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HAROLD A. SCHERAGA

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Non-Newtonian Viscosity of Solutions of Ellipsoidal Particles*

HAROLD A. SCHERAGA
Department of Chemistry, Cornell University, Ithaca, New York

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The specific viscosity, and its dependence on velocity gradient, plays an important role in studies of the structure of macromolecules in dilute solution. A satisfactory theoretical interpretation of the non-Newtonian viscosity of solutions of ellipsoidal particles has been given by Kuhn and Kuhn, and also by Saito, who made use of Peterlin's distribution function for the orientation of particle axes in the streaming liquid and calculated the energy dissipation due to both the hydrodynamic orientation and the Brownian motion. Also, a theory for the non-Newtonian viscosity of solutions of rod-like particles has been developed by Kirkwood. These theories involve extensive computations which have been carried out here with the aid of a computing machine by expressing Saito's results in terms of Legendre coefficients previously evaluated in the related problem of double refraction of flow. As a result, data are available for the dependence of the viscosity factor ν on axial ratio and on the parameter α, where $\alpha=G/\Theta$, G being the velocity gradient in sec^{-1} and Θ being the rotary diffusion constant in sec^{-1}. With these data it will be possible to determine the rotary diffusion constants of ellipsoidal particles from the non-Newtonian viscosity of their solutions, and also to correct viscosity measurements to zero velocity gradient in order to obtain the intrinsic viscosity. Data are also included for the evaluation of Θ from the dependence of ν at $\alpha=0$ on the frequency of periodic shear waves.

INTRODUCTION

THE interpretation of the hydrodynamic properties of solutions of macromolecules has usually been based upon a knowledge of the behavior of reasonable models under the same experimental conditions. If the macromolecule does not possess too much flexibility, as seems to be the case for proteins, the rigid ellipsoid of revolution appears to be a good model. Measurements of two independent quantities permit one to compute the size and shape of a rigid ellipsoid which has the same hydrodynamic properties as the protein.[1] One of these quantities is the intrinsic viscosity, obtainable from the specific viscosity which, in general, depends on the velocity gradient in the flowing solution. The dependence of the viscosity of solutions on the size and shape of the dissolved ellipsoidal particles and on the velocity gradient has been treated by several investigators.[2–8] The dependence on the velocity gradient involves computational problems which have been resolved in the present work with the aid of a computing machine.[9] For this purpose the theory of Saito,[7] making use of the hydrodynamic treatment of Jeffery[2] and the distribution function of Peterlin,[3] is easiest[10] to put into convenient form for computation. The calculation is very similar to that previously carried out for the related problem of double refraction of flow[11] with the aid of the Mark I computer of the Harvard Computation Laboratory, and makes use of some of the results of the previous computations. As a result, data are available for the dependence of the viscosity factor on axial ratio and on velocity gradient. With these data it will be possible to correct experimental measurements to zero velocity gradient to obtain the intrinsic viscosity which is easily related to the particle size and shape, and also to determine the rotary diffusion constants of asymmetrical particles from the dependence of the viscosity on velocity gradient. Thus, such viscosity experiments will provide two hydrodynamic quantities useful in studies of the configurations of proteins in dilute solution.[1]

EXPERIMENTAL OBSERVATION

If a viscous liquid is maintained between two parallel planes of area A, one of which moves relative to the other with a velocity V, the velocity gradient in the liquid will be $G=dV/dr$ in sec^{-1}, where r is taken in a direction normal to the two planes. The viscosity coefficient η_0 of the liquid is a measure of the internal friction which determines the value of the tangential force $\mathfrak{F}$ required to maintain the velocity gradient G between the planes. According to Newton,

$$\mathfrak{F}=\eta_0 GA. \tag{1}$$

This situation is most easily realized experimentally if the liquid is placed in the annular gap between two concentric cylinders of a Couette-type apparatus, and one of the cylinders rotated. If the gap is large G

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[1] H. A. Scheraga and L. Mandelkern, J. Am. Chem. Soc. 75, 179 (1953).
[2] G. B. Jeffery, Proc. Roy. Soc. (London), A102, 161 (1922–23).
[3] A. Peterlin, Z. Physik 111, 232 (1938).
[4] R. Simha, J. Phys. Chem. 44, 25 (1940).
[5] W. Kuhn and H. Kuhn, Helv. Chim. Acta 28, 97 (1945).
[6] J. G. Kirkwood, Rec. trav. Chim. 68, 649 (1949); J. G. Kirkwood and P. L. Auer, J. Chem. Phys. 19, 281 (1951).
[7] N. Saito, J. Phys. Soc. Japan 6, 297 (1951).
[8] B. H. Zimm (private communication) has obtained an asymptotic solution for ellipsoidal particles at very high velocity gradients, and Kirkwood (private communication) has obtained a solution for thin rods as a function of velocity gradient.
[9] These calculations were carried out at the Cornell Computing Center with the aid of an IBM card-programmed calculator under the direction of R. Lesser.
[10] Kuhn and Kuhn (see reference 5) have also given a complete treatment for the dependence of viscosity on velocity gradient for dilute solutions of ellipsoidal particles. See their Eqs. (73) and (74). The equivalence of their treatment and that of Saito (see reference 7) and Kirkwood (see reference 6) has been demonstrated by Saito and Sugita [J. Phys. Soc. Japan 7, 554 (1952)].
[11] Scheraga, Edsall, and Gadd, J. Chem. Phys. 19, 1101 (1951); Annals of the Computation Laboratory of Harvard University, 26, 219 (1951).

varies with r, but if it is small compared with the cylinder radius, the behavior of G approaches that for the ideal case of two parallel planes of infinite extent, where it is constant. The determination of η_0 in the Couette apparatus is carried out by rotating the outer cylinder (the inner one being suspended freely by a torsion wire) and measuring the torque transmitted by the liquid from the outer to the inner cylinder.[12]

If η_0 is independent of G the liquid is said to be Newtonian in its viscous behavior; if η_0 depends on G it is said to be non-Newtonian. If G exceeds a certain critical value in a given experiment the flow becomes turbulent; we are concerned here only with values of G below this critical region so that the flow is laminar. Most pure liquids in laminar flow exhibit Newtonian behavior whereas many solutions of macromolecules are non-Newtonian. Dilute solutions of relatively small and symmetrical molecules like serum albumin approach Newtonian behavior whereas dilute solutions of large asymmetrical molecules like tobacco mosaic virus are non-Newtonian.

