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# Rheology of Dilute Solutions of Rod-Like Macromolecules[1]

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The rheological properties of dilute solutions of rod-like macromolecules are treated on the basis of a new model of macroparticle dynamics. Calculations are presented of the rigidity modulus, the shear viscosity, and the first and second normal stresses.

**KEY WORDS:** non-Newtonian fluid; rheology; solutions; viscometric functions.

## 1. INTRODUCTION

In recent years, there has been a resurgence of interest in the dynamical and rheological properties of solutions of axisymmetric molecules. The stores of experimental information on these subjects, although far from complete, have been steadily increasing, and visible progress has been recorded in the ability to describe theoretically the transport and relaxation properties of such solutions.

Because of the extraordinary microscopic complexity of macromolecular systems, the introduction of simplifying approximations and assumptions is unavoidable. Thus, one invariably uses quite crude mechanical models for the macromolecules themselves, for their mutual interactions, and for their interactions with the solvent as well. These models and the mathematical theories based upon them can be judged successful (and potentially useful) provided that only a few experiments are

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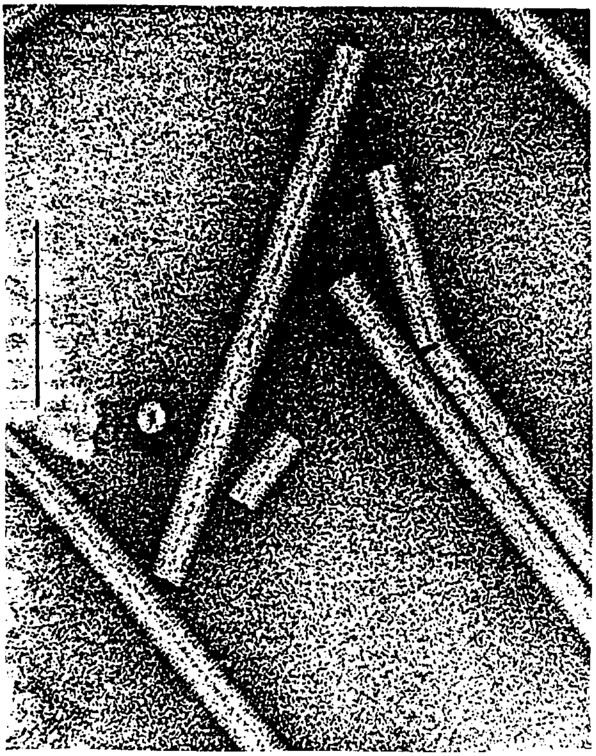
needed to establish the numerical values of whatever adjustable parameters are left unspecified. Once these values have been determined, the theory then can be used to predict the results of other experiments. A model which succeeds in accounting for a single property but fails for all others is obviously inadequate.

In this note, results are reported which we recently have obtained using a relatively simple dynamical model for dilute solutions of rod-like macromolecules. Since details of our theory have been presented elsewhere [1], we present here only a few of our computational results together with the most important of the conclusions that can be drawn from our investigation.

## 2. THE MODEL

In the dilute solutions to which our attention is restricted, the mutual interactions of the solute particles are negligible. In this limit each macromolecule makes its separate contribution to the stress tensor. Thus, the only theoretical requirements are a kinematic model for a single rod-like macromolecule and a description of how its motion will be affected by the solvent in which it is immersed. The best-known way of addressing these questions is based on the two-bead dumbbell model [2] of a macromolecule or on the more elaborate multibead generalization [3]. These models evidently incorporate features which mimic characteristics of real axisymmetric solute particles. According to the theories based upon these models, the rods or springs which connect adjacent beads are without mass and serve only to transmit "backbone" forces from one bead to another. The connecting links are assumed to be "porous" and in no way affect the motion of the solvent. The beads are local centers of mass and of the frictional drag which results from their motions relative to that of the surrounding solvent. The solvent is treated as a (Newtonian) continuum and Stokes' law is used to compute the frictional forces on the beads.

