LETTERS TO THE EDITORS

The Editors do not hold themselves responsible for opinions expressed by their correspondents. No notice is taken of anonymous communications.

Molecular Weight of Native Cellulose

THE molecular weight of cellulose is of great interest to cellulose chemistry, and many attempts have been made to determine it. The cellulose derivatives, esters and ethers, can in general be dissolved in simple organic solvents, and their molecular weights determined by the osmotic pressure method. It is questionable, however, if the derivatives can be prepared without degradation of the cellulose molecule. Therefore the study of cellulose in cuprammonium solutions is of very great interest. It has never been possible to carry out osmotic measurements of these solutions, owing to their high vapour pressure and the difficulties of membrane materials. Staudinger¹ has extrapolated his 'viscosity rule' from measurements of relatively low molecular weight materials and obtained degrees of polymerization of 2,000–3,000 for native cotton and ramie. Sedimentation equilibrium measurements were performed by Kraemer², who obtained values up to 1,300 for purified cotton linters, and estimated the molecular weight of native cellulose to be at least 570,000 (D.P. 3,500). Later, Mosimann³ showed that sedimentation equilibrium experiments with filament molecules (nitrocelluloses) of very high molecular weights give doubtful results owing to swelling-pressure effects.

We have measured the sedimentation and diffusion velocities of different celluloses in cuprammonium solution. The complexity of the solution and the thread-like shape of the cellulose molecules make the measurements difficult. In order to achieve reliable results it is necessary to extrapolate sedimentation and diffusion measurements to zero concentration of cellulose. Both sedimentation and diffusion of these highly asymmetrical molecules are strongly affected by concentration. On dilution, the sedimentation velocity increases and the diffusion velocity decreases. The sedimentation velocity at free sedimentation (zero concentration) may be graphically extrapolated. By experience it has been found that the concentration function obeys approximately the formula

$$s = \frac{s_0}{1 + kc'}$$

where s is the sedimentation constant determined at the concentration c , k is a constant and s_0 is the sedimentation constant at complete dilution. The diffusion constant at zero concentration may be determined from a single experiment by using the Boltzmann equation⁴. The diffusion constant has been found to be almost linearly dependent on concentration.

For calculation of molecular weights the formula

$$M = \frac{RTs}{D(1 - \bar{V}\rho)}$$

(Svedberg⁵) has been used. This formula is independent of the shape of the molecules. The partial specific volume $\bar{V}$ of cellulose in cuprammonium solution was determined by Stamm⁶ to be 0.642. Refractive index measurements have made it very probable that one copper atom is bound to every glucose unit. The cellulose copper complex has a lower specific volume than pure cellulose, and by taking

the copper ion radius into consideration it was calculated to be 0.485.

All experiments were performed in a purified nitrogen atmosphere, and special arrangements were made for complete exclusion of air when filling centrifuge and diffusion cells. The results for different celluloses are given in the accompanying table.

Cellulose	$s_0=0$	$D_0=0$	M (cellulose)	D.P.
Unbleached cotton linters	10.7	0.23	1.50×10^6	9,200
Raw Georgia cotton	10.4	0.33	1.00	6,200
Nettle fibre cellulose	13.7	0.25	1.76	10,800
Ramie	10.3	0.18	1.84	11,300
Sulphite wood pulp	6.2	0.43	0.46	2,900

The sedimentation constants are given in Svedberg units (10^{-13} cm./sec. dyne), the diffusion constants in units of 10^{-7} cm.²/sec.

It will be noticed that the molecular weights reported here are appreciably higher than those earlier reported for cellulose. For comparison, viscosity measurements were made. The results are given in the accompanying diagram. From this it is obvious that our results do not correspond to Staudinger's hypothesis of a linear relation between relative viscosity and molecular weight. At least for these giant molecules, the molecular weight increases very much faster than viscosity. From the sedimentation data it can also be deduced that the longer the molecules are, the more do they tend to become curled.

The free native celluloses in seed hairs and bast fibres have larger molecules than the prepared wood pulp. If wood is treated directly with cuprammonium, some of the cellulose goes into solution, and its sedimentation constant is about 8, suggesting a D.P. about 5,000.

The investigations are in progress, and full details will be published elsewhere. Financial support has been received from the Royal Swedish Institute for Engineering Research, the Rockefeller Foundation and the Wallenberg Foundation.

NILS GRALÉN.
THE SVEDBERG.

Institute of Physical Chemistry,
University of Uppsala.
Sept. 11.

¹ Staudinger and Feuerstein, *Ann. Chem.*, **526**, 72 (1936).

² Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

³ Mosimann, *Helv. Chim. Acta*, **26**, 369 (1943).

⁴ Boltzmann, *Ann. Phys.*, **53**, 959 (1894).

⁵ Svedberg and Pedersen, "The Ultracentrifuge" (Oxford, 1940).

⁶ Stamm, *J. Amer. Chem. Soc.*, **52**, 3047 (1930).