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Structural temperature transformation of the cellulose–water system using time-resolved SAXS

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Abstract

The main goal of the work was to examine the structural changes induced by water (D_2O and H_2O) in the dense cellulose film, Tomophan I, using temperature time-resolved SAXS and WAX measurements. We found that dry cellulose and water-saturated cellulose contains hydrophobic microregions at room temperature. At increasing temperature microphase separation was observed, as a formation of a broad peak on the SAXS curves, with T_c of about 55 and 60°C, depending on the kind of water. Further heating, up to 85°C, causes an appearance of a set of very small peaks, generated by the cubic structure, in SAXS. The structural changes of the system are typical for the thermo-associative process, observed in the copolymer–water systems. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose–water; Microphase separation; SAXS method

1. Introduction

Recently studies of the copolymer–solvent structure have been done which detected the existence of mesophases in such systems as a result of attractive self-organization. The mesophases can be detected by SAXS and SANS, so these methods have emerged as the most powerful techniques for studying such structures.

The large number of published experimental results, obtained by these methods, initiated some generalizations and theoretical studies of this new class of structures [1–5]. The theory of microphase separation in block copolymers, which defined the criterion for the separation was elaborated [6]. The determination of critical transition, e.g. triple point LP and regions of stability of various phases on the phase diagram were proposed, as well [6,7]. These phase diagrams reflect the transitions between the high temperature disordered phase and the microphases, characterized by the occurrence of an ordered structure at lower temperatures [8]. In spite of its importance the theory has not been fully experimentally documented, which is probably due to the fact that it does not take into account thermal fluctuations of the structure which cause essential ordering changes [9].

The self-assembling leads, very often, to the formation of micelles from copolymer coils. No sharp boundary but rather a broad coexistence region of aggregates and single chained polymers can be expected. Most often the micelles have spherical shape, but depending on the polymer structure they can be rod-like. A model developed by Mortensen [10] represents a micelle with a core surrounded by a looser layer—the shell. Another model “cape and gown” [11] assumes a gradual decrease in the polymer density in the shell.

The isolated, noninteracting micelles in the surrounding medium bring about the effect of broadening of the primary beam on SAS curves and, for some copolymers, the intramicellar effect—the form-factor generated from the mutual packing of various segments of the copolymer in the micelle. Further ordering of the micelles can be treated as hard-sphere crystallization, which leads to a cubic structure for spherical micelles and a hexagonal structure for the rod-like ones [10–12], with a lattice constant of the order of 10 nm. Commonly, the crystallization should not be considered as a complete process but leads to very distorted quasi-crystal structures shown as a formation of a set of small peaks on the SAS curve. The mutual positions of the peaks depend on the structure type. In addition to the above types of structures the formation of a gel structure of peculiar macroscopic properties has been observed, particularly in polymer–solvent systems. Ordering phenomena in gels also lead to progressive intermicellar crystallization [13–15]. Also a statistical–mechanical analysis pertaining to gels, formed by instantaneous cross-linking of semidilute

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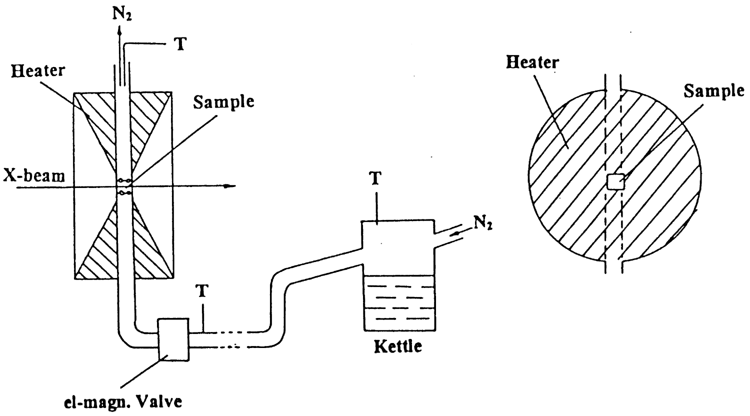

Fig. 1. The temperature chamber.

polymer solutions has been elaborated. According to this analysis the structural ordering of gels can be divided into two components: frozen inhomogenities of density and time-dependent thermal density fluctuations [16,17]. Some experimental works that confirmed this theory have already appeared [18,19].

