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Abstract

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HYDRODYNAMIC PROPERTIES OF SEMI-RIGID MACROMOLECULES IN SOLUTION

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Existing theories of the hydrodynamic properties of macromolecules in solution have been developed for very flexible and long chains, modeled by Gaussian coils. In the present work a theory is proposed for the intrinsic viscosity $[\eta]$ and the translational friction constant F of real macromolecules, taking into account their rigidity and finite length.

The general equations for F and $[\eta]$, applicable to chains of arbitrary type, ($^{1-4}$)* are

$$F = \frac{\xi n}{1 + \frac{\xi}{6\pi\eta_0 n} \sum_{p,t=1}^{n}{}' \overline{(1/r_{pt})}}, \tag{1}$$

$$[\eta] = \frac{N_A \overline{R^2}\, n\xi}{6M\eta_0 \left[1 + \frac{4\xi}{9\pi\eta_0 n^2} \sum_{t=1}^{n/2_i} \sum_{p=1}^{n}{}' (n-2p)\, \overline{(1/r_{pt})}\right]}, \tag{2}$$

where N_A is Avogadro' s number; $\overline{R^2}$ is the mean square radius of gyration of the chain; n is the number of monomer units in it; $M = nM_0$ is the molecular weight of the polymer; ξ is the friction coefficient of a monomer unit; η_0 is the viscosity of the solvent; r_{pt} is the distance between the p-th and t-th monomer units, and the averaging is carried out over all conformations of the chain. Using as the distribution function of r_{pt} a linear combination of Gaussian and δ-functions (^{12}), which gives the correct values of $\overline{r_{pt}^2}$ and $\overline{r_{pt}^4}$ for a wormlike chain (^{13,14}), we obtain $\overline{(1/r_{pt})} = \psi(x)/\sqrt{\overline{r_{pt}^2}}$, where $\psi(x) = 0.4270 + 0.5730[45x^2 - 156x +$

$$+214 - 54(4+x)e^{-x} + 2e^{-3}]/[27(x - 1 + e^{-x})^2].$$

Substituting these expressions into equations (1) and (2), we obtain

$$A \equiv \frac{6\pi\eta_0 n}{F} = \frac{1}{r_0} + \frac{8f(\lambda, n)}{\sqrt{3\pi}} \frac{n^{1/2}}{b\sqrt{\lambda}}, \tag{3}$$

$$f(\lambda, n) = \frac{\sqrt{6\pi}}{8} \frac{1}{\sqrt{\lambda}\, n^{3/2}} \sum_{k=1}^{n-1} \frac{(n-k)\psi(k/\lambda)}{\sqrt{k/\lambda - 1 + \exp(-k/\lambda)}}; \qquad (4)$$

$$[\eta] = \Phi \frac{(6\overline{R^2})^{3/2}}{M}, \qquad (5)$$

$$\Phi = \frac{\Phi_0}{\left[\varphi(\lambda, n) + \frac{45}{32}\sqrt{\frac{2\pi}{3}}\, \frac{1}{3-\sqrt{2}}\, \frac{b}{r_0}\right] \sqrt{\frac{\lambda}{n}}\, \chi^{1/2}(n/\lambda)}; \qquad (6)$$

$$\Phi_0 = N_A \left(\frac{\pi}{3}\right)^{3/2} \frac{45}{64(3-\sqrt{2})} \simeq 2.86 \cdot 10^{23}\ \mathrm{mol}^{-1}; \qquad (7)$$

* The nonrigorous equation (2) gives results practically coinciding with those of rigorous theories $(^{5-11})$.

