The diffusion of solute through wood saturated with water III

(2) Effects of thickness of test specimen on the diffusion of electrolytes in the transverse directions of wood

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Summary The effects of thickness of the test specimen on the diffusion of potassium chloride (KCl) through water-saturated wood have been measured for both transverse directions of Hinoki and Buna woods at a constant temperature of 50°C.

The results obtained are as follows:

(1) The variations of the diffusion coefficient in both transverse directions of Buna were generally greater than those of Hinoki (Table 2).

(2) There was no significant difference between the diffusion rates in the radial and tangential directions on Hinoki. However, in the case of Buna the diffusion coefficient in the radial direction was slightly greater than that in the tangential direction (Table 2 and Fig. 3).

(3) The ratio of the diffusion coefficient for each species and direction of diffusion to that of KCl into water in bulk was about 1/73 for Hinoki-radial, about 1/71 for Buna-radial, about 1/82 for Hinoki-tangential, and about 1/115 for Buna-tangential (Table 2).

(4) The values of the diffusion coefficient for each species and direction of diffusion were independent of the thickness of the test specimen (Table 2 and Fig. 3).

(5) According to the measurements of the diffusion rate by means of the two-ply specimen combined the two specimens in which the diffusion coefficient is known respectively, the diffusion coefficient was approximately equal to that of each specimen (Table 3). From these results, it was suggested that the effects of the specimen thickness on the diffusion coefficient were probably due to the difference of the relative effects between the effective capillary cross-sectional area and the thickness for the resistance of the diffusion and that the effects of thickness would be appeared when the diffusion coefficient of KCl through wood is greater than about 1/20 of that into water in bulk.

Introduction

In the previous report[3], the effects of thickness of the test specimen on the diffusion rate of potassium chloride (KCl) through water-saturated wood have been determined for the longitudinal direction of Hinoki and Buna woods at a constant temperature of 50°C. These data showed that the diffusion rate of Buna was considerably smaller than that of Hinoki having the same thickness and furthermore the

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diffusion coefficient of Hinoki for the transfer of the solute decreased gradually with an increase in thickness of the test specimen, but that of Buna was not affected by the changes in thickness. From these results, it was suggested that the diffusion rate of solute through or into water-saturated wood might be dependent upon the difference in the size between the mean free path of the diffusing molecule or ion and the dimension of the effective capillaries in the direction of diffusion. In other words, in Buna the influence of thickness of the test specimen on the diffusion rate would not appeared, because the solute molecules or ions have to pass through very many narrow paths compared with those of Hinoki.

In order to make clear the results described above, the present paper deals with the effects of thickness of the test specimen on the diffusion rate in the transverse directions (radial and tangential directions) using the similar method to that described already[1-3].

Experiments

1 Specimens

The test specimens were disks having the radial and tangential sections which were cut from air-dried blocks of Hinoki (*Chamaecyparis obtusa* ENDL.) and Buna (*Fagus crenata* BLUME) heartwoods. These Hinoki and Buna woods were quite similar to those used in the previous report[3]. They were prepared to the nominal sizes of 5 cm in diameter and six different thicknesses on the basis of preliminary tests, namely 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 mm. All specimens were selected to be almost similar to thickness, annual ring width (Hinoki: 1.5 mm, Buna: 1.6 mm), and specific gravity in air-dry (Hinoki: 0.38 g/cm^3, Buna: 0.65 g/cm^3), and then submerged in distilled water under a vacuum of 10^{-3} mmHg until they are completely saturated with water before use. The moisture contents of the test specimens were thus about from 200% to 230% for Hinoki and about from 105% to 125% for Buna.

2 Apparatus

The apparatus used for measurements of the diffusion rate was essentially the same as that described in the previous report[1-3] except for some modifications in the electric circuit (see Table 1), and its outline was as follows:

Table 1 Set of resistances

Set	Variable resistance (KΩ)	Resistance (KΩ)
a	0—1	0.05, 0.1, 0.3, 0.5, 1.0
b	0—5	0.3, 0.5, 1.0, 3.0, 5.0
c	0—30	5.0, 10.0, 15.0, 20.0, 30.0

(a) On the basis of the reason described already[2], vitreous cells were used as the diffusion cells.