A native cellulose is to a great extent crystalline. Many ways of preparation and treatment of cellulose usually lead also to partly crystalline structure. Up to now, at least seven cellulosic polymorphs of monoclinic and triclinic structure are described. The unit cells comprise parallelly located molecular chains of various orientations to each other. The partly crystalline cellulose can form crystal mesophases of rod- or band-like shape (microfibrils), immersed in the amorphous medium. Cellulose reactivity is heterogeneous due to its two-phase nature. The crystalline regions, due to their close packing and extensive interchain hydrogen bonding, are not readily accessible, contrary to the disordered region, in which the hydroxyl groups react readily with various substances [20]. Some derivatives of cellulose form thermotropic liquid crystalline phases below a characteristic temperature [21].

The regenerated cellulose, Tomophan I, which is the object of our present study, was investigated in our earlier works, using the SAXS method [22] and the radial distribution function method (RDF) [23]. From RDF it was found that Tomophan I is amorphous, without any crystalline parts. The amorphous structure can be heterogeneous, but no regions with a long-distance ordering exist. We also found that after saturation of the cellulose with water, the structure became heterogeneous in the mesoscopic scale, which can be caused, for example, by water droplets inside it [22].

Much of the research observed nowadays has brought about an essential progress in elucidating the processes of microphase separation in complex polymers and polymer–solvent systems. These processes are complicated and, at present, there are no sufficient generalizations that would enable one to predict them in definite systems. It is therefore of importance to accumulate and analyse experimental data for definite systems.

This work is a continuation of our previous studies on the cellulose–water system [22,23]. The purpose of this work is to examine the structural, temperature-dependent processes of ordering in the system. The measurements were carried out on the ELETTRA synchrotron at Triest, Italy, using the SAXS method in the time-resolved mode, with increasing temperature.

2. Experimental

Materials: The membrane of the cellulose dense film, Tomophan I, dry and swollen in H_2O or D_2O, was studied. The same materials were examined in our previous works [22,23]. The cellulose, swollen in water to saturation, e.g. to 2.5 times its volume, exhibited a broadening of the primary beam on SAXS, as we found. On the WAX curves a decrease of both cellulose peaks at 0.45 and 0.72 nm and additionally an emergence of halo from the bulk water were observed. The latter effect suggested that inclusions that result in the broadening on SAXS curves may be due to water.

A temperature chamber, home made, was constructed for the synchrotron measurements (Fig. 1). In this chamber a sample container is placed at the centre of a heated concave cylinder. The container is 2.5-mm long, and has small openings on its cylindrical wall, joined with a canal for vapour, which assures the vapour flow across the container. Hot water vapour produced in a heated kettle is blown through the sample container by means of nitrogen. The flow of vapour is initiated by the opening of the electromagnetic valve. The temperature of the vapour in the kettle, conducting tubing and sample, are controlled. The chamber makes it possible to continuously supply the sample with wet vapour as well as to increase its temperature.

Synchrotron beamline: The SAXS and WAX measurements were carried out using the Austrian SAXS Beamline at the ELLETRA synchrotron. The line is mainly dedicated for time-resolved studies of fast structural transitions in non-crystalline systems. A high power wiggler is used as the

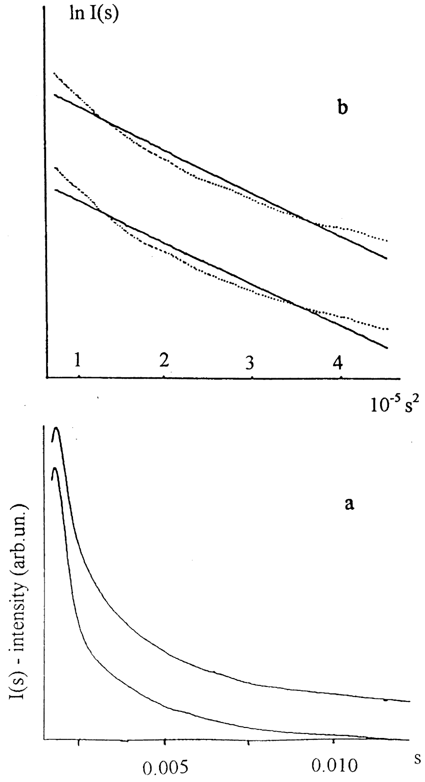

Fig. 2. (a) SAXS. (b) Fitting straight line to obtain R_g, for dry cellulose (bottom) and that saturated with water (top), at room temperature. The curves are shifted for better clarity, their maxima are equalized, *I*—intensity, *s*—2 sin θ/λ.

beamline source. Two one-dimensional gas-filled detectors enabled us to simultaneously perform fast, time-resolved SAXS and WAX measurements [24].