One expects the rod-like polymers to exhibit translational anisotropy. Because the connecting links are porous, the only means by which the linear arrays of beads can acquire this anisotropy is through hydrodynamic interactions among the centers of friction, namely, the beads. A great advantage of the connector-bead models is the relative ease with which these interactions and the associated translational anisotropy can be computed. However, this virtue must be weighed against the discouraging fact that real rod-like macromolecules such as tobacco mosaic virus (TMV), pictured in Fig. 1, do not closely resemble the bead-rod or bead-spring models, exemplified by the porous rods shown in Fig. 2. The interiors of these molecules certainly are not channels through which solvent can freely



$2L = 3000\,\text{A}$

$d = 180\,\text{Å}$

$2m = 6.48 \times 10^{-12}\,\text{g}$

$D_{\text{ROT}} = 350\ \text{s}^{-1}$

$D_{\text{TR}} = 3.4 \times 10^{8}\ \text{Å}^{2}\cdot\text{s}^{-1}$

**Fig. 1.** An electron micrograph of tobacco mosaic virus. [After F. S. Allen, Electro-optics of viruses and bacteriophege, in *Molecular Electrooptics*, S. Krause (ed.) (Plenum, New York, 1981).]

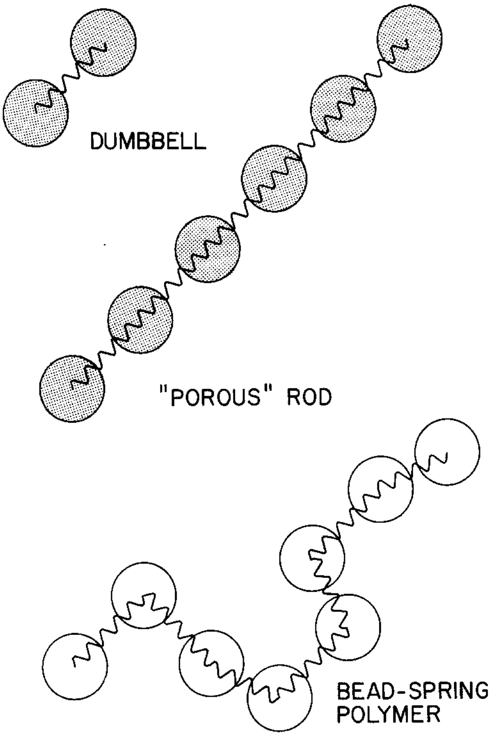


**Fig. 2.** Porous rod models.

flow. Furthermore, in order to calculate the hydrodynamic (Oseen) interactions among the beads—or any other objects—one must specify boundary conditions at the bead–solvent interface. But how is this to be done for a bead surrogate of a portion of a macromolecule such as TMV? Finally, there remains a nagging uncertainty about the applicability of ordinary hydrodynamics very near the surfaces of macromolecules and to the calculation of interactions between closely spaced objects. The inescapable conclusion is that, although the models provide well-defined procedures for computing solvent-transmitted interactions between different parts of the macromolecule, the numerical results of any such computations must be viewed as no more than sensible first approximations to the exact values of quantities which may be as impossible to compute as they are to precisely define.

An alternative approach has been developed by Brenner *et al.* [4] as well as by others. The idea is to model the macroparticles as rigid axisymmetric bodies and compute their translational anisotropic (and rotational mobilities, as well) using macroscopic fluid mechanics. An appealing feature of this approach is that the surface geometries of the models more closely resemble those of real macromolecules than do the surfaces associated with the bead-connector models. However, the issue of boundary conditions and the possible inapplicability of conventional fluid mechanics are as much parts of this theory as they are of its connector-bead counterpart. As far as we are aware this second approach has not been subjected to experimental tests. However, our own calculations [1] do cast doubt upon the accuracy of macroscopically derived formulas for the mobilities of rod-like macromolecules.

