THE INFLUENCE OF MEMBRANE PREPARING SOLVENT ON THE SORPTION, PERMEATION AND MEMBRANE POTENTIAL OF GLUTAMIC ACID-METHYL L-GLUTAMATE COPOLYMER MEMBRANES

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Two types of membranes of glutamic acid - methyl L-glutamate copolymers were obtained by the saponification of poly(γ-methyl L-glutamate) (PMLG) membranes in aqueous alcoholic systems. One is iM membrane and the other is E membrane. The iM membranes were obtained by the saponification in a mixture (2:2:1 in volume fraction) of methyl alcohol, isopropyl alcohol and water containing NaOH at various concentrations. The E membranes were obtained in a mixture (4:1 in volume fraction) of ethyl alcohol and NaOH aqueous solution. The sorption and the permeation behavior of these copolymer membranes depends on the glutamic acid content in these membranes, but not on the membrane preparing process. The membrane potential, however, depends on the membrane preparing method. That is, the absolute values of membrane potential of the E membranes were higher than those of the iM membranes. This difference could be ascribed to the difference in the surface character of the iM and of the E membranes.

INTRODUCTION

We have reported the sorption and the permeation behavior of various small molecular substances in and through several polypeptide membranes. The results have shown that the membrane properties of polypeptides are controlled by the chemical and structural features of their side chains. The present paper aims to clarify at first the sorption and the permeation behavior of copolymer membranes in which hydrophilic and hydrophobic residues are systematically arranged. Secondly, the influence of membrane preparing solvent to the membrane properties, such as sorption, diffusion and membrane potential, will be examined. The latter is considered to be a basic subject in the field of fiber and membrane technology.

EXPERIMENTAL

Preparation of the membranes

Glutamic acid - methyl L-glutamate copolymer membranes were obtained by the saponification of PMLG membranes with sodium hydroxide at 20°C. Using mixtures containing different contents of alcohols and aqueous solution of various concentration of NaOH, two types of the membrane were obtained. Fig. 1 shows schematically the methods of the preparation. The iM membrane was obtained with a mixture (2:2:1 in volume ratio, Method I in Fig. 1) of methyl alcohol, isopropyl alcohol and NaOH aqueous solution. The E membrane was obtained in a mixture (4:1 in volume ratio, Method II in Fig. 1) of ethyl alcohol and aqueous solution of NaOH. The sodium type copolymer membranes, which were obtained by these saponifications, were well washed with ethyl alcohol and were transformed to the acid type ones by soaking in 1.0 N HCl solution at 25°C and were washed with ethyl alcohol thoroughly. The content of glutamic acid residue in the copolymer was adjusted by regulating the concentration of NaOH in the mixed solvent. The membranes whose glutamic acid content are x% (in mole fraction) are denoted by (A-x)IM and (A-x)E for the cases of iM and E membranes, respectively. To obtain a disordered surface on the membrane, (A-10)E, (A-16)E and (A-45)E membranes were immersed into a mixture (5:3 in volume fraction) of methyl alcohol and ethylene dichloride at 25°C for one minute and then washed with methyl alcohol (Method III in Fig. 1). The membrane with about 30μ thickness was used for sorption and permeation experiments and that with about 5μ thickness for
membrane potential experiments.

Sorption and Permeation

A gravimetric sorption apparatus2) with a quartz spring balance was used to determine the amounts of sorption of water and methyl alcohol. The isotherms were observed at 25°C. For permeation experiments, Rouse's apparatus3) was used. The permeability coefficient $P$ (bar means concentration average) was calculated as usual, and the diffusion coefficient $D$ was obtained by $P$/$S$, where the solubility coefficient $S$ was calculated from the sorption isotherms.

Membrane potential

A H type cell was used to determine the membrane potentials. The cell was constructed with two sections made of pyrex glass between which the membrane was placed. Using a Ag-AgCl electrode with salt bridge, the potential was measured for KCl solutions with concentration ratio $c_1/c_2 = 4$ by a pH meter (F-7, type of Hitachi-Horiba Co. Ltd., Japan) at 25°C, where $c_1$ and $c_2$ are the high and low salt concentrations. In the case of high external concentrations compared with the fixed charge density of the membrane, membrane potential, $\Delta \phi$, for KCl solution systems is given by $^{4)}$:

$\Delta \phi = \frac{RT}{F} \left( \frac{\Phi X}{2K_2} \right) \frac{r-1}{r} \frac{1}{c_2}$

where $r = c_1/c_2$, $\Phi X$ is the effective charge density and $K_2$ is the equilibrium partition coefficient.

