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# THE $Al^{3+}$ SENSITIVITY OF CHITOSAN-SILK FIBROIN COMPLEX MEMBRANE ON SWELLING AND ITS APPLICATION ON CHEMICAL VALVE FOR THE SEPARATION OF ISOPROPANOL-WATER MIXTURE

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## ABSTRACT

A novel natural biopolymer complex membrane, namely, a crosslinked chitosan-silk fibroin complex membrane (semi-IPN membrane) was prepared. The complex membranes manifested a good ion sensitivity when swelled in $AlCl_3$ aqueous solutions with different concentrations. According to its different swelling values with different $Al^{3+}$ concentrations, the complex membrane could act as a chemical valve to control the flux of isopropanol-water mixture when separated by pervaporation. The pervaporation results indicated that the flux also showed an ion sensitivity when the $Al^{3+}$ content in the feed was changed. In the meantime, the ion sensitivity of the flux expressed the same tendency as that of the swelling ratio. In addition, the flux of isopropanol-water mixture was significantly improved while the high selectivity was maintained when suitable amount of $AlCl_3$ was added to the feed.

## INTRODUCTION

Stimuli-responsive polymer gels and their application to chemomechanical systems have attracted considerable attention in recent years. Much attention has



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(A) (B)

**FIGURE 1.** Structure of chitosan (A) and chitin (B).

been paid to polymer gels which exhibit a volume change on changing temperature, solvent, electric field, ion concentration and/or pH [1]. In the meantime the use of natural biopolymer such as proteins and polysaccharides for the preparation of polymer gels have attracted investigators [2]. This is due to the fact that natural biopolymers have abundant sources and unique properties, such as nontoxicity and good biological compatibility. For instance, some studies of natural biopolymer complex membranes, such as chitosan-polyether, chitosan-poly(acrylic acid) polymer networks on pH and ion sensitivities have been reported recently [2-5]. The unique characteristics of these gels mentioned above allow them to be used as a mechanical system which converts chemical free energy into mechanical work. One of the chemomechanical system applications is valve function. By changing the environmental conditions, the polymer gels can expand and contract in order to separate solute mixtures with different molecular size. However, the polymer gels often used as the chemical valve are usually electrically controlled [1].

We also have prepared a novel natural biopolymer complex membrane-the chitosan-silk fibroin complex membrane. As we know, chitosan (Figure 1A) is a poly(aminosaccharide), normally obtained by alkaline deacetylation of chitin, (Figure 1B) the principle component of living organisms such as fungi and crustaceans. Silk fibroin is a protein from silk which consists of various amino acid residues such as alanine, glycine, serine, etc. In our previous study, it was found that chitosan and silk fibroin formed a complex due to the hydrogen bonding between their molecular chains, and showed good pH and ion sensitivity [6]. On the other hand, the chitoan-silk fibroin complex membrane was also used to separate the alcohol-water mixture by pervaporation [7]. The results showed that the selectivity of the complex membrane was rather good, but the flux was quite low, which was in agreement with the previous studies on chitosan membranes [8]. In this article, we discuss the $Al^{3+}$ sensitivity of chitosan-silk fibroin complex membrane on water

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swelling and the chemical valve function on the flux control, which related to the swelling property in the separation of isopropanol-water mixture by pervaporation.

## EXPERIMENTAL

### Materials

Chitosan was prepared from chitin according to the method described in our previous paper [9]. Its viscosity-average molecular weight was 3.0(10$^5$, and the *N*-deacelylation degree was 86% (mol/mol). The chitosan solution was prepared by dissolving chitosan in 2% (w/w) acetic acid.

Raw silk was degummed twice with 0.5% (w/w) $NaHCO_3$ solution at 100°C for 30 minutes, and washed with distilled water. Degummed silk was dissolved in 9.5 mol/L LiBr solution. After dialysis with distilled water for 3 days, the solution was filtered, then the silk fibroin solution was obtained.

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### Membrane Preparation

The membrane was prepared by casting a mixture of 2% (w/w) chitosan solution, 2% (w/w) silk fibroin solution and the crosslinking agent glutaraldehyde [1.5% (mol/mol) content to the amino group in chitosan], onto a PET plate and allowing the solvent to evaporate in the air. The thickness of the membrane is about 30 μm.

### Swelling Experiment

Equilibrium swelling ratios were measured as follows. Dry chitosan-silk fibroin complex membrane samples were weighed and subsequently immersed in $AlCl_3$ aqueous solutions with various concentration at 30 °C for 24 hours. The swollen samples were weighed immediately after careful blotting. The swelling ratio (SR) was estimated using the following equation:

$$SR = (W_s - W_d)/W_d$$

where $W_d$ and $W_s$ are the weights of the dry and swollen membrane, respectively.

