The Viscoelastic Properties of Solutions of Rodlike Macromolecules of Finite Diameter

Robert Ullman

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan 48121. *Received August 12, 1968*

ABSTRACT: The intrinsic viscosities, intrinsic rigidities and rotatory diffusion constants have been calculated for solutions of rodlike macromolecules. The results differ from the earlier calculation of Kirkwood and Auer by taking into account the finite cross-section of the rod. In doing this, the parametric dependence of the result on an arbitrary bond length, which was obtained by Kirkwood and Auer, is removed. The general form of the results remains unchanged. The magnitude of the rotatory diffusion constants and intrinsic viscosities can be used for comparison with experimental data.

An analysis of the rotatory diffusion and dynamic mechanical behavior of rodlike macromolecules was presented by Kirkwood and Auer.[1] This analysis was based on a modification by Kirkwood[2] of the Burgers[3]–Oseen[4] procedure for determining the hydrodynamic behavior of solutions of macromolecules as a function of molecular dimensions. Kirkwood assumed that the resistive force exerted on the fluid by a segment of the polymer chain could be concentrated at a single point along the axis of the chain. The mutual hydrodynamic interaction between two segments of a polymer chain was a function of the distance separating the two points of resistance; this function, neglecting angular effects, is proportional to the reciprocal of the distance between the points. The effect of concentrating the resistive force at a single point simplifies the subsequent mathematics considerably, has little effect on segments which are widely separated, but is very badly at fault when the distance between segments becomes small. This is of little consequence for the random coil polymer, but for the rigid rod or the wormlike chain, the solution of the intrinsic viscosity problem becomes impossible. Kirkwood and Auer, following an earlier procedure of Riseman and Kirkwood,[5] escape the dilemma by introduction of a cutoff in the hydrodynamic interaction. It was assumed that the hydrodynamic interaction between different parts of a single polymer segment may be ignored. This enables the problem to be solved but the result is unphysical in that the various viscoelastic properties become a function of an arbitrary segment length. For example, the intrinsic viscosity (for long rods) is proportional to $L^2/\ln(L/b)$, where b, the segment length, is not uniquely defined. A numerical estimate of the significance of bond length can easily be obtained by computing the ratio of intrinsic viscosities obtained for a rod of a given length by assuming two different bond lengths. For example if b_1 is taken to be 6.25 Å and b_2 taken to be 50 Å, $[\eta](b_2)/[\eta](b_1) = 1.85$ if the rodlike molecule is 625 Å in length, while this ratio is reduced to 1.22 if the molecule is 640,000 Å long.

Burgers, in his adaptation of the Oseen formula to the treatment of hydrodynamic interaction, took the source of hydrodynamic interaction as originating on the axis of an elongated molecule and acting at a point on the surface.[6] The further approximation of Kirkwood–Auer, in which the hydrodynamic interaction is presumed to originate at a point on the chain axis and to act on another point on the axis, leads to an unphysical result and will not be made here. As a consequence, our modification of the Kirkwood–Auer calculation leads to formulas for viscoelastic properties which are a function of the diameter of the molecular cross section, and not dependent on the artifact of a bond length.

The unsuitability of an artificial bond length in the formula for hydrodynamic properties has been remarked upon earlier.[7] Also, Hearst and Stockmayer[8] in their analysis of sedimentation and diffusion of wormlike molecules identified the bond length with chain diameter explicitly, a procedure subsequently adopted in other places.

The Hydrodynamic Calculation. The equations for the forces acting on a rodlike molecule are identical with those of Kirkwood–Auer with two modifications. The quantity $|l - l'|$ in eq 5 is replaced by $[(l - l')^2 + (d/2b)^2]^{1/2}$ where d is the cross-section diameter. Similarly $|l - s|$ in eq 10 is replaced by $[(l - s)^2 + (d/2b)^2]^{1/2}$.

The rotatory diffusion constants are obtained by replacing the sums in eq 5 of Kirkwood–Auer by integrals. Accordingly, it is found that (in the notation of Kirkwood–Auer)

$$\sigma = L^3/12b^3 \qquad (1a)$$

(1) J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).
(2) J. G. Kirkwood, *Rec. Trav. Chim. Pays-Bas*, **68**, 649 (1949).
(3) J. M. Burgers, Second Report on Viscosity and Plasticity, North Holland, Amsterdam, 1938, Chapter III.
(4) C. W. Oseen, "Hydrodynamik," Akademische Verlag, Leipzig, 1928, p 34.
(5) J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 512 (1950).
(6) This is actually the procedure used by Burgers in ref 3. See also C. M. Tchen, *J. Appl. Phys.*, **25**, 463 (1954).
(7) R. Ullman and J. J. Hermans, *J. Polym. Sci.*, **10**, 559 (1953), Appendix A.
(8) J. E. Hearst and W. H. Stockmayer, *J. Chem. Phys.*, **37**, 1425 (1962).

