan solution. After casting on a glass plate, solvents were dried in an oven controlled at 65°C , followed by treating this membrane with 1 N NaOH solution for three hours, rinsed with distilled water and then redried at room temperature.

Swelling Experiment

Complex chitosan membrane treated with NaOH solution for 0, 0.5, 1, 3, 6, 9, 12 and 24 hours were immersed in water, methanol, ethanol, isopropanol and propanol. The area and the thickness of the membrane was about 20 cm^2 and about $20\mu\text{m}$, respectively. Each membrane was tested triplicate at room temperature, 40, 60 and 70°C .

Samples were placed in a desiccator over anhydrous silica gel for 24 hours before use, and dry weights of the membranes were recorded before soaking in the liquids. The weights were recorded at various time intervals. When membranes were removed from the liquids, they were carefully blotted to remove the surface liquid before weighing. The mass of liquid uptake per mass of sample was determined as a function of time (t). Weight gains (Q) were then plotted versus the square root of time. Solubilities of liquids in the polymers were calculated at equilibrium. Diffusion coefficients were calculated as

$$D = \frac{\pi}{t} \left(\frac{\ell \cdot Q_t}{4 Q_\infty} \right)^2 = \pi \left(\frac{\ell \theta}{4 Q_\infty} \right)^2 \quad (1)$$

where ℓ is material thickness (cm), θ is slope of the plot of Q_t versus $t^{1/2}$, and Q_∞ is maximum weight gain at equilibrium.

RESULTS AND DISCUSSION

Acetic Acid Complex Membranes

Infrared spectra of chitin, chitosan and complex

membrane are shown in Fig. 2. For chitin (Fig. 2(a)), a broad $-OH$ stretching vibration at $3,280\text{ cm}^{-1} \sim 3,400\text{ cm}^{-1}$, $-NH$ stretching at $3,400$ and $1,550\text{ cm}^{-1}$, respectively, are seen. Carbonyl absorption peak at $1,660\text{ cm}^{-1}$ becomes apparently smaller for chitosan membrane (Fig. 2(b)). For chitosan membranes, deacetylation degree was about 54% as determined by the titration method.²⁰ $-NH$ bending vibration at $1,550\text{ cm}^{-1}$ becomes smaller and bending vibration caused by the primary amino group appears at $1,590\text{ cm}^{-1}$. Chitosan-acetic acid complex membrane shows similar absorption peaks with chitosan membrane due to relatively low degree of deacetylation (Fig. 2(c)).

Effect of Alkali Treatment

Figs. 3~6 show absorption of water, methanol, ethanol and propanol, respectively, measured at 25°C as a function of square root of time for chitosan-acetic acid complex membrane treated with NaOH solution for 0~24 hours. As alkali treating time is prolonged, equilibrium absorption generally decreases for water and alcohols. Water sorption values at equilibrium are about 190% of dry film for nonalkali treated samples and about 120% for 24 hour alkali treated chitosan membranes. How-

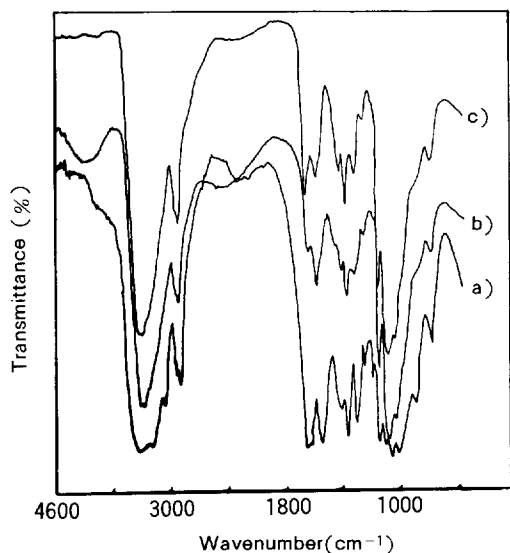


Fig. 2. IR spectra for (a) chitin, (b) chitosan and (c) chitosan complex membrane (3-hour alkali-washed).