Our model for a rod-like particle incorporates some of the more desirable features from both of the previously described models. We picture the macromolecule as a stiff rod of uniform mass density with different translational properties in directions transverse and parallel to its axis. The solvent velocity field is assumed to change only slightly over distances comparable to the length of the particle and to change not at all over distances comparable to its diameter. Thus, the rod-like particle is treated essentially as a "point rod," analogous to the point dipole model used in the theory of dielectrics. There are natural extensions of this model which have not yet been analyzed.

Subject to the assumptions of our model the equations of motion for a rod can be written as follows:

$$m\ddot{\mathbf{R}} = -\boldsymbol{\xi}\cdot[\dot{\mathbf{R}}-\mathbf{w}(\mathbf{R})]+\boldsymbol{\Phi}(\mathbf{R}) \tag{1}$$

$$m\ddot{\mathbf{r}} = -\boldsymbol{\xi}\cdot[\dot{\mathbf{r}}-\mathbf{r}\cdot\nabla_R\mathbf{w}(\mathbf{R})]+2\mathbf{F}(\mathbf{r})+\mathbf{r}\cdot\nabla_R\boldsymbol{\Phi}(\mathbf{R}) \tag{2}$$

Here, $2m$ denotes the mass of the particle, $\mathbf{R}$ the position vector of its center, and $\mathbf{r}$ the vector extending from the center of one-half of the rod to that of the other. The functional form of the rod's friction tensor is $\boldsymbol{\xi}=\xi_{\parallel}\hat{\mathbf{r}}\hat{\mathbf{r}}+\xi_{\perp}(\mathsf{I}-\hat{\mathbf{r}}\hat{\mathbf{r}})$, with $\hat{\mathbf{r}}=\mathbf{r}/|\mathbf{r}|$ denoting the unit vector in the axial direction and $\mathsf{I}$ the unit tensor.

The symbol $\boldsymbol{\Phi}(\mathbf{R})$ signifies the external force on the rod and can, in principle, include its interactions with other rods. $\mathbf{F}(\mathbf{r})$ is the "binding force" of interaction between the two halves of the rod and $\mathbf{w}(\mathbf{R})$ is the solvent velocity. Calculations for elastic and rigid rods must be performed somewhat differently. Here we limit our considerations to rigid rods for which $|\mathbf{r}|=l$ is a constant, equal to one-half of the total length $(L)$ of the macromolecule. We also restrict our attention to homogeneous flows $\mathbf{w}(\mathbf{R},t)=\mathbf{R}\cdot\alpha(t)$ for which the velocity gradient $\alpha=\nabla_R\mathbf{w}(\mathbf{R},t)$ may be a function of time but is independent of spatial location.

The constraint that $|\mathbf{r}|$ be constant reduces the number of degrees of freedom of a rod to three translational and two rotational. The equation of motion [from Eq. (2)] for displacements in directions transverse to the axis $\mathbf{e} \equiv \hat{\mathbf{r}}$ is

$$m\ddot{\mathbf{e}}_\perp = \xi_\perp[\dot{\mathbf{e}}_\perp - \mathbf{e} \cdot \boldsymbol{\alpha}(t)] + \mathbf{e} \cdot \nabla_R \cdot \boldsymbol{\Phi}_\perp(\mathbf{R}) \tag{3}$$

with $\mathbf{a}_\perp = (\mathsf{I} - \mathbf{ee}) \cdot \mathbf{a}$ denoting the transverse part (projection) of the vector $\mathbf{a}$.