Observation of the membrane surfaces

The membrane surfaces were observed with a scanning electron microscope (SSM-2 type Hitachi Co. Ltd., Japan) after vacuum deposition of platinum on the membrane surface.

RESULTS AND DISCUSSION

Sorption and Permeation

The isotherms for water and methyl alcohol vapor-iM membrane systems at 25°C are shown with solid lines in Fig. 2 (a) and (b). The dotted lines in Fig. 2 are the isotherms for $E$ membrane systems. The amounts of sorption of both vapors increase with increasing glutamic acid content in the membranes. If the saturated amounts of sorption of both vapors were obtained, we could estimate the maximum solvent (water and methyl alcohol in these cases) holding capacity of glutamic acid residue in $(A-x)_{iM}$ and $(A-x)_{E}$ membranes, which is denoted by the number of sorption site $N$ per glutamic acid residue. However, as the sorption isotherms in Fig. 2 (a) and (b) rapidly increased in
Fig. 2 Sorption isotherms (amount of sorbed vs. relative vapor pressure $P/P_0$) of glutamic acid - methyl L-glutamate copolymer membranes - diluent systems at 25°C: (a) water; solid lines are the isotherms of iM membrane systems and a broken line is that of (A-20)$_E$-water system, (b) methyl alcohol; solid lines are the isotherms of iM membrane systems and a broken line is that of (A-20)$_E$-methyl alcohol system.

In the high relative vapor pressure range, the amounts of sorption at $p/p_0 = 1$ could not be gained by the extrapolation method. Therefore, to obtain the value of $N$, we conveniently used the amounts of sorption at $p/p_0 = 0.9$ in Fig. 2 as the reliable values near the saturated amounts of sorption of both vapors. Thus the number of sorption site $N$ of (A-x)$_{IM}$ and (A-x)$_E$ membranes are obtained by the next relation using the values of sorption amount at $P/P_0 = 0.9$:

$$N = (Z - 143N_m \cdot M) \times 6.02 \times 10^{23}$$

where $Z$ (mole/g) is the amount of sorption of the solvent in (A-x) membranes at $P/P_0 = 0.9$, $M$ (mol/g) is that in PMLG at $P/P_0 = 0.9$, $N_m$ is the moles of methyl glutamate residue per 1 gram of (A-x) membrane and 143 indicates the molecular weight of methyl glutamate residue. Eq. (2) is based on the additivity of sorption capacities of methyl glutamate and glutamic acid residues. On the other hand, using the values of $v_m$, the amount of monolayer sorption in PMLG or (A-x) membranes, and a relation similar to Eq. (2), we can also calculate the sorption site which corresponds to the free polar groups in the membranes. Here, $v_m$ values were obtained from B.E.T. plots of the isotherms from $P/P_0 = 0$ to 0.35. Fig. 3 shows these site numbers, which level off as the number of $-COOH$ group in the membranes increases. This may indicate that the interactions between $-COOH$ groups in the membrane strengthen with the increase of the glutamic acid content in the copolymer. However, the sorption sites obtained from the isotherms at $P/P_0 = 0.9$ (straight lines in Fig. 3) show that about one molecule of water and methyl alcohol can bind to one $-COOH$ group in the copolymer after breaking of these interactions in the higher vapor pressure region. The squares ($\square$, ■) in Fig. 3, which indicate the sorption sites of E membranes, are located on the lines for iM membranes. This indicates that the membrane preparing solvent composition does not influence the sorption behavior.

Fig. 4 (a) and (b) show the diffusion coeffi-
Fig. 3 Relation between sorption site (site number per 1 gram of polymer) and number of $-\text{COOH}$ group per g of membrane: (a) water; (b) methyl alcohol. (---) is obtained from the values of sorption isotherms of iM membrane systems at $P/P_0 = 0.9$ and Eq. (2), (-----) is obtained from monolayer $v_m$ values of B.E.T. plots for iM membranes and (□ and ■) denote the sorption site of (A-20)$_E$ membrane.

