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Structural Features of Celluloses of Different Origin

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Abstract Parameters of supramolecular structure of celluloses isolated from various natural sources have been studied, such as type of crystalline allomorph, crystallinity and amorphicity degrees, interplanar distances and specific volume of crystalline unit cells, as well as sizes and area of specific surface of crystallites. It was found that in the sequence of various CIβ samples, from tunicate cellulose to celluloses of cotton, bast fibers (flax), wood and herbaceous plants, a gradual decrease in crystallinity degree and sizes of crystallites was observed, whereas the area of specific surface of crystallites, specific volume of crystalline unit cells and interplanar distance increased. Among CIα samples, the cellulose isolated from Valonia algae has the more ordered supramolecular structure than the isolated bacterial cellulose. Comparison of CIα and CIβ cellulose samples having the close crystallinity, lateral size of crystallites and area of specific surface showed that the CIα lattice is more distorted than CIβ lattice. It was found that independently on the type of crystalline allomorph; hydrophilic properties of isolated celluloses (sorption of water vapor and heat of wetting) are directly proportional to amorphicity degree, whereas specific gravity is directly proportional to crystallinity degree of celluloses. On the other hand, content of CII after alkalization of cellulose samples with 12% NaOH is inversely proportional to lateral size of crystallites.

Keywords Cellulose, Origin, Crystalline allomorph, Crystallinity degree, Sizes of crystallites, Area of specific surface of crystallites, Interplanar distances, Specific volume of unit cells, Distortion index, Properties

1. Introduction

Cellulose is a linear, stereoregular, semicrystalline polysaccharide composed of D-glucopyranose unitslinked by chemical β-1,4-glycosidic bonds [1, 2]. The glucopyranose units have a "chair" conformation. Macromolecules of natural celluloses of various origins may include from 2,000 to 30,000 elementary units. During the process of cellulose isolation from plant materials and cellulose modification, a partial depolymerization of the macromolecules is observed. Each glucopyranose unit of cellulose contains three hydroxyl functional groups: one primary and two secondary groups. The hydroxyl groups impart to cellulose materials a hydrophility and reactivity to various reagents.

The linear macromolecules joined by hydrogen bonds form supramolecular structure of cellulose that consists of thread-like elementary nanofibrils and their bundles called microfibrils [1, 2]. Statistically alternating nano-scale crystallites along with non-crystalline domains are integral constituents of long and thin nanofibrils. The nanocrystallites having three-dimensional order are strong and inaccessible structural elements. By contrast, the low-ordered non-crystalline nanodomains having twisted and curved segments are weak and accessible. Thereby, the cleavage of glycosidic bonds occurs mainly in non-crystalline domains of cellulose nanofibrils, which facilitates release of the individual crystallites having a level-off degree of polymerization.

Cellulose is the most abundant organic matter on Earth. The total resources of cellulose reach one trillion tons [3]. Moreover, the mass of this biopolymer increases approximately by 100 billion tons annually as a result of photosynthesis, but almost the same amount of cellulose biodegrades in the nature [4]. Cellulose is present in all terrestrial plants and algae; the so-called "animal" cellulose enters into the composition of the mantle of tunicates; in addition, chemically pure cellulose is synthesized by several microorganisms, for example, by the bacteria *Gluconacetobacter xylinus*.

Terrestrial plants are the main source of cellulose. The content of cellulose in herbaceous plants is 30–40%, in wood it is 45–50%, in bast fibers (flax, ramie, kenaf, jute, etc.) 60–70%, while the content of cellulose in cotton fibers is above 90% [5, 6]. This natural polymer is used as inexhaustible feedstock for producing of diverse types of substances, materials and compounds.

Pure celluloses isolated from various sources have the equal formula of repeat anhydroglucose unit (AGU): $C_6H_{10}O_5$, and the same chemical elemental composition: C=44.45 %, O=49.38% and H=6.17%. However, a wide variety of sources can lead to differences in the supramolecular structure of isolated celluloses. Therefore, the main purpose of this paper was to study the specific structural features of celluloses isolated from various natural sources.

