ARTICLE
Study of Structural Characteristics of Cellulose Esters with Different Degrees of Substitution

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ABSTRACT

In this article, structural characteristics of amorphous mono-, di-, and tri-substituted esters of cellulose have been studied. These esters were synthesized under homogenous conditions using anhydrides of various aliphatic acids. The specific gravity of the highly substituted samples was measured by a pycnometric method in the aqueous medium. To calculate the molar, Van der Waals, and free volumes, as well as the packing coefficient of amorphous esters the method of additive contributions of partial volumes of atoms and atom groups in the volumes of polymers was used. Based on the molar volume, also specific gravity of cellulose esters was calculated. The coincidence of calculated and experimental characteristics was shown. In addition, the relationship between glass transition temperature and free volume was found for the esters. The theoretical equations were derived, which provide predicting the structural characteristics of cellulose esters with different degrees of substitution.

1. Introduction

Being a renewable and inexhaustible natural raw material cellulose is widely used for the production of paper and board, powdered and microcrystalline cellulose, cellulose fibers, and films, water-soluble derivatives (carboxymethyl, hydroxyethyl, hydroxypropyl cellulose, etc.), and other products. However, increased hydrophilicity hinders the use of cellulose and its hydrophilic products in the creation of waterproof and vapor-proof materials. Temporary hydrophobization of hydrophilic cellulose

materials can be archived by their impregnation with solutions of hydrophobic substances, surface coating, and some other physical or physicochemical methods [1,2]. A more reliable method of cellulose hydrophobization is its chemical modification, especially esterification by replacing hydroxyl groups with hydrophobic substituents [2,3]. For example, it was shown that acetylation of cellulose increases its hydrophobicity and leads to a decrease in the sorption of water vapor [4-7]. As for other cellulose esters, when moving from acetates to higher cellulose esters, the hydrophobicity of cellulose derivatives rises [8].

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After chemical modification with hydrophobic acyl reagents, the hydrophobic cellulose derivatives can be used in the production of hydrophobic fillers, and reinforcements compatible with hydrophobic polymers, as well as in the compositions of hydrophobic coatings, paints, adhesives, and other hydrophobic materials. Moreover, various cellulose esters, such as acetates, propionates, butyrates, and others are applied in the production of thermoplastics, electronic device housings, spectacle frames, anti-fog goggles, cigarette filters, semi-permeable and separating membranes, optical films, heat, and rot-resistant fabrics, self-cleaning materials, protective coatings, and other materials [1,2,9-11].

Cellulose esterification can be performed under heterogeneous and homogeneous conditions. Heterogeneous esterification of cellulose proceeds in the solid phase according to the laws of topochemical reactions, namely, rapidly in amorphous domains and more slowly inside the cellulose crystallites [12]. In contrast, homogeneous esterification proceeds fairly uniformly in solvent media that swell or/and dissolve cellulose.

After esterification with various acyl reagents, usually, amorphous cellulose derivatives are formed [2]. The problem with studying the supramolecular structure of amorphous esters is that they do not contain crystalline domains, and therefore, the application of such well-known structural methods as X-ray diffraction, electron diffraction, NMR, and some others is difficult. Therefore, little information is currently available on the structure of various amorphous esters of cellulose.

The main purpose of this article was to characterize the structural state of amorphous cellulose esters with different degrees of substitution using such characteristics as molar, Van der Waals, and free volumes, as well as specific gravity.

2. Materials and Methods

The initial cellulose material was pure chemical grade cotton cellulose of Hercules Inc (98% Alfa cellulose, DP= 2700). Using this cellulose, various mono-, di-, and triesters of cellulose were synthesized and studied. Each repeating unit of these esters contained acyl substituents having a different number of carbon atoms (Table 1).

The esterification of the initial cotton cellulose was carried out in the medium of trifluoroacetic acid (TFAA) served as a solvent and also a catalyst [2]. Cotton cellulose was mixed with TFAA while stirring at room temperature for 1 h and then treated with anhydrides of various aliphatic acids at 50 °C 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 and con-

trolled by a method of chemical analysis [3]. The substitution degree (SD) of monoesters was 0.9-1.1, of diesters 1.8-2.2, and triesters 2.8-3.0. Finally, the cellulose esters were washed and dried in a vacuum chamber at 50 °C to constant weight.

