

Study of sorption of alcohols vapors by cellulose

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Abstract

In this article, the sorption of vapors of various alcohols by cellulose samples has been studied. Isotherms of vapors sorption of all studied alcohols have a sigmoid shape combining multilayer surface adsorption and absorption with capillary condensation at the final stage. To separate sorption from capillary condensation, the thermodynamic equation was used describing only the sorption process. It was found that sorption of methanol vapor was performed via absorption of alcohol molecules by accessible clusters of amorphous domains of cellulose. In contrast to methanol, the sorption of vapors of higher alcohols such as propanol and butanol by cellulose is carried out by the mechanism of multilayer surface adsorption. Sorption of ethanol vapor by cellulose combined multilayer surface adsorption and very limited absorption by accessible clusters of amorphous domains of cellulose.

Keywords: Cellulose; Alcohols vapors; Sorption; Mechanism of sorption; Calculations

1. Introduction

Considering that cellulose is a hydrophilic biopolymer, the main attention of researchers was devoted to the study of water vapor (WV) sorption by cellulose materials. Various models were proposed according to which the sorption of WV by cellulose was explained by surface adsorption [1], formation of hydrates and solid solutions [2, 3], and by mixed models combining various mechanisms such as surface adsorption, dissolution, clustering of water molecules, etc. [4, 5]. As a result of detailed studies, it was proved that the sorption process is carried out via the absorption of WV by amorphous domains of semi-crystalline cellulose materials [6].

Unlike water vapor, the process of sorption of vapors of various alcohols by cellulose has been studied to a much lesser extent. In particular, it was noted that the sorption of vapors of methanol (Me) and ethanol (Et) can be used to determine the specific surface area (S_{sp}) of cotton fibers [7]. It was discovered that for the same cellulose sample, the S_{sp} -value found by the sorption of Me vapor was several times higher than the S_{sp} -value obtained by the sorption of Et vapor. In another study, sorption of methanol vapor was used to determine the S_{sp} value for initial low-porous and special porous cellulose samples [8].

However, in general, the types of sorption isotherms and the sorption mechanism of vapors of various alcohols by cellulose are actually not known. Therefore, detailed studies are required to elucidate these issues.

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2. Materials and method

2.1. Materials

Three cellulose samples were used: the original sample of bleached spruce kraft pulp (OKP) of Weyerhaeuser, the modified pulp (MKP) obtained by mercerization of OKP with 20% NaOH followed by washing and drying, and rayon cellulose fibers (RCF) of Rayonier. Before testing, the samples were dried at 383 K to constant weight.

2.2. Characterization of cellulose samples

The crystallinity (X) and amorphicity (Y) degrees of the samples were determined by the method of wide-angle X-ray scattering (WAXS) [9]. The specific surface area, S_{sp} (H), was measured using adsorption of inert hexane vapor [10]. The content of α -cellulose was determined according to TAPPI standard method T-203 [11]. The average degree of polymerization (DP) of samples was studied by the viscosity method using diluted cellulose solutions in cupriethylenediamine [12]. The characteristics of the dry cellulose samples were shown in Table 1.

Table 1 Main characteristics of cellulose samples

Characteristics	OKP	MKP	RCF
X	0.63	0.53	0.36
Y	0.37	0.47	0.64
S_{sp} (H), m^2/g	5	3	2
DP	1100	1200	350
α -cellulose, %	97	98	-

As can be seen from Table 1, mercerization of the original cellulose causes a decrease in the degree of crystallinity and specific surface area, and also slightly increases the DP and the content of α -cellulose. Of all the used samples, rayon fibers have the lowest crystallinity and specific surface area.