The viscosity coefficient defined in Eq. (1) is also a measure of the dissipation of energy in the flowing liquid, the amount of work done in overcoming frictional resistance per unit time per unit volume being $G^2\eta_0$. When large particles are suspended in a flowing liquid made up of small molecules, there is an increased energy dissipation which depends on the size and shape of the dissolved particles.[13] The total energy dissipation per unit time per unit volume[14] in the *solution* is $G^2\eta$.

$$G^2\eta = G^2\eta_0 + n\left\langle\frac{dW}{dt}\right\rangle_{\mathrm{Av}}, \tag{2}$$

where η is the viscosity coefficient of the solution, η_0 is that for the pure solvent, n is the number of particles per unit volume, and $\langle dW/dt\rangle_{\mathrm{Av}}$ is the average increment in rate of energy dissipation per unit volume due to the presence of a single dissolved particle; $G^2\eta_0$ is that part of the energy dissipation due to the solvent when present alone and is assumed to be the same even when the particles are dissolved in the solvent. As a result, η will be greater than η_0. If each ellipsoidal particle has a volume of $v=4\pi ab^2/3$ where a is the semiaxis of revolution and b is the equatorial radius then[14]

$$\left\langle\frac{dW}{dt}\right\rangle_{\mathrm{Av}} = G^2\eta_0 v\nu, \tag{3}$$

where ν is a factor dependent on the shape of the particle. Inserting Eq. (3) in Eq. (2) we obtain[13]

$$\lim_{nv\to 0}\frac{\eta-\eta_0}{nv\eta_0}=\nu, \tag{4}$$

where nv is the volume concentration of the particles in the solution. If, in turn, the data are extrapolated to zero velocity gradient, then $\nu=[\eta]_v$ where $[\eta]_v$ is the intrinsic viscosity for volume concentration. Since concentration is usually expressed as c in g/100 cc and the quantity computed for a protein of molecular weight M is the equivalent hydrodynamic volume V_e, the working form of Eq. (4) will be

$$[\eta]= \lim_{\substack{c\to 0\\ G\to 0}}\frac{\eta-\eta_0}{\eta_0 c}=\left(\frac{N}{100}\right)\left(\frac{V_e}{M}\right)\nu, \tag{5}$$

where N is Avogadro's number and $[\eta]$ is the intrinsic viscosity for concentration in g/100 cc. Since the treatment here is confined to the rigid ellipsoid of revolution model, we are concerned only with the quantity ν for an ellipsoid of volume v. In the special case where the ellipsoid becomes a sphere, ν takes on the Einstein value of 2.5 and is independent of G; such a solution exhibits Newtonian viscous behavior. If the dissolved particles are asymmetrical, then the solution will exhibit non-Newtonian viscosity wherein ν will be larger than 2.5 at zero G and will decrease with increasing G, i.e., $\langle dW/dt\rangle_{\mathrm{Av}}$ decreases as the velocity gradient is increased due to increasing orientation of the asymmetrical particles in the streaming liquid. For any velocity gradient the average increment in rate of energy dissipation per unit volume, due to the presence of the particles, is given by Eq. (3) where ν depends on G and on the axial ratio[14] $p=a/b$. Therefore the factor ν is determinable from a knowledge of $\langle dW/dt\rangle_{\mathrm{Av}}$ as a function of G for particles of a given size and shape in a solvent of viscosity coefficient η_0.

THEORY

The evaluation of the increment in energy dissipation is based on the theory that a solution of ellipsoidal particles in laminar flow is in an equilibrium steady state dependent upon the magnitude of two opposing forces, one arising from the velocity gradient which tends to orient the particles in the direction of the stream lines, the other due to the Brownian motion which tends to produce a random orientation. The Brownian motion may be characterized by a rotary diffusion constant Θ (in sec^{-1}) which depends on the volume and shape of the ellipsoid.[15] To evaluate ν the distribution function $F(\vartheta,\varphi,t)$ for the orientation of the major axes of the

[12] For experimental details and results of viscosity measurements see A. E. Alexander and P. Johnson, *Colloid Science* (Oxford University Press, New York, 1949), Chap. XIII.

[13] In the treatment presented here it is assumed that there is no interaction between dissolved particles and, therefore, no increment in energy dissipation due to such interactions. This situation is realized experimentally by making viscosity measurements at various concentrations and extrapolating to infinite dilution.

[14] It should be pointed out that the notation for p differs among various authors. For example, several authors (see references 1 and 15) have defined p as b/a where a and b have the same meaning as used here.

[15] F. Perrin, J. phys. radium 5, 497 (1934).

particles at any time at a given value of G must first be computed.[16] This has been carried out by Peterlin[3] using Jeffery's[2] hydrodynamic treatment. Once the distribution function is known then $\langle dW/dt\rangle_{Av}$ may be evaluated for any distribution according to Saito's theory.[7,10] We shall thus outline the Jeffery-Peterlin-Saito treatment wherein the quantities required for the evaluation of ν have been obtained by means of a computing machine.