Measurements: The first measurements were performed at room temperature starting with dry cellulose and saturating it with wet water vapour during the measurement cycle. This enabled us to determine the time period of the structural transition: dry cellulose–cellulose swollen in H_2O or D_2O. The range was less than 1 s for both kinds of water.

Time-resolved temperature SAXS and WAX measurements were performed for the systems: cellulose–light water and cellulose–heavy water in the temperature range of 25–85°C and at a heating rate of about 15°C/min. Similar measurements were carried out for dry cellulose as reference.

The results of the measurements were displayed and subjected to a preliminary treatment using the OTOKO program [25].

The SAXS curves were obtained at room temperature for dry cellulose and after saturating it in water (Fig. 2a). Owing to the larger range and better resolution of the synchrotron measurement in comparison with our previous equipment [22,23], the effect of primary beam broadening was registered for dry cellulose, too. As one can see the difference between the slopes of the primary beam for both curves is insignificant and only a growth of intensity for swollen samples, similar for both kinds of water, is observed. By fitting a straight line to the measured curves in the scale: $\ln I(s^2)$, where $s = 2\sin\theta/\lambda$, according to Guinier, the gyration radius of domains, R_g, was obtained. It is equal to 5.40 and 5.45 nm for the dry and saturated cellulose, respectively (Fig. 2b). The WAX curves undergo rapid suppression during the saturation process, as shown previously [22].

Temperature time-resolved SAXS and WAX measurements are shown in Figs. 3 and 4 for the systems: cellulose–H_2O and –D_2O, respectively. They revealed the emergence and growth of a broad peak in SAXS. The critical temperature of the effect, T_c, occurred at about 60 and 55°C, for D_2O and H_2O, respectively. The peak has an elongated shoulder from the side of greater *s*. In Fig. 5, which is an enlarged insert of the main peak from Figs. 3 and 4, the SAXS peak for both the systems at the maximum temperature (85°C) is shown. Its specific shape there is visible: a step upturn in the small *s* region and a long back in the region of greater *s*. The *d*-value obtained from the peak is about 28 nm. A specific feature of the peak is the presence of its modulation in the form of a set of very small peaks, close to the peak maximum. The positions of the small peaks are the same for both systems, as seen in Fig. 5. The time-resolved temperature WAX curves for both kinds of water are also shown in Figs. 3 and 4. The recovery of both cellulose peaks, slightly stronger for D_2O, can be seen.

On the other hand the measurements carried out in the same way for dry cellulose (Fig. 6) did not reveal any effects.

3. Discussion

The existence of broadening of the primary beam on the SAXS curves for dry and saturated cellulose indicates that the cellulose contains microregions of different electron density. The gyration radii, R_g, determined from the slope of the broadened part of the primary beam, are the same for dry and saturated cellulose (Fig. 2b). No change in R_g after swelling shows that the microregions of different electron density are inaccessible to water and is an evidence of their hydrophobicity. The SAXS intensity, measured in the range of the broadening is weak, but was much smaller for dry cellulose, than for the saturated one, which is probably caused by the smaller density of the medium surrounding the microregions after swelling. In the case of dry samples the medium consists of cellulose, but in the case of saturated ones it consists of cellulose and water (density of cellulose is 1.5 g cm^{-3}, the number of electrons per atom is similar to that in water). In both cases weak intensity of the broadened part indicates that the number of the microregions is insignificant.