TABLE I
INTRINSIC VISCOSITIES OF RODLIKE MOLECULES AT ZERO FREQUENCY AS A FUNCTION OF L, λ_0 AND d[a]

λ_0	d = 6.25	d = 12.5	d = 25	d = 50	d = 6.25	d = 12.5	d = 25	d = 50
	L = 625				L = 2500			
0.2	0.3160	0.3650	0.4324	0.5304	3.987	4.458	5.055	5.840
0.4	0.3524	0.4145	0.5035	0.6417	4.342	4.906	5.639	6.632
0.8	0.3743	0.4451	0.5495	0.7192	4.546	5.168	5.988	7.121
1.6	0.3863	0.4622	0.5761	0.7664	4.656	5.311	6.188	7.396
3.2	0.3926	0.4714	0.5904	0.7929	4.713	5.385	6.282	7.542
6.4	0.3959	0.4761	0.5979	0.8069	4.724	5.423	6.334	7.617
12.8	0.3975	0.4785	0.6017	0.8142	4.757	5.443	6.360	7.655
	L = 10,000				L = 40,000			
0.2	52.67	57.70	63.79	71.32	717.9	775.3	842.8	923.2
0.4	56.50	62.32	69.47	78.49	761.9	826.9	904.0	997.1
0.8	58.64	64.93	72.74	82.69	786.1	855.5	938.3	1,039
1.6	59.78	66.33	74.50	84.97	798.8	870.6	956.5	1,061
3.2	60.37	67.06	75.41	86.16	805.4	878.3	965.9	1,073
6.4	60.67	67.42	75.88	86.77	808.7	882.3	970.7	1,079
12.8	60.82	67.61	76.12	87.08	810.3	884.3	973.1	1,082
	L = 160,000				L = 640,000			
0.2	10,000	10,690	11,490	12,400	141,800	150,400	160,100	171,100
0.4	10,530	11,300	12,190	13,230	148,400	157,800	168,500	180,800
0.8	10,820	11,630	12,580	13,690	152,000	161,900	173,200	186,100
1.6	10,970	11,810	12,780	13,930	153,800	164,000	175,600	188,900
3.2	11,050	11,900	12,890	14,050	154,800	165,000	176,800	190,400
6.4	11,090	11,940	12,940	14,120	155,200	165,600	177,400	191,100
12.8	11,110	11,970	12,970	14,150	155,500	165,900	177,700	191,400

[a] L and d are in ångströms; λ_0 is dimensionless; n = 20.

TABLE II
INTRINSIC VISCOSITIES OF RODLIKE MOLECULES AS A FUNCTION OF L AND λ_0, d = 6.25[a]

λ_0	L = 625	L = 2500	L = 10,000	L = 40,000	L = 160,000	L = 640,000
0.2	0.3162	3.989	52.70	718.1	10,006	141,803
0.4	0.3528	4.345	56.53	762.1	10,537	148,435
0.8	0.3746	4.549	58.67	766.4	10,826	152,003
1.6	0.3867	4.659	59.81	799.1	10,977	153,860
3.2	0.3931	4.717	60.40	805.7	11,054	154,800
6.4	0.3963	4.746	60.70	809.0	11,903	155,279
12.8	0.3980	4.760	60.84	810.6	11,111	155,519

[a] L and d are in ångströms; λ_0 is dimensionless; n = 40.

$$\gamma = 3\lambda_0 \int_{-1}^{1} \int_{-1}^{x} \frac{xy\,dy\,dx}{[(x-y)^2 + a^2]^{1/2}} \tag{1b}$$

$$a = d/L \tag{1c}$$

$$\lambda_0 = \zeta/8\pi\eta_0 b \tag{1d}$$

Equation 1b may be integrated in closed form. The result is

$$\gamma = 2\lambda_0\left[\ln\left(\frac{(4+a^2)^{1/2}+2}{a}\right) - \frac{(4+a^2)^{1/2}(7+a^2)}{6} + \frac{3a}{2} + \frac{a^3}{6}\right] \tag{2a}$$

The prime case of interest is for $a \ll 1$, whereupon eq 2a reduces to

$$\gamma = 2\lambda_0\left[\ln\left(\frac{4L}{d}\right) - \frac{7}{3}\right] \tag{2b}$$

Substitution of eq 2b into eq 5 of Kirkwood–Auer leads to

$$D = \frac{3kT}{\pi\eta_0 L^3}\left[\ln\left(\frac{4L}{d}\right) - \frac{7}{3} + \frac{1}{2\lambda_0}\right] \tag{3}$$

The rotatory diffusion constant D is written $D^{\theta\theta}$ in Kirkwood–Auer.

