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WATER-ETHANOL SEPARATION BY PERVAPORATION THROUGH SILK FIBROIN MEMBRANES

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Abstract

Silk fibroin membranes which were made insoluble by the treatments in saturated water vapor, in ethanol or in 50% ethanol were investigated for water-ethanol permseparation by pervaporation. Permseparation became effective for the feeds with ethanol concentration ranging up to 90% when the membrane thickness was more than 20 μm . The permselectivity was somewhat greater with the membranes treated in water vapor than those treated in ethanolic solutions. Activation energy for permeation obtained from the Arrhenius plots was between 5 and 8 kcal/mole. Separation factor for water was slightly smaller in the higher temperature range, and was correlated with the higher flux in the region.

1. Introduction

Silk fibroin is a natural polypeptide composed mainly of glycine (more than 40%), alanine (about 30%) and serine (more than 10%), and is one of the most popular natural fibers. Much study on the structure and properties has been undertaken for a long time¹⁾, and attention has also been given to its application besides the use for wear. Silk fibroin is originally insoluble in usual state, but can be dissolved in aqueous solutions of some inorganic salts like LiBr, which lead the hydration to break the hydrogen bonds between the amides on the fibroin chains. From the desalted solution by dialysis, films can be obtained by casting. Although the fresh film is soluble, it turns insoluble by some treatments with water vapor or with solvents like alcohols. Thus, the wider range of application of silk fibroin is expected. In fact, such insoluble fibroin has been applied to immobilization of enzymes²⁾. In addition, the

permeation should be interesting, since much portion of the amorphous region of silk fibroin is composed of bulky side chains³⁾. Minoura et al. have recently reported the O₂-permeation behaviors through the swollen fibroin membranes⁴⁾.

By the way, many efforts have been underway to find the effective water-ethanol permselective membranes. In order to enhance the water permseparation from water-ethanol mixtures, the membrane must be more hydrophilic to attract water preferentially. Since silk fibroin contains hydrophilic polyamide structures, it should be interesting to see the water permselectivity through the membrane. We have therefore investigated the permseparation behaviors of water through the silk fibroin membranes, and have already reported the possibility as a rapid communication⁵⁾.

In this paper, we would like to report the water permselective behaviors through the silk fibroin membranes further investigated after that⁵⁾ with respect to various factors such as the membrane

condition, temperature during pervaporation, and so on.

2. Experimentals

2.1 Preparation of Silk Fibroin Membranes

21 g of degummed silk fiber was dissolved in 900 mL of LiBr aqueous solution (9.3 mol/L) on standing overnight at room temperature. The solution was then warmed at 40°C for one hour to complete the dissolution. The fibroin solution was allowed to dialysis using cerophane film to remove LiBr. The completion of desalting was confirmed with silver nitrate. The desalted silk fibroin solution was casted on a plastic plate and dried. Thus the membranes with approximate thickness 10, 20, 50, 75 and 110 μm were obtained by changing the amount of casting solution. The dried fibroin membranes were treated with 100% ethanol and 50% aqueous ethanol as well as with saturated water vapor at room temperature for 24 hours, and were made insoluble.

2.2 Pervaporation

Water-ethanol separation was carried out with pervaporation. The details of this procedure have been described elsewhere⁶). A sheet of the membrane with 47 mm-diameter was fixed to a cell holder, and aqueous ethanol were put in it. The other face of the membrane was evacuated at higher than 10 Pa in blank experiments.

The permeation rate or the flux (Q , $\text{kg}/\text{m}^2\text{h}$) was obtained by weighing the amount of permeates collected in a cold trap. Concentrations of water and ethanol of both feeds and permeates were measured by a gas chromatography.

Permselectivity was evaluated by separation factor ($\alpha_{\text{EtOH}}^{\text{water}}$), which was calculated from the following equation;

$$\alpha_{\text{EtOH}}^{\text{water}} = (X_{\text{water}}/X_{\text{EtOH}})/(Y_{\text{water}}/Y_{\text{EtOH}})$$

where X_{water} and X_{EtOH} were the concentrations of water and ethanol in permeate respectively, and Y_{water} and Y_{EtOH} were those in feed. The higher value of α naturally implies the higher water permselectivity.