2.3. Sorption of vapors by cellulose

The sorption experiments were carried out at 298 K, on a vacuum *Mac-Ben* apparatus having helical spring quartz scales. Sorbates were vapors of chemically pure alcohols: methanol (Me), ethanol (Et), propanol (Pr), and butanol (Bu), purchased from Sigma-Aldrich. Some characteristics of alcohols such as molecular weight (MW), the diameter of molecules (d, nm), and the content of hydroxyl groups in alcohols (C_{OH} , weight parts) are shown in Table 2. Before starting the experiments, the cellulose samples were dried at 383 K up to constant weight and additionally degassed under vacuum in the sorption device. Three samples of the same cellulose were tested to calculate an average sorption value and standard deviation that was in the range ± 0.002 g/g. The specific surface area (S_{sp}) of the samples was calculated from sorption isotherms by the BET method, as follows:

$$S_{sp} = D a_m \dots \dots \dots (1)$$

where a_m (g/g) is the capacity of monomolecular sorption, and D (m^2/g sorbate) is the dimension coefficient (Table 2).

Table 2 Characteristics of molecules of alcohols

Sorbate	MW	C_{OH} , wt. p.	d, nm	D, m^2/g sorbate
Me	32	0.53	0.50	2900
Et	46	0.37	0.57	2570
Pr	60	0.28	0.62	2352
Bu	74	0.23	0.66	2195

3. Results and discussion

Experiments have shown that the sorption isotherms of alcohol vapors (AV) for cellulose samples had sigmoid shapes, and therefore they can be attributed to type II (see e.g., Figure 1).

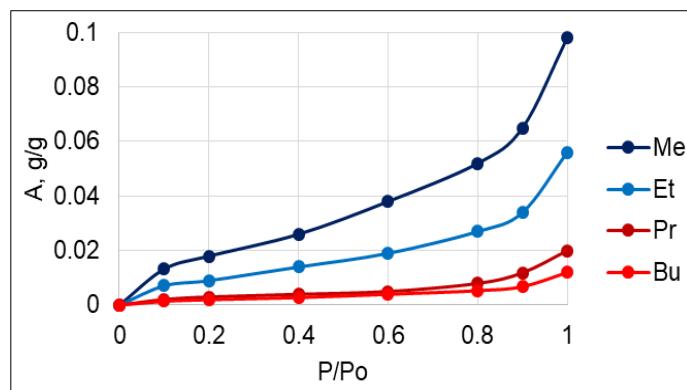


Figure 1 Experimental sorption isotherms of alcohol vapors by OKP

The sigmoid isotherms are usually explained by multilayer adsorption of sorbate molecules on the surface of pores. However, the absorption process of polar sorbates (e.g., water vapor) by amorphous domains (AD) of semicrystalline cellulose also gives a sigmoid isotherm of type II [6, 7, 10]. In addition, for various cellulose sorbents at high relative vapor pressures, $P/P_0 \geq 0.9$, the adsorption or absorption can be accompanied by capillary condensation.

If the sorption of vapors is accompanied by capillary condensation, these two processes should be separated. For this purpose, a universal thermodynamic equation (2) can be used [6, 13], which describes only sorption isotherms.

$$A = A_0(1 - K \ln \varphi)^{-1} \dots \dots (2)$$

or

$$A^{-1} = A_0^{-1} - (K/A_0) \ln \varphi \dots \dots (3)$$

where $\varphi = P/P_0$, A_0 is the maximum sorption value at $\varphi = 1$, and K is the coefficient

