5 Equilibrium and Kinetic Rigidity of the Cellulose Macromolecular Chain and Some of its Derivatives in Solution

Cellulose and its derivatives are the classic examples of macromolecules characterized by enhanced skeleton rigidity. This property is directly deduced from the configuration of its molecular chain presented in Fig. II.30. In order to calculate the statistic dimensions of the chain, its monomer unit can be substituted by an equivalent "effective" unit [68] consisting of two parallel bonds $b = 2.7 \text{ Å}$ around which the rotation takes place and a single bond $d = 1.45 \text{ Å}$ perpendicular to the two previous ones where rotation is excluded. It has been shown, using this scheme, [68] that, for a rather long chain on full freedom of rotation around O–C$_1$ and O–C$_4$ bonds, the mean square distance between its ends $h_f^2$ is equal to

$$h_f^2 = P \left[ d^2 + (2b)^2 + (1 + \cos v)/(1 - \cos v) \right]$$

where $P$ is the number of monomer units in the chain, $(\pi - v)$ is the valent angle between adjacent bonds O–C$_1$ and O–C$_4$. Substituting $b$ and $d$ values and assuming $v = 70^\circ$ we obtain $h_f^2 = 62P \times 10^{-6}$ and for a segment length of cellulose chain with full freedom of rotation.

$$A_f = h_f^2/P = h_f^2/(2b \cos v/2 + \sin v/2) = 12 \text{ Å}$$

This value corresponds to the number of glucoside units in the segment $S_f = 2.5$. In the case of the carbon chain polymer free of cycles in the chain, a similar calculation [69] affords $A_f = 3.8 \text{ Å}$ provided full freedom of rotation. Thus, even with full freedom of rotation the length of the segment of cellulose chain exceeds by more than 3 times that of flexible carbon chain (aliphatic) polymers, demonstrating the increased skeleton rigidity of cellulose derivatives.

The rigidity of polymer molecules is usually defined on the basis of their hydrodynamic properties in the solutions. It follows from analysis of dependence of coefficients of sedimentation ($S$), diffusion $D$ and intrinsic viscosity $[\eta]$ with the molecular weight $M$. The most widespread forms of these dependences are the empirical Mark–Kuhn expressions:

$$[\eta] = K \times M^a$$
$$D = K_D \times M^{-\beta}$$
$$[S] = K_s \times M^{1-\beta}$$
5.1 Hydrodynamic Properties of Cellulose Derivatives

When measurements are carried out in $\theta$-conditions i.e. without excluded volume effect, the high $\alpha$ and $\beta$-values demonstrate the significant influence of the permeability effect and thus may show the enhanced rigidity of the molecular chain. It is important that in many cases the excluded volume effect for rigid chain molecules does not play a significant role and it can be neglected in the first approximation [70]. The theory of hydrodynamic properties of persistent (wormlike) chains can be applied for evaluation of chain rigidity [71, 72]. In the area of rather high molecular weight when a molecule can be represented by a Gauss chain, this theory leads to the expressions

$$M/[\eta] = \Phi^{-1}(M/LA)^{3/2}M^{1/2} + 0.93[\ln(A/d) - 1.43]$$

$$\times (M/L)^2 A^{-1}$$  \hspace{1cm} (5.5)$$

$$DM/RT = (1.8433\pi \eta_0 N_A)(M/LA)^{1/2}M^{1/2} + (3\pi \eta_0 N_A)^{-1}$$

$$\times (M/L)[\ln A/d - 1.43]$$  \hspace{1cm} (5.6)$$

Apart from $L$ (contour chain length) and $A$ (length of statistic Kuhn segment) values, which characterize conformation and rigidity of the chain, the above formulas also contain the diameter $d$ of persistent chain, which should be taken into account for the proper description of its hydrodynamic properties.

One can see considering the left side of Eqs. (5.5) and (5.6) as function $M^{1/2}$ that the corresponding dependence is linear and one can determine the $M/L$-value on the basis of the curve slope — i.e. estimate the chain rigidity and $A/d$ value on the basis of segments intercepting at ordinate and thus chain diameter. In the case of small $M$ and significant chain rigidity, which is typical for cellulose type polymers, the role of the second term in the right side of Eqs. (5.5) and (5.6) is increased and this results in an increase of value $\alpha$ to about a unit in expressions for intrinsic viscosity.

5.1 Hydrodynamic Properties of Cellulose Derivatives

Since cellulose itself is soluble only in complex solvents (see for example, [73]) and these solutions are not true ones, information about the structure of cellulose macromolecules in the solution has been mainly obtained by analysis