Proton Diffusion in the Premelted State of 1-Hexadecanol

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Proton diffusion in the α-phase of polycrystalline 1-hexadecanol was studied using $C_{16}H_{33}O^3H$ and $C_{15}H_{31}$-$^{14}CH_2OH$. It was found that hydroxyl proton diffuses translationally more easily than the whole molecule. A value of $(7 \pm 5) \times 10^{-7}$ cm²/s was obtained for the diffusion coefficient of the hydroxyl proton in the α-phase. This fast diffusion is ascribed to the presence of molecular rotation involving hydrogen-bond networks in the α-phase of the crystal. Since the mechanism for the proton diffusion seems to be the same as that for the protonic conduction in this α-phase, proton mobility can be calculated from the diffusion coefficient, assuming that molecular rotation makes the rate determining step in both processes.

It has been shown in the literatures that proton conduction takes place in the premelted state (α-phase) of 1-hexadecanol (cetyl alcohol) through hydrogen bridges by way of the Grotthus mechanism.[1-3] Proton conduction is observed neither in the liquid state nor in the lower temperature solid phase of the alcohol. For the proton conduction to occur in solid, the presence of hydrogen-bond networks and their reorientation ability along the applied electric field are needed.[1,4-7] In the α-phase of 1-hexadecanol the molecules are known to be rotating around their hydrocarbon chains.[1,8] For further analysis of the mechanism of the proton conduction, it is necessary to know about the value of the proton mobility. There have been few data obtained about it so far on account of the small mobility and the occurence of electrode polarization, *etc.*[9-12] This study was made to obtain the diffusion coefficient of proton in the α-phase of 1-hexadecanol and also to calculate from it the value of the proton mobility.[13-16]

Experimental

1-Hexadecanol(guaranteed grade) used was obtained from Tokyo Kasei Co., Ltd. (Tokyo), and was used without further purification in this experiment. Two types of radioactive tracer were used in this experiment; tritiated 1-hexadecanol ($C_{16}H_{33}O^3H$), in which hydroxyl protons were tritium-labeled, and [1-^{14}C]-labled 1-hexadecanol ($C_{15}H_{31}$-$^{14}CH_2OH$).

Tritiated 1-hexadecanol was prepared by mixing 2 grams of melted 1-hexadecanol with 2 ml of tritiated water (100 mCi/ml) in an evacuated vessel (10^{-4} mmHg), followed by repeated annealing. The labeled alcohol was separated from the water and kept sealed in an evacuated flask until it was used for the experiment. The activity, obtained by this preparation, was about 3 μCi/mg and was ascertained before each experiment.

[1-^{14}C]1-Hexadecanol was obtained from the Radiochemical Centre(Amersham) as benzene solution whose radioactivity was 55.4 μCi/mg.

In order to distinguish the diffusion of the hydroxyl protons from that of the whole molecules, ^{14}C, ^3H-double labeled 1-hexadecanol was used. This double-labeled specimen was prepared in an evacuated vessel by mixing tritiated 1-hexadecanol with ^{14}C-labeled one in the liquid state and also sealed in the evacuated vessel. Its activity was 1.7 μCi/mg for ^3H and 2.4×10^{-1} μCi/mg for ^{14}C in the mixed state, respectively. During the measurement of diffusion coefficient, all handlings were carried out in a glove box where the atmosphere was replaced by nitrogen gas dried with P_2O_5. This is to prevent the tritium of 1-hexadecanol from being exchanged with protons of water molecules in the atmosphere followed by being re-exchanged with hydroxyl protons of other alcohol molecules at a distance.

A cyclinder-form cell made of polyethylene, the size of which was 1 cm in diameter and about 4 cm in height, was closed at one end and filled with melted 1-hexadecanol. The cell was put in an aluminium box and the temperature of the total system was controlled using thermister at 47±0.5 °C where 1-hexadecanol takes α-phase. Two or three drops of melted double-labeled 1-hexadecanol were dropped on the flat surface of the alcohol kept in the α-phase using a warmed glass syringe. The whole cell was immediately covered with the lid of acrylic resins and separated completely from the surroundings. After keeping the sample in this state for 2 weeks, it was sectioned, weighed and assayed for radioactivity using a liquid scintillation counter. The composition of the scintillation solution used in this experiment was dioxane 1 dm³, naphthalene 100 g, 2,5-diphenyloxazole 1 g, *p*-bis(4-methyl-5-phenyl-2-oxazolyl)benzene 0.25 g.

