

# Studies on the sorption of water vapour by hardwood hemicellulose

By

TAKESI SADOH

## Introduction

The sorption of water by wood has been studied by a large number of workers for many years on sorption isotherms, swelling, heat of sorption, and rate of sorption and diffusion. Most of these investigations have been interpreted in terms of wood itself or cellulose contained in wood. On the contrary, little attention has been paid to the sorptive nature of wood hemicellulose, although its high sorptive capacity is inferred from its molecular structure and state of aggregation in wood, namely, containing hygrophilic -OH groups and probably having an amorphous structure. Recently, the author and coworkers have reported a series of studies on the some sorptive behaviours of water vapour by wood hemicellulose<sup>4-12)</sup>, and in this paper these investigations are summarized.

## Materials

The samples used in these studies were filmy hemicellulose specimens which were prepared from wood meal of Buna (*Fagus crenata* BLUME), Shina (*Tilia japonica* SIMK.) and Makanba (*Betula Maximowicziana* REGEL) by the following procedures.

The wood was delignified with sodium chlorite and acetic acid at 75°C for four hours, and was extracted with 20 times its volume of 5 percent potassium hydroxide for three hours. After filtration, the solution was poured into three times its volume of methanol with acetic acid. The precipitate was centrifuged. The supernatant was decanted, and the residue resuspended in 85 % methanol and recentrifuged. In the same manner, the supernatant was replaced with pure methanol, and ethyl ether, successively. The resulting precipitate was suspended in ethyl ether, then, added into hot water. The aqueous solution of hemicellulose, obtained here, was condensed and dried on a glass plate to make transparent film, which had a well-oriented arrangement of molecules<sup>9)</sup>. The filmy specimen enables us not only to observe the sorption, but to examine the diffusion through it. Before each of the experiments, the specimen was sufficiently conditioned to give reproducible data. The conditioning was carried out by repeating moisture adsorption and redrying at room temperature.

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\* Contribution from the Laboratory of Wood Technology, Kyoto Prefectural University, Kyoto.

**Table 1 Hemicellulose samples used.**

	Buna ( <i>Fagus crenata</i> BLUME)		Shina ( <i>Tilia japonica</i> SIMK.)	Makanba ( <i>Betula</i> <i>Maximowicziana</i> REGEL)
	a	b		
Pentosans, %	84.5	84.4	83.2	85.5
Uronic anhydride, %	9.4	8.9	9.0	8.7
Ash, %	4.3	3.4	4.0	3.5
Degree of polymerization	90	110	100	110
Density, * (g/cm <sup>3</sup> )	—	1.51 1.52	1.52	1.51
Thickness of film, (mm)	0.09	0.08 0.14 0.21	0.10	0.08 0.10

\* By buoyancy in benzene, at 0% moisture content.

### Experimental procedures

1) Sorption isotherm and rate of adsorption: The determinations of the sorption isotherm and of the rate of adsorption were carried out in the absence of air. The amount of vapour adsorbed was determined from the increase of weight of specimen weighed by quartz helix-balance. The measurements were periodically conducted at constant vapour pressure and temperature until the equilibrium was established.

2) Swelling: The volumetric swelling of hemicellulose was measured by change in the volume which was calculated from buoyancy of specimens in benzene.

3) Diffusion: The diffusion of water through hemicellulose in steady state were measured by the cup-method. With the filmy specimen was sealed a glass cup containing water or calcium chloride. The cup was placed in a conditioned atmosphere and weighed periodically to determine the rate of change in weight.