### Pervaporation Experiment

A stainless steel cell with an effective area of a flat membrane of 36.5 cm$^2$ was used. At the down stream side, a pressure of below 30 Pa was maintained by

TABLE 1. Swelling Ratio o Chitosan-Silk Fibroin Complex Membranes in Different Salt Solution with Same Ionic Strength

| Silk fibroin content (%) | NaCl (1.5mol/L) | KCl (1.5mol/L) | $MgCl_2$ (0.5mol/L) | $CaCl_2$ (0.5mol/L) | $AlCl_3$ (0.25mol/L) |
|---|---|---|---|---|---|
| 25 | 74.38 | 66.69 | 72.97 | 73.68 | 344.41 |
| 50 | 69.62 | 63.53 | 71.52 | 68.88 | 338.28 |
| 75 | 53.18 | 82.65 | 56.36 | 57.01 | 206.97 |

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means of a mechanical pump. The permeate flux was calculated by weighing the permeate condensed in the cold trap. The water content in the feed and the permeate was analyzed by means of an Abbé refractometer. The isopropanol content in isopropanol-water mixture was 85.0% (w/w). Before testing, the chitosan-silk fibroin complex membrane was swollen in feed with various $AlCl^3$ concentrations for 24 hours. The performance of the membranes in pervaporation was evaluated by the water concentration in permeate (c') which could represent the separation factor α and the flux (J) calculated as following [10]:

$$J = \frac{W}{A\Delta t}$$

where W is weight of permeate (g), $\Delta t$ is permeation time (h), A is membrane area ($m^2$), respectively.

## RESULTS AND DISCUSSION

### Swelling in $AlCl_3$ Aqueous Solution

In the previous paper, it was found that the swelling ratio of chitosan-silk fibroin complex membrane in the trivalent ion solution was much larger than those in the monovalent andbivalent ion solutions with the same ionic strength (Table 1). Mochizuki *et al.* have reported that the multivalent metal ion could form a complex with the amino group of chitosan and the conformation was changed by the ionic repulsion and/or the steric hindrance of the complex formed [11]. Because the $Al^{3+}$

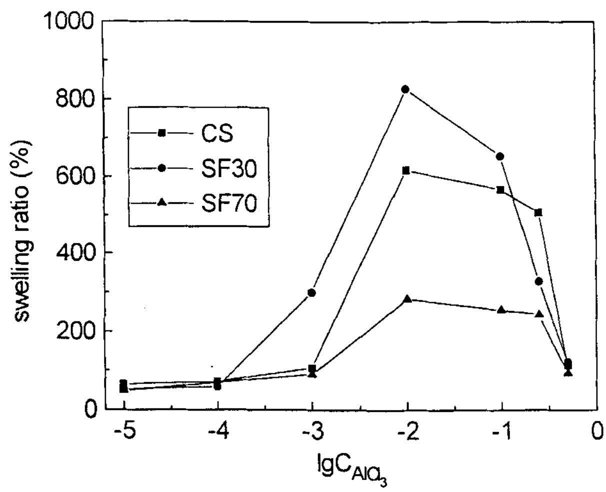


**FIGURE 2.** Swelling of chitosan-silk fibroin complex membrane in $AlCl_3$ aqueous solution [CS, SF30, SF70 denote the pure chitosan membrane, the chitosan-silk fibroin complex membrane which silk fibroin content was 30 and 70% (w/w), respectively].

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had larger electronegativity and molecule size than the monovalent and bivalent ions we studied, the free volume of chitosan was further enlarged more by complexing $Al^{3+}$, than that of monovalent and bivalent ions caused by ionic repulsion and/or steric hindrance. Therefore, this could explain why the complex membrane showed the largest swelling ratio in $AlCl_3$ aqueous. It could be also confirmed by $^{27}Al$ solid state high resolution NMR that $Al^{3+}$ could exist in chitosan membrane even if the membrane had been washed by solvent several times after swelling (X. Chen, Doctorate Thesis).