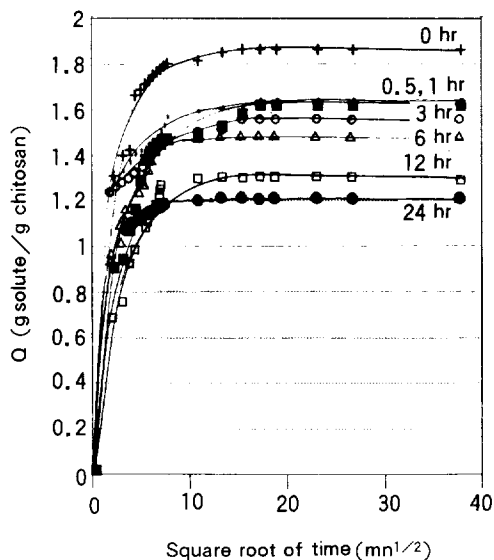


Fig. 3. Absorption (Q) of water measured at 25°C versus square root of time ($t^{1/2}$) for chitosan-acetic acid complex membrane treated with NaOH solution for different period.

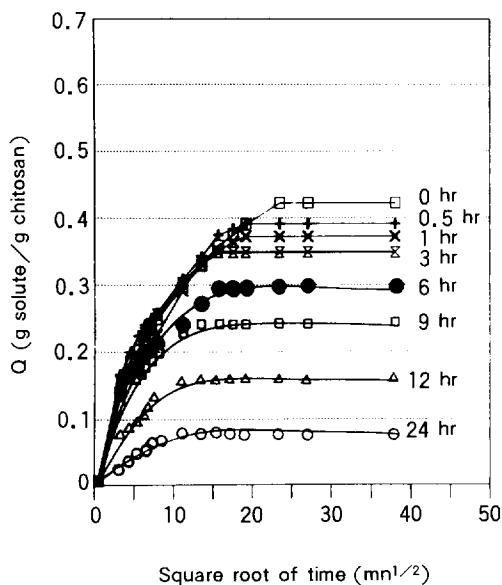


Fig. 4. Absorption (Q) of methanol measured at 25°C versus square root of time ($t^{1/2}$) for chitosan-acetic acid complex membrane treated with NaOH solution for different period.

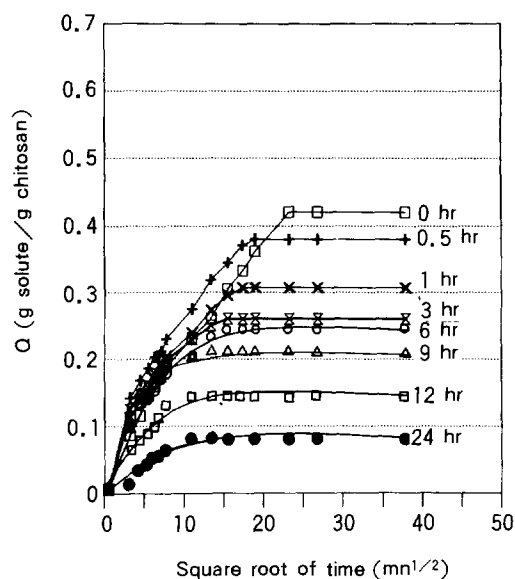


Fig. 5. Absorption (Q) of ethanol measured at 25°C versus square root of time ($t^{1/2}$) for chitosan-acetic acid complex membrane treated with NaOH solution for different period.

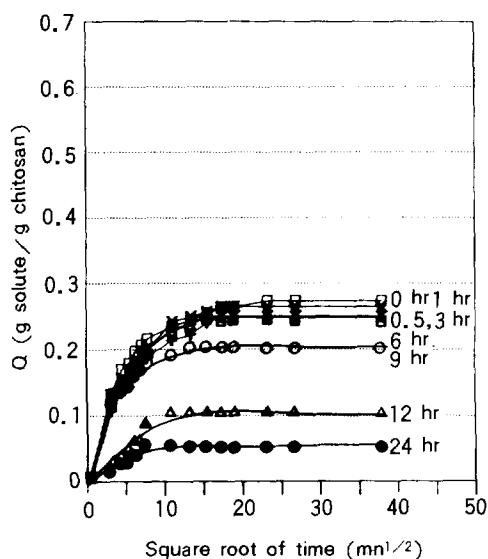


Fig. 6. Absorption (Q) of propanol measured at 25°C versus square root of time ($t^{1/2}$) for chitosan-acetic acid complex membrane treated with NaOH solution for different period.

ever, alcohol sorption at equilibrium is only up to about 40%. For alcohols with different carbon numbers, the amount of liquids sorbed depends mainly on the molar volume and the enthalpy of vaporization of alcohols^{21,22} as shown in Table 1. The sorption of alcohols in chitosan complex membranes is in the order of methanol > ethanol > isopropanol > propanol. Chitosan complex membrane sorbs water faster than alcohols. For water absorption, the time to reach an equilibrium is within an hour. For alcohols, however, it is prolonged to about 3~4 hours depending on the size of alcohols.