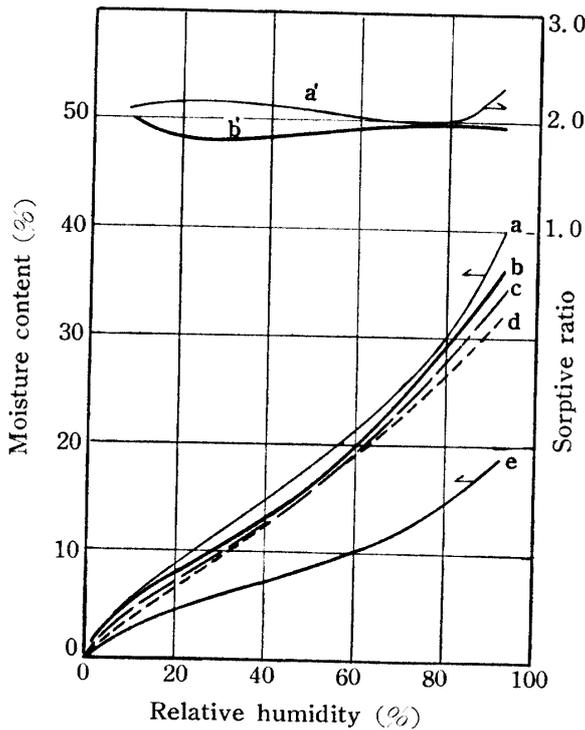
### Amount of vapour adsorbed<sup>1)</sup>

The amount of vapour adsorbed by hemicellulose were measured by increasing the relative humidity in steps within a range from 0 to 93% at 16, 20, 30, and 40 °C, and the sorption isotherms were plotted. The results were analyzed with the following equation<sup>2)</sup>,

$$u = \frac{v_m c x}{1 + c x} \cdot \frac{1 - x^n}{1 - x}, \quad (1)$$

where  $u$  is the moisture content,  $x$  the relative vapour pressure, and  $c$ ,  $v_m$ , and  $n$  are the parameters of the equation.

The sorption isotherm of hemicellulose shows such a typical sigmoid curve as those of wood and cellulose (Fig. 1). Only little differences in the isotherm are seen among species of original wood. The isotherms accord substantially with those



**Fig. 1** Sorption isotherms for wood hemicellulose (a and b, Buna; c, Shina; d, Makanba) and wood (e, Buna), and sorptive ratio based on wood (a' and b'; Buna). (16°C)

obtained by RUNKEL and LÜTHGENS<sup>3)</sup>, and CHRISTENSEN and KELSEY<sup>1)</sup>. The amounts of water adsorbed per a unit weight of hemicellulose are much more than those of wood for all relative humidity values, and the adsorption ratio basing on wood varies between 1.8 and 2.4.

The values of parameters of the equation (1) obtained from sorption isotherms of hemicellulose are compared with those of wood and cellulose in Table 2.  $V_m$  and  $nv_m$  are the number of grams of water adsorbed per gram of sorbent on the primary and the total sorption sites, respectively. The values for hemicellulose approximate to the corresponding values per gram of amorphous region of cellulose. The latter is calculated using the values of  $v_m$ ,  $nv_m$ , and the ratio of amorphous/

crystalline regions of the total cellulose. The area of the sorptive surface of hemicellulose is calculated to be ca.  $16 \times 10^6$  cm<sup>2</sup>/g, about twice the value for wood, with use of the equation,

$$A = \frac{sN}{M} nv_m, \tag{2}$$

where  $N$  is AVOGADRO number,  $s$  the projected area of one water molecule, and  $M$  the molecular weight of water (Table 2).

**Table 2** Values of parameters of equation (1) and area of sorptive surface.

	$v_m$	$n$	$nv_m$	$A$ (cm <sup>2</sup> /g)
<b>Hemicellulose</b>				
Buna, a	12.4	4.6	57.0	$15.3 \times 10^6$
Do, b	10.7	5.8	62.0	16.6
Shina	10.4	6.0	62.4	16.7
Makanba	9.9	6.0	59.4	15.9
<b>Wood</b>				
Buna	6.4	3.8	24.1	6.5
Makanba	7.8	4.0	31.4	8.2
<b>Cellulose</b>				
Regenerated	5.7	4.9	28.0	7.5
Cotton	4.0	4.1	16.4	4.4