The synthesis scheme of cellulose esters is shown in Figure 1.

Table 1. The studied cellulose esters

Esters of cellulose	Abbreviation	M	Nc
Monoacetate	MAC	204	2
Diacetate	DAC	246	4
Triacetate	TAC	288	6
Monopropionate	MPC	218	3
Dipropionate	DPC	274	6
Tripropionate	TPC	330	9
Monobutyrate	MBC	232	4
Dibutyrate	DBC	302	8
Tributyrate	TBC	372	12
Monovalerate	MVC	246	5
Divalerate	DVC	330	10
Trivalerate	TVC	414	15

M is the molar mass of repeating units (RUs) of various cellulose esters;

Nc is the number of carbon atoms in substituents of RUs
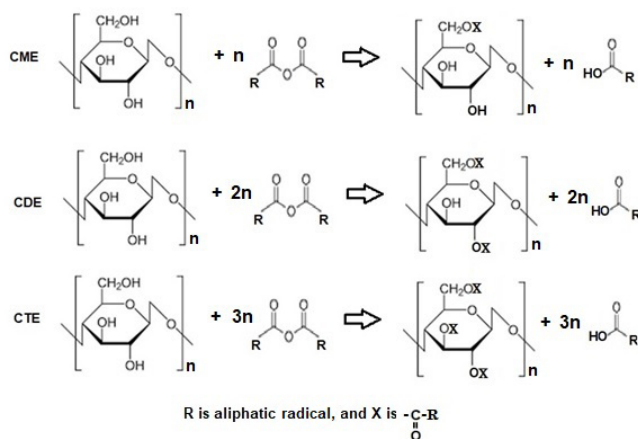
Figure 1. Scheme of cellulose esterification by anhydrides of various aliphatic acids to obtain cellulose mono- (CME), di- (CDE), and tri-(CTE) esters

To evaluate the hydrophobic properties of cellulose esters, the relative hydrophobicity index was used [8]:

$$HI = 100\%\{1 - (A_{es}/A_c)\} \qquad (1)$$

where A_{es} (mole H_2O/mole RUs) is the sorption value of water vapor at 25 °C and relative humidity of 80% for various amorphous esters having different SD from 1 to 3, while A_c (mole H_2O/mole RUs) is the sorption value for amorphous cellulose (SD=0) at the same sorption conditions.

The specific gravity of dry triesters was measured by a pycnometric method in the aqueous medium at 23 °C [13]. For this test, a glass pycnometer, i.e., measurement vessel, with a volume of 25.00 mL was used. The dry sample of cellulose triester having a mass of m (g) was weighed on an analytical balance and then it was placed in the pycnometer, filled with distilled water up to the mark, weighed on the analytical balance, and the weight P was measured. The weight of the empty pycnometer filled with distilled water up to the mark, P_w, was also measured. The specific gravity (G) was calculated as follows:

$$G = g \, m/(P_w + m - P) \qquad (2)$$

where g=1 g/cm^3 is the specific gravity of water.

From obtained G values also molar volumes of esters, $V_m = M/G$, were found; where M is the molecular mass of the repeating unit of the ester.

The glass transition temperatures (T_g) of amorphous triesters were determined using thermo-mechanical analysis [14].

To calculate the molar (V_m), Van der Waals (V_w), free (V_f) volumes, as well as packing coefficient of macromolecules ($K_p=V_w/V_m$) of amorphous cellulose esters, the Van Krevelen method of additive contributions of partial volumes of atoms and atom groups in the volumes of polymers was used [15]. The specific gravity of the esters was also calculated, as follows: $G = M/V_m$.

3. Results and Discussion

The results have shown that with an increase in the degree of substitution, the cellulose esters become more hydrophobic (Figure 2).
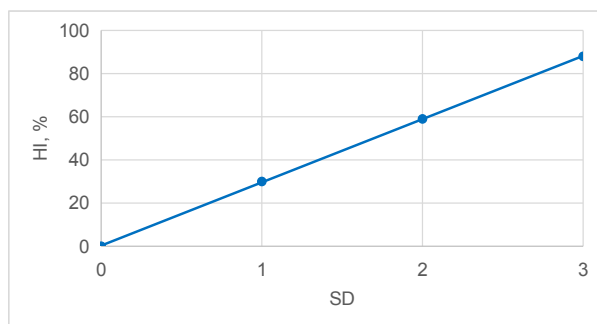
Figure 2. Dependence of relative hydrophobicity on the degree of substitution of esters

The experimental values of the specific gravity for some cellulose esters are shown in Table 2.