The tendency that alkali treatment drops the amount of equilibrium solvent uptake can be explained with an increased crystallinity of alkali-treated chitosan complex membranes as evidenced by the X-ray diffraction patterns of these membranes (Fig. 7). Studies on the crystal structure of chitosan have not been made so far except those reported by Samuels¹⁵ and Sakurai et al.¹⁶ Sa-

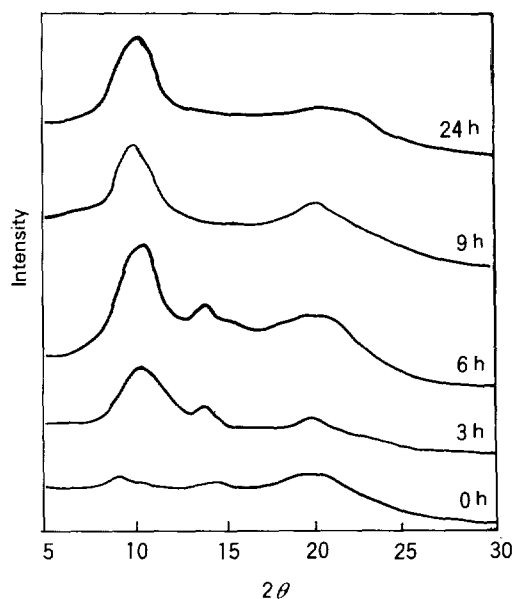


Fig. 7. X-ray diffraction patterns for chitosan-acetic acid complex membranes treated with NaOH solution. Numbers on the fig. indicate the duration of NaOH treatment.

Table 1. Physical Properties of Solvents ^{21, 22}

Liquid	Molecular Weight	Boiling Point °C	Density d g/cm ³	Molar Volume cc/g · mol	Heat of Vaporization cal/g	Solubility Parameters (cal/cm ³) ^{1/2}
Water	18.00	100.0	1.00000	18.000	540.50	23.4
Methanol	32.04	64.7	0.79150	40.480	284.29	14.5
Ethanol	46.10	78.5	0.78900	58.428	204.26	10.0
Propanol	60.09	97.2	0.80530	74.618	164.36	10.5
iso-Propanol	60.09	82.5	0.78505	76.543	159.35	10.0

muels proposed two types of crystals denoted as the form I and form II crystals, and also indicated that the unit cells of both crystal forms were orthorhombic. The appearance of two types of crystal forms depended largely on the preparation methods of chitosan films. Form I crystal is obtained by casting the aqueous formic acid solution. Form II crystal is obtained by precipitation, i.e., by immersing the solution into an aqueous NaOH solution. Sakurai et al. extended Samuels' earlier study and prepared several chitosan membranes with formic acid, acetic acid and butyric acid. They later used these membranes for gas separation¹⁷ and water vapour sorption study.¹⁸

Alkali treated chitosan complex membranes show X-ray patterns in the scattering angle (2θ) range of 9° to 11° and around 20° . According to Sakurai et al.'s analysis of X-ray patterns in chitosan-acid films, peaks appeared at around 10° are assigned to be (001) and (100), and those at around 20° are a mixture of (101) and (002). However, the maxima occurs at slightly different values in each films; at 8.88° , 9.64° , 9.64° , 10.10° and 10.64° in the complex membranes treated for 0, 3, 6, 9, and 24 hours, respectively. Using the formula: $n\lambda = 2d\sin\theta$ with $n=1$ and $\lambda=1.54\text{\AA}$, the d spacings of the films were determined to be 9.95, 9.17, 9.17, 8.75 and 8.3 \AA , respectively. The interchain packing can thus be seen to be tighter in the membranes treated with alkali for long time. These facts imply that the casting conditions bring out the formation of complex between acetic acid and amino groups not only in the amorphous

Table 2. Density of Chitosan Membranes Treated with NaOH Solution for Different Periods

Alkali Treating Time (hr)	Density (g/cm ³)
0	1.4155
0.5	1.4176
1	1.4165
3	1.4227
6	1.4259
9	1.4217
12	1.4176
24	1.4176

region but also in the crystalline region of chitosan.