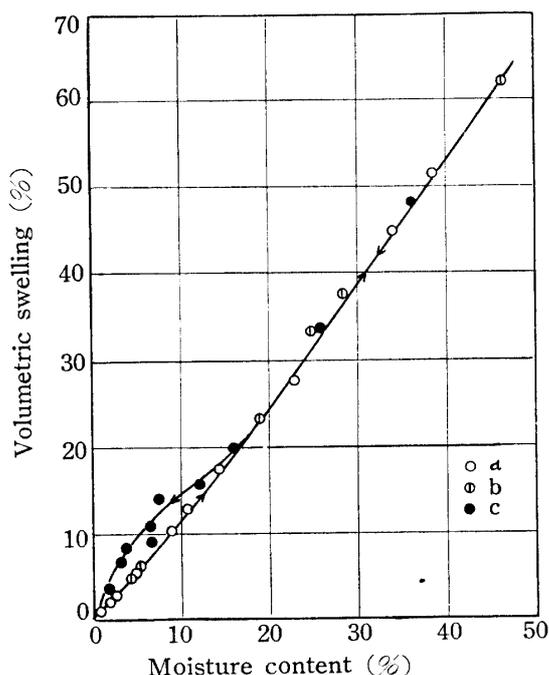


Fig. 2 Volumetric swelling in process of adsorption (a), at adsorption equilibrium (b), and in process of desorption (c). (Buna hemicellulose at 20°C)

### Swelling<sup>11)</sup>

The volumetric swellings of the specimens in the course of adsorption and at the equilibrium are plotted against the moisture content in Figure 2. All experimental points are located on a smooth curve. The fact suggests that the swelling of hemicellulose coincides with adsorption of water on it. Increase in the volume with adsorbing a unit weight of water ( $dV/dW$ ) is less than unity, which is equal to the specific volume of free water in liquid phase. The value of  $dV/dW$  is 0.6 near the zero moisture content, and it increases rapidly towards the constant value of about 0.9 with increasing moisture content.

The hemicellulose swells infinitely when it is placed in saturated water vapour or in water, and dissolved finally. The aqueous solution of hemicellulose transfers reversibly to jelly with increase in concentration or decrease in temperature, and it is also able to transfer reversibly from jelly to such a solid of well-oriented structure as the original film.

### Heat of adsorption<sup>10)</sup>

It is found that the reduction in equilibrium moisture content of hemicellulose with a rise of every 10°C in temperature at 10, 30, and 50% relative humidities is 0.5, 0.8, and 1.3% respectively. The sorption isostere is obtained by plotting the logarithm of relative humidity at which a given amount of vapour is adsorbed versus the reciprocal of the absolute temperature, and then differential heat of adsorption at given moisture content are calculated from the slope of the line with the following equation,

$$\frac{dQ}{du} = -\frac{R}{M} \cdot \frac{d \ln x}{d(1/T)}, \quad (3)$$

where  $dQ/du$  is the differential heat of adsorption,  $x$  the relative humidity,  $T$  the absolute temperature,  $M$  the molecular weight of water, and  $R$  the gas constant.

The differential heat of adsorption decreases with increasing moisture content. The relation between the differential heat of adsorption and relative humidity is similar to that found by CHRISTENSEN and KELSEY for *Eucalyptus* hemicellulose<sup>11)</sup> (Fig. 3). The relation is also similar to those for cellulose and wood. The fact suggests that there is an analogous distribution of energy of sorption site in those