The distribution function for ellipsoidal particles suspended in a continuous liquid medium under the condition of laminar flow obeys the general diffusion equation

$$\frac{\partial F}{\partial t}=\Theta\Delta F-\operatorname{div}(F\omega) \tag{6}$$

where Δ is the Laplacian operator and ω is the angular velocity of the rotating ellipsoid due to the hydrodynamic forces and has been computed by Jeffery as a function of G and R, where

$$R=\frac{p^2-1}{p^2+1}. \tag{7}$$

For a prolate ellipsoid $a>b$, whereas for an oblate one $a<b$. Therefore, $R=1$ for an infinitesimally thin rod, 0 for a sphere, and -1 for an infinitesimally flat disk.

If the particles are relatively small (no dimension greater than 10 000 A), then within a very short time after initiation of the rotation of the cylinder a steady state is reached in which $\partial F/\partial t=0$. For the steady state Peterlin,[3] making use of Jeffery's results for ω, expressed the solution of the diffusion equation in terms of slowly converging series of spherical harmonics.

$$F=\sum_{j=0}^{\infty}R^j\left[\frac{1}{2}\sum_{n=0}^{j}a_{n0,j}P_{2n}\right.$$
$$\left.+\sum_{n=1}^{j}\sum_{m=1}^{n}(a_{nm,j}\cos 2m\varphi+b_{nm,j}\sin 2m\varphi)P_{2n}^{2m}\right]. \tag{8}$$

The Legendre coefficients $a_{nm,j}$ and $b_{nm,j}$ are functions of the parameter $\alpha=G/\Theta$. P_{2n} are spherical functions of $\cos\vartheta$ and P_{2n}^{2m} are their derivatives of order $2m$. Recurrence relations are available[3,11] for computation of these Legendre coefficients. Evaluation of these coefficients gives F as a function of α and R. This distribution function has been used previously for flow birefringence calculations[11] based on the theory of Peterlin and Stuart.[17]

Using this distribution function for the particle orientation as a function of α, Peterlin[3] computed ν by taking into account the energy dissipation due only to the rotation of the particle in the hydrodynamic field. His results were at variance with those of Simha[4] who took into account the energy dissipation arising also from the Brownian motion. Simha's treatment was applied only to the limiting case of $\alpha=0$ where the particles have random orientation due to the Brownian motion and can be considered as rotating with uniform angular velocity. A complete theory for ν as a function of α was finally obtained by Kirkwood and Auer[6] for rods, and by Kuhn and Kuhn,[5] and also by Saito,[7] for ellipsoids.[18] These theories consider that Peterlin's distribution function F correctly describes the orientation of ellipsoidal particles, and that the increment in energy dissipation, $\langle dW/dt\rangle_{Av}$, contains contributions not only from the hydrodynamic orientation but also from the Brownian motion.[19] The result obtained by Saito[7] is

$$\nu=(J+K-L)\int F\sin^4\vartheta\sin^2 2\varphi d\Omega$$
$$+L\int F\sin^2\vartheta d\Omega+M\int F\cos^2\vartheta d\Omega$$
$$+\frac{N}{\alpha}\int F\sin^2\vartheta\sin 2\varphi d\Omega \tag{9}$$

where the coefficients J, K, L, M, N depend *only* on the axial ratio p of the ellipsoid[20] and are defined as follows:

$$\begin{aligned}
J&=\frac{1}{ab^2}\frac{\alpha_0''}{2b^2\alpha_0'\beta_0''},\\
K&=\frac{1}{ab^2}\frac{1}{2b^2\alpha_0'},\\
L&=\frac{1}{ab^2}\frac{2}{\beta_0'(a^2+b^2)},\\
M&=\frac{1}{ab^2}\frac{1}{b^2\alpha_0'},\\
N&=\frac{6}{ab^2}\frac{a^2-b^2}{a^2\alpha_0+b^2\beta_0}.
\end{aligned} \tag{10}$$

[16] See reference 11 for the definition of the coordinate system in the Couette cylinder apparatus.

[17] A. Peterlin and H. A. Stuart, Z. Physik **112**, 1 (1939).

[18] This problem was discussed extensively at the International Rheological Congress, Scheveningen (Holland), 1948, the Proceedings of which have been published.

[19] For further justification that there is a contribution to the energy dissipation from the Brownian motion see Kuhn and Kuhn (reference 5) and also Saito and Sugita (reference 10). An apparent disagreement over the effect of the rotary Brownian motion on the viscosity of solutions of rod-like macromolecules was reported in the discussion following Kirkwood's paper [J. Polymer Sci. **12**, 1 (1954)] which was presented at the Uppsala Symposium on Macromolecules. This disagreement has been resolved by Saito [J. Polymer Sci. **14**, 212 (1954)].

[20] While Eqs. (10) appear to be functions of a and b, rather than of p, the substitution of Eqs. (12) into Eqs. (10) leads to a dependence on only the *ratio* a/b.

The quantities α_0, α_0', α_0'', β_0, β_0', β_0'' are functions of a and b defined by Jeffery.[2]

$$
\begin{aligned}
\alpha_0&=\int_0^\infty \frac{dx}{(a^2+x)^{3/2}(b^2+x)},\\
\beta_0&=\int_0^\infty \frac{dx}{(a^2+x)^{1/2}(b^2+x)^2},\\
\alpha_0'&=\int_0^\infty \frac{dx}{(a^2+x)^{1/2}(b^2+x)^3},\\
\beta_0'&=\int_0^\infty \frac{dx}{(a^2+x)^{3/2}(b^2+x)^2},\\
\alpha_0''&=\int_0^\infty \frac{x\,dx}{(a^2+x)^{1/2}(b^2+x)^3},\\
\beta_0''&=\int_0^\infty \frac{x\,dx}{(a^2+x)^{3/2}(b^2+x)^2}.
\end{aligned}
\tag{11}
$$