Burgers[3] has calculated the rotatory diffusion constant of a long cylindrical particle.[9] He obtains

$$D = \frac{3kT}{\pi\eta_0 L^3}\left[\ln\left(\frac{2L}{d}\right) - 0.80\right] \tag{4}$$

The parameter, λ_0, written in terms of a bond length b (eq 1d) to conform to Kirkwood–Auer is in fact a dimensionless constant since ζ is proportional to b in a segmented molecule. Reasonable values for λ_0 are 0.375 and 0.5, 0.375 corresponding to that obtained if the segment is assumed to have the friction constant of a sphere of a radius $b/2$. Substitution in eq 3 yields

$$D = \frac{3kT}{\pi\eta_0 L^3}\left[\ln\left(\frac{2L}{d}\right) - 0.31\right] \tag{5a}$$

$$D = \frac{3kT}{\pi\eta_0 L^3}\left[\ln\left(\frac{2L}{d}\right) - 0.64\right] \tag{5b}$$

for λ_0 = 0.375 and 0.5, respectively. If λ_0 were taken equal to 0.6, eq 3 and 4 would be the same.

(9) The present results are compared with those of Burgers because of the similarity of the hydrodynamic method. In fact, the calculation of S. Broersma [*J. Chem. Phys.*, **32**, 1626 (1960)] is a better one as has been demonstrated by A. J. Haltner and B. H. Zimm [*Nature*, **184**, 265 (1959)] using macroscopic models.

TABLE III
INTRINSIC RIGIDITIES[a] OF RODLIKE MOLECULES AS A FUNCTION OF L, λ_0 AND d[b]

λ_0	d				d			
	6.25	12.5	25	50	6.25	12.5	25	50
	L = 625				L = 2500			
0.2	0.2294	0.2635	0.3097	0.3753	2.916	3.250	3.670	4.216
0.4	0.2597	0.3045	0.3680	0.4652	3.213	3.624	4.156	4.871
0.8	0.2781	0.3302	0.4065	0.5294	3.386	3.846	4.450	5.283
1.6	0.2884	0.3447	0.4290	0.5692	3.480	3.967	4.614	5.516
3.2	0.2938	0.3525	0.4412	0.5916	3.529	4.031	4.700	5.640
6.4	0.2966	0.3565	0.4476	0.6036	3.554	4.063	4.645	5.705
12.8	0.2980	0.3586	0.4509	0.6099	3.566	4.080	4.767	5.737
	L = 10,000				L = 40,000			
0.2	38.70	42.30	46.65	51.99	529.1	570.6	619.2	676.9
0.4	41.92	46.18	51.41	57.98	566.2	614.1	670.7	738.9
0.8	43.74	48.40	54.18	61.53	586.9	638.4	699.8	774.4
1.6	44.71	49.59	55.68	63.47	597.8	651.3	715.4	793.5
3.2	45.21	50.21	56.46	64.49	603.3	657.9	723.4	803.4
6.4	45.47	50.53	56.86	65.01	606.2	661.3	727.5	808.4
12.8	45.60	50.69	57.06	65.28	607.6	663.0	729.5	811.0
	L = 160,000				L = 640,000			
0.2	7,390	7,892	8,466	9,130	104,920	111,190	118,250	126,260
0.4	7,839	8,406	9,060	9,825	110,540	117,510	125,430	134,490
0.8	8,085	8,689	9,390	10,214	113,580	120,960	129,360	139,020
1.6	8,213	8,837	9,564	10,420	115,160	122,750	131,420	141,400
3.2	8,279	8,914	9,653	10,527	115,970	123,670	132,470	142,620
6.4	8,313	8,952	9,698	10,580	116,380	124,140	133,000	143,240
12.8	8,329	8,972	9,721	10,608	116,580	124,370	133,270	143,550

[a] The numbers in the table are in reduced form. The intrinsic rigidity is obtained by multiplying the appropriate number by $\omega^2\tau\eta_0/(1 + \omega^2\tau^2)$. [b] L and d are in ångströms; λ_0 is dimensionless; n = 20.