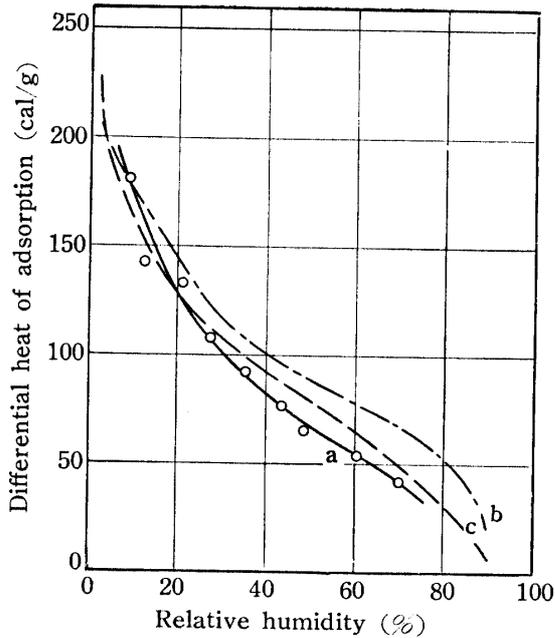


Fig. 3 Relation between relative humidity and differential heat of adsorption for hemicelluloses of Buna (a) and *Eucalyptus* (b, and c)<sup>1)</sup>.

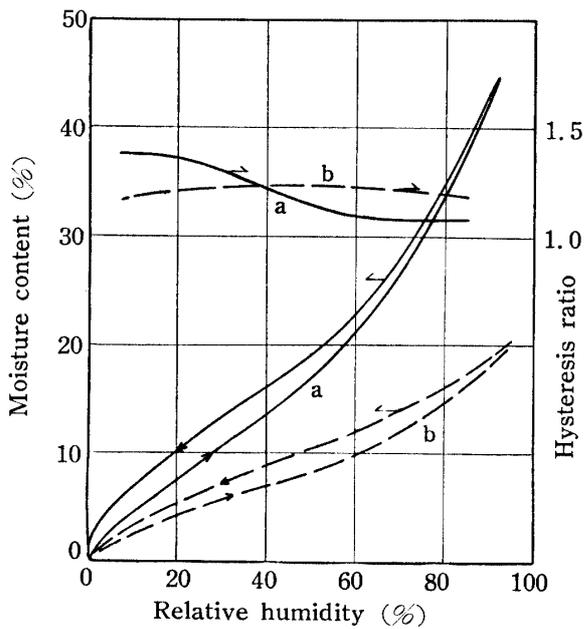


Fig. 4 Adsorption and desorption isotherms, and hysteresis ratio for hemicellulose (a) and wood (b). (Buna at 20°C)

substances.

**Hysteresis<sup>12)</sup>**

Both adsorption and desorption isotherms are determined at 20°C and the range between 0 and 93.0% relative humidities, and the desorption/adsorption ratio are calculated. The value for the hemicellulose are compared with those for wood in Figure 4. It is shown that the hysteresis effect on sorption isotherm of the former is more remarkable at lower relative humidity range.

The volumetric changes with variation of moisture content are determined during the processes of both adsorption and desorption. As shown in Figure 2, the moisture content vs. the volumetric change curve of desorption accords with that of adsorption above 20% moisture content. Below the moisture content, however, the volume of specimen conditioned by desorption are greater than the volume by adsorption. Thus, the volumetric shrinkage might proceed still so slowly after separation of water molecules, that the shrinkage would not complete within the usual period of experiment.

**Diffusion<sup>6)</sup>**

The rate of movement of water in a steady state through the filmy specimen of hemicellulose was measured under various moisture-content gradients and temperatures. The average diffusion coefficient is calculated with the following equation,

$$D = \frac{-ml}{A(c_2 - c_1)t}, \tag{4}$$

where  $D$  is the average diffusion coefficient,  $m$  the weight of water moved through the specimen for the time  $t$ ,  $A$  the effective diffusion area,  $l$  the thickness of specimen, and  $c_1$  and  $c_2$  are the concentrations of water at the both surfaces of specimen.