$$\chi\left(\frac{n}{\lambda}\right) = \frac{3\overline{R^2}}{b^2 \lambda n} = 1 - \frac{3}{(n/\lambda)^3}\left[\left(\frac{n}{\lambda}\right)^2 - 2\left(\frac{n}{\lambda} - 1 + e^{-n/\lambda}\right)\right]; \qquad (8)$$

$$\varphi(\lambda, n) = \sqrt{\frac{\pi}{3}}\, \frac{15}{4(3-\sqrt{2})}\, \frac{1}{\sqrt{\lambda}\, n^{5/2}} \left\{ \sum_{k=1}^{n-1} \frac{(k^2 + k - nk - 2n)\, \psi(k/\lambda)}{\sqrt{k/\lambda - 1 + \exp(-k/\lambda)}} + \sum_{k}^{n/2-1} \frac{(n^2/2 - 2k^2 + n)\, \psi(k/\lambda)}{\sqrt{k/\lambda - 1 + \exp(-k/\lambda)}} \right\}, \qquad (9)$$

where $\lambda = a/b$; a is the "persistence length" $^{(13)}$; b is the distance between neighboring monomer units; $r_0 = \xi/6\pi\eta_0$. For $n \gg 1$ and any (fixed) λ, formulas (3)–(9) pass into the corresponding formulas for Gaussian coils$^{(5,6)}$.

In Figs. 1 and 2, where the functions $f(\lambda, n)$ and $\varphi(\lambda, n)$ are given, it is seen that for an infinitely flexible coil ($\lambda = 0$) $f(\lambda, n)$ and $\varphi(\lambda, n)$ are appreciably smaller than unity if n is not very large, i.e., the finiteness of the chain lowers both these functions. At fixed n, or at a fixed number of statistical segments in the chain n/λ, $f(\lambda, n)$ and $\varphi(\lambda, n)$ increase with increasing λ, i.e., the rigidity of the chain increases these functions. At $\lambda \cong 4$ (which corresponds to the rigidity of most so-called flexible polymers$^{(15)}$) compensation of both factors takes place, so that in this case the hydrodynamic properties of the polymer obey the Kirkwood–Riseman equations$^{(5,6)}$ down to very low n. This explains, in particular, the fact noted in $^{(16)}$, according to which, at the same number of statistical segments, short molecules of polyvinyl chains obey the Kirkwood–Riseman equations appreciably better than long cellulose molecules.

Fig. 1. Dependence of the function $f(\lambda, n)$ on n. Numbers at the curves are the values of λ.

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Fig. 2. Dependence of the function $\varphi(\lambda, n)$ on n. Numbers at the curves are the values of λ.

Figure 2: Fig. 2. Dependence of the function $\varphi(\lambda, n)$ on n. Numbers at the curves are the values of λ.

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From formulas (3), (5), and (6) it follows that λ and r_0 can be determined from the slope and initial ordinate of the dependence of A on $f(\lambda, n)n^{1/2}$, or of $2^{3/2}\Phi_0(b^3/M_0)(n/[\eta])\chi(n/\lambda)$ on $\varphi(\lambda, n)n^{1/2}$. In doing so, for the treatment of experimental

the data one must apply the trial method, i.e., seek the λ that leads to self-consistent results. By this method we found from $S(M)$ for trinitrocellulose in ethyl acetate (16) and acetone (17), respectively, $r_0 = 3.5$ Å, $\lambda = 55$ and $r_0 = 2.7$ Å, $\lambda = 32$, and from $[\eta](M)$ for the latter system (17), $r_0 = 5$ Å, $\lambda = 26$. Thus, the proposed theory makes it possible in this case to obtain a reasonable value of r_0, and from viscosity data—molecular dimensions close to those obtained from light scattering ($\lambda = 22.5$ (16,18)).

It follows from equations (3)–(6) that, for reasonable values of $r_0(\sim b/2)$, the chain stiffness is responsible for the deviation of Φ and $P \equiv F/(6\overline{R^2})^{1/2}\eta_0$ from their limiting values Φ_0 and $P_0 = (3\pi)^{3/2}/2^{1/2}$ to no lesser degree than the hydrodynamic permeability for the solvent. The quantity $\Phi^{1/3}P^{-1}$ deviates only slightly from $\Phi_0^{1/3}P_0^{-1}$. In the case of hydrodynamically impermeable molecules ($\sqrt{n/\lambda}\, r_0/b \gg 1$), $F \sim n^{1/2}f(\lambda, n)$ and $[\eta] \simeq n^{1/2}\chi(n/\lambda)/\varphi(\lambda, n)$, i.e., the stiffness of the macromolecules increases the exponents b and especially a in the equations $[\eta] \sim M^a$ and $F \sim M^b$.

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

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