Evaluation of these integrals gives

$$
\begin{aligned}
\alpha_0&=\frac{1}{b^3(p^2-1)}\left\{-\frac{2}{p}-A\right\},\\
\beta_0&=\frac{1}{b^3(p^2-1)}\left\{p+\frac{A}{2}\right\},\\
\alpha_0'&=\frac{p^4}{4a^3b^2(p^2-1)^2}\left\{(2p^2-5)-\frac{3A}{2p}\right\},\\
\beta_0'&=\frac{2p^2}{a^3b^2(p^2-1)^2}\left\{1+\frac{p^2}{2}+\frac{3pA}{4p}\right\},\\
\alpha_0''&=\frac{2p^2}{ab^2(p^2-1)^2}\left\{\frac{p^2}{4}+\frac{1}{8}+\frac{(4p^2-1)}{16p}A\right\},\\
\beta_0''&=\frac{2p^2}{ab^2(p^2-1)^2}\left\{-\frac{3}{2}-\frac{(2p^2+1)}{4p}A\right\},
\end{aligned}
\tag{12}
$$

where

$$A=\frac{1}{(p^2-1)^{1/2}}\ln\frac{p-(p^2-1)^{1/2}}{p+(p^2-1)^{1/2}} \quad \text{for prolate ellipsoids } (p>1)$$

$$=\frac{-2\arccos p}{(1-p^2)^{1/2}} \quad \text{for oblate ellipsoids } (p<1).$$

The integrals in Eq. (9) represent mean values of the given trigonometric functions which may be expressed in terms of spherical harmonics and evaluated after F is known.

$$
\begin{aligned}
&\langle\sin^4\vartheta\sin^2 2\varphi\rangle_{\text{Av}}\\
&=\int F\left[\frac{4}{15}P_0-\frac{8}{21}P_2+\frac{4}{35}P_4-\frac{\cos 4\varphi}{210}P_4^4\right]d\Omega\\
&=\frac{4}{15}\left[1+4\pi\sum_{j=1}^{\infty}R^j\left(-\frac{a_{10,j}}{7}+\frac{a_{20,j}}{42}-40a_{22,j}\right)\right].
\end{aligned}
\tag{13}
$$

$$
\begin{aligned}
&\langle\cos^2\vartheta\rangle_{\text{Av}}\\
&=\int F[\tfrac{1}{3}P_0+\tfrac{2}{3}P_2]d\Omega\\
&=\frac{1}{3}\left[1+\frac{4\pi}{5}\sum_{j=1}^{\infty}R^j a_{10,j}\right].
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
&\langle\sin^2\vartheta\rangle_{\text{Av}}\\
&=1-\langle\cos^2\vartheta\rangle_{\text{Av}}.
\end{aligned}
\tag{15}
$$

$$
\begin{aligned}
&\langle\sin^2\vartheta\sin 2\varphi\rangle_{\text{Av}}\\
&=\int F\left[\frac{\sin 2\varphi}{3}P_2^2\right]d\Omega\\
&=\frac{16\pi}{5}\sum_{j=1}^{\infty}R^j b_{11,j}.
\end{aligned}
\tag{16}
$$

Whereas a complete set of Legendre coefficients $a_{nm,j}$ and $b_{nm,j}$ would be required to determine the distribution function F, it can be seen from Eqs. (13) to (16) that, after integration, the only ones which are required for the evaluation of ν are $a_{10,j}$, $a_{20,j}$, $a_{22,j}$, $b_{11,j}$.

RESULTS AND DISCUSSION

As α approaches zero Eq. (9) reduces to the form

$$\nu=r-s\alpha^2\cdots \tag{17}$$

where r and s are constants; i.e., ν shows a quadratic dependence on α with a horizontal tangent at $\alpha=0$.[5,7] As α increases, the complete solution for ν as a function of α in Eq. (9) is obtainable by evaluation of the coefficients $a_{10,j}$, $a_{20,j}$, $a_{22,j}$, $b_{11,j}$ of Eqs. (13) to (16). These coefficients have all been previously computed[11] for values of α up to 200 in connection with the related problem of double refraction of flow. As reported previously,[11] a sufficient number of j-values required to attain the limiting values of the summations appearing in Eqs. (13) to (16) was obtained for $\alpha\leqq 60$. However, for $\alpha>60$, the additional j-values required could not be obtained because of the limited internal storage capacity of the Mark I computer. Therefore, no results are reported here for $\alpha>60$. For $\alpha\leqq 60$ the values obtained are probably accurate to well within 1%.[21]

[21] See the Appendix and also reference 11 for some discussion of the convergence of these series.

TABLE I. Prolate ellipsoids; ν as a function of α for various axial ratios, p.