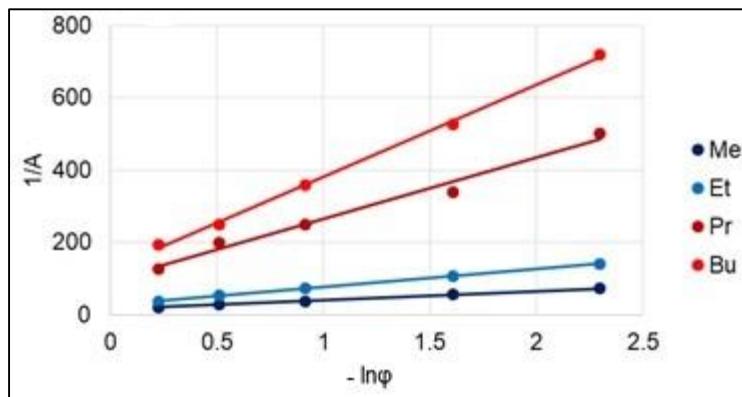


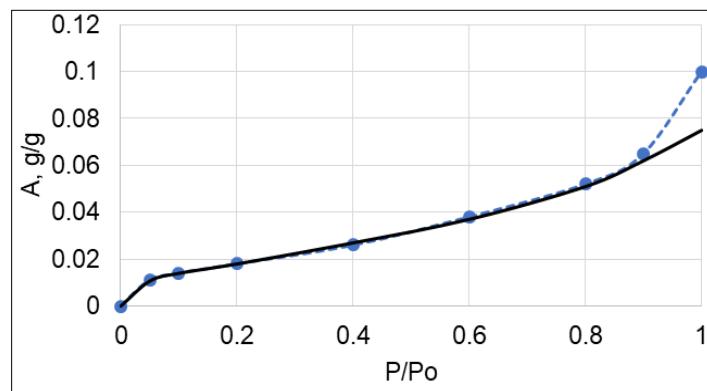
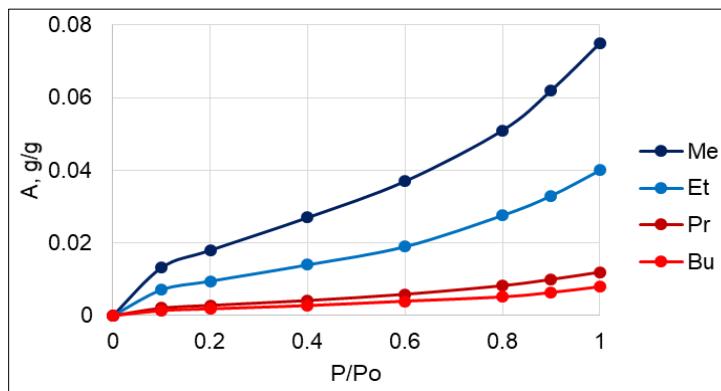
Figure 2 Linear form of sorption isotherms of AV by OKP

The sorption isotherms can be presented in a linear form of eq. (3), as shown for example in Figure 2. Extrapolation of the linear plot $1/A = F(-\ln \varphi)$ to $\ln \varphi = 0$ gives the value $1/A_0$, from which the maximum sorption value, A_0 , can be found. In addition, the coefficient $K = n A_0$ can be calculated from the slope coefficient, n (Table 3).

Table 3 Parameters A_o and K of eq. (2) for AV sorption by OKP

Sorbate	A_o , g/g	K
Bu	0.008	2
Pr	0.012	2
Et	0.040	2
Me	0.075	2

Using parameters A_o and K , the sorption isotherm can be calculated to compare it with the experimental isotherm and separate its final capillary condensation stage at $\varphi=P/P_o \geq 0.9$ (see, e.g., Figure 3). After exclusion of capillary condensation, only sorption isotherms can be plotted (Figure 4).

**Figure 3** Experimental (dashed line) and calculated (solid sine) sorption isotherms of methanol vapor by OKP**Figure 4** Sorption isotherms of AV by OKP without capillary condensation stage

As follows from Figure 4, with an increase in the molecule size and a decrease in the content of hydroxyl groups (Table 2), the sorption of alcohol vapor by cellulose decreases. In order to elucidate the sorption mechanism, the dependences of sorption values on the degree of amorphicity, Y , and the specific surface area, $S_{sp}(H)$, of cellulose samples were studied.

A study of sorption of methanol (Me) vapor by cellulose samples showed that with an increase in the amorphicity degree of the samples, the amount of sorbed vapor proportionally increases (Figures 5 and 6).

