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The Diffusion Behavior of Ag^+ Ions in a Polymer Membrane Containing Valinomycin

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The diffusion behavior of Ag^+ ions in a polymer membrane containing valinomycin (VAL) has been studied by X-ray microanalysis. Ag^+ ions are transported rapidly into the membrane along with Cl^- ions. The saturated amount of Ag^+ ions in the membrane is estimated to be equal to that of VAL. It is found that the rate determining step of Ag^+ ion transport is the diffusion process.

Various kinds of ions are known to be transported across the membrane.[1,2] Especially, the ion transport across a liquid membrane containing an ion carrier has been investigated vigously.[3-7] For example, potassium ions are transported by valinomycin (VAL) across the liquid membrane. On the contrary, silver ion which does not form a stable complex with VAL cannot be transported across the liquid membrane.

We found, by X-ray microanalysis, that the silver ion diffuses into a polymer membrane which cotains VAL and a solvent of VAL, whereas potassium ion does not migrate into the membrane.[8] The mechanism of the ion transport in the polymer membrane should be different from that in the liquid membrane. The ion carrier, which can diffuse across the liquid membrane, would not move in the polymer membrane, but acts as a hopping site for the ions.[8]

The Ag/AgCl layer and the polymer membrane containing VAL was prepared as shown in Fig. 1. The preparation method of the sample was the same as reported in the previous paper.[8] The Ag/AgCl layer was prepared as follows. Ag metal (layer thickness = 800 nm) was vacuum evaporated onto the polyethylene terephthalate (PET) film. Then, the surface of the Ag metal layer was oxidized to AgCl by $K_2Cr_2O_7$ and HCl (conversion ratio = 25%). The AgCl layer was coated with polymer solution consisted of methyl ethyl ketone (5.0 ml), copolymer (polyvinyl chloride : polyvinyl acetate = 9 : 1) (0.9 g), VAL (33 mg) and dioctyl phthalate (solvent of VAL) (1.8 g). The

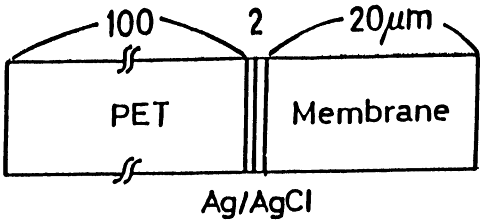


Fig. 1. Cross section of the membrane configuration.