α \ p	1	2	3	4	5	6	7	8	9	10	12	14	16	18	20	25	50	100	300
0.00	2.500	2.908	3.685	4.663	5.806	7.099	8.533	10.10	11.80	13.63	17.67	22.19	27.18	32.63	38.53	55.19	176.8	593.7	4279
0.25	2.500	2.907	3.683	4.661	5.802	7.094	8.526	10.09	11.79	13.62	17.65	22.17	27.15	32.60	38.49	55.13	176.6	593.0	4274
0.50	2.500	2.906	3.679	4.653	5.791	7.078	8.506	10.07	11.76	13.59	17.60	22.10	27.07	32.50	38.37	54.96	176.0	591.0	4260
0.75	2.500	2.903	3.672	4.641	5.773	7.053	8.474	10.03	11.71	13.53	17.52	22.00	26.94	32.34	38.18	54.68	175.1	587.7	4235
1.00	2.500	2.899	3.663	4.624	5.748	7.019	8.429	9.973	11.65	13.45	17.41	21.85	26.76	32.12	37.91	54.29	173.8	583.2	4202
1.25	2.500	2.895	3.651	4.604	5.717	6.977	8.374	9.904	11.56	13.34	17.28	21.68	26.54	31.84	37.59	53.81	172.1	577.6	4161
1.50	2.500	2.890	3.637	4.579	5.681	6.927	8.310	9.823	11.46	13.23	17.11	21.47	26.28	31.53	37.21	53.25	170.3	571.1	4113
1.75	2.500	2.884	3.621	4.552	5.640	6.872	8.237	9.732	11.35	13.09	16.94	21.24	25.98	31.17	36.78	52.62	168.1	563.8	4059
2.00	2.500	2.877	3.604	4.522	5.596	6.811	8.158	9.633	11.23	12.95	16.74	20.98	25.66	30.78	36.31	51.93	165.8	555.8	4000
2.25	2.500	2.871	3.586	4.490	5.548	6.746	8.074	9.528	11.10	12.80	16.53	20.71	25.32	30.36	35.81	51.20	163.4	547.4	3938
2.50	2.500	2.863	3.566	4.457	5.499	6.678	7.986	9.418	10.97	12.64	16.31	20.43	24.97	29.93	35.29	50.44	160.8	538.5	3873
3.00	2.500	2.848	3.526	4.387	5.396	6.537	7.804	9.190	10.69	12.31	15.86	19.84	24.24	29.03	34.22	48.86	155.5	520.3	3738
3.50	2.500	2.832	3.485	4.316	5.291	6.395	7.619	8.958	10.41	11.97	15.41	19.25	23.49	28.12	33.13	47.26	150.1	501.8	3602
4.00	2.500	2.816	3.444	4.246	5.188	6.254	7.437	8.731	10.13	11.64	14.96	18.67	22.77	27.24	32.07	45.70	144.9	483.8	3470
4.50	2.500	2.801	3.405	4.179	5.089	6.119	7.263	8.514	9.868	11.32	14.53	18.12	22.07	26.38	31.05	44.21	139.9	466.6	3343
5.00	2.500	2.787	3.367	4.115	4.995	5.991	7.097	8.307	9.617	11.03	14.12	17.59	21.41	25.58	30.09	42.80	135.2	450.3	3223
6.00	2.500	2.760	3.299	3.999	4.824	5.759	6.797	7.933	9.162	10.48	13.39	16.64	20.22	24.12	28.35	40.24	126.6	421.0	3007
7.00	2.500	2.738	3.240	3.897	4.675	5.558	6.537	7.608	8.768	10.01	12.75	15.82	19.19	22.87	26.84	38.04	119.2	395.7	2822
8.00	2.500	2.718	3.189	3.810	4.547	5.383	6.312	7.328	8.427	9.608	12.21	15.11	18.30	21.78	25.55	36.14	112.9	374.0	2663
9.00	2.500	2.702	3.145	3.734	4.435	5.232	6.117	7.085	8.132	9.257	11.73	14.49	17.53	20.85	24.42	34.50	107.5	355.3	2527
10.00	2.500	2.688	3.107	3.668	4.338	5.100	5.947	6.872	7.874	8.950	11.32	13.96	16.86	20.03	23.45	33.07	102.7	339.1	2408
12.50	2.500	2.661	3.031	3.536	4.143	4.834	5.603	6.444	7.355	8.332	10.48	12.88	15.51	18.38	21.48	30.21	93.19	306.7	2171
15.00	2.500	2.642	2.975	3.435	3.989	4.623	5.329	6.101	6.936	7.833	9.804	12.00	14.42	17.05	19.90	27.89	85.54	280.7	1983
17.50	2.500	2.629	2.934	3.361	3.880	4.476	5.139	5.866	6.652	7.496	9.350	11.42	13.69	16.17	18.84	26.34	80.43	263.3	1856
20.00	2.500	2.619	2.900	3.300	3.788	4.349	4.974	5.660	6.402	7.199	8.949	10.90	13.05	15.38	17.90	24.98	75.93	248.0	1746
22.50	2.500	2.611	2.874	3.250	3.712	4.245	4.839	5.491	6.198	6.956	8.621	10.48	12.52	14.74	17.13	23.86	72.28	235.7	1657
25.00	2.500	2.605	2.852	3.208	3.647	4.155	4.723	5.346	6.021	6.745	8.337	10.11	12.06	14.18	16.47	22.90	69.12	225.0	1580
30.00	2.500	2.597	2.819	3.142	3.545	4.012	4.536	5.112	5.736	6.406	7.878	9.520	11.32	13.29	15.40	21.35	64.05	207.9	1457
35.00	2.500	2.591	2.795	3.092	3.465	3.900	4.389	4.927	5.511	6.138	7.517	9.054	10.74	12.58	14.56	20.12	60.39	194.5	1361
40.00	2.500	2.587	2.777	3.053	3.401	3.809	4.269	4.776	5.327	5.918	7.220	8.671	10.27	12.00	13.87	19.12	56.80	183.6	1283
45.00	2.500	2.584	2.763	3.021	3.348	3.733	4.167	4.646	5.167	5.728	6.960	8.336	9.847	11.49	13.26	18.24	53.94	174.0	1214
50.00	2.500	2.582	2.752	2.995	3.303	3.667	4.078	4.533	5.028	5.560	6.732	8.039	9.477	11.04	12.73	17.46	51.40	165.5	1154
60.00	2.500	2.579	2.736	2.955	3.232	3.560	3.933	4.345	4.794	5.278	6.344	7.535	8.845	10.27	11.81	16.12	47.04	151.0	1050

From Eq. (7) it can be seen that $R(p) = -R(1/p)$. This transformation from prolate to oblate does not affect the summations in Eqs. (13) to (15) since these a-coefficients have nonzero values only for even powers of j. However, the b-coefficient in Eq. (16) has nonzero values only for odd powers of j. Therefore, the contribution of this term to ν in Eq. (9) is of opposite sign for prolate and oblate ellipsoids (as far as the effect of R^j

TABLE II. Oblate ellipsoids; ν as a function of α for various axial ratios, p.