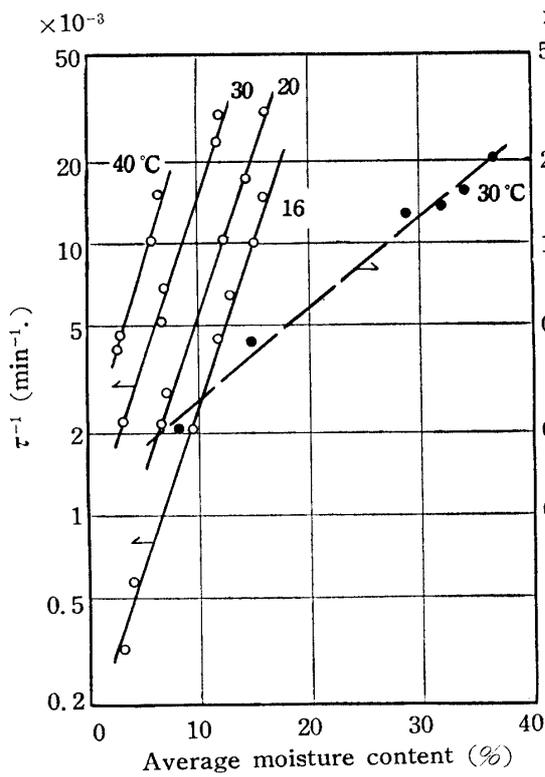


Fig. 5 Relations between average moisture content and  $\log \bar{D}$ , and  $\log \tau^{-1}$  at given temperature. (Buna hemicellulose)

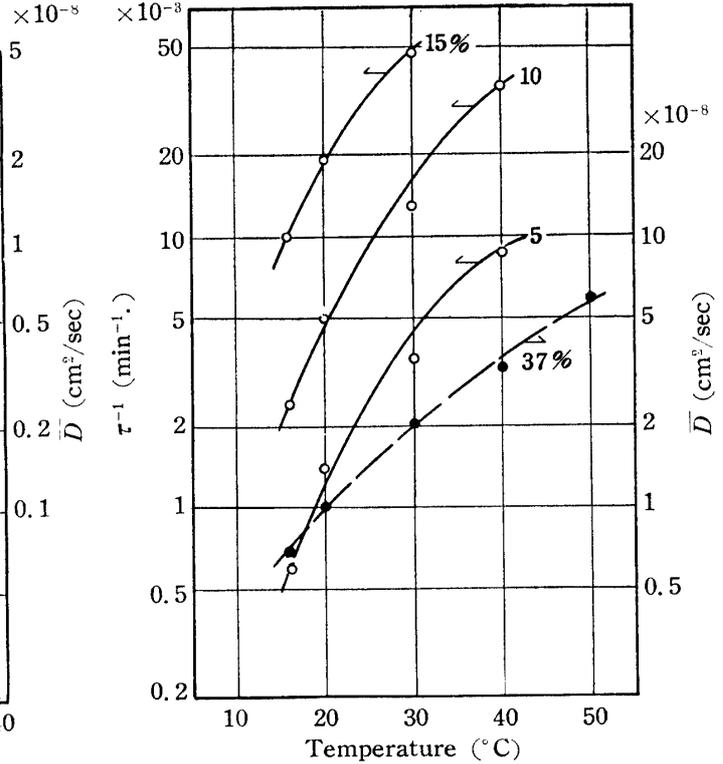


Fig. 6 Relations between temperature and  $\log \bar{D}$ , and  $\log \tau^{-1}$  at given average moisture content. (Buna hemicellulose)

The results obtained are shown in Figure 5 and 6. The average diffusion coefficient increases in an exponential manner with increasing average moisture content (Fig. 5). The diffusion coefficient ranges between  $10^{-9}$  and  $10^{-8}$   $\text{cm}^2/\text{sec}$  at  $30^\circ\text{C}$ . The activation energy of diffusion of water is 10.7 kcal/mol, which is obtained from the increase of diffusion coefficient with temperature at a given moisture content (Fig. 6), using equation,