We assume the rod–rod interactions to be negligible and that there are no external forces. The stress is then uniform and can be written in the form

$$\begin{aligned} \sigma(t) = ck_\mathrm{B}T\{ &-\mathsf{I} + 3\langle \mathbf{ee} - \tfrac{1}{3}\mathsf{I}\rangle + \kappa\langle \mathbf{eee} \cdot \boldsymbol{\alpha}^* \cdot \mathbf{e}\rangle \\ &- \nu\langle \mathbf{e} \cdot \boldsymbol{\alpha}^* \mathbf{e} \cdot \boldsymbol{\alpha}^* - \mathbf{ee}(\mathbf{e} \cdot \boldsymbol{\alpha}^*)^2\rangle\} \end{aligned} \tag{4}$$

Here $c$ is the number of rods per unit volume, $k_\mathrm{B}$ is the Boltzmann constant, and $\kappa = \xi_\parallel/\xi_\perp$ is a measure of the translational anisotropy. The dimensionless quantity $\nu = D_\mathrm{rot}^2(ml^2/2k_\mathrm{B}T)$ is defined in terms of the rotational diffusion coefficient

$$D_\mathrm{rot} = 2k_\mathrm{B}T/l^2\xi_\perp \tag{5}$$

The quantity $\boldsymbol{\alpha}^* = \boldsymbol{\alpha}(t)/D_\mathrm{rot}$ appearing in Eq. (4) denotes the dimensionless velocity gradient tensor, which for simple shear flow (in the $xz$ plane) is related to the rotary Péclet number $\dot{\alpha}^*(t)$ by the formula $\boldsymbol{\alpha}^* = \dot{\alpha}^*(t)\,\mathbf{n}_x\mathbf{n}_z$, where $\mathbf{n}_i$ is the unit vector in the direction of the coordinate axis $i$.

Finally, the bracket $\langle \cdots \rangle$ indicates orientational averaging over a rod distribution function $f(\mathbf{e}, t)$ which satisfies the kinetic equation

$$D_\mathrm{rot}^{-1}\,\partial_t f(\mathbf{e}, t) = (S_0 + \delta S)\, f(\mathbf{e}, t) \tag{6}$$

wherein

$$S_0 = \nabla_e^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{7}$$

and

$$\begin{aligned} \delta S &= 3\dot{\alpha}^*(\mathbf{e} \cdot \mathbf{n}_x)(\mathbf{e} \cdot \mathbf{n}_z) - \dot{\alpha}^*(\mathbf{e} \cdot \mathbf{n}_x)(\mathbf{n}_z \cdot \nabla_e) \\ &= \dot{\alpha}^* \sin\phi\left(3\sin\theta\cos\theta - \sin^3\theta\,\frac{\partial}{\partial\cos\theta}\right) \end{aligned} \tag{8}$$

## 3. TESTING/PREDICTIONS OF THE THEORY

Our formula given by Eq. (4) is a generalization of the expression for the single-particle contributions to the stress which was employed by Doi and Edwards [5] and by Jain and Cohen [6]. The formula which these authors used is obtained from Eq. (4) by setting $\kappa = 1$ and $\nu = 0$. This limiting form of Eq. (4) is identical to the expression obtained by Bird *et al.* [2] for a dilute solution of rigid dumbbells. While the term proportional to $\nu$ is usually negligible ($\nu = 2 \times 10^{-8}$ for TMV), the viscometric functions depend sensitively on the value of the parameter $\kappa$, $0 \leqslant \kappa \leqslant 1$. For the TMV solutions considered here, the experimental value of $\kappa$ is 0.313.

In recent calculations performed by Doi and Edwards [5] and by Kuzuu and Doi [7], the task of computing the fourth rank tensor $\langle \mathbf{eeee} \rangle$ was obviated by discarding all but the first and second terms from Eq. (4). Jain and Cohen [6] and Dahler *et al.* [8] obtained much better agreement with experiment (for PBLG in *m*-cresol) at high rates of shear by retaining the third term, with $\kappa = 1$. All of these studies used a semiempirical procedure due to Doi and Edwards [5] which corrects for polymer interactions by introducing a concentration-dependent rotational diffusion coefficient. The calculation of Dahler *et al.* [8] incorporated hydrodynamic screening as well.