α \ $1/p$	1	2	3	4	5	6	7	8	9	10	12	14	16	18	20	25	50	100	300
0.00	2.500	2.854	3.431	4.059	4.708	5.367	6.032	6.700	7.371	8.043	9.391	10.74	12.10	13.45	14.80	18.19	35.16	69.10	204.9
0.25	2.500	2.854	3.430	4.058	4.706	5.365	6.029	6.697	7.367	8.039	9.386	10.73	12.09	13.44	14.79	18.18	35.13	69.06	204.8
0.50	2.500	2.853	3.427	4.053	4.700	5.357	6.019	6.686	7.354	8.025	9.369	10.72	12.07	13.42	14.77	18.15	35.06	68.91	204.3
0.75	2.500	2.850	3.422	4.045	4.689	5.344	6.004	6.668	7.334	8.002	9.341	10.68	12.03	13.37	14.72	18.09	34.95	68.68	203.6
1.00	2.500	2.847	3.415	4.034	4.675	5.326	5.983	6.643	7.306	7.971	9.304	10.64	11.98	13.32	14.66	18.01	34.79	68.36	202.7
1.25	2.500	2.844	3.406	4.021	4.657	5.304	5.956	6.613	7.272	7.933	9.257	10.59	11.92	13.25	14.58	17.91	34.59	67.97	201.5
1.50	2.500	2.839	3.396	4.005	4.636	5.278	5.926	6.577	7.231	7.887	9.203	10.52	11.84	13.16	14.49	17.80	34.36	67.51	200.1
1.75	2.500	2.834	3.384	3.988	4.613	5.249	5.891	6.537	7.186	7.837	9.141	10.45	11.76	13.07	14.38	17.67	34.10	66.99	198.6
2.00	2.500	2.829	3.371	3.968	4.587	5.217	5.853	6.493	7.136	7.781	9.074	10.37	11.67	12.97	14.27	17.52	33.82	66.42	196.9
2.25	2.500	2.823	3.358	3.948	4.560	5.183	5.813	6.447	7.083	7.722	9.003	10.29	11.57	12.86	14.15	17.37	33.51	65.82	195.0
2.50	2.500	2.817	3.344	3.926	4.531	5.147	5.770	6.398	7.028	7.660	8.928	10.20	11.47	12.75	14.02	17.22	33.20	65.18	193.1
3.00	2.500	2.804	3.314	3.881	4.471	5.073	5.682	6.296	6.912	7.531	8.772	10.02	11.26	12.51	13.76	16.89	32.54	63.87	189.2
3.50	2.500	2.790	3.283	3.834	4.410	4.997	5.592	6.192	6.795	7.399	8.613	9.830	11.05	12.27	13.49	16.55	31.87	62.53	185.2
4.00	2.500	2.777	3.253	3.788	4.349	4.922	5.503	6.089	6.678	7.269	8.456	9.647	10.84	12.03	13.23	16.22	31.21	61.20	181.2
4.50	2.500	2.764	3.224	3.744	4.290	4.850	5.417	5.990	6.566	7.144	8.304	9.469	10.64	11.80	12.97	15.90	30.57	59.92	177.4
5.00	2.500	2.751	3.196	3.701	4.234	4.781	5.335	5.895	6.458	7.024	8.159	9.299	10.44	11.59	12.73	15.60	29.96	58.70	173.7
6.00	2.500	2.729	3.144	3.623	4.131	4.653	5.184	5.720	6.260	6.803	7.893	8.987	10.08	11.18	12.28	15.04	28.84	56.46	167.0
7.00	2.500	2.709	3.099	3.555	4.040	4.541	5.050	5.566	6.086	6.608	7.657	8.712	9.769	10.83	11.89	14.54	27.85	54.48	161.0
8.00	2.500	2.692	3.060	3.494	3.960	4.442	4.933	5.430	5.932	6.436	7.450	8.469	9.490	10.51	11.54	14.11	26.97	52.73	155.8
9.00	2.500	2.678	3.026	3.442	3.890	4.354	4.829	5.310	5.796	6.284	7.266	8.254	9.244	10.24	11.23	13.72	26.20	51.19	151.2
10.00	2.500	2.666	2.996	3.395	3.827	4.277	4.737	5.204	5.675	6.149	7.103	8.062	9.025	9.990	10.96	13.38	25.51	49.82	147.1
12.50	2.500	2.642	2.936	3.300	3.699	4.117	4.546	4.983	5.424	5.868	6.764	7.665	8.570	9.477	10.39	12.66	24.08	46.96	138.5
15.00	2.500	2.626	2.891	3.225	3.597	3.988	4.390	4.801	5.217	5.636	6.482	7.334	8.190	9.049	9.909	12.07	22.89	44.57	131.3
17.50	2.500	2.614	2.856	3.169	3.520	3.892	4.276	4.669	5.066	5.468	6.279	7.096	7.918	8.742	9.568	11.64	22.03	42.86	126.2
20.00	2.500	2.605	2.829	3.123	3.455	3.809	4.176	4.552	4.933	5.319	6.097	6.883	7.674	8.467	9.262	11.26	21.27	41.33	121.6
22.50	2.500	2.598	2.807	3.084	3.400	3.739	4.091	4.453	4.820	5.192	5.944	6.703	7.467	8.234	9.002	10.93	20.62	40.03	117.7
25.00	2.500	2.593	2.789	3.051	3.352	3.677	4.017	4.365	4.720	5.079	5.806	6.541	7.281	8.023	8.768	10.64	20.03	38.86	114.2
30.00	2.500	2.585	2.760	2.998	3.275	3.577	3.894	4.221	4.554	4.893	5.579	6.273	6.973	7.676	8.381	10.15	19.06	36.91	108.4
35.00	2.500	2.580	2.740	2.957	3.215	3.497	3.795	4.104	4.420	4.741	5.393	6.054	6.721	7.391	8.064	9.753	18.24	35.32	103.60
40.00	2.500	2.577	2.724	2.925	3.165	3.431	3.712	4.005	4.306	4.612	5.235	5.867	6.505	7.147	7.792	9.411	17.57	33.94	99.50
45.00	2.500	2.574	2.712	2.899	3.124	3.375	3.643	3.922	4.209	4.501	5.098	5.705	6.318	6.935	7.555	9.114	16.97	32.75	95.92
50.00	2.500	2.572	2.703	2.878	3.090	3.327	3.581	3.848	4.122	4.403	4.975	5.559	6.149	6.743	7.341	8.844	16.43	31.66	92.65
60.00	2.500	2.570	2.690	2.846	3.036	3.251	3.483	3.727	3.980	4.240	4.772	5.316	5.867	6.423	6.982	8.391	15.51	29.82	87.15

