

## Study of water vapor sorption by cellulose esters with different degrees of substitution

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### Abstract

In this research, the sorption of water vapor (WV) by various cellulose esters with different degrees of substitution (SD) has been studied. It was found that if the sorption value is measured in moles of H<sub>2</sub>O per mole of repeating units of the esters, then sorption properties depend only on the degree of substitution and not on the type of substituent. The lowest sorption is observed for triesters due to the absence of hydroxyl groups, which have the greatest contribution to the sorption process. To describe sorption isotherms, a calculating equation  $A = A_0(1 - K \ln \varphi)^{-1}$  was derived, where  $A_0$  is the maximum sorption value at relative vapor pressure  $\varphi=1$ , and  $K$  is the coefficient. This equation allows adequately describing experimental S-shaped sorption isotherms of WV for various esters having different SD. It was shown that the most probable sorption mechanism is the binding of polar water molecules by polar groups of various esters.

**Keywords:** Cellulose esters; Degree of substitution; Sorption of water vapor; Mechanism; Calculations

### 1. Introduction

Being a renewable and inexhaustible natural raw material cellulose is widely used for the production of diverse materials such as paper and board, powdered and microcrystalline cellulose, cellulose fibers and films, water-soluble ethers, etc. However, increased hydrophilicity hinders the use of cellulose and its hydrophilic materials in the creation of waterproof and vapor-proof packaging and other hydrophobic products [1]. Another shortcoming of cellulose is the impossibility of its processing from the melt, which distinguishes this biopolymer from the common plastics used for the manufacture of packaging and other goods [2].

These disadvantages of cellulose can be overcome by its chemical modification, and especially by esterification. After that, the hydrophobic cellulose derivatives can be used in the production of hydrophobic fibers and films, fillers and reinforcements compatible with hydrophobic polymers, as well as in the compositions of hydrophobic coatings, paints, adhesives, and other hydrophobic materials. Currently, various cellulose esters, such as acetates, propionates, butyrates, and others are applied in the production of packaging materials, thermoplastics, eyeglass frames, cigarette filters, semi-permeable and separating membranes, optical films, water- and rot-resistant fabrics, self-cleaning materials, protective coatings, etc. [3-6].

An important method for characterizing the hydrophobicity of cellulose derivatives is to study the sorption of water vapor (WV). The main attention was paid to the sorption of WV by cellulose acetates (CA) [7-10]. It was shown that with an increase in the degree of substitution of CA, the sorption ability of WV decreases due to an increase in hydrophobicity of this ester [10]. As for other cellulose esters, when moving from acetates to mixed esters, aceto-propionates and aceto-butyrate, the hydrophobicity rises, and as a result, the sorption of WV declines, while the isotherms look less concave [2]. In addition, the sorption hysteresis reduces and even disappears.

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Various models of WV sorption for cellulose esters have been proposed, such as multimolecular surface adsorption, clustering of water molecules, as well as mixed models combining monomolecular and multimolecular surface adsorption, or monomolecular surface adsorption and dissolution of water molecules in amorphous polymers, and some others [2, 7-10]. Thus, the WV sorption mechanism by various esters remains still a subject of discussion. Another still poorly studied issue is the effect of the degree of substitution of different cellulose esters on the sorption of water vapor.

Therefore, the main purpose of this research was to study the dependence of WV sorption on the substitution degrees for various cellulose esters, as well as to elucidate the sorption mechanism.

## 2. Material and methods

### 2.1. Materials

The various mono-, di-, and triesters of cellulose were synthesized and studied. These esters have different characteristics such as molar ( $V_m$ ), van-der-Waals ( $V_w$ ) and free ( $V_f$ ) volumes, molecular masses of repeating units (MU), and the total number of carbon atoms ( $N_c$ ) in the substituents (Table 1).