During temperature increase the emergence and growth of the broad peak can be observed in the SAXS for cellulose

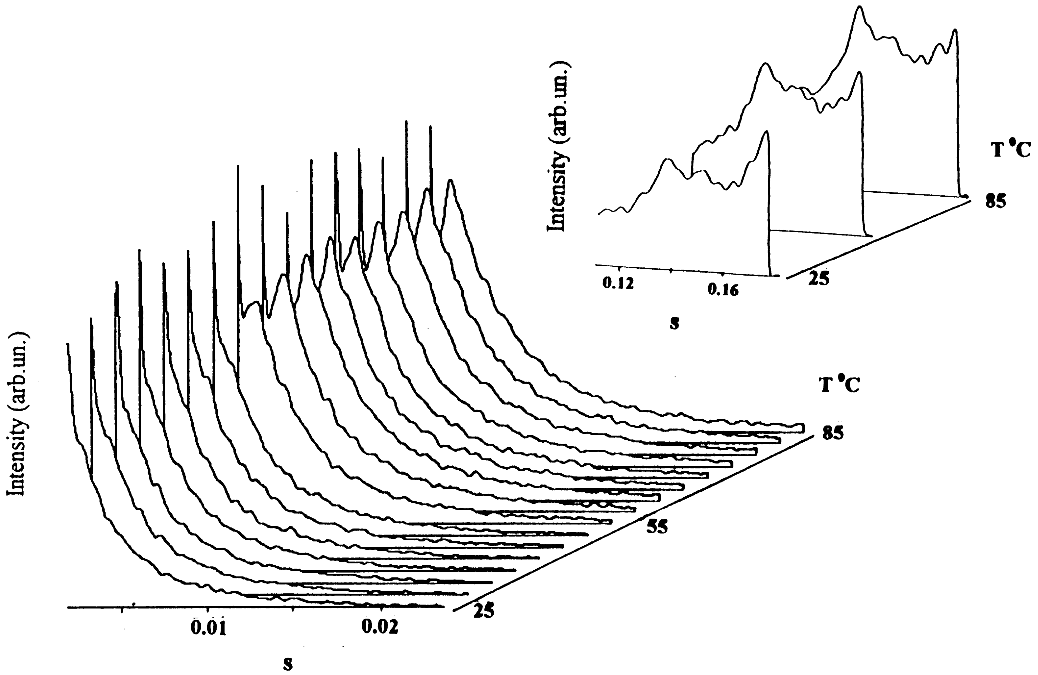

Fig. 3. Time-resolved temperature measurements for the cellulose–H_2O system: SAXS (left) and WAX (right).

swollen in H_2O and D_2O (Figs. 3 and 4). The position of the peak ($d = 28$ nm) is the average distance between the domains that are formed. The growth of the peak indicates a dramatic increase in the number of domains and a progress in the domains ordering towards the narrow distribution of their distances. Simultaneously the WAX curves of both samples show a gradual recovery of the cellulose double peak (Figs. 3 and 4) towards the shape observed for dry cellulose (Fig. 6). It is an evidence for the increase of the material hydrophobicity, which is a well-known