To study the swelling property of chitosan-silk fibroin complex membrane in $AlCl_3$ aqueous solution more carefully, the concentration of $AlCl_3$ aqueous solution has been changed extensively. The result indicated that the membranes showed ion sensitivity (Figure 2). At first, the swelling ratio was low and increased slightly with the $AlCl_3$ concentration increased, and when the $AlCl_3$ concentration changed from $10^{-3}$ mol/L to $10^{-2}$ mol/L, the swelling ratio increased sharply. At last, when the $AlCl_3$ concentration was larger than $10^{-2}$ mol/L, the swelling ratio de-creased with the $AlCl_3$ concentration increased. This phenomenon could be explained by the swelling mechanism of complex membrane [3, 6]. When the

$AlCl_3$ concentration was low ($<10^{-3}$ mol/L), the complexing of $Al^{3+}$ on chitosan was less, so that the dissociation of the hydrogen bond between chitosan and silk fibroin was weak, which resulted in a low swelling ratio. When the $AlCl_3$ concentration was large, more $Al^{3+}$ was complexed onto chitosan, so that the dissociation of the hydrogen bond between chitosan and silk fibroin became significant. In addition, due to the Donnan equilibrium [3] between the $Al^{3+}$ in chitosan-silk fibroin complex membrane and the exterior solution phase, there was a maximum difference in the total ion concentration between the two phases when $AlCl_3$ concentration was $10^{-2}$ mol/L and it decreased with a further increase of the $AlCl_3$ concentration. As a result, the swelling ratio reached the maximum value when $AlCl_3$ concentration was $10^{-2}$ mol/L and induced deswelling in the region where $AlCl_3$ concentration was larger than $10^{-2}$ mol/L.

From Figure 2, it was also found that the swelling ratio of chitosan-silk fibroin complex membrane, in which silk fibroin content was 30% (w/w), was larger than the pure chitosan membrane, though in the complex membrane the chitosan content was less. This was the characteristic property of complex membrane in swelling, as a result of dissociation of two components in membrane, and not only the ionic repulsion and/or steric hindrance of chitosan chain. However, when the chitosan content in membrane was much less, for instance, the silk fibroin content was 70% (w/w), the swelling ratio was rather low.

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**Separation of Isopropanol-Water Mixture by Pervaporation**

The separation mechanism of pervaporation is based on the solution-diffusion theory, i.e., the adsorption-diffusion-desorption process of the components in the feed coming across the membrane from one side to another [12]. According to the mechanism, the pervaporation properties can be improved by enhancing the adsorption of one component in the feed to the membrane or/and accelerating the diffusion of one component in the feed through the membrane. From the swelling property of chitosan-silk fibroin complex membranes in $AlCl_3$ aqueous, it can be seen that the free volumes of the complex membranes changed by changing $Al^{3+}$ concentrations. Thus, the chitosan-silk fibroin complex membrane had the possibility to act as a chemical valve to control the solute amount diffused across the membrane when the pervaporation process occurred, i.e., to control the pervaporation flux.

First, the swelling ratio of chitosan-silk fibroin complex membrane in the feed (isopropanol-water mixture) containing various amounts of $AlCl_3$ was measured (Figure 3). When the $AlCl_3$ concentration in the feed was less than $10^{-3}$

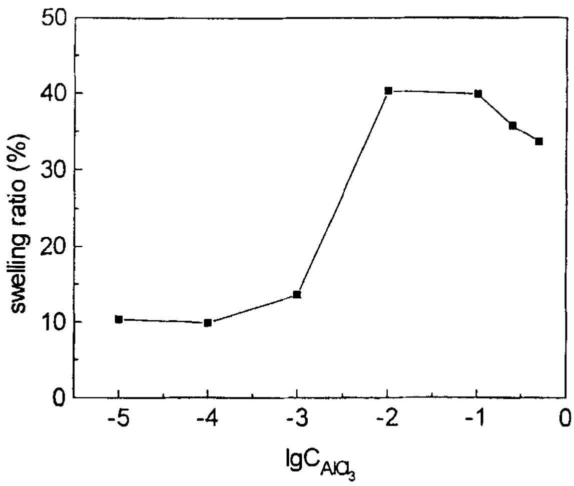


**FIGURE 3.** Swelling of chitosan-silk fibroin complex membrane in isopropanol-water mixture [silk fibroin content in membrane: 30% (w/w), $C_{AlCl_3}$ denote the $AlCl_3$ concentration in the water part of isopropanol-water mixture].

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mol/L, the swelling ratios were almost the same as that of complex membrane which was swollen in the feed without $AlCl_3$ in it [SR=10.48% (w/w)]. When the $AlCl_3$ concentration in the feed was larger than $10^{-3}$ mol/L, the swelling ratio increased dramatically and then decreased slightly, similar to those of the complex membrane in $AlCl_3$ aqueous solutions. Because the chitosan-silk fibroin complex membrane was a alcohol permselective membrane [7], it could be assumed that the chitosan-silk fibroin complex membrane adsorbed more water from the feed containing $AlCl_3$ than from the feed without $AlCl_3$, especially when the $AlCl_3$ concentration in the feed was larger than $10^{-3}$ mol/L. In the meantime, the free volume of the membrane was enlarged with the increase of swelling ratio. As a result, the permeat molecule could diffuse more freely.

