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OPTICAL ROTATORY DISPERSION OF WATER-SOLUBLE CELLULOSE DERIVATIVES

G. R. Rakhmanberdyev, N. A. Fedyakova, N. V. Myagkova, and A. Sidikov

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Dilute solutions of water-soluble cellulose esters and also solutions of model compounds – glucose and cellobiose – have been investigated. It has been shown that a definite influence on optical rotatory dispersion is exerted by the conformational difference of the pyranose rings of cellulose arising when the hydroxy groups in the macromolecule are partially replaced by functional groups of different natures.

Optical activity characterizing features of the spatial structure of simple molecules was known even during the last century from the work of J. Biot, L. Pasteur, J. H. Van't-Hoff, A. M. Butlerov, and others. It is also known that features of the spatial structure of molecules determine various properties of a substance and play a major role in processes of synthesis.

This question has been little studied as applied to cellulose and its derivatives. In the dissertation [1], which gathers together practically all the material on the optical activity of cellulose and cellulose acetate, there is no information on the connection of optical activity with the conditions of synthesis, the properties of the polymer, and the quality of the products. There are no clear ideas on the role of the functional groups of cellulose esters in the optical activities of their solutions.

In order to elucidate the causes of the change in the optical activity of cellulose derivatives on the replacement of certain functional groups by others in the pyranose rings of the cellulose macromolecule, we have studied by the method of optical rotatory dispersion (ORD) dilute solutions of cellulose acetates (CAs) with different degrees of substitution, cellulose aminoacetate, and cellulose acetophthalate, and also solutions of model compounds – α-glucose and cellobiose.

In this connection, we investigated solutions in acetic acid of CAs with various degrees of substitution obtained by the successive saponification of cellulose triacetate at temperatures of 59 and 20°C.

The results of the optical rotatory dispersion investigations are given in Table 1, from which it can be seen that CAs with the same qualitative and quantitative compositions of the macromolecules can have negative or positive values of the ORD, depending on the conditions of synthesis. For solutions of CAs obtained at a low saponification temperature – 20°C – a transition is observed from the negative to the positive region of optical rotatory dispersion. It can also be seen from Table 1 that the samples containing 54-56% of bound acetic acid obtained at 20°C were dextrorotatory, while those obtained at 59°C were levorotatory.

In order to elucidate the factors causing CAs to change from levorotatory to dextrorotatory in the process of saponification, we studied model compounds of one functional composition – glucose and cellobiose – in acetic acid (Table 2). A difference in the optical activities of substances with one functional composition can be explained by a change in the conformational state of the pyranose rings and by rotational isomerism. However, rotational isomerism is excluded for glucose. It can therefore be stated that the optical activity of solutions of carbohydrates is most probably determined by the conformational state of the pyranose rings [2].

To determine the contribution to optical activity of the rotation of the functional groups and the rotation of the rings relative to one another, we have carried out a mathematical treatment of the optical rotatory dispersion curves for the above solutions in acetic acid by means of Drude's equation [3]. The rotational constants A, responsible for the stereoregularity of the polymer, and λ_0, characterizing the contribution of the functional groups to the optical rotation, were calculated (Table 3).

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TABLE 1. Specific Rotations of Solutions of Cellulose Acetates in Acetic Acid (λ = 400 nm)

Saponification temperature, °C	Content of bound acetic acid, mass-%							
	54	55	56	57	58	59	60	61
59	−5	−6	−8	−12	−15	−17	−18	−19
20	+24	+17	+4	0	−9	−13	−16	−19

TABLE 2. Optical Rotatory Dispersion of Solutions of Cellulose Derivatives in Acetic Acid

Compound	Specific rotation ($[\alpha]^{20}$, degrees) at wavelength, nm							
	576	546	510	495	481	454	414	400
Glucose	+51	+57	+68	+72	+76	+88	+109	+114
Cellobiose	+31	+39	+46	+52	+57	+63	+72	+78
Cellulose acetate	0	−2	−2	−5	−7	−11	−21	−29
Cellulose aminoacetate	+3	+4	+3	+4	+5	+3	+2	+2
Cellulose acetophthalate	−14	−15	−21	−24	−27	−35	−49	−54

TABLE 3. Rotational Constants (solvent: acetic acid)

Compound	Mass fraction of bound acetic acid	$A \cdot 10^{-5}$	λ_0, nm
Glucose	–	222.0	373
Cellobiose	–	15.0	309
Cellulose acetate	61	−15.0	301
	59	−13.0	321
	58	−10.8	349
	56	−2.3	390
	55	−6.3	302
	54	2.0	369
	50	25.0	343

The close values of λ_0 for carbohydrates with different functional compositions show that a change in the ratio of functional groups exerts no appreciable influence on optical activity. And, conversely, the wide interval of change in the constant *A* for carbohydrates both with the same and with different functional compositions may indicate a considerable difference in the stereoregularity of the polymers and, in particular, in the conformational state of the pyranose rings of the compounds studied.

The results obtained (see Table 2) also show that the substitution of the hydroxy groups in the pyranose rings of the cellulose macromolecule by functional groups of different natures leads to a change in the magnitude and sign of the specific rotations of solutions of cellulose esters. However, in the series considered, no link was found between optical activity and the volume of the functional groups introduced into the macromolecule.

There are contradictory statements on this question in the literature. Thus, Malm et al. [4, 5] attempted to show an influence of the nature of the esterifying agent on the optical activity of cellulose derivatives. They obtained triesters of cellulose with aliphatic acids from acetic to palmitic. With an increase in the number of carbon atoms in the esterifying acid the magnitude of the negative specific rotation gradually decreased. These authors give no discussions whatever of the reasons for the change in optical rotation in the series of cellulose triesters. In an earlier paper [6] it was also shown that the replacement of light functional groups by relatively heavy ones frequently does not cause a change in optical rotation and, conversely, a change between two different groups with approximately the same molecular weights may have a considerable influence on optical rotation.

Thus, the results that we have obtained permit the conclusion of a determining role for the conformational state of the pyranose rings in the optical activity of cellulose derivatives.

EXPERIMENTAL

For the investigation we used solutions with a concentration of 0.5 mass-%. Angles of optical rotation were measured on an SPU-E spectropolarimeter in the range of λ from 400 to 600 nm. The source of light was a DRSh-250 mercury lamp.

A glass cell 1 dm long with quartz windows was used. Optical activities were evaluated from specific rotations calculated by means of the formula [2]:

$$[\alpha]_{\lambda}^{t} = \frac{\alpha \cdot 100}{l \cdot c},$$

where α is the observed angle of rotation of the plane of polarization, degrees;
λ is the wavelength of the incident light, nm;
l is the path length of the light in the optically active medium;
C is the concentration of the optically active substance, g/dl of solution; and
t is the temperature of the solution investigated, °C.

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