**Table 1** Characteristics of studied cellulose esters

Esters of cellulose	Abbreviation	$N_c$	MU	$V_m$	$V_w$	$V_f$
Monoacetate	MAC	2	204	149.4	103.3	46.1
Diacetate	DAC	4	246	186.6	127.3	59.3
Triacetate	TAC	6	288	223.8	151.3	72.5
Monopropionate	MPC	3	218	165.3	113.6	51.7
Dipropionate	DPC	6	274	218.3	147.9	70.4
Tripropionate	TPC	9	330	271.4	182.2	89.2
Monobutyrate	MBC	4	232	181.1	123.9	57.2
Dibutyrate	DBC	8	302	250.0	168.5	81.5
Tributyrate	TBC	12	372	318.9	213.1	105.8
Monovalerate	MVC	5	246	197.0	134.2	62.8
Divalerate	DVC	10	330	281.7	189.1	92.6
Trivalerate	TVC	15	414	366.5	244.0	122.5

Note:  $V_m$ ,  $V_w$ , and  $V_f$  are expressed in  $\text{cm}^3/\text{mol}$

### 2.2. Esterification

The esterification of the original cotton cellulose was carried out in the medium of trifluoroacetic acid (TFAA) served as a solvent and also a catalyst [6]. Cotton cellulose was mixed with TFAA while stirring at room temperature for 1 h and then treated with anhydrides of various aliphatic acids at 323 K for 1 h using a liquid to cellulose ratio of 50. The degree of substitution was adjusted using different molar ratios of anhydrides to cellulose. Finally, the cellulose esters were washed and dried in a vacuum chamber at 323 K to constant weight. The substitution degree (SD) of esters was controlled by a method of chemical analysis [11]. The SD value of monoesters was 0.9-1.1, diesters 1.8-2.2, and triesters 2.8-3.0.

### 2.3. Sorption of water vapor

The sorption experiments were carried out at 298 K using a vacuum *Mac-Ben* apparatus equipped with spring quartz balances. Before starting the experiments, the samples were dried at 323 K up to constant weight and additionally degassed under vacuum in the sorption device. Three of the same sample were tested to calculate an average sorption value and standard deviation that was in the range  $\pm 0.002$  g/g.

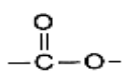
### 2.4. Calculations

A number of moles of water ( $a_i$ ) bound by one mole of a polar group of cellulose ester at a certain relative vapor pressure ( $\varphi=P/P_0$ ) and 298 K was calculated by the equation [12]:

$$a_i = a_{o,i} (1 - C_i \ln\varphi)^{-1} \dots\dots\dots (1)$$

where  $a_{o,i}$  is the maximum sorption value at  $\varphi =1$  expressed in mol H<sub>2</sub>O per mol of the group, and  $C_i$  is the coefficient (Table 2).

**Table 2** Parameters of eq. (1)

Polar groups	RC	$a_{o,i}$ , mol/mol	$C_i$
-OH	1.00	1.44	2.6
-O-	0.08	0.12	16
	0.17	0.24	7

Note: RC denotes the relative contribution of the polar group in sorption

Parameters of eq. (1) allow the calculation of the sorption values ( $A$ , mol/mol) of WV for amorphous polymer or amorphous domains (AD) of the semicrystalline polymer at various relative vapor pressures ( $\varphi$ ) knowing only the chemical formula of the repeating unit of this polymer including the type and number ( $n_i$ ) of polar groups, as follows:

$$A = \sum n_i a_i = \sum n_i a_{o,i} (1 - C_i \ln\varphi)^{-1} \dots\dots\dots (2)$$

$$\text{or } A = n_h a_{o,h} (1 - C_h \ln\varphi)^{-1} + n_{et} a_{o,et} (1 - C_{et} \ln\varphi)^{-1} + n_{es} a_{o,es} (1 - C_{es} \ln\varphi)^{-1} \dots\dots\dots (3)$$

where subscripts h, et, and es refer to hydroxyl (-OH), ether (-O-), and ester (-COO-) groups, respectively.