The pervaporation properties of isopropanol-water mixture were shown in Figure 4. The results indicated that the flux agreed with the swelling property in $AlCl_3$ aqueous and in the feed containing $AlCl_3$ discussed above (Figures 2 and 3). When the $AlCl_3$ concentration in the feed was less than $10^{-3}$ mol/L, the flux was small. When $AlCl_3$ concentration was larger than $10^{-3}$ mol/L, the flux increased sharply and reached the maximum value when $AlCl_3$ concentration was $10^{-2}$ mol/L, then decreased with an increase of $AlCl_3$ concentration. That is, the chitosan-silk fibroin complex membrane could act as a chemical valve to adjust the flux of

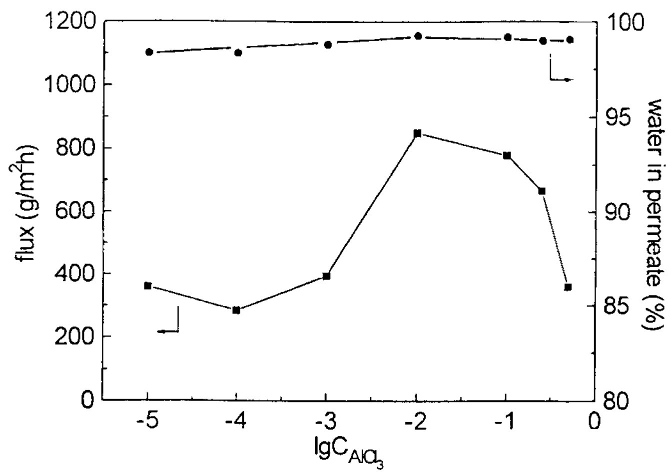


**FIGURE 4.** Separation properties of isopropanol-water mixture through chitosan-silk fibroin complex membrane by pervaporation [silk fibroin content in membrane: 30% (w/w), isopropanol in feed: 85% (w/w), $C_{AlCl3}$ denote the $AlCl_3$ concentration in the water part of isopropanol-water mixture].

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isopropanol-water mixture in the pervaporation by controlling the $AlCl_3$ concentration in the feed.

Second, it was found that both the fluxes and the separation factors of the isopropanol-water mixture containing $AlCl^3$, though chitosan-silk fibroin complex membranes, were no less than that of the "pure" isopropanol-water mixture, i.e., the one containing no $AlCl_3$ in the feed [J=383.9g/m$^2$h, c'=98.33% (w/w)]. When pervaporation flux reached maximum when the $AlCl_3$ concentration in the feed was $10^{-2}$ mol/L, the separation factor also had the maximum value [J=848.8g/m$^2$h, c'=99.28% (w/w)]. As mentioned above, when the chitosan-silk fibroin complex membrane swelled, with the increase of the swelling ratio, the free volume of the membrane enlarged. As the molecule size of the isopropanol was quite large, it was still difficult to pass through the membrane when the free volume of the membrane was enlarged, whereas the small water molecule could pass through the membrane more freely. Therefore, the flux and separation factors of the chitosan-silk fibroin complex membrane could have improved because more water was diffused across the membrane with the enlargement of the free volume caused by the increase of the swelling ratio when $AlCl_3$ was added in a isopropanol-water mixture and, the feed was separated by pervaporation.

## CONCLUSION

A novel natural biopolymer complex membrane–chitosan-silk fibroin complex membrane (semi-IPN membrane) was prepared via crosslinking chitosan with glutaraldehyde and interpenetrating silk fibroin. The chitosan-silk fibroin complex membrane showed a good ion sensitivity when swelled in $AlCl_3$ aqueous solutions. It was found that the complex membrane manifested the similar ion sensitivity when swelled in a isopropanol-water mixture which contained $AlCl_3$. Furthermore, the flux though the complex membrane also expressed the same ion sensitivity when separated isopropanol-water mixture containing $AlCl_3$ by pervaporation. According to the ion sensitivity of the flux, the chitosan-silk fibroin complex membrane can act as a chemical valve to control the pervaporation flux of isopropanol-water mixture by changing the $AlCl_3$ content in the feed. Moreover, adding appropriate amount of $AlCl_3$ in the feed can improve the flux of isopropanol-water mixture significantly while the high selectivity was retained.

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