The fourth rank tensor $\langle \mathbf{eeee} \rangle$ can be eliminated from Eq. (4) by invoking the relationship

$$D_{\text{rot}}^{-1} \frac{d}{dt} \langle \mathbf{ee} \rangle - [\alpha^{*T} \cdot \langle \mathbf{ee} \rangle + \langle \mathbf{ee} \rangle \cdot \alpha^{*}] = 2[\mathbf{I} - 3\langle \mathbf{ee} \rangle] - 2\langle \mathbf{eee} \cdot \alpha^{*} \cdot \mathbf{e} \rangle \tag{9}$$

which follows directly from the kinetic equation (6). Here $\alpha^{*T}$ denotes the tensor transpose of $\alpha^{*}$. The relationship (9) allows us to transform the stress tensor expression (6) into the computationally convenient Giesekus form

$$\sigma(t) = ck_{\text{B}} T \Big\{ -(2-\kappa)\,\mathbf{I} + 3(1-\kappa)\langle \mathbf{ee} \rangle + \tfrac{1}{2}\kappa[\alpha^{*T} \cdot \langle \mathbf{ee} \rangle + \langle \mathbf{ee} \rangle \cdot \alpha^{*}] - \nu\langle \mathbf{e} \cdot \alpha^{*}\mathbf{e} \cdot \alpha^{*} - \mathbf{ee}(\mathbf{e} \cdot \alpha^{*})^{2} \rangle - \tfrac{1}{2}\kappa D_{\text{rot}}^{-1} \frac{d}{dt} \langle \mathbf{ee} \rangle \Big\} \tag{10}$$

This stress tensor and the associated viscometric functions are simple to compute only in the linear response (l.r.) approximation. Thus, with $\boldsymbol{a}(t)=\boldsymbol{a}_0(\omega)\exp(i\omega t)$, we find that

$$\boldsymbol{\sigma}^{\text{l.r.}}(\omega)= -\mathsf{I}2\pi ck_{\mathrm{B}}T\,\delta(\omega)+\frac{1}{18}c\xi_{\parallel}l^2\mathsf{I}\;Tr\boldsymbol{a}_0(\omega)$$
$$+\left[\frac{1}{30}c\xi_{\parallel}l^2+\frac{3}{5}ck_{\mathrm{B}}T\frac{1}{i\omega+6D_{\mathrm{rot}}}\right]\left[\boldsymbol{a}_0(\omega)+\boldsymbol{a}_0^T(\omega)-\frac{2}{3}\mathsf{I}Tr\boldsymbol{a}_0(\omega)\right] \tag{11}$$

From this one concludes that the shear viscosity contribution of the rods is

$$\delta\eta(\omega)=\frac{1}{30}c\xi_{\parallel}l^2+\frac{3}{5}ck_{\mathrm{B}}T(i\omega+6D_{\mathrm{rot}})^{-1} \tag{12}$$

that the corresponding contribution to the coefficient of bulk viscosity is

$$\delta\eta_{\mathrm{b}}(\omega)=\frac{1}{18}c\xi_{\parallel}l^2 \tag{13}$$

and that the Trouton (elongational) viscosity is related to the coefficient of shear viscosity by

$$\eta_T(\omega)=3\delta\eta(\omega) \tag{14}$$

The two rigidity moduli are given by the formulas

$$[G'(\omega)]=\frac{3}{5}\left(\frac{k_{\mathrm{B}}T}{m}\right)\frac{(\omega/6D_{\mathrm{rot}})^2}{1+(\omega/6D_{\mathrm{rot}})^2} \tag{15}$$

and

$$[G''(\omega)]=\frac{2}{5}\left(\frac{k_{\mathrm{B}}T}{m}\right)(\omega/6D_{\mathrm{rot}})\left[\kappa+\frac{3}{2}\frac{1}{1+(\omega/6D_{\mathrm{rot}})^2}\right] \tag{16}$$

These moduli are plotted in Fig. 3 as functions of the dimensionless frequency $\omega^*=\omega/6D_{\mathrm{rot}}$, for a number of values of the anisotropy parameter $\kappa$. The theoretical results have been tested against experimental data for TMV solutions. The tobacco mosaic virus particle is a good example of a rigid-rod macromolecule: its length is $2l=3000$ Å and its diameter is $d=180$ Å. The measured values of its rotational and translational diffusion coefficients are[10] $D_{\mathrm{rot}}=350\pm3.05\ \mathrm{s}^{-1}$ and $D_{\mathrm{tr}}=(3.4\pm0.1)\times10^8\ \text{Å}^2\cdot\mathrm{s}^{-1}$, respectively. These are specific to a water solution at 20°C in the presence of sodium phosphate buffer (pH = 7.5).