As can be seen from Table 2, with an increase in the number of carbon atoms in the substituents, the specific gravity of the studied triesters decreases, and their molar volume increases due to the steric effect of bulk substituents causing enhancement of distances between chains of the esters.

Table 2. Specific gravity (G) and molar volume (V_m) of studied cellulose triesters

Esters of cellulose	M	Nc	G, g/cm^3	V_m, cm^3/mol
TAC	288	6	1.26	228.5
TPC	330	9	1.23	268.0
TBC	372	12	1.16	320.1
TVC	414	15	1.13	365.7

An X-ray study of amorphous cellulose triesters revealed two diffuse scatterings, which are characteristic of a mesomorphic rather than a completely amorphous structure [2]. As a result, model of the mesomorphous structure of cellulose esters was proposed [16]. According to this model, the substituted anhydroglucose units (AGUs) form layers with an approximately constant distance (ca 0.4 nm) between them. However, in the plane of the layers, the distance between substituted AGUs increases directly proportional to the number of carbon atoms, Nc, in the substituents. Based on this model the molar volume and specific gravity of the cellulose triesters were calculated [17], which were actually the same as those presented in Table 2, despite the different investigation methods.

Using the method of additive contributions of partial volumes of atoms and atom groups [15], the molar ($V_{m,sk}$), Van der Waals ($V_{w,sk}$), and free ($V_{f,sk}$) volumes of the skeletons of anhydroglucose units, AGUs, for mono-, di-, and triesters (Figure 3) were calculated (Table 3).
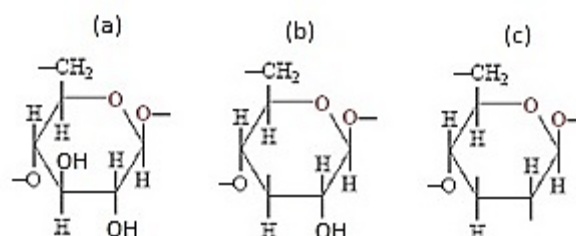
Figure 3. Skeletons of AGUs for mono- (a), di- (b), and tri- (c) esters of cellulose

Table 3. Partial volumes of skeletons of AGUs for cellulose esters

Esters	Skeletons	$V_{m,sk}$, cm^3/mol	$V_{w,sk}$, cm^3/mol	$V_{f,sk}$, cm^3/mol
Monoesters	$C_6H_9O_4$	102.5	73.1	29.4
Diesters	$C_6H_8O_3$	92.8	66.9	25.9
Triesters	$C_6H_7O_2$	83.1	60.7	22.4

The partial volumes of atom groups present in substituents of amorphous esters are shown in Table 4.

Using data presented in Tables 3 and 4, the characteristics of various cellulose esters can be calculated. For example, TBC consists of the skeleton (c), six CH_2-groups,

Table 4. Partial volumes of atom groups of acyl substituents

Group	$V_{m,g}$, cm^3/mol	$V_{w,g}$, cm^3/mol	$V_{f,g}$, cm^3/mol
-CH$_2$-	15.85	10.3	5.55
-CH$_3$	23.9	14.2	9.7
$\underset{-C-O-}{\overset{O}{\parallel}}$	23.0	16.0	7.0

and three CH$_3$- and COO-groups. Summing up the contributions of partial volumes of the skeleton and all groups of tributyrate, the molar volume, V_m=318.9 cm^3/mol, Van der Waals volume, V_w = 213.1 cm^3/mol, and free volume, V_f = 105.8 cm^3/mol, for amorphous TBC were calculated. Knowing the Van der Waals and mole volumes, the packing coefficient, K_p = 0.670, and specific gravity, G=1.17 g/cm^3, of TBC were also calculated.