Fig. 4 Relation between steady state diffusion coefficient $D$ at 25°C and relative vapor pressure $P/P_0$: (a) water; (b) methyl alcohol.

cients, which are calculated from the permeation coefficients and solubility coefficients, as a function of relative vapor pressure. It is clear that the diffusion coefficients of water and methyl alcohol decrease with the increase of glutamic acid content in the membrane, even when the amount of sorption of these solvents become higher. This behavior may also show the presence of the strong interactions between $-\text{COOH}$ groups in these copolymer membranes. For the variation of $D$, too,
no influence of membrane preparing solvent seems to be observed. Previously, we interpreted the diffusion behavior of polypeptide membrane - organic solvent systems with the free volume theory. A similar treatment may apply to the diffusion behavior of these copolymer membranes. Here the additivity of free volume fractions of glutamic acid and methyl L-glutamate residues in the copolymer is assumed:

\[ f = f_M (1 - v_A) + f_A v_A \quad (4) \]

where \( f, f_M \) and \( f_A \) are the free volume fractions of the system, methyl glutamate residue and glutamic acid residue, respectively, \( v_A \) is the volume fraction of glutamic acid residue in the copolymer. The relation between the diffusion coefficient \( D \) and \( f \) can be written as:

\[ \frac{D}{RT} = A_d \exp\left(-\frac{B_d}{f}\right) \quad (5) \]

where \( B_d \) is the critical size of the diffusant molecule and \( A_d \) is a constant which is independent of temperature and diluent concentration. Substitution of Eq. (4) into Eq. (5) yields Eq. (6) and Eq. (7):

\[ \frac{D_{OM}}{RT} = A_d \exp\left(-\frac{B_d}{f_M}\right) \quad (6) \]

\[ \frac{D_{OMA}}{RT} = A_d \exp\left(-\frac{B_d}{f_M - f_A}\right) \quad (7) \]

where \( D_{OM} \) and \( D_{OMA} \) are the diffusion coefficients of PMLG and of the copolymers at zero penetrant concentration, respectively. \( \beta \) is the difference between the free volume fractions of methyl glutamate and glutamic acid residue:

\[ \beta = f_M - f_A \quad (8) \]

From Eq. (6) and Eq. (7) we can obtain Eq. (9):

\[ \left(\ln\frac{D_{OM}}{D_{OMA}}\right)^{-1} = -\frac{f_M}{B_d} + \frac{f_M^2}{B_d} \beta \cdot \frac{1}{v_A} \quad (9) \]

Eq. (9) predicts a linear relationship between the left hand side and \( 1/v_A \). The \( D_{OM} \) and \( D_{OMA} \) values can be obtained by the empirical extrapolations of the experimental \( D \) values to the values at \( P/P_0 = 0 \) (broken lines in Fig. 4). Application of Eq. (9) to each system is shown in Fig. 5. The expected linear relations between \( \left(\ln\frac{D_{OM}}{D_{OMA}}\right)^{-1} \) and \( 1/v_A \) are obtained for both systems.

Using the values of the slope and the intercept of these straight lines and Eq. (9), \( f_A/f_M \) value, the ratio of the free volume fraction of glutamic acid to that of methyl L-glutamate, can be obtained. The values of \( f_A/f_M \) for water and methyl alcohol systems are almost the same, 0.34 and 0.35, respectively. Therefore, the free volume fraction of methyl glutamate residue is about three times larger than that of glutamic acid residue. Furthermore, Fig. 5 shows that the values of \( \left(\ln\frac{D_{OM}}{D_{OMA}}\right)^{-1} \) calculated for E and iM membrane systems are on the same straight lines for both water and methyl alcohol systems. Thus, the permeation and the diffusion behaviors of the membranes are clearly independent of the kind of membrane preparing solvent, as in the case of the sorption behavior. Therefore, the amount of sorption and the rate of permeation of the solvents in these membranes are dependent only on the glutamic acid content in the membranes, as assumed in deriving Eq. (2) and Eq. (9).
Membrane potential

Fig. 6 shows the KCl concentration dependence of the membrane potentials when the $c_1/c_2$ value is fixed to 4. In the E and iM membrane systems, increasing glutamic acid content in the membrane raise the absolute values of $d(\Delta \phi)$, since glutamic acid residue has the dissociable side group. It is remarkable, however, that there are great difference between the values of E and iM membranes that have the same glutamic acid content. In terms of Eq. (1), the experimental relations between $d(\Delta \phi)$ values and $c_2$ result in straight lines, from which the values of the effective charge density of the membranes are obtained. Fig. 7 shows that the effective charge densities, $(\Phi X)$, of the E membranes are higher in one order than those of iM membranes. Thus the membrane potential is strongly dependent on the membrane preparing solvent, in contrast to the sorption and permeation properties.