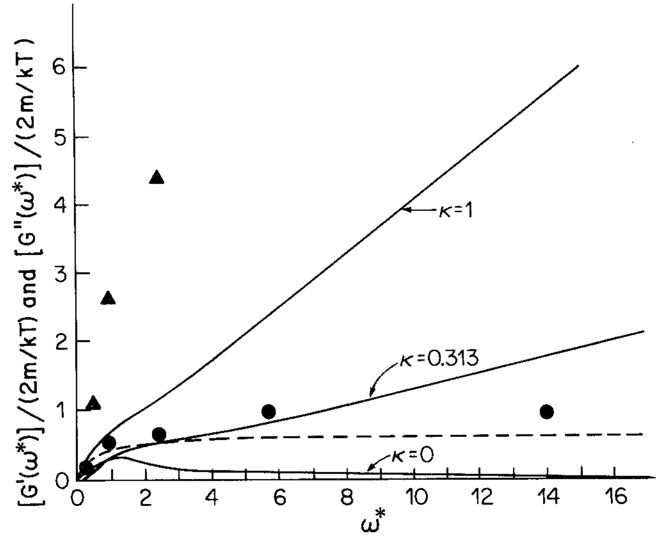


**Fig. 3.** Loss and storage moduli versus reduced frequence $\omega^* = \omega/6D_{\mathrm{rot}}$. The dashed curve and filled circles, respectively, indicate the theoretical predictions and experimental values of $[G'(\omega)](2m/kT)$. The solid curve and filled triangles indicate the $\kappa$-dependent theoretical predictions and experimental values of $[G''(\omega)](2m/kT)$. (After Ref. 1.)

From formula (5) for $D_{\mathrm{rot}}$ and the corresponding expression

$$D_{\mathrm{tr}} = \frac{k_{\mathrm{B}}T}{6}\left[\xi_{\|}^{-1} + 2\xi_{\perp}^{-1}\right] \tag{17}$$

for the translational diffusion coefficient, we conclude that $\xi_{\perp} = 1.03 \times 10^{-6}\,\mathrm{g \cdot s^{-1}}$ and $\xi_{\|} = 3.22 \times 10^{-7}\,\mathrm{g \cdot s^{-1}}$. Consequently, the "experimental value" of the anisotropy parameter is $\kappa = 0.313$.

From these data and the mass[11] $2m = 6.48 \times 10^{-12}$ g of a TMV particle, we obtain a theoretical estimate of $22\,\mathrm{cm^3 \cdot g^{-1}}$ for the intrinsic viscosity

$$[\eta] = \frac{k_{\mathrm{B}}T}{30mD_{\mathrm{rot}}\eta_0}(1.5 + \kappa) \tag{18}$$

This value differs by approximately 25% from the experimentally observed value of $27\,\mathrm{cm^3 \cdot g^{-1}}$. The difference may be due, at least in part, to the fact that we have used for $\eta_0$ the viscosity of pure water, whereas the experiments were done for buffered sodium phosphate solutions.

The experimental measurements and theoretical predictions of the rigidity moduli are displayed in Fig. 3. There is little more than qualitative agreement between the two. The high-frequency asymptotic limit of the storage modulus is equal to the Kirkwood–Auer result $\lim_{\omega\to\infty}[G'(\omega)](2m/k_B T) = 3/5$, but the experimental value is 0.99. Similarly, the asymptotic limit of the loss modulus is given by the expression $\lim_{\omega\to\infty}[G''(\omega)](2m/\omega^* k_B T) = (2/5)\,\kappa$. The numerical value of this quantity is 0.2 for the Kirkwood–Auer theory ($\kappa = 0.5$), and our estimate, based on $\kappa = 0.313$, is 0.13. The experimental value [9] of approximately 3 is far greater than either of these predictions.