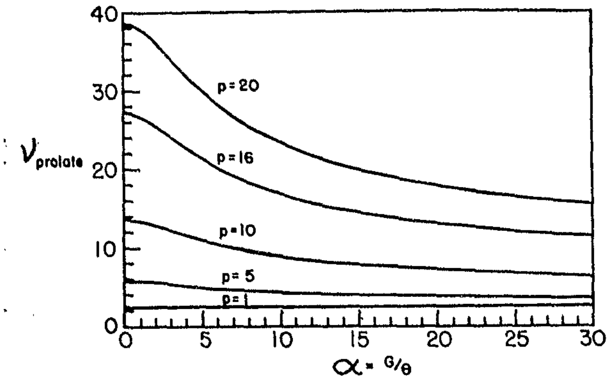

FIG. 1. Dependence of ν on α for prolate ellipsoids of various axial ratios.

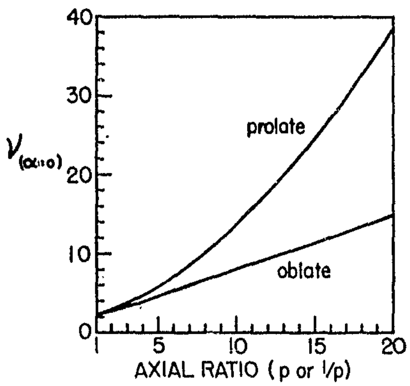

FIG. 3. Dependence of ν at $\alpha=0$ on axial ratio for prolate and oblate ellipsoids.

is concerned). However, the quantity N is positive for prolate and negative for oblate ellipsoids so that this term always increases the value of ν. As α increases, the last term of Eq. (9) (arising from the energy dissipation due to the Brownian motion, and neglected by Peterlin) becomes negligible. The values of J, K, L, M, N of Eqs. (10) are different for prolate and oblate ellipsoids. Therefore, the numerical values of ν as a function of α will differ for prolate and oblate ellipsoids. The results of the computations of ν as a function of α for various axial ratios p are given in Table I for prolate and in Table II for oblate ellipsoids. Some of these results are also shown in Figs. 1 and 2 which are qualitatively similar to those of Kuhn and Kuhn[5] and Saito.[7]

The special case where $\alpha=0$ is of interest. Taking the limiting forms of the summations in Eqs. (13) to (16) for $\alpha=0$, and substituting in Eq. (9), the following result is obtained

$$\nu=\frac{4}{15}(J+K-L)+\frac{2}{3}L+\frac{1}{3}M+\frac{RN}{15}. \tag{18}$$

This equation is identical with that obtained previously by Simha[4] for the case of complete Brownian motion. Computations of ν as a function of p, for $\alpha=0$, have

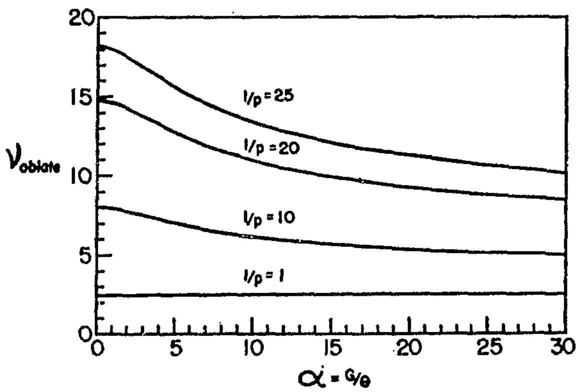

FIG. 2. Dependence of ν on α for oblate ellipsoids of various axial ratios.

been reported by Mehl, Oncley, and Simha.[22] An expanded form of their results was obtained during the course of the present computations and is reported in Table III and Fig. 3.

It has been pointed out by Zimm[8] that the frequency dependence of ν at $\alpha=0$ provides an alternative method to that of non-Newtonian viscosity for the determination of rotary diffusion constants. If one uses periodic shear waves of frequency ω [not the same ω as used in Eq. (6)], then the frequency dependence is expressible by a modified form of Eq. (18) in terms of a complex

TABLE III. Dependence of viscosity factors ν, ν_A, and ν_B on axial ratio for prolate and oblate ellipsoids at $\alpha=0$ and $\omega=0$.