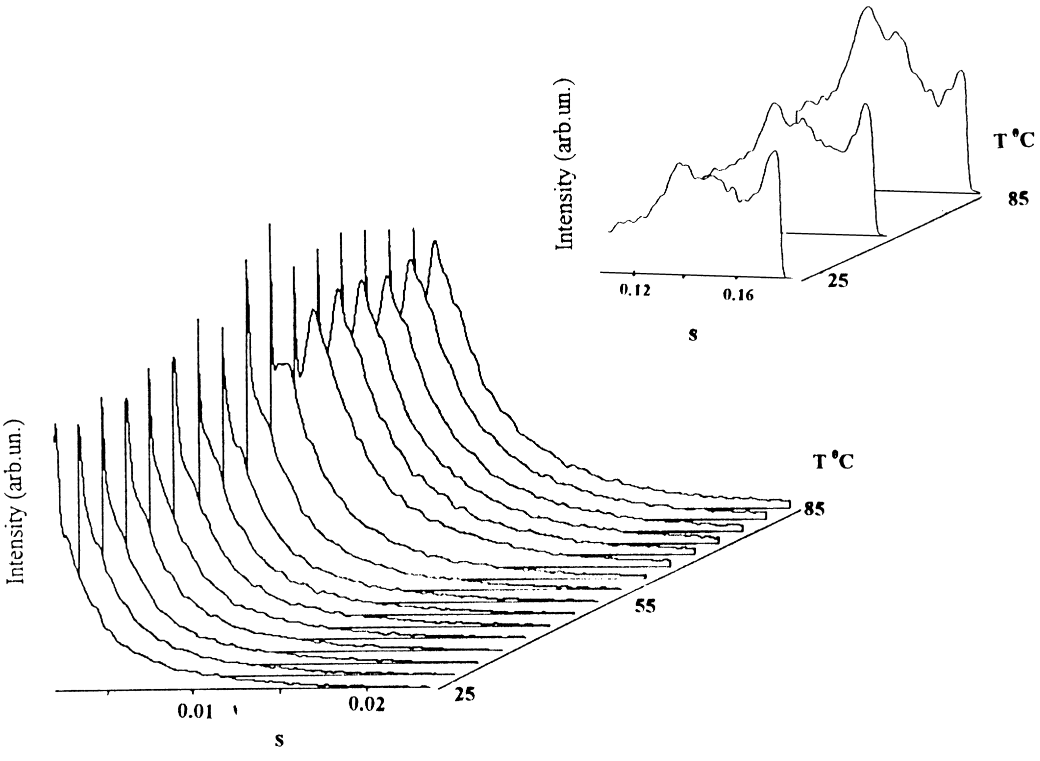

Fig. 4. Time-resolved temperature measurements for the cellulose–D_2O system: SAXS (left) and WAX (right).

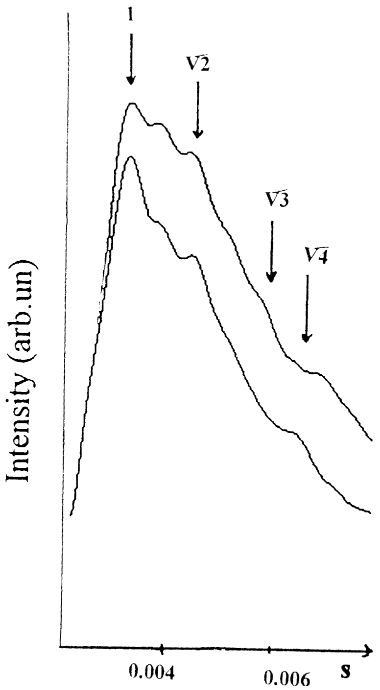

Fig. 5. SAXS peak at 85°C, for cellulose–H_2O (bottom) and cellulose–D_2O (top). The small maxima are marked by arrows. The curves are shifted for better clarity.

phenomenon observed when swollen polymers are heated. The increase of the number of domains together with the increase of the samples' hydrophobicity suggest that the domains are of reduced hydration.

Fig. 5 shows the peak that emerged at the highest temperature, for cellulose saturated with light and heavy water. On each curve, one can see small modulations at the same position. The modulations form a set of very small peaks and are marked in the figure by arrows. The successive *d*-values, calculated from the positions of the small peaks follow the proportions: $1{:}2^{1\backslash 2}{:}3^{1\backslash 2}{:}4^{1\backslash 2}$, which are characteristic for a cubic crystal structure. It is the first indication that the domains order to the mesophase cubic structure. Its lattice constant is about 30 nm. Because a cubic structure can be formed by spherical centres only, the domains must be of spherical shape, which suggests their non-crystalline structure, because cellulose nanocrystals are formed from bundles of chains and are of rod-like shape. This suggestion is confirmed by only a small change of the WAX, from the direction of the WAX curves obtained for dry cellulose (Figs. 3 and 4).

Identical structural effects in SAXS were observed and explained earlier for copolymers saturated with water [10,11,26,27], i.e. generation of a broad, asymmetric peak with step upturn from lower angles, above the temperature of association. The intensity of the peak increases with the further raising of temperature, but the position is the same, and then a set of small peaks is generated. The effect is due to self-association as a consequence of the increased hydrophobicity of the copolymer at higher temperatures. During heating, hard segments self-associate to form thermodynamically stable aggregates of reduced hydration. The soft segments form a common medium with water. The