$$E = -R \frac{d \ln \bar{D}}{d(1/T)} \quad (5)$$

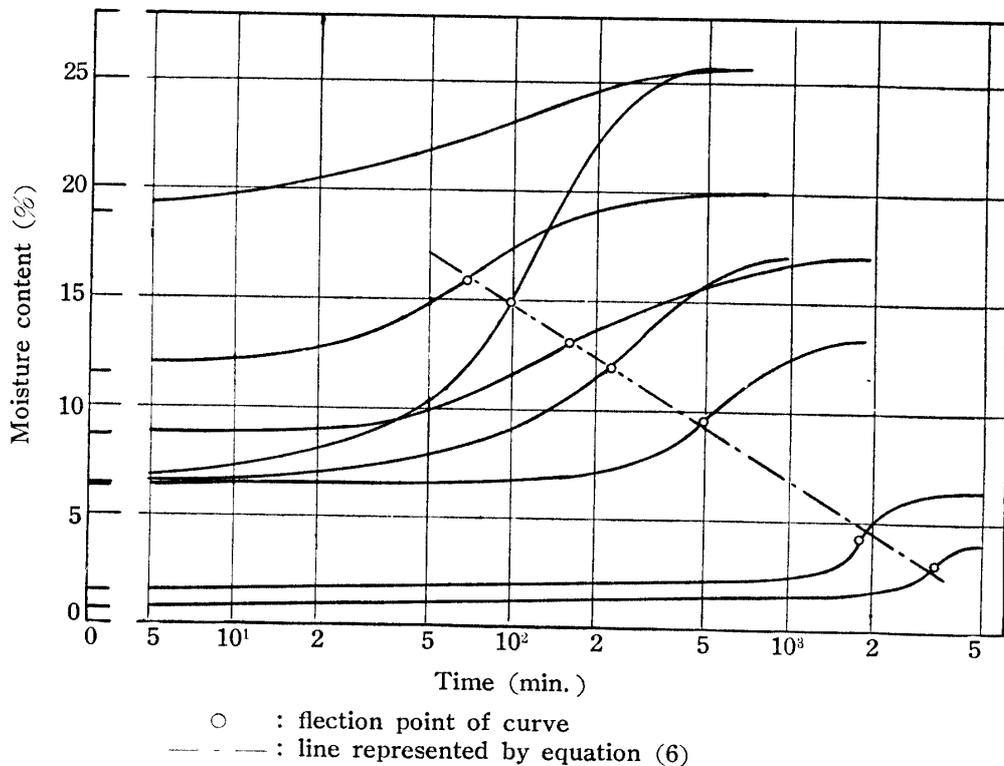
This value of activation energy is nearly coincident with the energy of hydrogen bond. The coincidence indicates that sorbed water moves probably through combination and separation of bonds between water molecules and sorption sites; in other words, the movement of water through hemicellulose might consist of such series of molecular jumps of water from a sorption site to another, as demonstrated by STAMM<sup>13)</sup> on the movement of bound water into cell wall of wood.

#### Rate of adsorption<sup>4,5,7)</sup>

The amount of water vapour adsorbed by the hemicellulose was measured periodically until the equilibrium was established under various temperatures and increments of moisture content. To determine the diffusion coefficient by unsteady-state stream with BOLTZMANN'S form of FICK'S equation, the moisture content is plotted against the square root of time. However, the relation between them is far

from showing any linearity even at the initial stage of adsorption, especially the average moisture content is low. The adsorption processes are scarcely affected by the variation of thickness of specimen under 15% moisture content. Therefore, the rate of moisture adsorption is taken to be independent on the diffusion of water into the specimen, and presumably controlled by a rheological deformation of molecular networks of hemicellulose during the swelling<sup>4,7</sup>.

In order to analyse the rate of adsorption for this system, the adsorption processes are represented graphically in the form of moisture content vs. logarithm of time curves. Each of them have an inflection point in the neighbourhood of average moisture content, so the time  $\tau$  of the inflection point is used as a measure of adsorption rate. Some examples of the experimental results are given in Figure 7, and the inflection points of all the adsorption curves, except at higher average



**Fig. 7** Adsorption processes plotted in form of relation between moisture content and logarithm of time. (Buna hemicellulose at 16°C)

moisture content, have place on a straight line which is represented by the equation,

$$\log \tau = k u_{\tau} + c, \quad (6)$$

where  $u_{\tau}$  is moisture content at time  $\tau$ , and  $k$  and  $c$  are constants. And  $u_{\tau}$  is given approximately by

$$u_{\tau} = 0.55(u_{\infty} - u_0) + u_0, \quad (7)$$

where  $u_0$  and  $u_{\infty}$  are the initial and the equilibrium moisture contents respectively. The increase of adsorption rate with moisture content may be accounted for by assuming that the molecules of sorbed water weaken the intermolecular bondings of the network of hemicellulose, and this causes the decrease in the resistance

against the swelling.