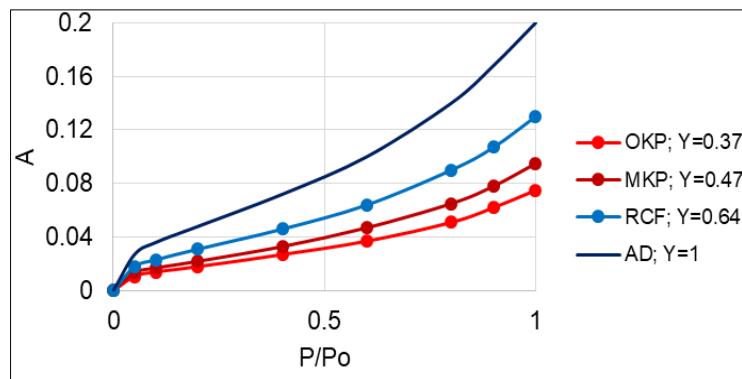


Figure 5 Sorption isotherms of methanol vapor by cellulose samples having different amorphicity degrees (Y)

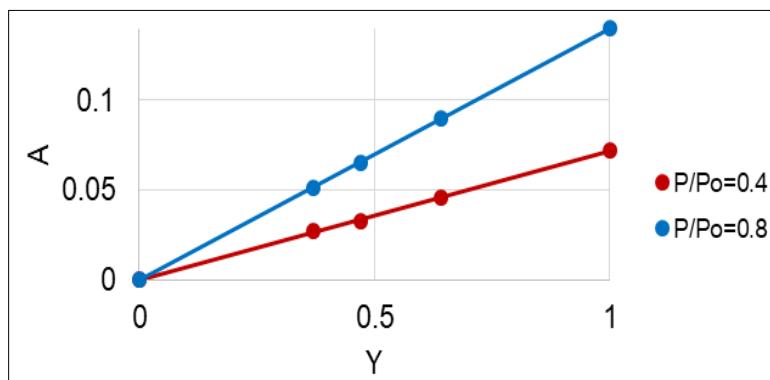


Figure 6 Dependence of sorption value of methanol vapor on amorphicity degree of samples at relative vapor pressures P/P_o : 0.4 and 0.8

In addition, there is no correlation between the Me vapor sorption value and the initial specific surface area of cellulose samples, $S_{sp}(H)$. However, if the specific surface areas of cellulose samples were measured from the linear parts of BET isotherms of Me vapor, then quite high areas of specific surface can be obtained (Table 4).

Table 4 Specific surface area of cellulose samples measured by sorption of methanol vapor, $S_{sp}(Me)$

Cellulose	Y	$S_{sp}(H)$	$S_{sp}(Me)$
OKP	0.37	5	45
MKP	0.47	3	60
RCF	0.64	2	78

As follows from Table 4, there is no correlation between $S_{sp}(H)$ and $S_{sp}(Me)$. On the other hand, the linear dependence between the $S_{sp}(Me)$ value and the amorphicity degree of samples is observed (Figure 7). Thus, in fact, the $S_{sp}(Me)$ does not characterize the initial porous structure of cellulose samples. The high value of $S_{sp}(Me)$ is an index of the accessibility of the internal structure of cellulose to moderately polar Me molecules, which depends on the amorphicity degree of the sample.

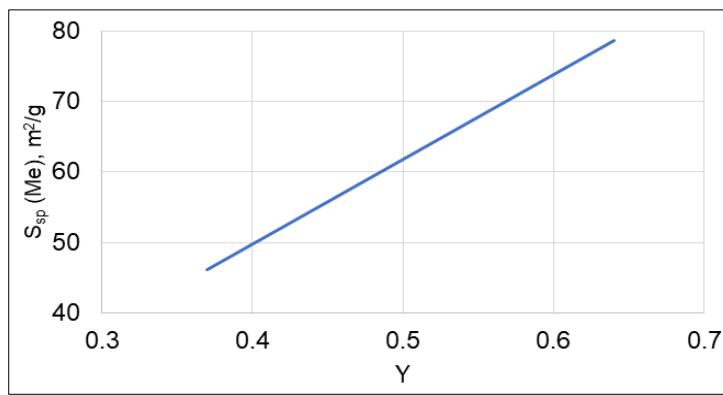


Figure 7 Dependence of specific surface area of cellulose samples measured by sorption of methanol vapor on amorphicity degree

The discovered dependencies indicate the absorption of the sorbate in the amorphous domains of cellulose. Thus, the sorption process can be explained by the absorption of methanol molecules by the polar groups inside accessible regions of amorphous domains (AD). If at different relative vapor pressures, the linear dependence $A=F(Y)$ is extrapolated to the A -values corresponding to $Y=1$, then the general isotherm of Me vapor absorption by AD of cellulose can be obtained (Figure 5).