Results and Discussion

The equation which described the tracer diffusion from an infinitely thin surface layer into a semi-infinitely thick solid is given by

$$C(x, t) = \frac{C_0}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right), \tag{1}$$

where $C(x,t)$ is the concentration of the tracer at a distance of x into the solid at time t, C_0 is the initial concentration of the tracer present and D is the diffusion coefficient. The diffusion coefficient can, therefore, be obtained from a plot of $\ln C$ *vs.* x^2. From the measurement of the ^3H-diffusion rate, it was found that $\ln C$-x^2 plots were almost linear except for their initial part where possible existence of micro-cracks through the thin specimens gave larger values. Carbon-14-labeled molecules did not diffuse at all during the same period of experiments. These results are shown in Fig. 1 and Table 1.

Since a cold sample used as a blank test in parallel run showed no radioactivity, the water vapor in the environment seemed to have been almost perfectly removed. The proton diffusion observed in this experi-

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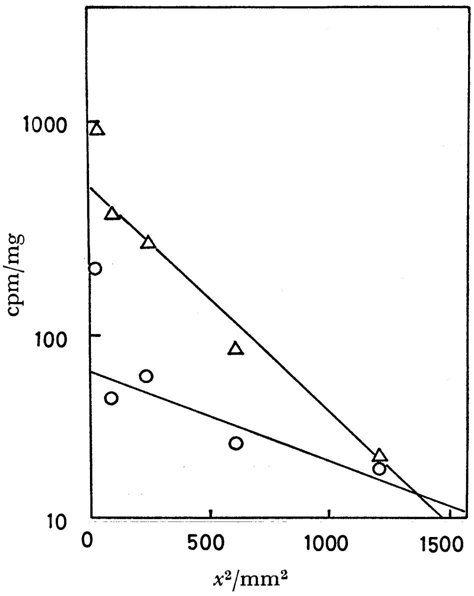

Fig. 1. Profile of the diffusion of ^{3}H in the α-phase of 1-hexadecanol.
○: After 14 days, △: after 12 days.

TABLE 1. DIFFUSION OF ^{3}H, ^{14}C IN THE α-PHASE OF 1-HEXADECANOL

Distance mm	^{3}H $^{a)}$ cpm·mg^{-1}	^{14}C $^{a)}$ cpm·mg^{-1}
5	198.3	<0.1
10	46.4	<0.1
15	60.1	<0.1
25	28.4	<0.1
35	20.8	<0.1

a) Initial activity was 1.7 μCi/mg for ^3H and 2.4×10^{-1} μCi/mg for ^{14}C, respectively.

ment is considered to have taken place through the bulk without involving proton exchanges with water vapor in the atmosphere. Moreover, tritium diffusion through the partially molten spots in the sample can be ignored, because the ^{14}C-labeled molecules had scarcely diffused despite the temperature was kept just below the melting point. It was concluded, therefore, that hydroxyl protons diffuse rather fast and independently of the whole molecule in the α-phase of the alcohol, presumably *via* the hydrogen-bond networks extending through the crystals.

The diffusion coefficient, D, was calculated in accordance with Eq. 1 as

$$D = (7\pm5)\times10^{-7}\,\mathrm{cm^2/s}. \qquad (1)$$

Measurements of the diffusion coefficient for proton using radioisotope as a tracer have been reported with other crystals such as ice,[14,15] imidazole,[16] and pivalic acid.[13] In the plastic phase of pivalic acid, it was reported that the diffusion coefficient of carboxyl protons is about 10^{-7} cm^2/s at 25 °C, which is approximately 10^2 times faster than that of the whole molecules. The diffusion coefficient is related to the mobility of charge carrier by Einstein's equation

$$\mu kT = qD, \qquad (2)$$

where μ is the mobility, k is the Boltzmann constant, and q is the charge of the ion. Using this equation, the proton mobility in the α-phase of 1-hexadecanol is calculated as follows from the value of the diffusion coefficient obtained in this experiment.

$$\mu = (3\pm2)\times10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}.$$

It seems that Eq. 2 can only be applied when the independent charged-particles diffuse through the material. Charge transfer is not necessarily involved in the present diffusion process because diffusion can also be effected by some non-ionic exchange mechanism. However, if the rate-determining step in both the electric conduction and the concentration diffusion through the hydrogen-bond networks is not in the proton transfer process, but in the process of molecular rotation or reorientation of the hydrogen-bonded portion,[5] then Eq. 2 can be used to evaluate the effective mobility for the electric conduction of 1-hexadecanol in the α-phase.

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