Theoretical equation (2) can be transformed into the following calculating equation of the sorption isotherm for an amorphous cellulose derivative [12]:

$$A = A_o (1 - K \ln\varphi)^{-1} \dots\dots\dots (4)$$

where  $A_o = \sum n_i a_{o,i}$  is the maximum amount of water molecules sorbed by amorphous ester at  $\varphi=1$ , and  $K$  is the coefficient.

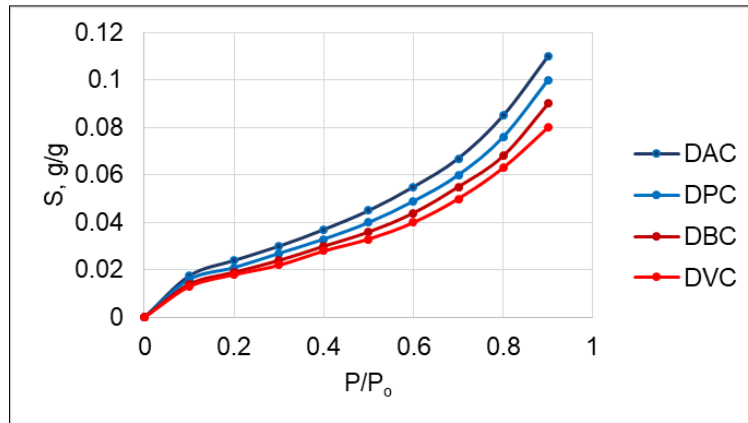
The bulk characteristics of the cellulose esters (see Table 1) were calculated using the Van Krevelen method of additive contributions of partial volumes of atoms and atom groups in the volumes of amorphous polymers [1, 13]. From these characteristics also fraction of free volume was found, as follows:

$$F = V_f/V_m \dots\dots\dots (5)$$

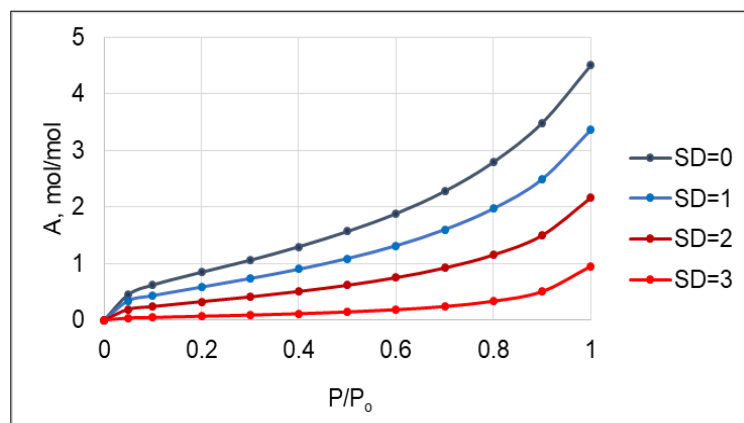
### 3. Results and discussion

The experimental isotherms of WV sorption by amorphous cellulose esters were S-shaped (Fig.1). At the same degree of substitution (e.g., SD=2), an increase in  $N_c$  of substituents leads to a decrease in the sorption ability of the esters, expressed in g H<sub>2</sub>O per g sample. However, if the sorption value is measured in moles H<sub>2</sub>O per mole repeating units of the polymers, then sorption properties depended only on the degree of substitution and not on the type of substituent, or  $N_c$  (Fig. 2). It was found when passing from mono- and diesters to triesters, the sorption of water vapor declines most sharply due to the vanishing of hydroxyl groups that have the greatest contribution to the sorption process (see RC from Table 2).

Using eq. (2) or (3), the sorption isotherms can be also calculated. For example, one repeating unit of cellulose diesters (CDE) contains one hydroxyl group (-OH), two ether groups (-O-), and two ester groups (-COO-). Then, the following sorption values ( $A$ , mol/mol) at various relative vapor pressures ( $\varphi$ ) can be obtained (Table 3).