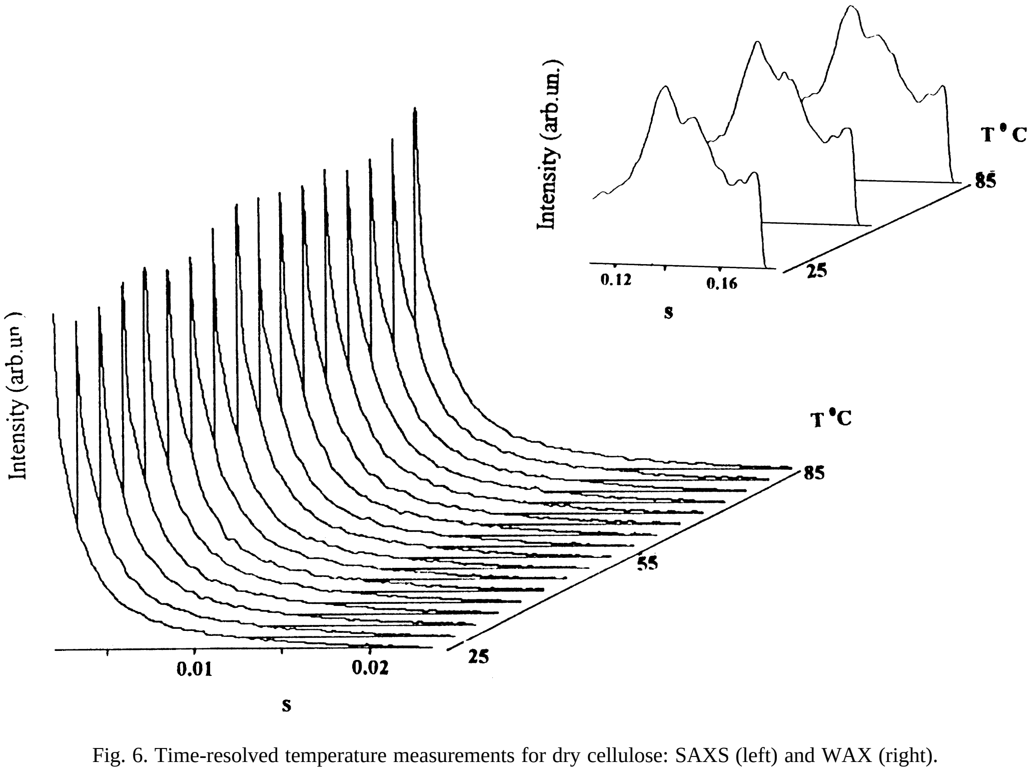

Fig. 6. Time-resolved temperature measurements for dry cellulose: SAXS (left) and WAX (right).

aggregates are commonly micelles that can order themselves to a mesophase crystal structure at high temperature. The characteristic feature of the thermo-associative process is that the crystal mesophase structure appears at higher temperature rather than the amorphous one. The mutual incompatibility of various segments is considered to be essential to the structural changes.

In the case of Tomophan I, the identical behaviour suggests the same process. The existence of the two phases in the material at room temperature was stated by us from the SAXS results of the present work (Fig. 2) and from that of Ref. [22]. The WAX curves [22] and RDF results [23] indicated a lack of crystallinity of both phases. During heating, the more ordered and hydrophobic domains act probably in a similar way as the hard-segment cores in copolymers, leading to association. Also, ordering of the mesophase to crystal structure, whose first signals are visible in Fig. 5, at further increase of temperature, is typical for the thermo-associative process.

From our study the action of D_2O and H_2O on the cellulose structure is very similar, in spite of fact that both kinds of water show different permeation rates. However, there are some differences: a slightly higher critical temperature T_c and a slightly better recovery of the cellulose peak at WAX during the heating of cellulose swollen in heavy water.

4. Concluding remarks

1. In the amorphous, homogenous structure of the dense cellulose film hydrophobic properties of microregions, not accessible to water, exist even at room temperature.
2. The mesophase domain structure of the close distribution of the interdomain distances is formed during the heating of swollen cellulose above the critical temperature.
3. Further increase of temperature results in ordering of the domains and then to the first stage of the cubic crystal structure formation. The cubic structure can be generated by domains of spherical shape only.
4. The spherical shape of the domains, their WAX curves of non-crystalline shape and our earlier result of RDF analysis suggest an amorphous structure of the domains, but of a greater degree of ordering than medium.
5. The structural changes of the cellulose–water system are identical to those observed in the thermo-associative process of some copolymer–water systems.
6. The structural changes in the cellulose–water system are very fast, both at room temperature and at higher temperatures.
7. The action of D_2O and H_2O on the cellulose structure is similar.

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