The  $u_\tau$  vs.  $\log \tau$  line shifts in parallel towards shorter time with increasing temperature, as shown in Figure 5. The activation energy for moisture adsorption by hemicellulose is about 18 kcal/mol, which is obtained from the variation of  $\tau$  at a given  $u_\tau$  with temperature using the equation,

$$E = -R \frac{d \ln \tau}{d(1/T)} \quad (8)$$

The value is evidently higher than those of the diffusion and it may represent the activation energy for the deformation of molecular network to swell.

Generally, the main limiting factors for the rate of adsorption may be as follows<sup>7)</sup>: i) The rate of movement of water molecules in hemicellulose, which is expressed as the diffusion coefficient determined under steady state movement ( $D$ -effect). ii) The rate of development of sorptive ability at each sorption site on hemicellulose, which is controlled by the rate of deformation of the molecular network of hemicellulose in order to make a space accepting sorbed water, namely, the rate of swelling, and which is expressed as the above mentioned time  $\tau$  ( $\tau$ -effect). iii) The rate of sorption of water molecule on active sorption site which may be too rapid to limit the whole adsorption rate.

According to the temperature or the moisture content range, either  $D$ - or

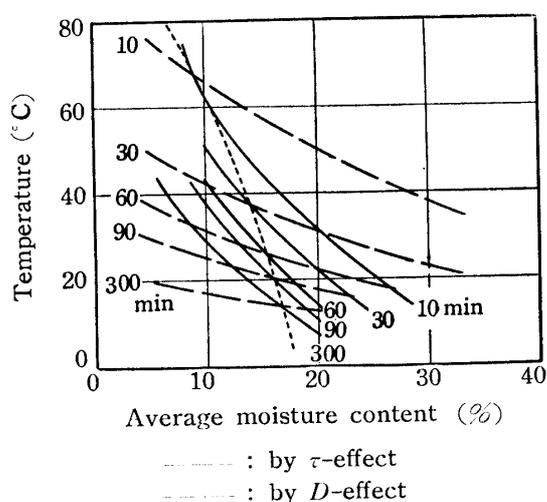


Fig. 8 The isochronals for the adsorption equilibrium. (0.1 mm thick)

$\tau$ -effect limits the rate of adsorption of water by hemicellulose. In Figure 8, isochronal curves, which show the time necessary to establish an adsorption equilibrium either by  $D$ - or by  $\tau$ -effect, are plotted for 1.0 mm thick of the ideal filmy specimen of the hemicellulose using the experimental values of  $D$  and  $\tau$ . At higher temperature and moisture content, or more precisely, on the right of the dotted line which get through intersecting points of two corresponding isochronals, the rate of movement of water molecules limits the rate of adsorption, and on the left of it, namely at lower temperature

and moisture content, the rate of deformation of hemicellulose network is predominate.

### Acknowledgement

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## 広葉樹材ヘミセルロースの吸湿に関する研究

佐 道 健

**要 約** 広葉樹材から抽出，フィルム状に調製したヘミセルロースについて種々の吸湿特性，すなわち吸湿量，膨潤量，微分吸着熱，ヒステレシス，拡散および吸湿速度に関する一連の研究をおこない，これらを木材，セルロースでみられる吸湿特性と比較検討した結果をとりまとめたものである。

本研究の結果，吸湿量，膨潤量，吸着熱の値からヘミセルロースの吸湿挙動がセルロースの非結晶領域のそれと類似していることがしられた。また，ヘミセルロースは膨潤，すなわちネットワークが変形することから，吸湿速度，ヒステレシスの研究においてはネットワークの変形速度を考慮する必要のあることが明らかとなった。