All isotherms presented in Figure 5 can be described by the following thermodynamic equation [6, 13]:

$$A = A_{o,a} Y (1 - K \ln \varphi)^{-1} \dots \dots (4)$$

where $A_{o,a}=0.2$ (g/g) is the maximum sorption value of Me vapor by amorphous domains at $\varphi=1$, Y is the amorphicity degree of the sample, while coefficient $K=2$.

Based on $A_{o,a}=0.2$ (g/g), it can be calculated that the maximum vapor absorption by amorphous domains will be about 1 mol Me per 1 mol of anhydroglucosidic units (AGU) in AD of cellulose. Taking into account that one AGU contains five polar groups, three hydroxyl, and two ether groups, it can be concluded that one polar group of AGU can attach one Me molecule if only 20 vol. % of AD are accessible for the sorbate molecules.

Structural studies have shown that amorphous domains of cellulose have a heterogeneous packing since they consist of densely and loosely packed clusters with different energies of hydrogen bonds [10]. The densely packed clusters accounting about 80 vol. % of AD are in a glassy state, and therefore they are inaccessible to alcohol molecules. For this reason, only loosely packed clusters accounting no more than 20 vol. % of AD are accessible for Me vapor. This distinguishes moderately polar ($C_{OH}=0.53$ wt. p.) and relatively large ($d=0.50$ nm) molecules of methanol from highly polar ($C_{OH}=0.94$ wt. p.) and small ($d=0.38$ nm) molecules of water, for which the amorphous domains of cellulose are completely accessible.

When studying the process of ethanol (Et) vapor sorption by cellulose samples, no obvious dependence of the sorption value on either the amorphicity degree, Y , or the initial specific surface area, S_{sp} (H), of the samples was established. Nevertheless, the specific surface area determined by the sorption of ethanol, S_{sp} (Et), was higher than it was found by the sorption of inert hexane vapor, S_{sp} (H) (Table 5).

Table 5 Specific surface area of cellulose samples measured by sorption vapors of various alcohols

Alcohol	S _{sp} (A), m ² /g		
	OKP	MKP	RCF
Et	20	18	19
Pr	6	4	2
Bu	5	4	2
H	5	3	2

Thus, the sorption of ethanol vapor by cellulose probably proceeds according to a mixed mechanism combining the multilayer adsorption on the surface of pores and very limited absorption in AD of cellulose. With a decrease in the specific surface area of the sample, sorption should decrease, but a simultaneous increase in the degree of amorphicity leads to an increase in absorption. As a result of mutual compensation of opposite effects, the sorption isotherms of Et vapors for the studied cellulose samples differ little from each other and, after the exclusion of the capillary condensation stage, they look similar to the isotherm shown in Figure 4. However, if the cellulose samples have the same amorphicity degree, but the different specific surface areas, S_{sp} , then it can be expected that with an increase in the S_{sp} value the sorption of Et vapor will increase.

Unlike lower alcohols, methanol and ethanol, the sorption of vapors of higher alcohols, propanol (Pr) and butanol (Bu), is carried out exclusively by the mechanism of multilayer adsorption on the surface of pores. As can be seen from Table 5, the specific surface areas determined by the sorption vapors of these low-polar alcohols, were very close to the S_{sp} (H) values obtained by sorption of inert hexane vapor. Therefore, the absorption mechanism of Pr and Bu vapors by AD of cellulose can be excluded.