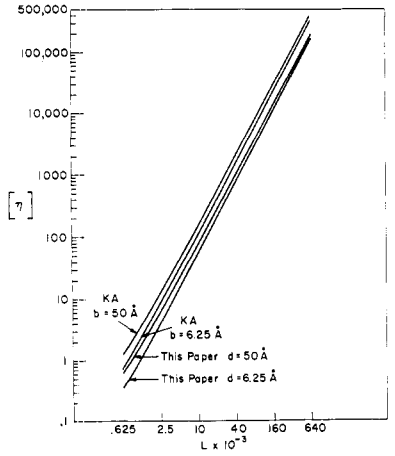

Figure 1. A plot of $[\eta]$ *vs.* length of rod on a log–log scale. The upper two curves are from the Kirkwood–Auer asymptotic formula; the lower two are from this paper, λ_0 = 0.4. $[\eta]$ is in units of deciliters per gram.

The intrinsic viscosity and intrinsic rigidity are given by

$$[\eta] = \frac{\pi NL^2\lambda_0}{2250M_L}\left[F(2\lambda_0,L,d) + \left(\frac{3}{2}\right)\frac{F(\lambda_0, L, d)}{1 + \omega^2\tau^2}\right] \quad (6a)$$

$$[\mu] = \frac{\pi NL^2\lambda_0\eta_0}{1500M_L}\left[\frac{\omega^2\tau}{1 + \omega^2\tau^2}F(\lambda_0, L, d)\right] \quad (6b)$$

Equations 6a and 6b are similar to equation 13 of Kirkwood–Auer with one important difference. In eq 6a and 6b, M_L is molecular weight per unit length. N is Avogadro's number, $\tau = 1/(6D)$, L is the length of the rodlike polymer molecule, and ω is frequency. It is significant that the bond length b which plays an important role in the calculation of Kirkwood–Auer is missing in eq 6.

$F(\lambda_0, L, d)$ is defined by the relationship

$$F(\lambda_0, L, d) = \frac{3}{2}\int_{-1}^{1} x\varphi(x)\,dx \quad (7a)$$

$$\varphi(x) = x - \lambda\int_{-1}^{1} \varphi(y)/[(x - y)^2 + a^2]^{1/2}\,dy \quad (7b)$$

Equation 7b is solved by converting the integral to a sum. The set of simultaneous equations thus generated is solved using Gaussian quadratures. The arithmetic was carried out for several values of λ, L and d using a Philco 212 computer. To check accuracy the integral was divided into 20 and 40 divisions and the results were compared. In no case was the difference between the two more than a few tenths of a per cent. The details of the procedure are presented in the Appendix.

Results and Discussion

Computed results on intrinsic viscosity are presented in Table I for rods of varying length as a function of the friction constant and cross-section diameter. It was assumed that the rod has a molecular weight of 100 atomic units per Å. A few of these results are shown on a log–log plot in Figure 1 together with that obtained by Kirkwood and Auer in the asymptotic limit

of very long chains.[10] In Table II, some data are presented on intrinsic viscosity for rods of cross section 6.25 Å. These calculations are made to a higher degree of approximation than those in Table I. In Table I, $n = 20$; in Table II, $n = 40$. It is clear by comparing corresponding results in Table I and Table II that the mathematical approximation of replacing integral equation by simultaneous equations is accurate to 0.2% or better. Table III contains the intrinsic rigidities of the rodlike molecules.

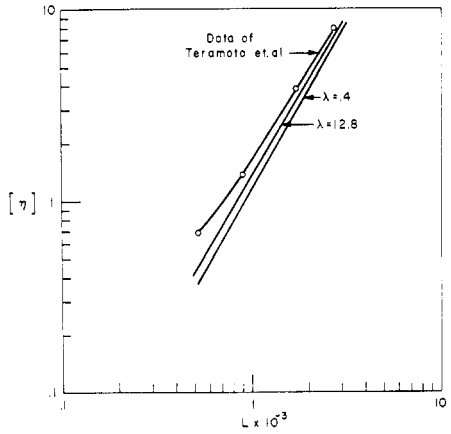

Figure 2. A plot of $[\eta]$ *vs.* length of rod for $d = 25$ Å, $\lambda_0 = 0.4$ and 12.8. The third curve contains experimental data from Teramoto, *et al.*,[8] on poly(γ-benzyl-L-glutamate) in dimethylformamide.