2. Experimental

2.1. Raw-materials

The following natural sources were used for isolation of cellulose:

- Wheat straw (WS)
- Corn stover (CS)
- Bagasse of sugar cane (BG)
- Chips of soft (spruce) wood (SW)
- Chips of hard (poplar) wood (HW)
- Bast fibers of flax (FL)
- Cotton fibers *Acala* (CT)
- Tunicate *Halocynthia roretzi*(TN)
- Pellicles of bacterial cellulose *Gluconacetobacter xylinus* (BC)
- Algae sample of *Valonia ventricosa* (AL)

The initial materials were dried, cut, knife-milled and screened through a sieve of 2mm.

2.2. Isolation of cellulose from raw-materials

To isolate the cellulose from plant materials and tunicate, the two-stage pulping, with nitric acid and alkali, was used [7]. Dried raw-material was put into 1L Pyrex autoclave flask, and 5% nitric acid was added to liquid/solid ratio (LSR) 4. The flask closed hermetically with a thermostable cap was placed in an oil bath having the temperature of 115 °C, and the material was treated for 30 min. The flask was removed from the bath, cooled and the content of the flask was filtered and washed with water using vacuum glass filter to neutral pH. The residue was quantitatively transferred into a 1L conical lab flask and 1.5% sodium hydroxide was added to LSR 7, and the content was boiled for 30 min. After alkaline treatment, the pulp was filtered, washed with water and neutralized with 1% sulphuric acid to pH 3-5. Then, the isolated cellulose was bleached with boiling1% sodium chlorite at LSR 10 for 30 min. Finally, the pure cellulose was washed with deionized water to neutral pH, rinsed with 95% ethanol and dried at 105 ^oC to constant weight. The obtained cellulose samples had 97-99 % of alpha-cellulose.

Pure bacterial cellulose (BC) was isolated from pellicles using cooking with 1.5 % sodium hydroxide and bleaching with 1% sodium chlorite. Then, the pure BC was washed with deionized water to neutral pH, rinsed with 95% ethanol and dried at 105 ^oC to constant weight.

Algae sample was preliminary extracted with organic solvents to remove lipids [8]. The defatted material was boiled with 1.5% sodium hydroxide and bleached with 1% sodium chlorite. Then, pure tunicate cellulose was washed with deionized water to neutral pH, rinsed with 95% ethanol and dried at 105 ^oC to constant weight.

Besides, two additional cellulose samples were studied, and namely microcrystalline celluloses prepared from isolated cotton cellulose (CM) and cellulose of softwood (WM) by hydrolysis with boiling 2.5 N HCl for 60 min (see subsection 2.3.2).

2.3. Methods of investigations

2.3.1. X-Ray diffraction

X-ray measurements have been carried out by Rigaku Ultima Plus- diffractometer in $\varphi = 2\Theta$ angle range from 5 to 80°. CuKα radiation with $\lambda = 0.15418$ nm generated at 35 kV and 25 mA was used. Collimation included a system consisting of three vertical slits and Soller slits. X-ray diffractograms of the samples were recorded using both transmission and reflection modes. Procedure of 0.02^o step-by-step scanning was used to determine the exact position of the peaks. The weak peaks were identified by a step-by-step scanning method with accumulation of impulses at the each step. The incoherent background scattering was subtracted from diffractograms. Then, corrections of diffractograms on absorption, combined PL factor and *Rietveld refinement were performed*. The angular positions of the peaks were checked using a narrow line of NaF standard at 2Θ of 38.83^o. Overlapped peaks were separated using a least-square program. Interplanar spacings (d) in crystallites were calculated by the Bragg equation:

$$d = \lambda /(2\sin \Theta) \quad (1)$$

The type of main crystalline allomorph (CA) of isolated celluloses, was evaluated on the basis of literature references [9-12]. Parameters a, b, c of the C1β crystalline unit cell were calculated by standard equations comprising interplanar spacings and Miller indices of reflections [13], whereas specific volume (V) of C1β crystalline unit cell were calculated as follows:

$$V = (k\, N\, a\, b\, c \sin \boldsymbol{\gamma})/(n\, M) \quad (2)$$

where k is dimension coefficient; N is Avogadro number; n=4 is number of AGU in the unit cell; M=162 is molecular mass of AGU.