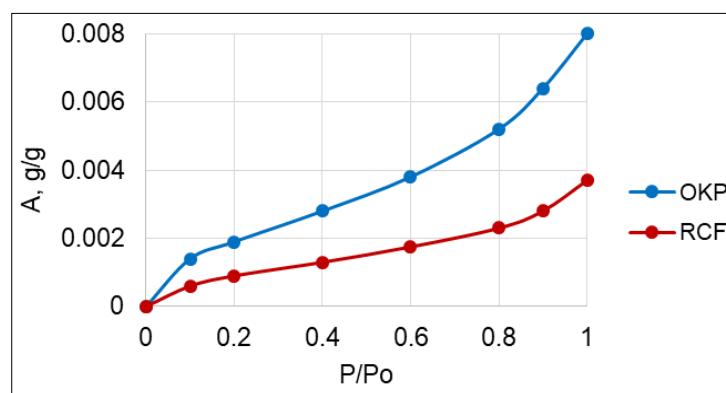


Figure 8 Sorption isotherms of butanol vapor for two cellulose samples having different specific surface areas: OKP with S_{sp} (H) = 5 m^2/g , and RCF with S_{sp} (H) = 2 m^2/g

Due to the mechanism of surface adsorption, a decrease in S_{sp} (H) value of the samples will cause a corresponding decrease in the sorption value (see e.g., Figure 8).

Finally, for all the studied samples and sorbates, a linear relationship was found between the maximum sorption value at $\varphi=1$, A_0 , g/g, and the specific surface area, $S_{sp}(A)$, m^2/g , determined by sorption of given alcohol vapor (Figure 9):

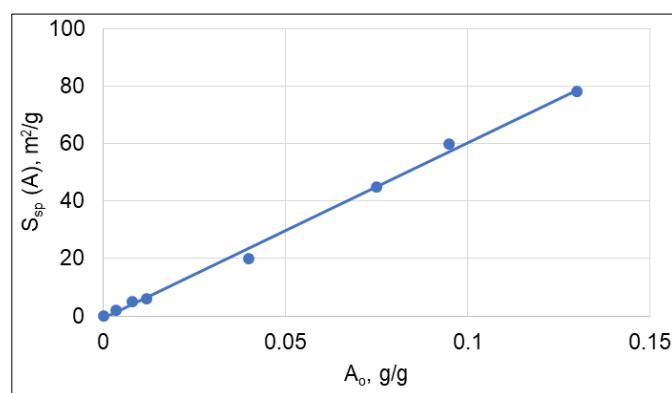


Figure 9 Dependence of $S_{sp}(A)$ on A_0

This linear dependence can be described by the following correlation equation:

$$S_{sp}(A) = k A_0 \dots \dots (5)$$

where coefficient $k=612$.

4. Conclusion

The study showed that isotherms of alcohols vapors by cellulose samples have a sigmoid shape combining multilayer surface adsorption and absorption with capillary condensation at the final stage. To separate sorption from capillary condensation, the following thermodynamic equation was used describing only the sorption process: $A = A_0 (1 - K \ln \varphi)^{-1}$, where A_0 is the maximum sorption value at $\varphi = P/P_0 = 1$, and K is the coefficient.

A study of the sorption mechanism revealed that the sorption of methanol vapor was performed via absorption of alcohol molecules by accessible clusters of amorphous domains of cellulose. In contrast to methanol, the sorption of vapors of higher alcohols such as propanol and butanol by cellulose is carried out by the mechanism of multilayer surface adsorption. Sorption of ethanol vapor by cellulose combined multilayer surface adsorption and very limited absorption by accessible clusters of amorphous domains of cellulose.

In addition, for all the studied samples and sorbates, a linear relationship was found between the maximum sorption value at $\varphi = 1$, A_0 , g/g, and the specific surface area, $S_{sp}(A)$, m²/g, determined by sorption of given alcohol vapor: $S_{sp}(A) = k A_0$, where coefficient $k = 612$.

Compliance with ethical standards

Disclosure of conflict of interest

The author of this paper hereby declares that there is no conflict of interest.

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