In theory, Eq. (1) was derived with the assumption that the values of the membrane potential can be determined by the Donnan potentials at the membrane/solution interfaces. On the other hand, the sorption and the permeation behaviors of these copolymer membranes are mainly determined by the natures of the inner part of the membrane. Thus, the difference of the membrane potentials between E and iM membranes may be attributable to the difference in their surface structures. So that, it is quite interesting to examine the relation between the membrane potential and the surface structure in more detail.
order to change the surfaces of the membranes, \((A-10)E\), \((A-16)E\) and \((A-45)E\) membranes were immersed in a mixture of ethylene dichloride and methyl alcohol (Method III in Fig. 1). The swelling and shrinking process in method III is expected to enhance the disorder on the membrane surfaces of \(E\) membranes. Resulting membranes, denoted by \((A-x)_{EDC}\), had lower potential (absolute) values comparing with those of \(E\) membranes (Fig. 8). The \(\Phi X\) values obtained with Eq. (1) are also shown in Table 1. It is noticed that the relative values of \(\Phi X\) of \((A-x)_{EDC}\) to \((A-x)E\) are approximately the same, about 0.3, for all glutamic acid contents. This seems to indicate that a certain membrane treating process causes the same degree of disorder irrespective of the glutamic acid content of the membrane. Thus, it is confirmed that the membrane potential depends on the surface characters of the membrane.

**Observation of the membrane surfaces**

To examine the difference of the surface structures of \(E\), \(iM\) and \(EDC\) membranes, the surfaces were observed with a scanning electron microscope. The surfaces of \((A-45)E\), \((A-45)_{EDC}\) and \((A-50)_{iM}\) membranes are shown in Fig. 9 (a), (b) and (c), respectively. Fig. 9 shows that the surface of \(E\) membrane is relatively smooth in comparison with that of the \(EDC\) treated membrane, \((A-45)_{EDC}\). Furthermore, a typical surface of \(iM\) membrane is clearly coarse, in the sense that which has many small plaits on the surface, as is shown in Fig. 9 (c). Thus, it may be contended that the difference of the membrane potentials of \(E\) and \(iM\) membranes in Fig. 6 and also those of \(E\) and \(EDC\) membranes in Fig. 8 are ascribed to the differences of the surface structures of these membranes. The relation between the surface structure and the membrane potential must be a very interesting problem in the fields of fiber and membrane science and of their applications.

In conclusion, though the sorption and the
The diffusion behavior of glutamic acid-methyl L-glutamate copolymer membranes are controlled by the glutamic acid content in the membranes, the membrane potential is not only dependent on the content but also on the kind of preparing solvent. The observations of the membrane surfaces suggest that the membrane potential is affected by the surface character of the membrane, while the sorption and diffusion properties are mainly determined by the nature of the inner part of the membrane.

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REFERENCES

グルタミン酸-メチルL-グルタミート共重合体膜の低分子収着透過性及び膜電位に及ぼす膜調製溶媒の影響

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グルタミン酸-メチルグルタミート共重合体膜が、ポリ（γ-メチルレグルタミート）膜のアルコールを用いた混合溶媒中におけるケン化反応により調製された。この際、ケン化溶媒として、メチルアルコール、イソプロピルアルコール、NaOH水溶液（2:2:1、体積比）を用いた場合と、エタノール、NaOH水溶液（4:1）を用いた場合とでは、得られた共重合体膜の物性に若干の差異が生じた（前者の調製法で得た膜を iM膜、後者のそれをE膜とする）。つまり、ケン化溶媒の相違は、水蒸気、メタノール蒸気の、膜透過性や、収着量にはまったく影響を与えないが、膜電位に関してはその影響があらわれ、E膜の方が、iM膜に比べ比較的大きな値を示した。

また、エチレンジメラライド（EDC）-メチルアルコール（3：5）混合溶媒中で処理された膜（EDC処理膜と略）の膜電位の値は、E膜に比べて低かった。さらに電子顕微鏡を用いて観察した膜表面構造は、E膜が最もなめらかであり、iM膜には数多くの細かな乱れが、そしてEDC処理膜には比較的大きな乱れが見られた。これらの結果は、E膜、iM膜、EDC処理膜の膜電位の差が、この表面構造の差に起因することを示唆した。低分子の収着透過性に処理溶媒の差に基づく影響があらわれなかったのは、おそらくこれらの膜物性が、主に膜内部の性質に伴われるためであろう。