The degree of crystallinity (X) and amorphicity (Y) were calculated by the equations [14]:

$$X = \int J_c\, d\varphi \,/\, \int J_o\, d\varphi \quad (3)$$

$$Y = 1 - X \quad (4)$$

where J_c and J_o are the corrected and normalized diffraction intensities for crystalline regions and sample respectively.

To calculate the true lateral size of crystallites (D) a diffraction peak at $2\Theta_o$ of 22.5-23^o was isolated, its integral width (B) in radians was measured and corrections for instrumental factor (Δ) and lattice distortion (δ_d) were introduced; then a D-value was calculated according to equation [15]:

$$D=\lambda/[(\cos \Theta_o (B^2 - \Delta^2)^{0.5})^2 – (2\delta_d \sin \Theta_o)^2]^{0.5} \quad (5)$$

The distortion index (DI) of crystalline lattice was determined as follows:

$$DI= 100\% [(V/Vo) – 1] \quad (6)$$

were V and Vo is specific volume of crystalline unit cell of distorted crystallites of cellulose sample andminimal specific volume of hypothetical perfect macrocrystals of CI, Vo=0.604 cm^3/g [16], respectively.

2.3.2. Acid hydrolysis

Hydrolysis of the cellulose samples up to level-off degree of polymerization (LODP) was carried out by boiling 2.5 N HCl for 60 min followed by washing and drying. The LODP value was measured by Cuen-viscosity method [17]. Determination of LODP enables to estimate the average length of cellulose crystallites (L, nm) [18]:

$$L = 0.517\, LODP \quad (7)$$

2.3.3. *Content of* alpha-cellulose

The content of alpha-cellulose was analyzed according to TAPPI T-203 standard method after treatment of the cellulose samples with 17.5% NaOH at 25°C for 1h

2.3.4. Sorption of water vapor

The sorption of water vapor by cellulose samples (A) was measured at 25°C for 1 month using saturated aqueous solution of sodium chloride giving RH=75 %.

2.3.5. Wetting heat

The heat effect of cellulose wetting with water (Q) was studied at 25°C by the method of microcalorimetry [19].

2.3.6. Specific gravity

The specific gravity (ρ) of the dry samples was tested at 25°C by the pycnometry method in a hexane medium [15].

2.3.7. Alkalization

The alkalization of samples was carried out with 12% sodium hydroxide at 25°C, LSR20 for 1h. The CII content was determined by X-ray method of inner standards [20].

3. Results and Discussion

According to data of chemical analysis, all isolated cellulose samples have a high content of alpha-cellulose, 97-99%, indicating their chemical purity. Since the crystallites of isolated celluloses are rod-like, where L > D (Table 1), the area of specific surface of the crystallites can be calculated, as follows [21]:

$$S=4/D \quad (8)$$

Study of structural parameters of the samples showed (Table 1) that tunicate cellulose has the most ordered supramolecular structure among all studied CIβ celluloses.

Table 1: Structural characteristics of isolated celluloses

Origin	CA	X	D, nm	L, nm	S x 10^8, m^2/m^3	d, nm	V, cm^3/g
TN	CIβ	0.82	13	400	3.0	0.387	0.611
CM	CIβ	0.75	10	98	4.0	0.388	0.613
WM	CIβ	0.73	8	75	5.0	0.391	0.615
CT	CIβ	0.70	7.5	96	5.3	0.391	0.616
FL	CIβ	0.67	6.8	90	5.9	0.392	0.619
SW	CIβ	0.63	6.7	74	6.0	0.392	0.619
HW	CIβ	0.62	5.6	70	7.1	0.393	0.621
BG	CIβ	0.54	4.8	58	8.3	0.394	0.623
WS	CIβ	0.53	4.5	55	8.9	0.395	0.624
CS	CIβ	0.52	4.3	54	9.3	0.395	0.625
AL	CIα	0.84	15	500	2.7	0.392	0.625
BC	CIα	0.76	8	100	5.0	0.394	0.627

X-ray diffractogram of this cellulose type contains sharp, narrow and well resolved peaks (Fig. 1). As it follows from the obtained results, cellulose isolated from tunicate is highly crystalline (X=0.82); besides, it has large crystallites (D=13 nm and L=400 nm),the smallest area of specific surface of crystallites (S=3 x 10^8 m^2/m^3), as well as the smallest specific volume (V=0.611 cm^3/g) and distance (d=0.387 nm) between [200] planes of crystalline unit cell. These results are confirmed by data of other researchers [16, 22].