Studies have shown that the structural characteristics of cellulose esters depend both on the degree of substitution and the type of substitute. So, an increase in SD and/or length of the substitute leads to an increase in the molar volume of the esters (Figure 4).
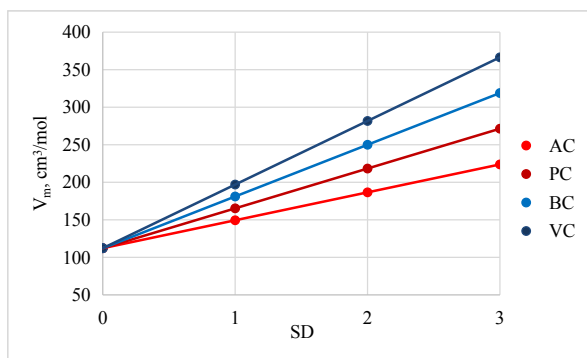
Figure 4. Dependence of molar volume on substitution degree for acetates (AC), propionates (PC), butyrates (BC), and valerates (VC) of cellulose

These dependences can be also expressed by the following theoretical equation:

$$V_m = V_{m,c} + (K_{m,AC} + N\,V_{m,CH2})\,SD \tag{3}$$

where $V_{m,c}$ =112.2 (cm^3/mol) is molar volume of amorphous cellulose; $K_{m,AC}$ = 37.2 is slope factor of dependences V_m = F(SD) for cellulose acetates; and $V_{m,CH2}$ = 15.85 (cm^3/mol) is contribution of partial volume of the CH$_2$-group in V_m. N is the number of CH$_2$-groups in one substitute.

Similarly, the theoretical equations for the Van der Waals (V_w) and free ($V_f = V_m – V_w$) volumes were derived.

$$V_w = V_{w,c} + (K_{w,AC} + N\,V_{w,CH2})\,SD \tag{4}$$

where $V_{w,c}$ =79.3 (cm^3/mol) is Van der Waals volume of amorphous cellulose; $K_{w,AC}$ = 24.0 is slope factor of de-

pendences V_w = F(SD) for cellulose acetates; and $V_{w,CH2}$ = 10.3 (cm^3/mol) is contribution of partial volume of the CH$_2$-group in V_w.

$$V_f = V_{f,c} + (K_{f,AC} + N\,V_{f,CH2})\,SD \tag{5}$$

where $V_{f,c}$ =32.9 (cm^3/mol) is free volume of amorphous cellulose; $K_{f,AC}$ = 13.2 is slope factor of dependences V_f = F(SD) for cellulose acetates; and $V_{f,CH2}$ = 5.55 (cm^3/mol) is contribution of partial volume of the CH$_2$-group in V_f.

The Equations (3), (4), and (5) provide predicting the structural characteristics of cellulose esters with different degrees of substitution. For example, in acetates the number of CH$_2$-groups in one substitute, N=0. Then from Equation (3) it follows that for cellulose acetates the dependence V_m = F(SD) will be:

$$V_m \text{ (cm}^3\text{/mol)} = 112.2 + 37.2\,SD \tag{6}$$

Another example is cellulose laurates having N=8. In this case, the following dependence can be derived from Equation (3) for these esters:

$$V_m \text{ (cm}^3\text{/mol)} = 112.2 + 164\,SD \tag{7}$$

Considering that $K_p = V_w/V_m$ and $G = M/V_m$, the theoretical equations for calculating the packing coefficient of macromolecules (K_p) and specific gravity (G) of various cellulose esters will be the following:

$$K_p = \frac{V_{w,c} + (K_{w,AC} + N V_{w,CH2})SD}{V_{m,c} + (K_{m,AC} + N V_{m,CH2})SD} \tag{8}$$

$$G = M/\{V_{m,c} + (K_{m,AC} + N\,V_{m,CH2})\,SD\} \tag{9}$$

It was found that the packing coefficient has a slight tendency to decrease with increasing SD and/or length of the substitute increases due to the steric effect of bulk substituents. Nevertheless, for studied cellulose esters the average value of K_p = 0.681 ± 0.004, i.e., it is equal to the average K_p value for various solid amorphous polymers [18].

From the Equation (9), it follows that the specific gravity of esters should naturally decrease with an increase in the degree of substitution and/or the length of the substituent (Figure 5).