X-ray diffraction patterns also show that alkali treating time serves to increase the peak intensity at 2θ of around 10° . Accordingly, we can see that the relative crystallinity goes up as the acetylate ion attached to amino group of chitosan (Fig. 1) was removed. In other words, as chitosan membrane has more amino groups in the chain, it becomes more capable of hydrogen bonding with each other, resulting in an increased crystallinity. This result is somewhat similar to what Sakurai et al. reported¹⁷ for gas separation.

For some reasons, however, the peak intensity in X-ray diffraction patterns and density (Table 2) was the highest for six-hour alkali-treated sample. When pervaporation experiment was conducted using this membrane (not shown here), the permeation rate was the lowest while the separation

factor was the highest for six-hour alkali-washed membrane.¹² Accordingly, the pervaporation performance coincides well with the density and X-ray measurements. It is well known that the swelling degree of water and alcohols depends on the volume fraction of amorphous region (or crystallinity) since the crystalline region is usually recognized to be independent of permeation. The swelling becomes less as chitosan membrane was further treated with alkali solution due to an increased crystallinity. However, we did not observe any minima in the swelling experiment.

Effect of Temperature

We measured sorption of water and alcohols in chitosan complex membrane at different temperatures: 25, 40, 60 and 70°C. Fig. 8 illustrates the effect of temperature on equilibrium sorption of water and alcohols in chitosan-acetic acid complex membranes treated with NaOH solution for three hours. As can be seen in the Fig., an equilibrium sorption of liquids in the membrane is to a small extent increased with temperature ranging up to 70°C. Fig. 9 represents typical data for temperature dependence of apparent diffusivity of water and

alcohols as calculated from slopes of initial linear portions of the curve in Figs. 3~6. Diffusivity values of liquids in the membrane increased with temperature due mainly to the thermal motion of the chitosan membrane. Since chitosan is a semi-crystalline material, the activation energy is not so much.

Metal Ion Complex Membrane

Metal ions are known to form a complex with hydroxyl groups or amino groups in chitosan, and this is the main reason why chitosan has long been known and used as a heavy metal adsorbent.⁴ To form a complex membrane it is essential that the metal ion should be di-valent.¹³ Monovalent ions such as Li^+ or Na^+ do not form a complex. There are several researches reported recently about metal ion complex chitosan membranes used for gas separation^{8,9} and for water-ethanol separation.^{11,12} But for water-ethanol separation, the researchers used metal salts in the feed mixture rather than mixed metal salts in the membrane itself. Thus metal ion complex membrane is formed on the surface rather than inside of the membrane. The result of the separation characteristics of this

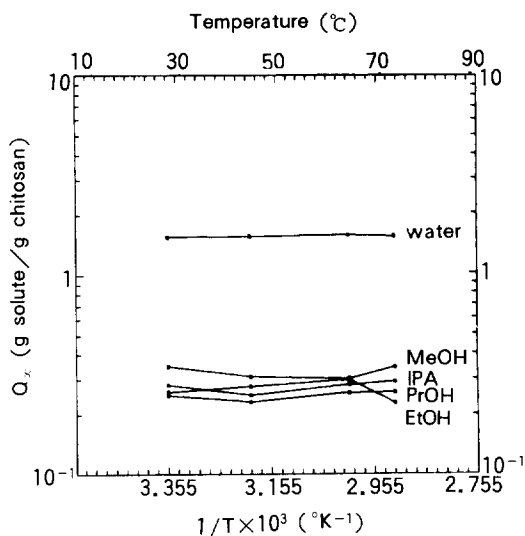


Fig. 8. Effect of temperature on equilibrium solvent uptake in chitosan-acetic acid complex membrane treated with NaOH solution for 3 hours.

