At present there is no single point of view on the question of conformational change in the unit during the process of cellulose triacetate (CTA) hydrolysis. Information is lacking about a possible change in the steric disposition of side groups in the chain conformation on replacement of the acetate groups by hydroxyl groups.

Thus, some Japanese workers [1], on the basis of x-ray structural analysis and IR spectroscopy, indicate a change in the conformation of the glucopyranoside unit during nitration. On the other hand, in [2, 3], on the basis of theoretical calculations of the conformational state of dimeric fragments of the trinitrate and of CTA, the conclusion was drawn that there is a large number of steric forms, due to large conformational possibilities of the side groups, which is the reason for conformational polymorphism. At the same time, the authors of [2, 3] consider that the high cooperative nonvalence interactions hinders the formation of stereoregular conformations, and replacement of nitrate groups by acetate groups does not lead to a change in the stability of the Cl,1C group conformation.

Another problem is the preparation of chemically uniform, high-quality acetates (CA) with stable properties. In this connection, a study of the structural features of the macromolecules and their change during the process of CTA hydrolysis is of interest.

One of the methods for evaluating the structure of a polymer in solution is the method of optical rotation dispersion (ORD).

Specimens for study were prepared by acetylation of cellulose, with subsequent hydrolysis of the CTA by the continuous homogeneous method in acetic acid medium.

Absolutely dry cellulose (26 g) was activated for 1 h at 100°C in 12 ml of glacial acetic acid. The mixture was cooled to 25°C and, with agitation, was treated over a 10-min period with the catalyst — a mixture of 190 ml of acetic acid and 1.7 ml of sulfuric acid — after which 94 ml of acetic anhydride was added, and the acetylation process was carried out to complete disappearance of the cellulose fibrils.

Hydrolysis was effected by adding 116 ml of a 70% aqueous solution of acetic acid to the CTA solution so obtained, over a 5-min period, with thorough mixing. Then the solution was divided into two parts and was hydrolyzed at temperatures of 25 and 59°C. The first samples of about 0.5 g were taken 30 min after the start of the hydrolysis process and diluted with

Fig. 1. Optical rotation dispersion of cellulose acetates prepared at the indicated values of CHOAc (in % by wt.): 1) 62.25; 2) 60.9; 3) 59.8; 4) 58.8; 5) 56.6; 6) 53.4; 7) 52.5.
Fig. 2. Optical rotatory dispersions of CA specimens prepared at 25°C at the indicated acetic acid concentrations (in % by wt.): 1) 62.3; 2) 61.2; 3) 58.8; 4) 57; 5) 56.3; 6) 54.6; 7) 52.

Fig. 3. Dependence of \([\alpha]_\lambda^{25}\) of CA solutions on \(C_{\text{HOAc}}\) at 25°C (1) and at 59°C (2).

Acetic acid to 50 g/liter. The taking and preparation for measurement of subsequent samples was carried out similarly after definite time intervals. Measurement of the optical activity of the solutions was carried out on a type SPU-E spectro-polarimeter by the method of [4], at various wavelengths of the incident light. The optical activity of the solutions was evaluated from the magnitude of the specific molecular rotation, \([\alpha]_\lambda^{25}\), calculated by the formula of [5, p. 90]

\[
[\alpha]_\lambda^{25} = \frac{\alpha}{100/C}
\]

where \(l\) is the working length of the cuvette, in dm; \(C\) is the concentration of the polymer, in g/ml; and \(\alpha\) is the angle of rotation of the plane of polarization, in deg.

Bearing in mind the change in molecular weight of the elementary unit during the hydrolysis process, we made a calculation of the specific molecular rotation, which did not lead to a change in the character of the ORD.

In performing the CTA hydrolysis process at 59°C, it was found that the optical rotation changes as hydrolysis proceeds. From levorotatory, the CA solutions are transformed into dextrorotatory (Fig. 1). This complex character of change in ORD is not the result of quantitative change in the ratio of functional groups alone, since there is a small positive contribution of the hydroxyl groups to the total magnitude of the optical rotation [4].

It is to be noted that the hydrolysis process is one of the polymer-analog transformations (PAT). It is natural, therefore, that during the course of the PAT a change takes place in the basic stereochemical characteristic — the local configurations, superposition of which affects the configuration of the macromolecules as a whole. Moreover, replacement of some functional groups by others can lead to definite changes in the free rotation of groups of atoms around individual bonds and rotations of units with respect to the \(\beta\)-glucoside bond. This assists in the appearance of new steric forms, which, obviously, may be the reason for the transition of CA from levorotatory forms into dextrorotatory ones. To check the suggestion which has been made, we carried out the hydrolysis process at a low temperature so as to reduce intramolecular mobility and change in the conformation of the macromolecules.

It turned out that the character of change in the ORD of CA solutions obtained at various hydrolysis temperatures was the same: A similar transition of levorotatory forms into dextrorotatory forms takes place (Fig. 2). This indicates structural changes of the macromolecules during PAT. At the same time, the transition of the ORD curves from normal (levorotatory) into anomalous and normal ones (dextrorotatory) takes place at different contents of bound acetic acid (\(C_{\text{HOAc}}\)).