Vapor Permeation of Bioethanol with Quaterinized Chitosan–Lipid Complex Membranes

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Membranes from quaterinized chitosan (QCh), which was a derivative of marine (natural) polymer, and sodium 1-dodecylsulfate (C12SNa) transported ethanol in preference to water by vapor permeation. Membrane performance, such as permselectivity and flux, was enhanced with the increase in amphiphile (C12S) content in the membrane. The results suggested that the QCh–C12S complex membranes were applicable to selective separation of bioethanol from fermentation broth.

Key words : bioethanol / chitosan / permselectivity / quaterinized chitosan / vapor permeation

1. Introduction

There are various polymeric materials, such as synthetic polymers and derivative of natural polymers, which are used as candidate materials for membranes¹⁾. It is an interesting and an important subject to obtain membranes from natural polymers, in other words, environmentally-friendly ‘green’ polymers, or derivative of those. To this end, the authors’ research group have been studying molecularly imprinted membranes from cellulose acetate^{2~4)} or proteins from *Geobacillus thermodenitrificans* DSM465^{5, 6)}, pervaporation membranes from agarose^{7~9)}, agarose/hydrophilic polymer¹⁰⁾, or agarose/derivative of natural polymer¹¹⁾, and vapor permeation membranes from gelatin/polyamideimide¹²⁾ or *G. thermodenitrificans* DSM465/polyamideimide¹³⁾. Chiral separation was studied adopting egg shell membranes¹⁴⁾. DNA, which was considered as a polyanion with a huge molecular weight, was adopted as membrane materials and chiral separation^{15~17)} and selec-

tive transport of oxygen with DNA complex membranes¹⁸⁾ were investigated. Contrary to this, polycation of natural polymer or derivative of that was also expected to give a chiral separation membrane. Quaterinized chitosan/lipid complex membranes, of course, showed chiral separation ability¹⁹⁾.

Ion exchange membranes such as Nafion with metal cations from group 1, 2, and 13 of the periodic table^{20, 21)} and sulfonated polyethylene with metal cations from group 1²²⁾ always demonstrated selective transport of water from aqueous alcohol solutions (e.g. aqueous 2-propanol and aqueous ethanol) by pervaporation. Incorporation of hydrophobic organic counterions, such as quaternary ammonium cations with longer alkyl groups (butyl–octyl), changed the pervaporation performance of the ion exchange membranes²³⁾; in other words, instead of water, alcohol was transported in preference to water and the selectivity toward alcohol was correlated to the hydrophobicity of counterions and alcohols. From this²³⁾, membranes from quaterinized chitosan–lipid complexes are expected to show permselectivity toward alcohol in separation of aqueous alcohol mixtures since they consisted of hydrophobic longer alkyl chains (dodecyl–hexadecyl)¹⁹⁾. Selective separation of alcohol is interesting and indispensable in connection with production of bio-

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fuels, which are produced *via* fermentation of biomass. To this end, in the present rapid communications, vapor permeation performance of bioethanol through membranes from quaterinized chitosan-lipid complexes was investigated. In the present study, aqueous ethanol solution was adopted as a model mixture of biofuel/water mixture.

2. Experimental

Quaterinized chitosan (QCh) with 2-hydroxypropyl-trimethylammonium cationic charge sites, of which degree of quaterinization being 1.3, was kindly supplied by Dainichiseika Color & Chemicals Mfg. Co. Ltd. and used as received. Anionic amphiphile, sodium 1-dodecansulfate (C12SNa), was used without further purification. Dimethylsulfoxide (DMSO) and ethanol were used without further purification. Water purified with an ultrapure water system (Simpli Lab, Millipores S. A., Molsheim, France) was used.

QCh

C12SNa

The preparation of QCh-C12S complex is simple like that of DNA-lipid complex^{24, 25}: an aqueous solution of QCh and an aqueous C12SNa one were mixed at ambient temperature. The precipitate was washed with water by centrifugation and dried *in vacuo* at 80 °C for 1 d. Dimethylsulfoxide (DMSO) was adopted as a solvent for the QCh-C12S complexes. The composition of QCh-C12S complex was determined by using intensity of methyl protons for C12S (0.92 ppm) and that for QCh (3.17 ppm) in ¹H NMR spectra of QCh-C12S complexes, using DMSO-d₆ as a deuterated solvent.

A 0.4 g of QCh-C12S complex was dissolved in 7.6 g

of DMSO. The DMSO solution was poured into a TeflonPFA 75 mm diameter laboratory dish and the solvent was allowed to evaporate at 80 °C for 24 h. The thickness of the membrane, δ (m), was 76 ~ 83 μm , which were determined by using micrometer.