(b) The combinations of variable resistance and resistances in the electric circuit were as shown in Table 1.

(c) The measurements were made with Am-Type potentiometer capable of being read to 1/1000 of full scale of the variable resistance.

(d) An ammeter with a range of 0-50 μA was used to facilitate the detection of null-point.

3 Experimental procedure and calculation of diffusion coefficient

Potassium chloride (KCl) was the solute used at a concentration of 0.5 mol. and the diffusion rate was measured in the radial and tangential directions at a constant temperature of 50°C. The measurements of the diffusion rate were made in a manner similar to those described previously[1-3], i.e. a water-saturated disk specimen heated to the desired temperature was inserted between the cells, clamped, and an external circumference of the disk specimen was then sealed with a paraffin to prevent the loss of solution from the specimen and the cell. To obtain results at the steady-state condition, the solution of 50°C with the given concentration was poured in one side of the diffusion cell (cell-A) and distilled water at the same temperature in the other (cell-B). These diffusion cells were then enclosed in a thermostat controlled to within 0.5°C of the desired temperature. All of the procedures described above were made as fast as possible to avoid fluctuation of the temperature of the solution in the cells and of the test specimen. Furthermore, in order to avoid the change of the concentration gradient in the specimen due to the difference of thickness of each water-saturated test specimen and the transfer of the solute during the measurements, the solution in cell-A and distilled water in cell-B were removed two or three times after convenient periods of time and replaced.

As indicated previously[1-3], the transfer of the solute from cell-A to cell-B resulting from the concentration gradient was determined by measuring the electric resistance of the solution in cell-B at suitable time intervals. The diffusion was allowed to continue until seven or ten consecutive readings at the steady-state were obtained.

Besides the measurements described above, a calibration curve (i.e. a plot of the electric resistance against the concentration of solution) in relation to the individual

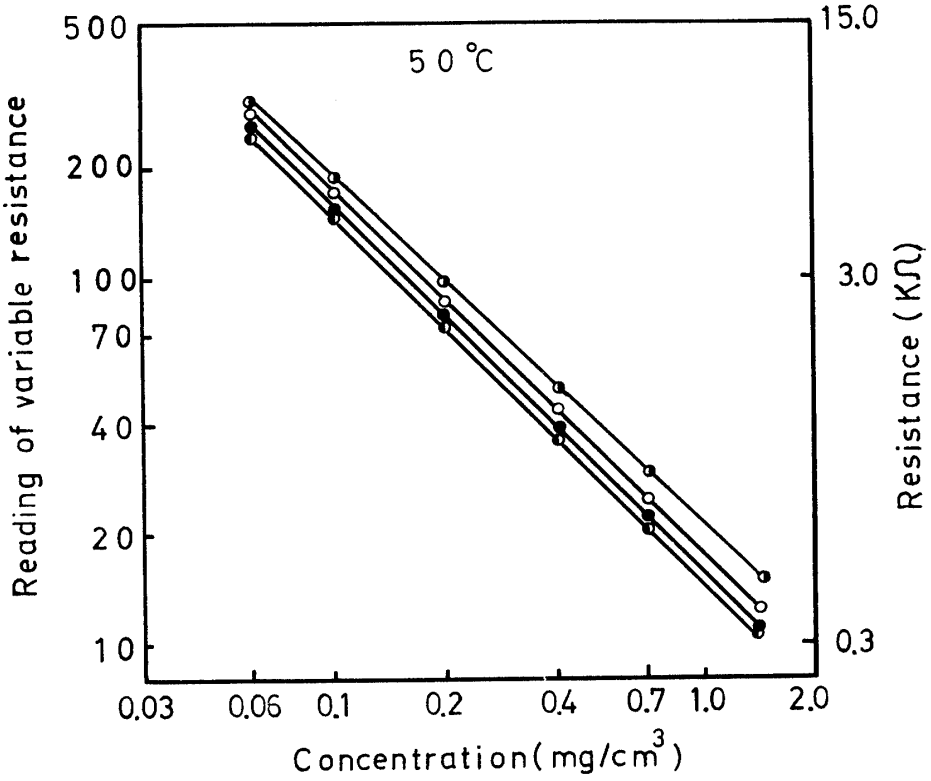

Fig. 1 An example of calibration curves for KCl

cell-B was preliminarily measured by the method that has been described already[1-3]. Fig. 1 illustrates an example of calibration curve. And, examples of the diffusion curves (i.e. a plot of the amount of solute-transfer against time) are as shown in Fig. 2.