**Figure 1** Experimental isotherms of VW sorption for various diesters of cellulose



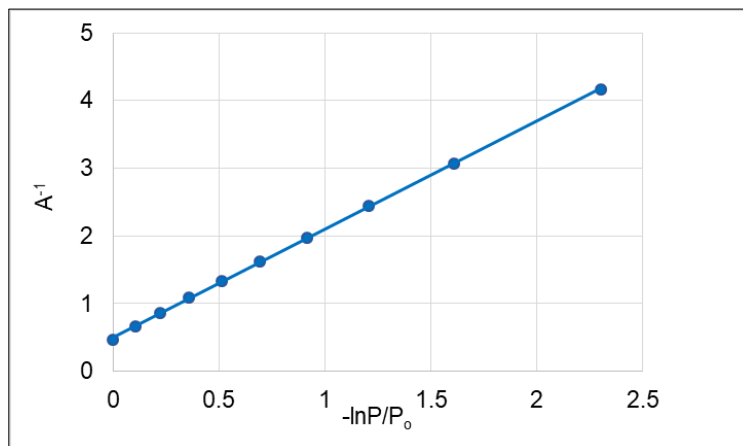
**Figure 2** Experimental (lines) and calculated (points) isotherms of WV sorption for AD of cellulose (SD=0) and various amorphous cellulose esters having different SD

**Table 3** Calculated sorption values (A) for CDE

$\varphi$	$a_h$	$2a_{et}$	$2a_{es}$	A
0	0	0	0	0
0.05	0.164	0.005	0.022	0.191
0.1	0.206	0.006	0.028	0.240
0.2	0.278	0.009	0.039	0.326
0.3	0.349	0.012	0.051	0.411
0.4	0.426	0.015	0.065	0.506
0.5	0.514	0.020	0.082	0.616
0.6	0.618	0.026	0.105	0.749
0.7	0.747	0.036	0.137	0.920
0.8	0.912	0.052	0.187	1.151
0.9	1.130	0.089	0.276	1.496
1.0	1.440	0.240	0.480	2.16

In Table 3,  $a_h$  is the contribution of one hydroxyl group in the sorption value  $A$  of CDE;  $2a_{et}$  is the contribution of two ether groups in the sorption value  $A$  of CDE;  $2a_{es}$  is the contribution of two ester groups in the sorption value  $A$  of CDE.

Summing up the values of  $a_{o,i}$  at  $\varphi=1$ , the maximum sorption value  $A_o = 2.16$  (mol/mol) for CDE was calculated. Further, from the linear form of eq. (4)  $A^{-1} = A_o^{-1} (1 - K \ln\varphi)$ , where  $\varphi = P/P_o$ , the coefficient  $K=3.2$  for cellulose diesters was found (Fig. 3).



**Figure 3** Linear graph  $A=f(-\ln P/P_o)$  for CDE

Thus, the final equation for calculating the isotherm of WV sorption for CDE will be the following:

$$A = 2.16 (1 - 3.2 \ln\varphi)^{-1} \dots\dots\dots (6)$$

In a similar way, the parameters  $A_o$  and  $K$  of the sorption equation (4) also for other esters can be obtained (Table 4).

**Table 4** Parameters of sorption eq. (4):  $A = A_o (1 - K \ln\varphi)^{-1}$

SD	$A_o$ , mol/mol	K
0	4.50	2.7
1	3.35	2.9
2	2.16	3.2
3	0.95	8.0

The comparison showed that the calculated isotherms practically coincide with the experimental ones (see Fig. 2), which indicates the adequacy of the derived calculating equations. In addition, from the obtained results it follows that with increasing SD the sorption ability of the esters decreases, while isotherms become less curved.