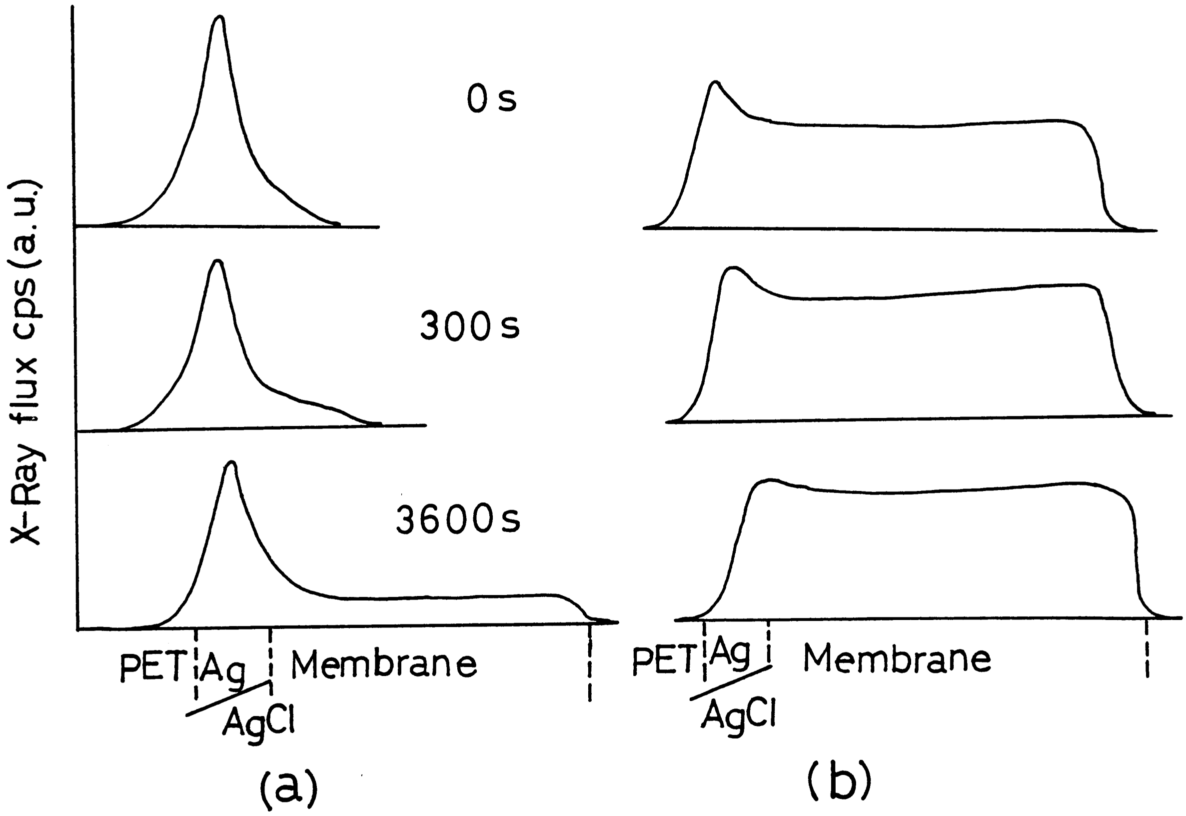
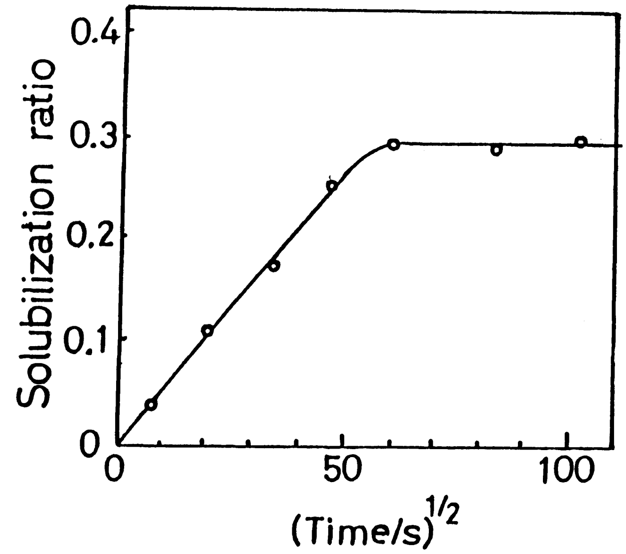


Fig. 2. Characteristic of X-ray flux of Ag+ ions (a) and Cl- ions (b). Time 0 s is without water contact. Time 300 and 3600 s indicate the period for water contact.

layer was dried at 60 ℃ for 1 h. The thickness of the membrane was 20 μm. The membrane was in closely contact with Ag/AgCl layer which acted as an Ag^+ ion source for the membrane. The concentration of VAL in the membrane was 6.0×10^{-7} mol/cm^3. After distilled water was contacted on the surface of the membrane for a specified time, the water was removed by suction into filter paper. A piece of the contacted portion was embedded in epoxy resin (Semedine Super) for 16 h and, then, cut with a diamond knife to obtain a cross section of the membrane. The distributions of the ions in the membrane were measured by XMA (Hitachi HSM 2B, wavelength dispersion type). The amounts of Ag^+ ions were measured by comparing the internal stand-