The experimentals were carried out usually at 40°C, and also in the range from 30°C to 50°C to investigate the temperature dependence. Activation energies of permeation were determined from the Arrhenius plots.

3. Results and Discussion

3.1 Water Permselectivity

Figures 1 and 2 show the dependence of pervaporation on the feed ethanol concentration, respectively, for the 50 and 75 μm thickness membranes of silk fibroin being made insoluble by the treatments in ethanol (50%, 100%) and in saturated water vapor. Ethanol concentration in permeate was generally lower than that in feed throughout the concentration range, and the water permselectivity was suggested in these membranes. The ethanol concentration in permeate was always lower when the membranes treated in water vapor were used. Flux generally decreased as the ethanol concentration in feed increased, and such permeation behavior is usual for the water-permselective membranes.

Permselectivity for water was presented with separation factor, and the dependence on the feed ethanol concentration was obtained. The results are shown in Figure 3, respectively for the membranes with various thicknesses. Separation factor was naturally dependent on the preparation of the

Fig. 1. Dependence of flux and separation by pervaporation at 40°C on the ethanol concentration in feed for the 50 μm -thickness fibroin membranes, respectively treated in 50% ethanol (50%et) and in saturated water vapor (wv).

Fig. 2. Dependence of flux and separation by pervaporation at 40°C on the ethanol concentration in feed for the 75 μ m-thickness fibroin membranes, respectively treated in 100% ethanol (et) and in saturated water vapor (wv).

membrane, and the higher values were obtained with the membranes being treated in water vapor.

Maximum of separation factor generally appears at around 60–70% ethanol in feed in usual water-permselective membranes, while the behaviors are somewhat different in these fibroin membranes. The higher values were obtained in both side of water-rich and ethanol-rich solutions. The reason for such behaviors observed in silk fibroin mem-

Fig. 3. Dependence of separation factor for water on the ethanol concentration in feed for the fibroin membranes.

branes can not be given at present exactly, but the unusual behaviors may result from some morphological changes of the membrane due to contact with feeds.

When fibroin membranes were made insoluble in aqueous ethanol with different concentrations, the α -type and the β -type amide structures were observed at 1650 cm^{-1} and 1630 cm^{-1} in infrared spectra, respectively^{7,8}). The absorption peak was not observed at 1630 cm^{-1} practically in the original membrane, and the peak depth according to this absorption increased with increasing the concentration of ethanol used for treatments as

Fig. 4. Infrared spectra of the silk fibroin membranes; original (a), treated in 50% ethanol (b), in 100% ethanol (c), and in saturated water vapor (d).

shown in Figure 4. The material permeation takes place naturally in the amorphous region. Although the changes observed in infrared spectra are only for the amide forms, these morphology changes might induce the changes in the amorphous region to affect the permseparation behaviors. Further investigation is however necessary for proving this assumptions.

The fibroin membranes showed water-permsepation ability by pervaporation, and the separation factor reached more than 10 as far as investigated in this study.

3.2 Membrane Thickness Dependence

As mentioned above, the permsepation was dependent on the state of membranes. Then the dependence on the membrane thickness was investigated. Figures 5 and 6 show the dependences of flux and separation factor, respectively, for the feeds with approximate 20, 50, 70 and 90% ethanols. Flux decreased from about 5 kg/m²h to 0.1 kg/m²h with increasing the thickness. When a 10 μ m-thickness membrane was used, flux was abnormally high and the permsepation did not take place practically. This suggests that some defects are formed on the membrane during pervaporation or during the preparation of membranes.

Separation factor became larger as the membrane thickness increased, and this was closely related to

Fig. 5. Dependence of flux on the membrane thickness of silk fibroin membranes respectively for the feeds with about 20, 50, 70, and 90% ethanol concentrations.

Fig. 6. Dependence of separation factor for water on the membrane thickness of silk fibroin.

the decrease of flux. As pointed out before, the value of separation factor was greater for the membranes treated in water vapor. It also should be noticed that the values of separation factor for the membrane treated in 50% ethanol was rather similar to that for the membrane treated in water vapor. This is possibly correlated with the structure as observed in infrared spectra; in other words, the peak shapes according to the β -form at 1630 cm⁻¹ are similar to each other as shown in Figure 4.