Vapor permeation experiments were carried out following the procedure described in the previous paper¹². The performance of membranes was determined by the flux, J ($\text{kg m}^{-2} \text{h}^{-1}$), and the separation factor toward ethanol against water, $\alpha_{\text{EtOH}/\text{H}_2\text{O}}$. The flux is defined as

$$J = Q/At \quad (1)$$

where Q (kg) denotes the collected amount of the permeate, A (m^2) is membrane area, and t denotes time (h), respectively.

The separation factor $\alpha_{\text{EtOH}/\text{H}_2\text{O}}$ is defined as

$$\alpha_{\text{EtOH}/\text{H}_2\text{O}} = (Y_{\text{EtOH}}/Y_{\text{H}_2\text{O}}) / (X_{\text{EtOH}}/X_{\text{H}_2\text{O}}) \quad (2)$$

where Y_i s are the weight fractions in permeate and X_i s are those in vapors in feed, respectively.

3. Results and Discussion

As for the composition of the QCh-C12S complex, the ratios of the amount of anionic site to that of cationic site (-/+ for the QCh-C12S complexes studied in the present study ranged from 1.12 to 1.56. As reported previously¹⁹, it was very hard to obtain a QCh-C12S complex with a prescribed composition. The composition of the formed complex was inclined to exceed the feed composition; in other words, the ratios of the amount of anionic site to that of cationic site in the complex preparation process were 0.90, 1.00, 1.10 and 1.20, respectively. And the ratios for the QCh-C12S complex were determined to be 1.12, 1.25, 1.40, and 1.56, respectively. Some anionic amphiphiles were thought to be existed in QCh-lipid complex as a form of micell. It is an unsolved problem to obtain complexes with the prescribed ratio of sulfate anions to ammonium cations. In a future study, it is requisite to prepare QCh-lipid complexes below the critical micell concentration of around $7.22 \times 10^{-3} \text{ mol dm}^{-3}$ at ambient conditions²⁶.

The results of vapor permeation of aqueous ethanol solution with weight fraction of ethanol in the feed of

Table 1 Results of vapor permeation of aqueous ethanol solution through the membranes

-/+	Weight fraction of EtOH in feed liquid	Weight fraction of EtOH in feed vapor	Weight fraction of EtOH in permeate	$\alpha_{\text{EtOH/H}_2\text{O}}^a$	J/kg m ² h ⁻¹	δ/m
1. 12	0.0947	0.4916	0.6023	1.6	2.8	83.1 x 10 ⁻⁶
1. 25	0.0922	0.4828	0.6558	2.0	3.4	82.8 x 10 ⁻⁶
1. 40	0.0939	0.4887	0.6873	2.3	4.3	79.8 x 10 ⁻⁶
1. 56	0.0943	0.4903	0.6971	2.4	6.1	76.1 x 10 ⁻⁶
PDMS ^b	0.0958	0.4953	0.6546	1.9	1.0	76.2 x 10 ⁻⁶

^a $\alpha_{\text{EtOH/H}_2\text{O}} = (Y_{\text{EtOH}}/Y_{\text{H}_2\text{O}})/(X_{\text{EtOH}}/X_{\text{H}_2\text{O}})$; X_i , weight fraction of i in feed vapor; Y_i , weight fraction of i in permeate.

^b Polydimethylsiloxane membrane supplied by General Electric Co.

around 0.095 through the various QCh–C12S membranes are summarized in Table 1. In the present study, it was very hard to obtain an aliquot of the vapor equilibrated with the boiling feed solution. The composition of the feed vapor was determined by using the feed liquid composition, which was analyzed by a gas chromatography and vapor-liquid equilibrium data²⁷⁾. As expected, those four types of QCh–C12S complex membrane transported ethanol vapor in preference to water vapor like pervaporation of aqueous alcohol solution through Nafion with hydrophobic organic counterions²³⁾. Both flux value and permselectivity toward ethanol increased with the increase in the amount of amphiphile molecule in the membrane. The permselectivity toward ethanol was thought to be expressed as follows: hydrophobic alkyl chains sorbed ethanol preferentially from feed vapor mixtures and ethanol was, as a result, selectively transported through the QCh–C12S complex membranes.

There were reported various alcohol permeable membranes^{28–37)}. Among those membranes, polydimethylsiloxane (silicone) membrane was perceived as a typical alcohol permeable membrane^{28, 29)}. Vapor permeation performance of polydimethylsiloxane membrane, which was kindly supplied by General Electric Co., was also studied. As shown in Table 1, polydimethylsiloxane membrane transported ethanol preferentially from aqueous ethanol mixture not only by pervaporation but also vapor permeation. QCh–C12S complex membranes with higher lipid content showed higher flux and permselectivity than polydimethylsiloxane membrane. The present results suggested that QCh–lipid complex membranes were applicable to separation of bioethanol from fermentation broth by vapor permeation.

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(Received 19 April 2010 ;

Accepted 8 June 2010)