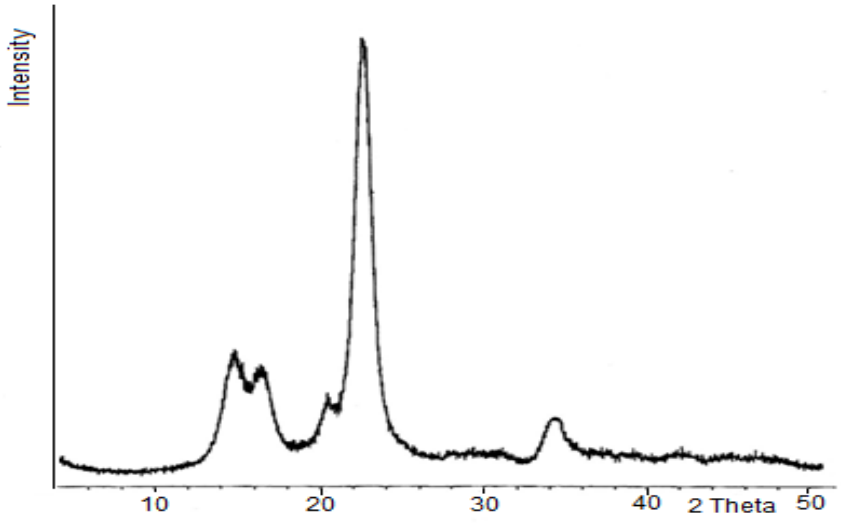

Figure 1: X-ray diffractogram of isolated tunicate cellulose

Others isolated CIβ celluloses of various origins were less ordered than tunicate cellulose **(**see e.g. Fig. 2, 3).

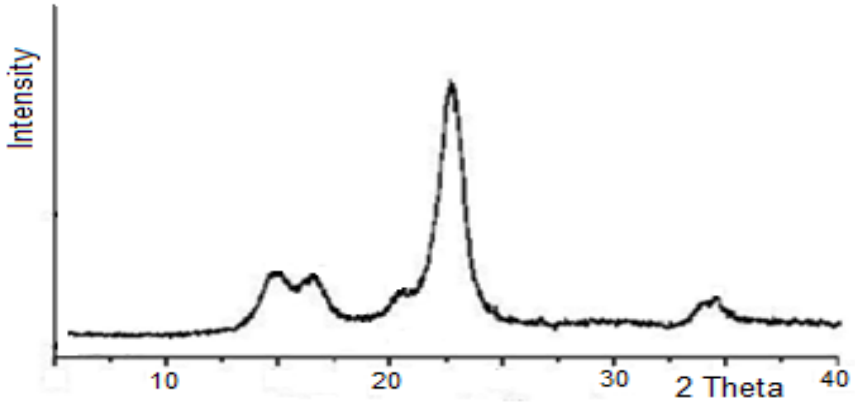

Figure 2: X-ray diffractogram of isolated cotton cellulose

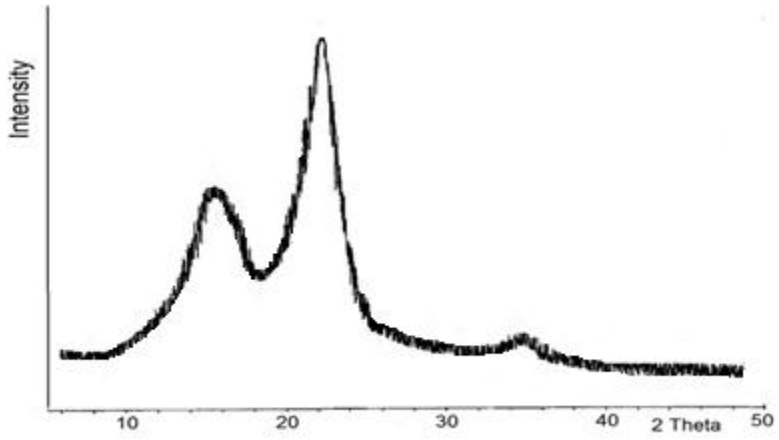

Figure 3: X-ray diffractogram of isolated wheat straw cellulose

In the sequence from cellulose of tunicate to celluloses of cotton, bast fibers (flax), wood and herbaceous plants, a gradual decrease incrystallinity degree and sizes of crystallites was observed, whereas the area of specific surface of crystallites, specific volume of crystalline unit cell interplanar distance increased (Table 1).