An attempt was made to compare the calculated intrinsic viscosities with experiment using data of Teramoto, *et al.*,[11,12] on poly(γ-benzyl-L-glutamate)-PBG in dimethylformamide solution. The cross section of the PBG molecule, using 0.9445 as an estimate of the dry density, is 18 Å. Assuming that one or two monolayers of solvent adhere to the polymer molecule, the hydrodynamic cross section is about 25 Å. In Figure 2, experimental results on PBG are plotted together with the calculated quantities at two different values of the friction constant, $\lambda = 0.4$ and $\lambda = 12.8$. The agreement between the absolute value of intrinsic viscosity and the calculated result is not too good, but the dependence on molecular weight is very close to that of the theory. The samples are somewhat polydisperse and a correction for polydispersity would bring the two curves closer together. Since the highest chain length reported on is only 2750 Å, it is difficult to judge to what extent the PBG molecule deviates from linearity. It does seem certain that if the molecule is curved, the persistence length is greater than 2500 Å.[13]

Experiments on dielectric relaxation of PBG have been carried out by Marchal and Marchal.[14] The rotatory diffusion constants calculated therefrom are not in accord with the theory for a rigid rod, but seem to indicate the PBG molecule is somewhat coiled.

Appendix I

Equation 7b is solved by a numerical procedure used by Schlitt[15] for singular integral equations. Rewriting eq 7b, one has

$$\varphi(x) = x - \lambda\int_{-1}^{1} \frac{[\varphi(y) - \varphi(x)]\,dy}{[(x-y)^2 + a^2]^{1/2}} - \lambda\varphi(x)J(x) \quad \text{(A1)}$$

$$J(x) = \int_{-1}^{1} \frac{dy}{[(x-y)^2 + a^2]^{1/2}} = \ln\left\{\left[1 + \left(\frac{1+x}{a}\right)^2\right]^{1/2}\left[1 + \left(\frac{1-x}{a}\right)^2\right]^{1/2}\right\} \quad \text{(A2)}$$

On rearranging terms one has

$$\varphi(x) = \frac{x}{1 + \lambda J(x)} - \frac{\lambda}{1 + \lambda J(x)}\int_{-1}^{1} \frac{[\varphi(y) - \varphi(x)]\,dy}{[(x-y)^2 + a^2]^{1/2}} \quad \text{(A3)}$$

In this form, errors which would be large in a finite numerical approximation of eq 5b in the neighborhood of $x = y$ (small a) are minimized.

Equation A3 is replaced by the set of simultaneous equations[16]

$$\left.\begin{aligned} \sum_{j=i}^{n} A_{ij}\varphi_j &= f_i \\ f_i &= \frac{x_i}{1 + \lambda J(x_i)} \\ A_{ij} &= \left[\frac{\lambda}{1 + \lambda J(x_i)}\right]\left[\frac{1}{(x_i - x_j)^2 + a^2}\right]^{1/2} w_j \quad (\text{where } i \neq j) \\ A_{ii} &= 1 - \sum_{j \neq 1} A_{ij} \end{aligned}\right\} \quad \text{(A4)}$$

The weight function for the Gaussian quadrature formula is designated by w_i. The functions φ_j are obtained by solution of eq A4. The quantity $F(a_0, L, d)$ in eq 7a is obtained from the φ_j by Gaussian quadrature also.

(10) No attempt is made to use the Kirkwood–Auer result except in the asymptotic case. The solution that Kirkwood–Auer give for the integral equation is incorrect in general as pointed out by R. Ullman, *J. Chem. Phys.*, **40**, 2422 (1964). The correct solution, however, agrees with the Kirkwood–Auer result in the asymptotic limit for long chains.

(11) A. Teramoto, K. Nakagawa, and H. Fujita, *J. Chem. Phys.*, **46**, 4197 (1967).

(12) H. Fujita, A. Teramoto, T. Yamashita, K. Okita, and S. Ikeda, *Biopolymers*, **4**, 781 (1966).

(13) This conclusion can be established by comparison with some calculations on intrinsic viscosity of wormlike chains: R. Ullman, *J. Chem. Phys.*, in press.

(14) E. Marchal and J. Marchal, *J. Chim. Phys.*, **64**, 1607 (1967).

(15) D. W. Schlitt, *J. Math. Phys.*, **9**, 436 (1968).

(16) The values of the coordinates and weights for the Gaussian quadrature calculations are given by P. Davis and P. Rabinowitz, *J. Res. Nat. Bur. Stand.*, **56**, 35 (1956).