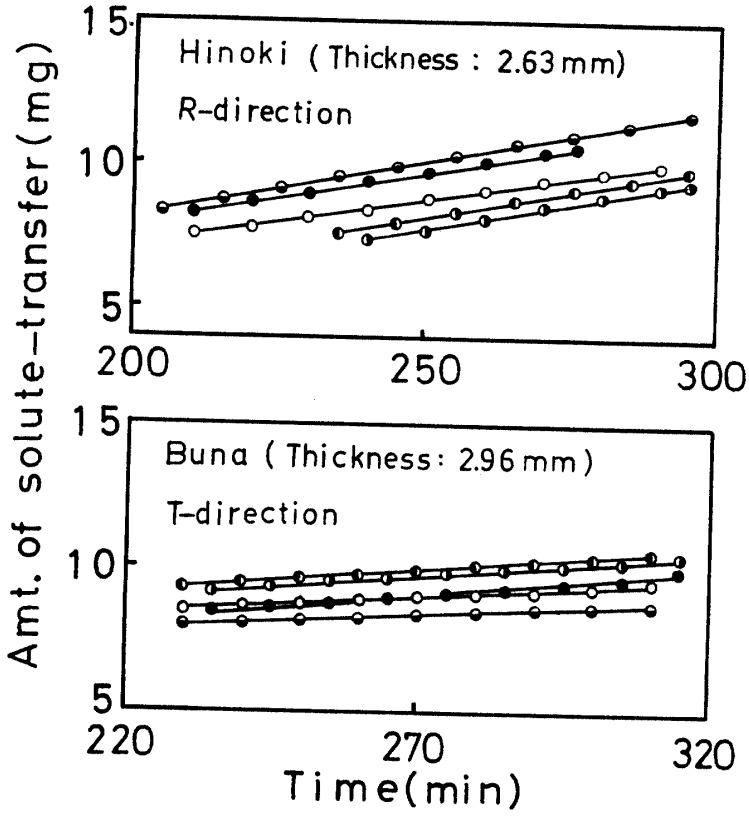

Fig. 2 Examples of diffusion curves

Since the linear portion of the diffusion curve shows that the transfer of solute through the test specimen perhaps was under the steady-state condition, the diffusion coefficient (D) for the transfer of the solute can be calculated by using Fick's first law (Eq.(1)).

$$\frac{dm}{dt} = -D \cdot A \cdot \frac{dc}{dx} \quad \cdots\cdots\cdots\cdots (1)$$

Therefore, $$D = \frac{1}{A} \cdot \frac{l}{C_1 - C_2} \cdot \frac{dm}{dt} \quad \cdots\cdots\cdots\cdots (2)$$

in which dm/dt is the rate of transfer of solute passing through the test specimen per unit time (g/sec), dc/dx the concentration gradient set up across the test specimen ($g/cm^3/cm$), A the effective area of the test specimen (cm^2), l its thickness in the direction of diffusion (cm), C_1 and C_2 the concentrations in equilibrium of the solutions in cell-A and cell-B (g/cm^3) respectively.

Results and discussion

1 Diffusion coefficient

The values of the diffusion coefficient of KCl at a constant temperature of 50°C for each species, direction of diffusion and thickness, and of the standard deviation are as shown in Table 2. Each value of the diffusion coefficient is the mean of values from at least five test specimens. Since the test specimens of 3.0 mm-thick in the radial direction and of 2,5 mm-thick in the tangential direction of Hinoki have

Table 2 Diffusion coefficient (D) and standard deviation (σ) for each species, direction of diffusion and thickness