The obtained results also have shown that reducing in the area of specific surface of the crystallites lead to lineal decrease of interplanar distance (Fig. 4) and specific volume of crystalline unit cell (Fig. 5). Furthermore, extrapolation of the dependences d=f(S) and V=f(S) to S=0 gives do=0.384 nm and Vo=0.604 cm^3/g corresponding to hypothetical perfect macrocrystals of CI.

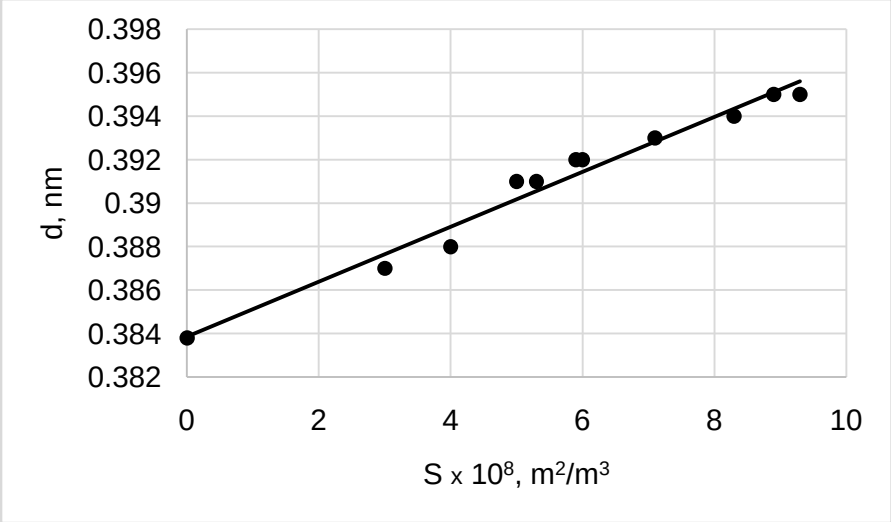

Figure 4: Dependence of interplanar distance on area of specific surface of crystallites

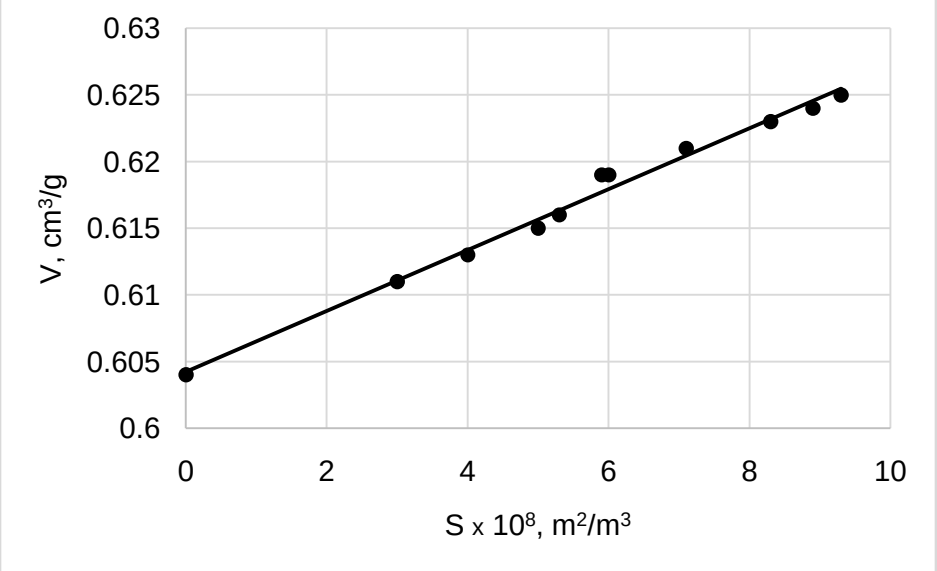

Figure 5: Dependence ofspecific volume of unit cell on area of specific surface of crystallites

Among studied CIα samples, the cellulose isolated from Valonia algae has a more ordered supramolecular structure than the isolated bacterial cellulose (Fig. 6, 7).