The large discrepancies between the experimental results and the predictions of linear response theory may indicate that the simple diffusion-type theories currently used by most rheologists are incapable of providing quantitative predictions of polymer transport coefficients. Although we doubt that this is so, more refined measurements of the rigidity moduli are needed before a final conclusion can be drawn.

In order to compute the non-Newtonian response of the fluid, the kinetic equation (11) must be solved for large rates of shear. We have examined the nonlinear response of a rod-polymer solution to the time-independent rate of strain $a = \dot{\alpha} n_x \mathbf{n}_z$. An approximate solution of the kinetic equation was obtained using the projection operator technique. This solution was then used to compute numerical values of the shear viscosity coefficient and of the two normal stresses. The results of these calculations are summarized in Figs. 4–6. The shear viscosity increment $\delta\eta$

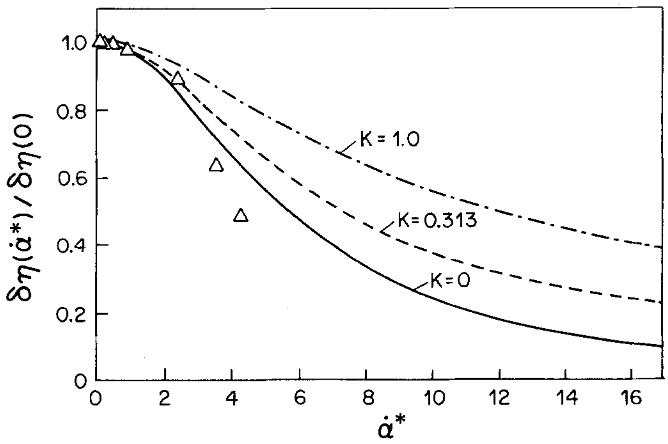


**Fig. 4.** The variation $\delta\eta(\dot{\alpha}^*)/\delta\eta(0)$ of the shear viscosity with the rotary Péclet number $\dot{\alpha}^* = \dot{\alpha}/D_{\rm rot}$. The open triangles represent experimental values. (After Ref. 1.)

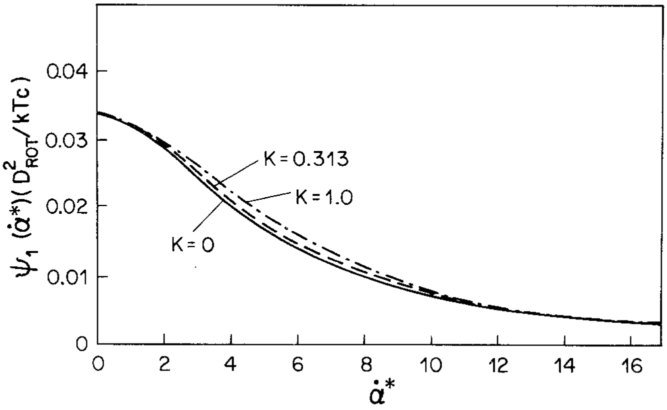


**Fig. 5.** The first normal stress coefficient $\psi_1(\dot{\alpha}^*)(D^2_{\text{rot}}/kTc)$ versus $\dot{\alpha}^*$. (After Ref. 1.)

is compared with the experimental data of Wada [12]. No experimental measurements of the normal stresses have been reported.

