SOME REMARKS CONCERNING FLATNESS OF CELLULOSE MICELLES

by

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In a recent paper in this Journal, MUKHERJEE AND WOODS[6] published electron micrographs of the micelles of cellulose sols, obtained by acid degradation of both native and regenerated cellulose. Although a shadowing angle of 1:4 had been used, the ratio of the widths of the micelles and their shadows was not ¼, but about 1, which seemed to prove that the micelles are not rod-like, but tabular. This was in line with the fact that X-ray diagrams of dried films of precipitated micelles showed tangential orientation of the 101-crystal planes. These planes were supposed to be oriented parallel to the largest face and for obvious reasons tabular particles will lie flat when settling down.

However, we cannot accept these facts as conclusive evidence of the tabular form of the micelles.

Firstly WILLIAMS[8] has shown that in the case of 200-mesh screens, filmed with collodion, the local shadowing angle may vary by as much as 20–40 % over one grid opening while using a shadowing angle of about 1:2. Much greater variation is to be expected if a 1:4 angle is used. Therefore, for precise measurement of the shadow width the shadowing angle must be determined locally *e.g.* with polystyrene latex particles. This was not done. Many small round particles, accidently present in the electron micrographs of MUKHERJEE AND WOODS and also a big one in Fig. 6 of that paper, throw a shadow of not much greater width than their diameters. These particles might all be flat, but this is not very likely and one is inclined to believe that the shadowing angle in reality was often closer to 1:1.5 than to 1:4 angle adopted.

Secondly, the observed tangential orientation of the 101 crystal plane in precipitates of the cellulose sol is no proof of micelle flatness either. It may equally well be explained along the same lines as FREY-WYSSLING[1] explains the same phenomenon in dried films of native cellulose, viz. with a tendency of rod-like micelles to aggregate with the 101^{-}-planes facing each other.

Thirdly, according to RÅNBY's[7] extensive measurements, the fibrils of ultrasonically desintegrated plant cellulose have a mean thickness of 77–88 A, which is at variance with a mean micelle width of 130 A as measured by MUKHERJEE AND WOODS, unless the fibrils are supposed to be flat too. This has in fact been claimed already[5], but it has not been accepted since there was more evidence to the contrary. Fibrils will undoubtedly twist along their axis and, if flat, will produce a shadow, locally varying in width. Usually, however, the shadow is uniform.

With regenerated cellulose a tabular shape of the crystallites has already been claimed by several authors[3,4]. KRATKY *et al.*[4] base their conclusion on the greater intensity of the small angle scattering in the direction perpendicular to the 101-plane. However, if HEYN[2] is right in deducing that in cellulose the period of the small angle scattering does not indicate the mean crystal-size, but the mean distance between the crystallite centres, then the phenomenon described by KRATKY *et al.* might also be due to a smaller mean distance between the surfaces of rod-like crystallites in the direction perpendicular to the 101-plane as compared with their mean distance parallel to this plane. This is a rather probable structure, since the cellulose film had been obtained by drying cellulose gel on a glass plate. The shrinkage was confined to one dimension.

HERMANS[3] based his conclusion on a theoretically too low intensity of the 101 X-ray interference as compared with that of the 101^{-} plus 002 interferences. In native cellulose the ratio was as could be expected with rod-like crystallites. However, since MUKHERJEE AND WOODS (*l.c.*) did not find any difference in shape of the micelles of these types of cellulose, one is left in doubt.

MUKHERJEE AND WOODS have projected further work on these lines and we hope that they will produce evidence refuting our criticism.

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Received November 24th, 1953