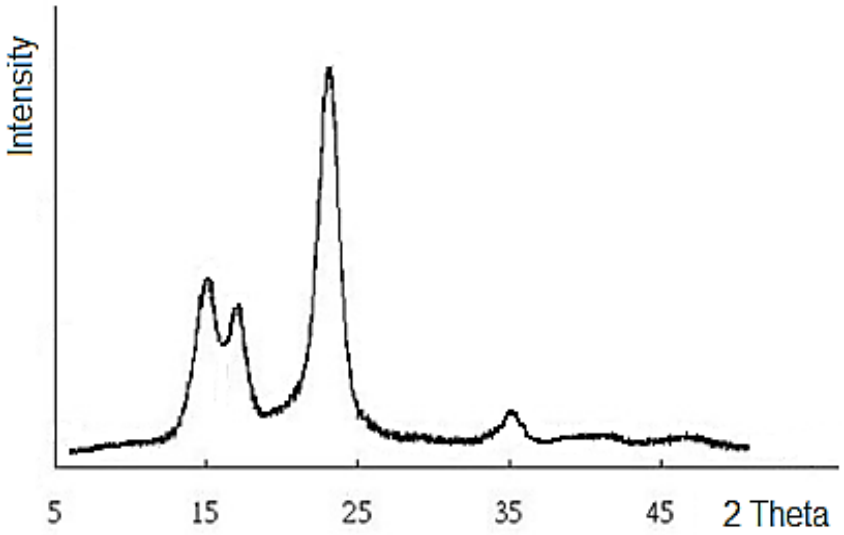

Figure 6: X-ray diffractogram of isolated Valonia cellulose

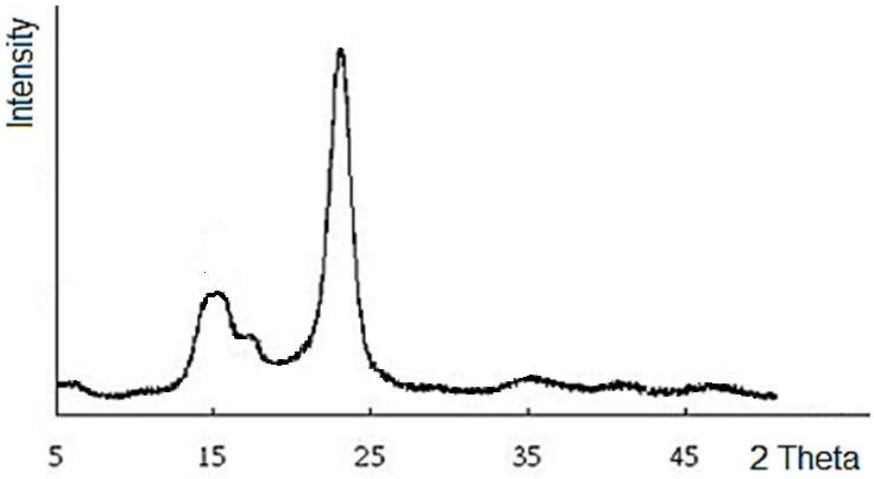

Figure 7: X-ray diffractogram of isolated bacterial cellulose

Comparison of CIα and CIβ samples having the close crystallinity, size of crystallites and area of specific surface (e.g. celluloses of AL and TC; BC and WM) revealed that the CIα lattice is more distorted than CIβ lattice (Table 2, Fig. 8). This conclusion is confirmed by results of other investigations [11, 16, 22].

Table 2: Lattice distortions of crystallites CIα and CIβ

Cellulose	CA	X	D, nm	S x 10^8, m^2/m^3	DI, %
TN	CIβ	0.82	13	3.0	1.1
AL	CIα	0.84	15	2.7	3.5
WM	CIβ	0.73	8	5.0	1.8
BC	CIα	0.76	8	5.0	3.8

From the study of hydrophilic properties of isolated cellulose samples it follows that sorption of water vapor (A) and heat of wetting (Q) are directly proportional to amorphicity degree (Y) of celluloses independently on the type of crystalline allomorph (Fig. 9). Such dependence can be explained by the fact that only non-crystalline (amorphous) domains of cellulose are accessible for water molecules.