A comparison of calculations with experimental results indicates a good concordance between them (see e.g., Table 5).
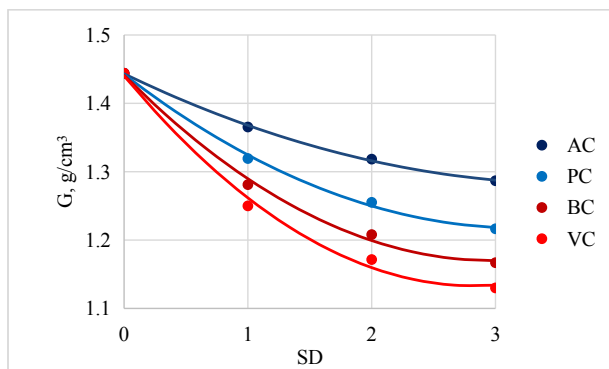
Figure 5. Dependence of specific gravity on substitution degree for acetates (AC), propionates (PC), butyrates (BC), and valerates (VC) of cellulose

Table 5. Calculated and experimental characteristics of cellulose triesters

Esters of cellulose	T_g, ℃	V_m, cm^3/mol		G, g/cm^3	
		Exp	Cal	Exp	Cal
TAC	167	228.5	223.8	1.26	1.28
TPC	130	268.0	271.4	1.23	1.22
TBC	100	320.1	318.9	1.16	1.17
TVC	76	365.7	366.5	1.13	1.13

According to the theory, the glass transition temperature should depend on the free volume of polymers [19]. In this study, an attempt was made to establish such a relationship also for cellulose esters. As a result, the best correlation was found if using the difference between glass temperatures (ΔT_g) and free volumes (ΔV_f) of amorphous cellulose and amorphous triesters (Figure 6).
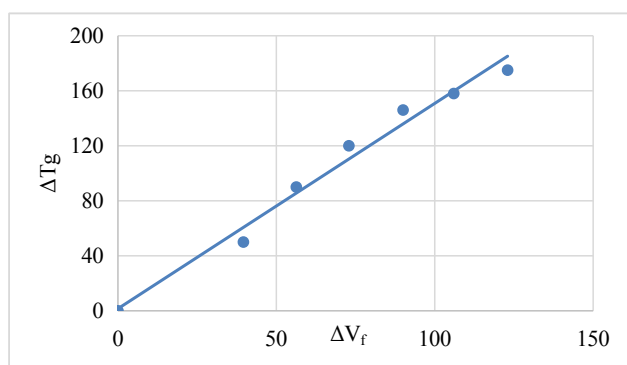
Figure 6. Dependence $\Delta T_g = F(\Delta V_f)$ for amorphous triesters of cellulose

This dependence can be expressed by the equation:

$$\Delta T_g = k \, \Delta V_f \qquad (10)$$

where slope factor k=1.5; while $T_{g,c}$ and $V_{f,c}$ for amorphous cellulose are 220 ℃ [20] and 32.9 cm^3/mol, respectively.

This result can be explained by the fact that a larger free volume of cellulose esters provides higher flexibility and mobility of chain segments, which contributes to a decrease in the glass transition temperature.

4. Conclusions

In this article, structural characteristics such as Van der Waals (V_w), molar (V_m), and free (V_f) volumes, as well as packing coefficient of macromolecules (K_p) and specific gravity (G) were used to describe the structural state of amorphous cellulose esters having different degrees of substitution. It was shown that with an increase in the degree of substitution (SD), the cellulose esters become more hydrophobic. Furthermore, the directly proportional dependences of bulk characteristics (V_m, V_w, and V_f) of the esters on SD were found. Conversely, the dependences of specific gravity on SD were nonlinear and inversely proportional. It was also discovered that the average value of packing coefficient K_p =0.681 ± 0.004 for studied cellulose esters is equal to the average K_p value for various solid amorphous polymers.

The theoretical equations were derived, which provide predicting the structural characteristics of cellulose esters with different degrees of substitution. The coincidence of calculated and experimental characteristics was shown. The relationship between glass transition temperature and free volume of cellulose esters was also found.

The introduction of bulk substituents to cellulose causes steric effects resulting in an increase in Van der Waals, molar, and free volumes, as well as a decrease in specific gravity. Moreover, the rise in the free volume of cellulose esters provides higher flexibility and mobility of chain segments, which contributes to a decrease in the glass transition temperature.

Author Contributions

The author conducted research and wrote this article.

Conflict of Interest

The author declares no conflict of interest.

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