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STUDY OF THE PACKING DENSITY OF MACROMOLECULES IN VARIOUS CELLULOSE PREPARATIONS

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The methods used until now for studying the packing density of cellulose macromolecules have unfortunately been indirect in character and have been based mainly on measurements of the internal surface by means of adsorption of vapors of nitrogen, water, and organic solvents (methanol, ethanol, benzene), absorption from aqueous solution of dyes, iodine, certain cations, determination of the heat of wetting, reactivity, etc. Meanwhile, one of the most reliable ways of measuring the packing density of macromolecules should be the determination of the true specific gravity of the preparations under investigation. Unfortunately, this method has not yet received the recognition it deserves.

In our study, the true specific gravity of cellulose was determined by the Hermans method, based on the principle of suspending pieces of cellulose in a medium of carbon tetrachloride, the specific gravity of which is varied by raising or lowering the temperature. In the course of the work we introduced into this method certain changes which considerably simplified it without reducing the accuracy of the measurements.

In all determinations of true specific gravity, the cellulose preparations were first carefully dried at 105°. Since many investigators regard cellulose as consisting of alternating regions with loose and dense packing, corresponding to their different reactivity, we measured the true specific gravity of various cellulose preparations after partial hydrolysis or alcoholysis. The use of alcoholysis was necessitated by the need to prevent the cleaved loose regions from their presumed densification under the influence of water under hydrolysis conditions. Hydrolysis of the cellulose preparations studied was carried out for various lengths of time with a 10% aqueous solution of H_2SO_4 at 100°, and alcoholysis in absolute ethanol containing 10% H_2SO_4 at 100°. Simultaneously with the specific gravity, the amount of cellulose remaining after hydrolysis or ethanolyis was determined.

Figure 1 shows the change in the true specific gravity of various cotton cellulose preparations during their hydrolysis and alcoholysis. As can be seen, the initial specific gravity of this cellulose, equal to 1.545, rapidly increases to 1.562 without appreciable loss in the weight of the starting preparation. Further deepening

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

of hydrolysis does not change the limiting value of the density of cellulose. This phenomenon indicates rapid densification of the loose regions of cotton cellulose that have undergone cleavage under hydrolysis conditions. In contrast to hydrolysis, the increase in the specific gravity of the residue of cotton cellulose during ethanolysis proceeds gradually, as the fraction readily susceptible to alcoholysis dissolves. After removal of ~7% of the weight of the cotton cellulose, the specific gravity of the residue becomes equal to 1.563 and thereafter practically does not change. Fig. 1,3 shows the change in the density of ethanolysed cotton cellulose that had first been subjected to dry grinding for 40 min in a vibratory mill of VNIIGS design. The ground cellulose before ethanolysis had a specific gravity of 1.502. Its Debyegram was characterized by the presence of a single amorphous ring and by the absence of interferences typical of cellulose I. Curve 3 sho-

shows that at the beginning of ethanolysis, with practically no loss of substance, rapid densification of the cellulose is observed to a specific gravity of 1.517, after which the density of the residue no longer changed appreciably upon dissolution of up to 85% of the weight of the preparation. Thus, in its structure, the milled cellulose is very homogeneous and differs sharply in density from the original cotton cellulose. The milled cotton cellulose was wetted with water at 50° (Fig. 1, 4) and 100° (Fig. 1, 5) for 1 hour, after which the water was displaced with absolute alcohol and the preparations were dried. During alcoholysis of these preparations, curves 4 and 5 in Fig. 1 were obtained. Under the influence of water at a temperature of 50°, the milled cellulose became densified to a specific gravity of 1.526, and at 100°—to 1.529. During subsequent ethanolysis of these preparations, their density did not change. Apparently, under the influence of water, the loose cellulose became compacted, forming a homogeneous structure.

Fig. 1. Change in the specific gravity of various preparations of natural cotton cellulose during their ethanolysis and hydrolysis. Explanations in the text.

During mercerization of the original cotton cellulose (Fig. 1, 6), its specific gravity decreases to 1.523. During subsequent ethanolysis of this preparation it forms a stable structure with a specific gravity of 1.540, occupying an intermediate position between the original and the milled cellulose.

Fig. 2. Change in the specific gravity of various celluloses during ethanolysis. 1—cotton cellulose, 2—bacterial cellulose, 3—ramie cellulose, 4—wood cellulose

Fig. 3. Change in the specific gravity of viscose silk preparations during

Fig. 3

Figure 3: Fig. 3

ethanolysis and hydrolysis. Specific gravity of the residue after: 1—ethanolysis of viscose silk I, 2—ethanolysis of viscose silk II, 3—hydrolysis of viscose silk I

Interesting results were obtained in the ethanolysis of various natural celluloses (Fig. 2). The data obtained show that the packing density of different natural celluloses is different.

A great variety in packing density was also established in different batches of viscose silk obtained from spruce cellulose. The results of measuring the specific gravity of two samples of viscose silk during their hydrolysis and alcoholysis are given in Fig. 3.

Comparison of the data obtained, presented in Figs. 1-3, shows that, depending on the method of preparation of the cellulose specimens, they form structures with different initial density, as well as with different behavior in the course of hydrolysis and alcoholysis.

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Note: Figure translations are in progress. See original paper for figures.