Hinoki wood				Buna wood			
Direction of diffusion	Thickness (mm)	D (cm^2/sec)	σ (cm^2/sec)	Direction of diffusion	Thickness (mm)	D (cm^2/sec)	σ (cm^2/sec)
Radial	1.08	$3.70^{\times 10^{-7}}$	$0.72^{\times 10^{-7}}$	Radial	1.05	$4.74^{\times 10^{-7}}$	$0.99^{\times 10^{-7}}$
	1.63	4.88	0.92		1.62	2.67	0.65
	2.08	4.43	1.20		2.16	3.93	1.38
	2.63	5.06	0.57		2.64	5.54	0.41
	—	—	—		3.01	4.64	1.46
	3.63	3.83	0.45		3.61	4.89	0.64
Tangential	1.13	3.96	0.75	Tangential	1.13	2.61	0.28
	1.63	3.79	0.39		1.70	2.87	0.30
	2.25	4.63	0.90		2.10	3.22	0.97
	—	—	—		2.75	2.37	0.39
	3.12	3.70	0.63		2.96	2.64	0.37
	3.68	3.59	1.10		3.70	2.47	1.18

not given enough data, these values are not shown in Table 2.

From the results shown in Table 2, it will be seen that the variations of diffusion coefficients among the test specimens are considerably greater and the coefficients of variation (standard deviation/mean value) for diffusion coefficient in both transverse directions of Buna are, with minor exceptions, generally greater than those of Hinoki, as described in the previous report[3]. Furthermore, in comparing the diffusion coefficients in both transverse directions, the results in Table 2 show that there is no significant difference between the diffusion rates in the radial and tangential directions on Hinoki, while in the case of Buna the diffusion rate in the radial direction is, with one anomalous exception, slightly greater than that in the tangential direction. Although there have not been enough data to explain the latter result in this stage, it may be considered that this difference is attributed to the following two causes, namely on one hand the wood rays whose orientation and thin walls would facilitate radial diffusion, and on the other hand the aspirated pit membrane openings existing on the walls of vessels because of the test specimens prepared from the heartwood blocks.

As the diffusion coefficient of KCl into water in bulk is 320.0×10^{-7} cm^2/sec at a temperature of 50°C, the diffusibility of KCl in the radial direction decreases by the wood structure to about 1/73 on an average in Hinoki, and to about 1/71 in Buna. And the tangential diffusion coefficient decreases to about 1/82 in Hinoki, and to 1/115 in Buna compared with the bulk diffusion coefficient. The longitudinal diffusion coefficient which has been measured using the same materials[3] decreased to about 1/2.5 (in 5.4 mm-thick) ~ 1/6 (in 30.2 mm-thick) in Hinoki and to about 1/18 on an average in Buna compared with that in the bulk state. The rate of diffusion of the solute through wood, as mentioned above, is considerably smaller in comparison with the bulk diffusion rate. But these phenomena are especially more conspicuous in the case of the transverse diffusion than the longitudinal one. As was previously

pointed out[2,3], it is assumed that the cause for these phenomena is probably dependent upon the dimension and the number of effective capillaries through which solute could diffuse.

The order of magnitude of the diffusion coefficient for each species and direction of diffusion is Buna-radial = Hinoki-radial = Hinoki-tangential > Buna-tangential. The reason that the tangential diffusion of Buna is difficult compared with others, is also possibly due partly to the decrease of the number of pit membrane openings where the solute passed through because of the aspirated pit-pair as abovementioned.

2 Thickness of test specimen and diffusion coefficient

Fig. 3 illustrates the plots of the diffusion coefficient against the thickness of the