At low values of the rotary Péclet number $\dot{\alpha}^* = \dot{\alpha}/D_{\text{rot}}$, we obtain the relatively simple expressions

$$\delta\eta(\dot{\alpha}^*) = \frac{ck_{\text{B}}T}{15D_{\text{rot}}}(1.5+\kappa)\left\{1 - \frac{\dot{\alpha}^{*2}}{1.5+\kappa}\frac{1}{7}\left[\frac{19}{60} - \frac{1}{15}\kappa + \frac{3}{2}\nu\right]\right\} \tag{19}$$

$$\psi_1(\dot{\alpha}^*) = \frac{ck_{\text{B}}T}{30D_{\text{rot}}}\left\{1 - 14\nu - \dot{\alpha}^{*2}\frac{1}{105}\left[\frac{841{,}555}{223{,}608} - \frac{1{,}103}{1{,}848}\kappa - 31\nu\right]\right\} \tag{20}$$

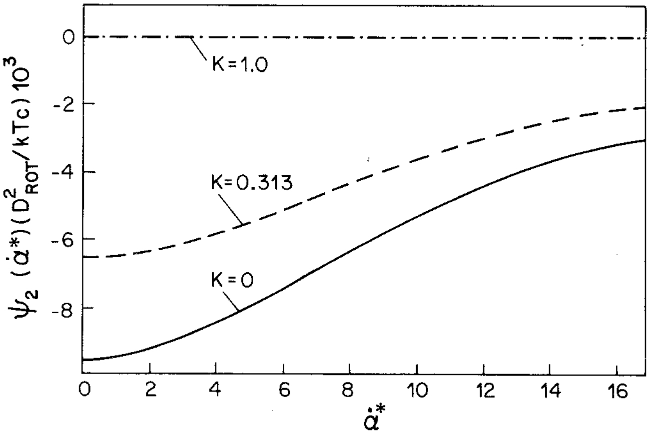


**Fig. 6.** The second normal stress coefficient $\psi_2(\dot{\alpha}^*)(D^2_{\text{rot}}/kTc)\,10^3$ versus $\dot{\alpha}^*$. (After Ref. 1.)

and

$$\psi_2(\dot{\alpha}^*) = \frac{-ck_{\mathrm{B}}T}{105D_{\mathrm{rot}}}\left\{1-\kappa-14\nu-\dot{\alpha}^{*2}\frac{1}{30}\left[\frac{1{,}891}{1{,}617}(1-\kappa)-11\nu\right]\right\} \quad (21)$$

These reduce to the well-known results for the rigid dumbbell model [2] when $\kappa = 1$ and $\nu = 0$.

Our calculations show that the agreement between theory and the data collected by Wada [12] is rather good for rotary Péclet numbers no greater than 4. At higher values of $\dot{\alpha}^*$ the theory underestimates the rate of viscous thinning. This difference may be due to finite concentration effects (Wada did not extrapolate his data to zero particle concentration) or to inadequacies of our approximate solution of the kinetic equation. According to our calculations the first normal stress is a positive definite, monotonically decreasing function of $\dot{\alpha}^*$. It also depends weakly on the anisotropy parameter $\kappa$. The second normal stress is negative semidefinite (vanishing for $\kappa = 1$) and strongly dependent on $\kappa$. It appears to increase monotonically with $\dot{\alpha}^*$ to the asymptotic limit $\psi_2(\infty) = 0$.

## 4. CONCLUDING REMARKS

The model, described in Section 2, appears to be a useful alternative to the conventional multibead model for rigid rod-like macromolecules. Our strategy of using experimental values for the particle mobilities eliminates the need for a theory of the obscure and very difficult to calculate solute–solvent interactions. In this we have followed the example set by the quasihydrodynamical theory of ionic transport in electrolyte solutions. The model parameters once established by this procedure permit us to make predictions of other measurable viscometric properties and this, in turn, allows us to test the consistency of the model. This program has been carried only partially to completion because there are not yet enough reliable experimental data for dilute solutions of rod polymers.

As the polymer concentration increases, so also does the difficulty of devising a realistic microscopic model and an associated, computationally tractable mathematical theory. As far as we are aware, no theory presently exists which is able to account satisfactorily for the effects of finite concentration.

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