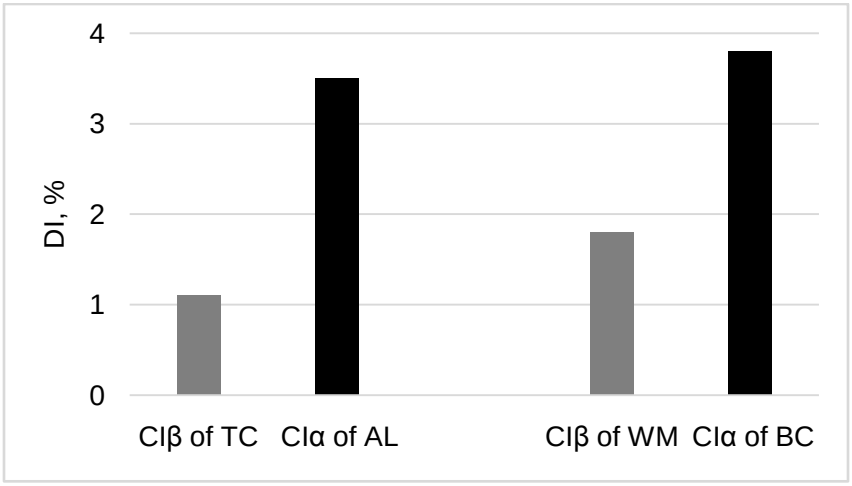

Figure 8: Comparison distortion indexes of crystallites having CM CIα and CIβ

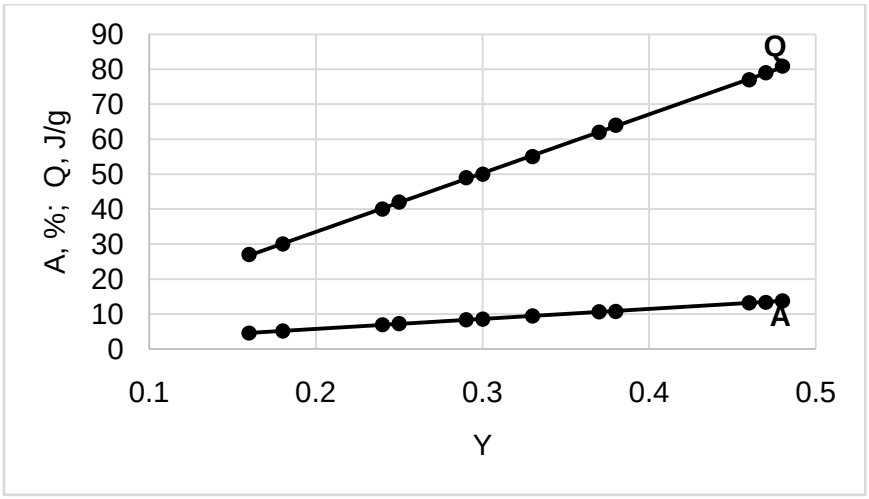

Figure 9: Dependence of hydrophilic properties of cellulose samples on amorphicity degree

On the other hand, the specific gravity of cellulose samples is directly proportional to crystallinity degree (Fig. 10).