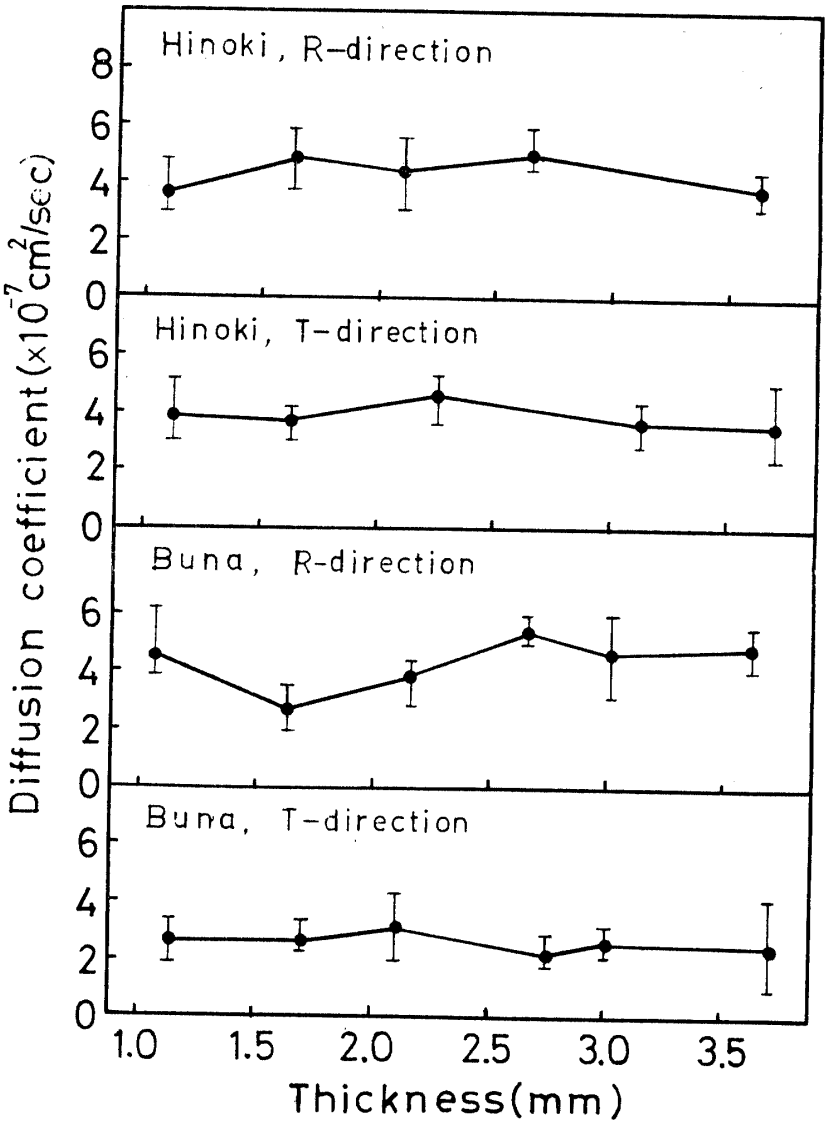

Fig. 3 Relationship between diffusion coefficient and thickness of test specimen for Hinoki and Buna woods

test specimen on the basis of the results indicated in Table 2. From the results in Fig. 3 and Table 2, it will be seen that the diffusion coefficient of KCl in both transverse directions for Hinoki and Buna is quite independent of the thickness of test specimen as well as that in the longitudinal direction of Buna indicated in the

previous report[3].

In order to make clear experimentally the effects of the specimen thickness on the diffusion coefficient described above, the measurements of the diffusion rate of solute were made by means of the two-ply specimen combined the two single specimens in which the diffusion coefficient is known respectively. The thicknesses of each single specimen used in these experiments were 1.0 mm and 1.5 mm in the case of the radial diffusion, and 1.5 mm and 2.0 mm in the tangential diffusion.

In the case of making up the two-ply specimen using the two single specimens, it was necessary to contact as closely as possible the connecting surface between each single specimen to avoid the experimental error and the variance of diffusion coefficient. According to the results of some preliminary tests on the technique for this, it was most convenient the method that two single specimens were given a suitable pressure from the upper side after they were piled each other, and then eight positions at suitable intervals on the edge-surface of the two-piled specimen were fixed by a nail. Thereafter, the external surface of this specimen was sealed with a paraffin except for the sectional area across the direction of diffusion as indicated previously.

The measurements of the diffusion rate of two-ply specimen were made in a manner similar to those described already. Examples of the diffusion curves measured using these methods are as shown in Fig. 4 and the results obtained in Table 3. From the results in Table 3, it will be seen that the diffusion coefficient of the two-ply specimen in both transverse directions of Hinoki and Buna shows, with minor excep-