To assess the hydrophobic properties of cellulose esters, the relative hydrophobicity index was used:

$$HI = 100\% \{1 - (A_{o,es}/A_{o,c})\} \dots\dots\dots (7)$$

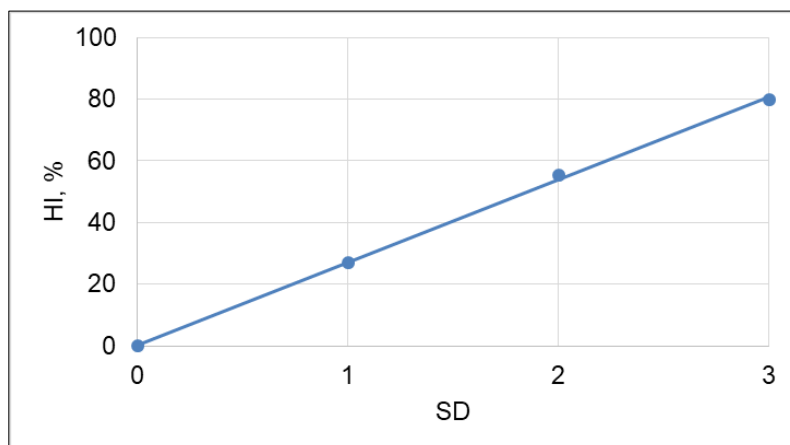
where  $A_{o,es}$  is the value of  $A_o$  for various amorphous esters having SD of 1 to 3, while  $A_{o,c}$  is the value of  $A_o$  for amorphous cellulose (SD=0).

As can be seen from Figure 4, with an increase in the degree of substitution, the esters become more hydrophobic.

Various mechanisms of WV sorption by cellulose esters have been proposed including multimolecular surface adsorption, clustering of water molecules, the combination of monomolecular with multimolecular surface adsorption, or monomolecular surface adsorption with the dissolution of water molecules in amorphous polymers, and some others [2, 7-10]. However, it has long been known that common cellulose esters are usually low- or non-porous materials with

a small specific surface area ( $<1 \text{ m}^2/\text{g}$ ) [14]. For this reason, the mechanism of surface adsorption is hardly suitable for explaining the VW sorption properties of the esters.

On the other hand, di- and especially triesters are characterized by increased hydrophobicity (see Fig. 4). Therefore, it is doubtful that polar water molecules can dissolve in these hydrophobic esters and cause a strong rise in sorption value according to the Flory-Huggins equation at enhanced relative vapor pressures, as postulated in reference [10].



**Figure 4** Dependence of relative hydrophobicity on the degree of substitution of esters

It was also assumed that the sorption of water vapor at the initial sorption stage ( $\varphi < 0.2$ ) is performed by filling the free volume [10]. In this case, the amount of water ( $A_{0.1}$ ) sorbed, e.g., at  $\varphi = 0.1$ , should be depended on the fraction of free volume (F) of the esters. However, the study shows that there is no such dependence since with an increase in the degree of substitution, the value of  $A_{0.1}$  decreases, but the F-value does not change (Table 5). Thus, the sorption mechanism by filling the free volume with water molecules is not confirmed.

**Table 5** Values of F and  $A_{0.1}$

SD	F	$A_{0.1}$ , mol/mol
1	0.32	0.43
2	0.32	0.24
3	0.32	0.05

The most probable sorption mechanism can be the binding of polar water molecules by polar groups of various esters. This is evidenced by the good agreement between calculated sorption isotherms based on such a mechanism and experimental isotherms of WV sorption for cellulose esters having different Nc and SD.

#### 4. Conclusion

In this research, the sorption of water vapor (WV) by various cellulose esters with different degrees of substitution (SD) was studied. It was found that if the sorption value is measured in moles of  $\text{H}_2\text{O}$  per mole of a repeating unit of ester, the sorption properties cease to depend on the type of substituent, and depend only on the degree of substitution. The lowest sorption is observed for triesters due to the disappearance of hydroxyl groups, which have the greatest contribution to the sorption process. A calculating equation of sorption isotherms was derived, that allows adequately describing experimental S-shaped sorption isotherms of WV for various esters having different SD. The most probable sorption mechanism was proposed, which consists of the binding of polar water molecules by polar groups of various esters. This mechanism is confirmed by the good agreement between calculations and experiments.

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