	Prolate				Oblate		
$p=a/b$	ν_A	ν_B	ν	$1/p=b/a$	ν_A	ν_B	ν
1.0	2.500	0.000	2.500	1.0	2.500	0.000	2.500
1.2	2.504	0.021	2.525	1.2	2.505	0.019	2.524
1.4	2.516	0.072	2.588	1.4	2.520	0.063	2.583
1.6	2.533	0.144	2.677	1.6	2.542	0.119	2.661
1.8	2.555	0.229	2.784	1.8	2.573	0.180	2.753
2.0	2.583	0.325	2.908	2.0	2.610	0.244	2.854
2.25	2.623	0.455	3.078	2.25	2.664	0.325	2.989
2.50	2.671	0.595	3.266	2.50	2.727	0.405	3.132
2.75	2.726	0.743	3.469	2.75	2.795	0.485	3.280
3.0	2.786	0.899	3.685	3.0	2.868	0.562	3.430
3.5	2.922	1.230	4.152	3.5	3.027	0.714	3.741
4.0	3.077	1.586	4.663	4.0	3.198	0.861	4.059
4.5	3.248	1.967	5.215	4.5	3.378	1.004	4.382
5.0	3.434	2.372	5.806	5.0	3.563	1.145	4.708
6.0	3.844	3.254	7.098	6.0	3.947	1.420	5.367
7	4.302	4.230	8.532	7	4.342	1.690	6.032
8	4.804	5.299	10.103	8	4.744	1.956	6.700
9	5.346	6.458	11.804	9	5.151	2.220	7.371
10	5.928	7.706	13.634	10	5.562	2.481	8.043
12	7.203	10.466	17.669	12	6.390	3.001	9.391
14	8.622	13.567	22.19	14	7.224	3.519	10.74
16	10.179	17.002	27.18	16	8.061	4.034	12.10
18	11.868	20.762	32.63	18	8.901	4.548	13.45
20	13.688	24.842	38.53	20	9.743	5.061	14.80
25	18.787	36.406	55.19	25	11.853	6.340	18.19
30	24.65	49.86	74.51	30	13.966	7.618	21.58
35	31.24	65.15	96.39	35	16.083	8.894	24.98
40	38.53	82.23	120.76	40	18.200	10.170	28.37
50	55.20	121.61	176.81	50	22.438	12.720	35.16
60	74.54	167.74	242.28	60	26.678	15.268	41.95
70	96.45	220.46	316.9	70	30.92	17.82	48.74
80	120.88	279.60	400.5	80	35.16	20.36	55.52
90	147.77	345.03	492.8	90	39.40	22.91	62.31
100	177.06	416.65	593.7	100	43.64	25.46	69.10
150	358.44	864.74	1223.2	150	64.86	38.19	103.05
200	595.6	1457.3	2052.9	200	86.08	50.93	137.01
300	1226.9	3052.5	4279.4	300	128.52	76.39	204.91

[22] Mehl, Oncley, and Simha, Science 92, 132 (1940).

viscosity factor whose real part is given by[23]

$$\nu=\nu_A+\frac{\nu_B}{1+\omega^2/36\Theta^2} \tag{19}$$

where

$$\nu_A=\frac{4}{15}(J+K-L)+\frac{2}{3}L+\frac{1}{3}M,$$

and

$$\nu_B=RN/15.$$

For zero frequency Eq. (19) reduces to Eq. (18); at high frequency ν approaches ν_A. As indicated by Cerf,[23] Θ is determinable from the slope of the curve of ν *vs* ω at the inflection point. For this purpose values of ν_A and ν_B as a function of p are also included in Table III.

Now that data are available for ν_A and ν_B as a function of p at $\alpha=0$, and for ν as a function of α and p, it will be very desirable to have extensive experimental tests to check the validity of the theory. Some preliminary results on non-Newtonian viscosity have already been obtained.[24]

APPENDIX

In connection with the convergence problem[24] it is of interest to examine the values of the summations of Eqs. (13) to (16) for increasing j-values for the case $R=1$. Such data are shown in Table IV for $\alpha=25$, 40, and 60, where each entry is the cumulative value of the summation as j increases. It can be seen that enough terms have been computed to obtain the limiting values of the summations within the precision of the data reported in Tables I and II.

TABLE IV. Values of summations as a function of j for several values of α.

α	$-\Sigma a_{10,j}$	$\Sigma a_{20,j}$	$\Sigma a_{22,j}$	$\Sigma b_{11,j}$
25	0.06449	0.01935	0.0005235	0.009029
	0.09624	0.03951	0.0006101	0.015774
	0.10956	0.05068	0.0005530	0.019813
	0.11145	0.05478	0.0004914	0.021399
	0.10923	0.05492	0.0004622	0.021545
	0.10742	0.05390	0.0004568	0.021256
	0.10670	0.05317	0.0004600	0.021017
	0.10658	0.05292	0.0004636	0.020918
	0.10669	0.05292	0.0004653	0.020908
	0.10678	0.05297	0.0004657	0.020923
	0.10681	0.05301	0.0004656	0.020934
				0.020939
40	0.06671	0.02001	0.0006295	0.005837
	0.10338	0.04490	0.0008667	0.010806
	0.12504	0.06255	0.0009241	0.014767
	0.13611	0.07356	0.0009037	0.017518
	0.13917	0.07915	0.0008639	0.019029
	0.13857	0.08093	0.0008301	0.019628
	0.13720	0.08075	0.0008093	0.019723
	0.13603	0.07999	0.0007998	0.019616
	0.13533	0.07934	0.0007971	0.019482
	0.13496	0.07894	0.0007974	0.019383
	0.13481	0.07874	0.0007984	0.019328
				0.019303
60	0.06753	0.02026	0.0006731	0.003939
	0.10599	0.04769	0.0009891	0.007460
	0.13104	0.06925	0.0011394	0.010583
	0.14748	0.08494	0.0011965	0.013208
	0.15578	0.09505	0.0012054	0.015137
	0.15917	0.10117	0.0011934	0.016389
	0.16021	0.10429	0.0011754	0.017107
	0.16023	0.10543	0.0011590	0.017461
	0.15983	0.10564	0.0011471	0.017597
	0.15933	0.10547	0.0011397	0.017620
	0.15889	0.10519	0.0011356	0.017595
				0.017563

[23] R. Cerf, Compt. rend. 234, 1549 (1952).

[24] E. Wada, J. Sci. Research Inst. (Tokyo) 47, 168 (1953); J. Polymer Sci. 14, 305 (1954).