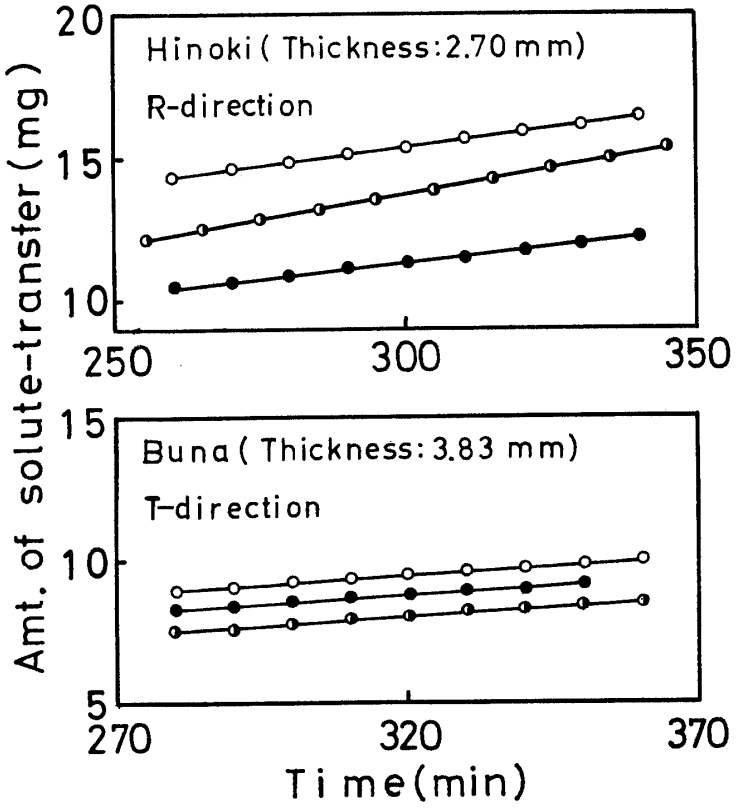

Fig. 4 Examples of diffusion curves of two-ply specimen for Hinoki and Buna woods

Table 3 Diffusion coefficient (D) of single and two-ply specimens for Hinoki and Buna woods.

Species	Direction of diffusion	Single specimen			Two-ply specimen		
		Thickness (mm)	D (cm^2/sec)	D_{mean} (cm^2/sec)	Thickness (mm)	D (cm^2/sec)	D'_{mean} (cm^2/sec)
			$\times 10^{-7}$	$\times 10^{-7}$		$\times 10^{-7}$	$\times 10^{-7}$
Hinoki	Radial	1.06	3.67	4.14	2.68	5.20	4.06
		1.65	5.37				
		1.08	3.43		2.71	3.43	
		1.60	3.72				
		1.07	3.54		2.72	3.55	
		1.63	5.14				
	Tangential	1.58	3.88	4.26	3.89	4.10	3.70
		2.25	4.97				
		1.65	3.83		3.87	6.06	
		2.23	6.15				
		1.66	3.14		3.85	3.94	
		2.19	3.61				
Buna	Radial	1.02	5.25	3.81	2.68	3.81	3.30
		1.63	2.97				
		1.07	4.38		2.76	2.91	
		1.58	2.74				
		1.04	3.96		2.67	3.19	
		1.61	3.56				
	Tangential	1.72	2.63	2.98	3.82	2.11	2.45
		2.09	1.99				
		1.73	3.42		3.89	2.23	
		2.07	3.49				
		1.71	2.57		3.78	3.00	
		2.10	3.81				

(D_{mean} and D'_{mean} are the mean of D for single and two-ply specimens respectively)

tions, the intermediate value between the diffusion coefficient for each single specimen combined. Therefore, the mean values (D'_{mean}) of the diffusion coefficient of two-ply specimen for each species and direction of diffusion are approximately equal to the corresponding values (D_{mean}) of the single specimen. Furthermore, these mean values (D'_{mean}) for the two-ply specimen are also in fairly close agreement with the corresponding values (Hinoki-radial : 4.37×10^{-7} cm^2/sec, Hinoki-tangential : 3.89×10^{-7} cm^2/sec, Buna-radial : 4.51×10^{-7} cm^2/sec, Buna-tangential : 2.45×10^{-7} cm^2/sec) of the diffusion coefficients for all specimens over the ranging from 1.0 mm to 3.5 mm in thickness indicated in Table 2 and Fig. 3, except for the values in the radial direction of Buna (Buna-radial : 4.51×10^{-7} cm^2/sec) in which the diffusion coefficient in 1.5 mm-thick is apparently smaller than others.