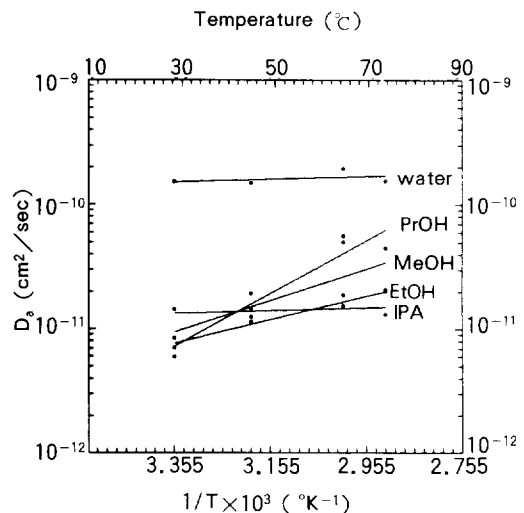


Fig. 9. Effect of temperature on apparent diffusion coefficient for water and alcohols in chitosan-acetic acid complex membrane treated with NaOH solution for 3 hours.

Table 3. Equilibrium Solvent Uptake of Chitosan-Metal Salt Complex Membrane Cast in 2 wt% Acetic Acid Solution and then Subsequently Treated with NaOH Solution for 3 Hours

Metal Ion Solvent	Ba	Mg	Fe	Co	Co*	Ni	Cu	Al
Water	1.14	1.31	1.14	0.99	0.99	1.10	1.91	1.65
Methanol	0.20	0.38	0.11	0.07	0.11	0.20	0.39	0.25
Ethanol	0.09	0.31	0.04	0.11	0.07	0.16	0.20	0.21
iso-Propanol	0.08	0.15	0.07	0.08	0.08	0.10	0.18	0.43
Propanol	0.07	0.12	0.07	0.48	0.05	0.11	0.11	0.40

* sorbed according to Mochizuki.¹⁸

membrane indicated that the long-term stability prevents this membrane from being used as a commercially available one because there is always a problem of removing excess metal ions in the feed mixture. It would be, of course, more advantageous to manufacture more stable complex membrane.

The effect of various metal sulfates added to chitosan-acetic acid casting solution and membrane therefrom on the solvent uptake at equilibrium was investigated and listed in Table 3. Except for aluminium ion, all the metal ions are divalent. Electronegativity increases from Ba^{++} to Al^{+++} which is from the left to the right of Table 3. In general Cu^{++} and Al^{+++} ion containing chitosan membranes show higher equilibrium solvent uptake than the membranes containing less electronegative ions. An increase of the equilibrium solvent uptake in the presence of the specific salts may be explained by an increase of the affinity of chitosan toward water and alcohols due to the formation of complex. Another reason might be the formation of physical macrovoids due to the insertion of metal ions. The scanning electron microscopic pictures(not shown here) indicated the formation of small voids for metal containing membranes.

We can compare the equilibrium solvent uptake of metal ion containing chitosan complex membrane with the membrane without metal ions. Generally metal ion containing complex membranes show less solvent uptake at equilibrium than that

of membranes without metal ions. The reduction in equilibrium solvent uptake may be explained by the crosslinking effect of metal ions on the chitosan. Despite of the formation of small voids in metal containing membranes, the presence of metal-chitosan interaction would reduce the extent of interaction of solvent molecules with the chitosan. Guthrie et al. observed the similar tendency for acid dye sorption in chitosan membrane.²³ Membranes with and without metals are treated with alkali for three hours. Thus, metal ion complex membrane is actually a membrane containing both salts and metal ion complex. We can see that the specific metal ion containing membrane is not as efficient as the membrane containing only salts. Notwithstanding a slight decrease in water uptake and a marked decrease in a certain alcohol uptake, metal ion containing membranes could be generally more effective in separating water from alcohol solution.

CONCLUSIONS

Sorption and diffusion of water and alcohols in chitosan-acetic acid complex membranes have been studied to assess potential applications of these membranes in separating water from alcohols. This study indicated that equilibrium sorption values in these membranes diminished as alkali treating time increased due to an increased crystallinity of these membranes. Water appears to be the highest absorbing liquid among the solvents

tested for chitosan complex membranes. Lower carbon alcohols sorb more liquids than higher carbon alcohols do due to smaller molar volumes and greater enthalpies of vaporization. Temperature dependence of sorption and diffusion of water and alcohols in chitosan-acetic acid complex membrane is seen. Metal ion complex membranes show a decreased equilibrium solvent uptake due to the chelating effect of metal ions.

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