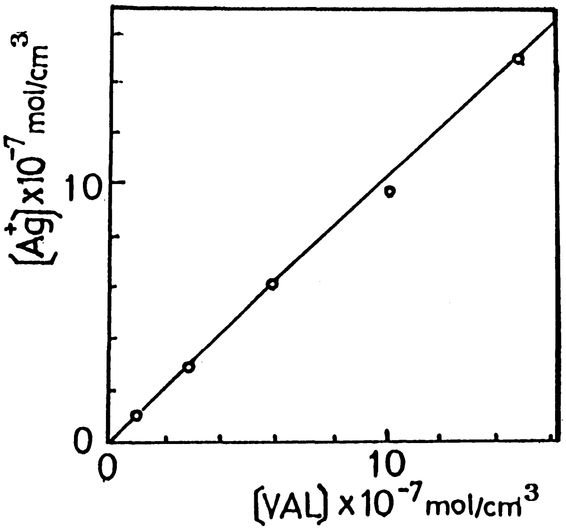


Fig. 3. Diffusion behavior of Ag^+ ions. Solubilization ratio indicates ratio of the amount of diffused Ag^+ ion and total Ag^+ ion.

Fig. 4. Relationship between the amount of Ag^+ ion and the concentration of VAL.

ard Ag/AgCl layers having no membrane with the measured ones. The diffusion of Cl^- ions were observed by the decrease in the X-ray flux of Cl^- ions of the Ag/AgCl layer.

The distribution changes of Ag^+ ions and Cl^- ions in the cross section of the membrane (corresponding to Fig. 1) on time were shown in Fig. 2a and 2b, respectivly. The amounts of Ag^+ ions diffused into the membrane were measured by the X-ray flux. These values were plotted in Fig. 3. The vertical axis indicates the solubilization ratio (= the ratio of the amount of Ag ions in the membrane and total Ag^+ ions). The horizontal axis indicates a square root of the period for water contact. The linearity of the two factors was obtained in the short period. The results show that the rate determining step of the transport of Ag^+ ions is a diffusion process. The diffusion coefficient (D) is estimated to be 7.9×10^{-11} cm^2/s (VAL concentration = 6.0×10^{-7} mol/cm^3) from this slope. However, the Cottrel plot of Ag^+ ions deviates from the straight line and approaches toward the saturated line (= constant value) after a definite time. The inflection point is estimated to be about 3600 s.

The dependence of Cl^- ion distribution on time was shown in Fig. 2b. It showed that X-ray flux of the Ag/AgCl layer containing Cl^- ions decreased and slightly increased in the membrane. The results suggest that the Cl^- ions diffuse into the membrane. Since Cl^- ion cannot be complexed with VAL, Cl^- ion should be attracted by Ag^+ ion in the membrane.

The time t, when $\sqrt{\pi Dt}$ becomes equal to the membrane thickness d (= 20 μm), is calculated as 16000 s. This time is in agreement with the inflection point of 3600 s. That is, it indicates that the amount of Ag^+ ions is saturated at that time in the membrane and, after 3600 s elapsed, Ag^+ ions cannot diffuse from the AgCl layer into the membrane.

When the various VAL concentrations are used in the membrane, the analogous behaviors are observed. The relationship between the saturated amount of Ag^+ ions and the VAL concentration is shown in Fig. 4. The horizontal axis indicates VAL concentration and the vertical axis indicates the amount of Ag^+ ions in the membrane. The amounts of Ag^+ ions give essentially straight line to the various contents of VAL. The amount of Ag^+ ions is proportional to the VAL contencentration. The slope is defined to 1.0. When Ag^+ ion recombines with Cl^- ion to form AgCl crystalline, the slope is splipping off from the straight line and should move up to 1.0. When the VAL is not fully occupied with Ag^+ ion, the slope is splipping off from the straight line and should move down in 1.0. This means that Ag^+ ion does not recombine with Cl^- ion to form AgCl crystlline and VAL is wholly used for complex formation in the membrane. That is, Ag^+ ions form 1:1 complex with VAL. Consequently, the amount of Ag^+ ion at the inflection point is equal to that of VAL. VAL is fully saturated with Ag^+ ion at this point. Above 3600 s, Ag^+ ions cannot diffuse into the membrane because of an absence of Ag^+ ion trap with VAL.

These diffusion phenomena are considered as follows. The VAL is complexed with Ag^+ ion to form a metastable trap. The energy of this state is enough high, so Ag^+ ion can jump over to the adjacent VAL by hopping process along with a counter Cl^- ion.

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