Accordingly, it seems reasonable to consider from the results indicated above and in the previous report[3], that the diffusion coefficient of KCl through or into water-saturated wood under the steady-state condition would be independent of the thickness of the test specimen except for the test specimen in which the diffusion coefficient of

KCl through wood is greater than about 1/20 of that into water in bulk, irrespective of the direction of diffusion. On the contrary, Christensen and Williams[4], who have determined the diffusion rate in the tangential direction using sodium chloride solutions ranging from 0.5 mol. to 4.0 mol. in concentration, found that the diffusion rate of the solute was slightly greater with an increase in thickness. Regarding this fact, they have assumed that the zone of wood under the lacquered margin was probably contributed to the diffusion path.

However, that the diffusion coefficient may be independent of the thickness of test specimen seems also can be explained by considering the relationship between the rate of transfer of the solute (dm/dt) and the concentration gradient (dc/dx) in Eq. (1). Under the steady-state condition that two different fixed concentrations are maintained at the two surfaces of the test specimen, the rate of transfer of the solute (dm/dt) would be greater the thinner the test specimen because of the increase of the concentration gradient (dc/dx), on the contrary this rate would be smaller the thicker the test specimen. As a result, the diffusion coefficient would be expected to be not affected considerably by the changes in thickness of the test specimen.

In general, the diffusion of liquids, vapors and dissolved materials into wood occurs predominantly through cell cavities and pit membrane openings, and probably very little through transient capillaries developed in swollen cell walls. But, it has been shown that the diffusion of an electrolyte through the complex network of water-filled capillaries of wood is analogous to electrical conduction through this same structure[5]. Therefore, considering the parallel and series combination of the various capillaries of wood, it can be assumed that the diffusion rate is approximately proportional to total cross-sectional area of the effective capillaries existing in the diffusion path and inversely proportional to the average path length (in other words, "thickness of test specimen") in spite of the complexity of the wood structure. Taking this viewpoint, it will be discussed below.

The experimental results indicate that the longitudinal diffusion coefficient of Buna and the transverse values of both species are not affected by the changes in thickness, in spite of the longitudinal value of Hinoki decreases gradually with an increase in thickness. This can probably be explained by the difference in the relative effects between the effective capillary cross-sectional area and the thickness (or path length) for resistance of the diffusion. For example, for the wood in which the capillary radius is much larger than that of the mean free path of the diffusing molecule or ion, the diffusion coefficient of the solute would be approximately equal to the bulk diffusion coefficient. Consequently, it may be considered that the diffusion rate in such case is mainly dependent upon the thickness of the test specimen. On the contrary, it will be expected that when the diffusion coefficient of the solute is considerably smaller in comparison with that in the bulk state, the rate of diffusion is mainly controlled by the dimension of the effective capillaries in diffusion path rather than the specimen thickness.

要旨：前報[1~3]に続き，飽水木材中の溶質拡散に及ぼす試片厚さの影響を0.5mol.のKCl溶液を用い，50°Cの一定条件下で，ヒノキおよびブナ材の繊維直角方向の場合について検討した。

得られた結果を要約すると次のとおりである。

(1) 木材組織に起因しての拡散係数の変動は前報[3]同様にヒノキよりもブナにおいてやや顕著であった（Table 2)。

(2) ヒノキでは半径，切線両方向の拡散係数に著しい差異はなかったが，ブナの場合には半径方向の拡散係数が切線方向のそれよりも若干大きかった（Table 2, Fig. 3)。

(3) ヒノキおよびブナの両方向の拡散係数をKClの水中におけるそれと比較すると，半径方向の場合：ヒノキ約1/73，ブナ約1/71，切線方向の場合：ヒノキ約1/82，ブナ約1/115であった（Table 2参照)。

(4) ヒノキおよびブナの両方向の拡散係数は，いずれも試片厚さによって影響されないことが認められた（Table 2, Fig. 3)。

(5) 拡散係数既知の2枚の試験片を重ね合わせた試料についての測定結果によると，その拡散係数はいずれも各試験片のそれにほぼ等しく，試片厚さの影響が認められなかった（Table 3)。拡散係数に及ぼす試片厚さの影響は拡散の抵抗に対する有効毛管断面と厚さとの相対効果の差異に起因し，KClの場合には水中における拡散係数の約1/20以上になるとその影響のあらわれることが推測された。

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