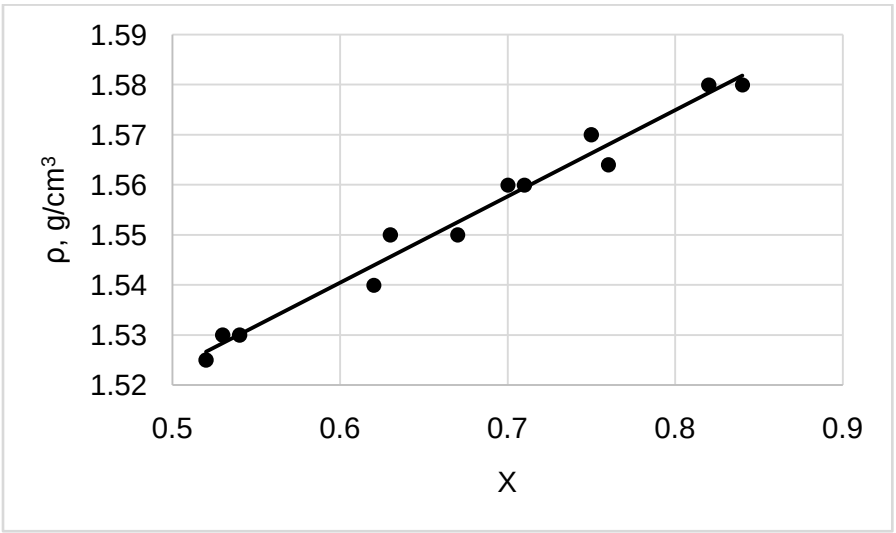

Figure 10: Dependence of specific gravity of cellulose samples on crystallinity degree

Study alkalization of cellulose samples with 12 NaOH showed that phase transition of CI in CII is inversely proportional to lateral size of crystallites (Fig. 11). Large CI crystallites of tunicate and Valonia celluloses do not form CII, while small CI crystallites of herbaceous plants transform completely in CII after alkalization with 12% NaOH. This result conforms to theory of phase transitions of nano-crystallites [21].

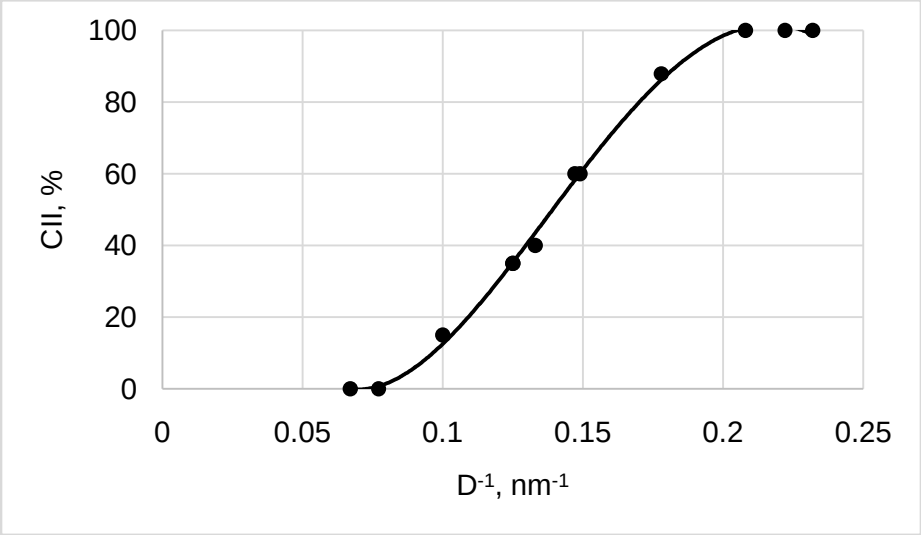

Figure 11: Dependence of CII-content in isolated celluloses after alkalization with 12% NaOH

4. Conclusions

Parameters of supramolecular structure of celluloses isolated from various natural sources have been studied. It was found that in the sequence of various CIβ samples, from tunicate cellulose to celluloses of cotton, bast fibers (flax), wood and herbaceous plants, a gradual decrease incrystallinity degree and sizes of crystallites was observed, whereas the area of specific surface of crystallites, specific volume of crystalline unit cells and interplanar distance increased. Among CIα samples, the cellulose isolated from Valonia algae has the more ordered supramolecular structure than the isolated bacterial cellulose. Comparison of CIα and CIβ cellulose samples having the close crystallinity, lateral size of crystallites and area of specific surface showed that the CIα lattice is more distorted than CIβ lattice. Study of cellulose properties revealed that independently on the type of crystalline allomorph, sorption of water vapor and heat of wetting are directly proportional to amorphicity degree, whereas specific gravity is directly proportional to crystallinity degree of celluloses. On the other hand, content of CII after alkalization of cellulose samples with 12% NaOH is inversely proportional to lateral size of crystallites.

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