3.3 Temperature Dependence

Pervaporation was further carried out with some membranes in the temperature range between 30°C and 50°C. Figures 7 and 8 show the Arrhenius plots of the permeation rates for the 50 μ m-thickness membranes being made insoluble with 50% ethanol and with water-vapor, respectively. Flux naturally increased as the temperature increased. It has been reported that there existed some transition temperatures for dye diffusion in silk fibroin⁹⁾, and that the transition was observed at around 35°C for the oxygen permeation through the swollen membranes⁴⁾. However in the pervaporation of water-ethanol mixtures, such transition was not clearly observed in the temperature range investigated in this study.

Activation energies were obtained from the slopes using the equation $Q = Q_0 \ln(-\Delta E_a/RT)$, where Q was flux, ΔE_a was activation energy for permeation, R was gas constant, and T was absolute

Fig. 7. Arrhenius plots of flux of the 0, 20, 50 and 70% ethanol feeds through the 50 μ m-thickness fibroin membrane treated in 50% ethanol.

Fig. 8. Arrhenius plots of flux of the 0, 20, 50 and 70% ethanol feeds through the 50 μ m-thickness fibroin membrane treated in saturated water vapor.

temperature. Since the number of experiments were restricted, deviation of the values was inevitable. The approximate energies obtained were as follows; 4.9, 5.2, 5.4 and 5.1 kcal/mole respectively for the feeds with 0, 20, 50 and 70% ethanol in the ethanol-treated membrane, and 6.3, 8.2, 8.5 and 7.6 kcal/mole in the water vapor treated membrane. Thus the energy for permeation was somewhat larger in the latter membrane. Minoura et al. have shown in the study of oxygen permeation that the permeation rate was reversely related with the activation energy, namely, the activation energy for permeation of oxygen was larger when permeation rate was smaller, and vice versa, for the silk fibroin membranes treated with methanol under various treatment time conditions⁴⁾. The same is true for pervaporation of water-ethanol. A membranes treated in 50%

Fig. 9. Temperature dependences of separation factor of water for the 20 μ m-thickness membrane treated with saturated water (1), and the 50 μ m-thickness membranes treated with water vapor (2) and 50% ethanol (3).

ethanol which had lower activation energies showed the higher flux generally.

Figure 9 shows the dependence of separation factor on temperature for pervaporation. It should be pointed out that the values were slightly larger in the lower temperature range, and that was related to the lower permeation rates in the range.

4. Conclusion

It was found that silk fibroin membranes which were made insoluble by the treatments with saturated water vapor or with aqueous ethanol were water-permselective from water-ethanol mixtures by pervaporation. Higher permselectivity was performed with the membranes treated in water vapor in general, and the selectivity seemed to be dependent on the physical structure arising from the treatments. Permselectivity became effective with the membranes of the thickness more than 20 μ m, and for the more effective permselectivity 50 micron was necessary. Activation energy for permeation was between 5 kcal/mole and 8 kcal/mole, and the temperature dependence of permselectivity of water was slight. Both flux and separation factor must be improved

simultaneously for the truly good permselective membranes, and therefore, further investigation is necessary to increase the two factors through making a careful study of the relations between the permseparation and the membrane structure by the treatments.

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絹フィブロイン膜を用いてのパーバレーションによる 水-エタノール分離

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水蒸気中およびエタノール中で不溶化を図った絹フィブロイン膜を用いてパーバレーション法により水-エタノール分離について検討を加えた。これらの膜は水を選択的に透過した。その選択性は膜の厚さ、不溶化の方法などに依存した。すなわち、膜厚 20 μm 程度より水の選択透過があらわれ、厚さとともに選択性が増加し透

過速度が減少した。また、水蒸気処理による不溶化が選択性向上のためにより有効であった。アレニウスプロットから求めた透過の活性化エネルギーは、5-8 kcal/mole であった。また、分離係数は高温側で幾分低下した。しかしその程度は小さく、これは高い透過速度と関連するものである。