generating functions times ϕ^i

$$B_i(\phi; y_0, y_1, \cdots, y_i) = \phi^i[B_0(\phi; y_0)][B_0(\phi; y_i)]\prod_{s=1}^{i=1}[B_0(\phi; y_s) - 1]/(y_s - 1) \qquad i > 1 \quad \text{(A10)}$$

where

$$B_0(\phi; y) = \frac{1}{y}\left[\frac{y(1 + \phi)}{1 - \phi} + \frac{2\phi(1 - \phi^y)}{(1 - \phi)^2}\right] \qquad \text{(A11)}$$

is the enumeration generating function of the number of paths of length n for an unvulcanized primary chain.

Intrinsic Viscosity of Wormlike Chains. Determination of the Shift Factor

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ABSTRACT: The intrinsic viscosity of stiff chains without excluded volume is evaluated by an application of the Oseen–Burgers procedure of hydrodynamics to wormlike cylinder models in the same spirit as that of the Yamakawa-Fujii theory of the translational friction coefficient. The molecular parameters involved are only the chain contour length L, the Kuhn segment length λ^{-1}, and the molecular diameter d. The final results are obtained only numerically by the use of a digital computer, but the semiempirical analytical expressions, which are very accurate, are presented for practical use. A method of determining a shift factor defined by $M_L = M/L$ with M the molecular weight is proposed, based on an analysis of intrinsic viscosities in conjunction with sedimentation coefficients. It is applied to DNA, poly(n-butyl isocyanate), and cellulose nitrate. It is concluded that the values of M_L determined for the latter two polymers are close to those corresponding to the all-trans conformation.

Analysis of the conformational and transport properties of stiff chain macromolecules has often been made on the basis of a continuous wormlike-chain model.[1] In doing this, however, a difficulty arises from the fact that the model chain is characterized by the contour length L and the Kuhn statistical segment length λ^{-1}, or the persistence length $(2\lambda)^{-1}$, while the relationship between L and the molecular weight M is not generally known except for molecules having rigid local conformations such as DNA and ladder polymers. We may define a shift factor M_L or f as the proportionality constant between L and M or the number n of bonds in the spine of the chain by[2,3]

$$M = M_L L \qquad (1)$$

$$n = fL\lambda \qquad (2)$$

In the case of flexible chains, values of the mean-square radius $\langle S^2\rangle$ are determined as a function of M if the characteristic ratio[4] is determined, whereas in the application of the wormlike-chain model to stiff chains, values of $\langle S^2\rangle$ as a function of M cannot be predicted unless proper values are assigned to both M_L and λ.[5] In many cases, once the value of M_L has been given, the determination of λ is not difficult.

For short broken chains of polymethylene, poly(oxymethylene), and the like (with a few exceptions), Maeda, Saito, and Stockmayer[3,6] have concluded that the best shift factor f may be obtained by taking L as the length of the chain fully extended to the all-trans conformation, based on a comparison of the second and fourth moments of the end-to-end distance of the broken and wormlike chains. However, there has not yet been established a method of determining the shift factor M_L from experiment. Thus, in the present paper, we propose a method for doing this, based on an analysis of intrinsic viscosities in conjunction with sedimentation coefficients. For this purpose, we first develop a theory of the intrinsic viscosity of wormlike chains in the same spirit as in the previous paper on the translational friction coefficient.[7]

The theory is developed by an application of the Oseen–Burgers procedure[8,9] of hydrodynamics to the wormlike cylinder model, and its formulation is given in section I. The discussion of this procedure in comparison with the Kirkwood procedure[10,11] and also the related references are given in detail in the previous paper,[7] and not repeated herein. However, we emphasize that our theories of the intrinsic viscosity and the sedimentation coefficient are consistent to be combined. Although such a consistent pair of theories for the two transport properties has also been presented by Ullman,[12] his theory is based on the wormlike-bead model with the use of the Kirkwood procedure, followed by the limiting process, and involves one more parameter than ours. In section II, numerical solutions of the derived integral equation, which cannot be solved analytically, are given, and in section III, the results are used to analyze the viscosity data for DNA. In section IV, we propose a method of determining M_L and apply it to DNA and several other stiff macromolecules.

I. Formulation

For convenience, all lengths are measured in units of the Kuhn segment length λ^{-1}, so that the unreduced con-

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tour length is L/λ from now on. Consider a wormlike cylinder of contour length L and diameter d in the unperturbed velocity field $\mathbf{v}^0$ of solvent with viscosity coefficient η_0

$$\mathbf{v}^0 = (\kappa y, 0, 0) \tag{3}$$

where the molecular center of mass is fixed at the origin of the Cartesian coordinate system ($\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$), and κ is the velocity gradient.

Following the Oseen-Burgers procedure, we replace the cylinder by a frictional force distribution $\mathbf{f}(s)$ per unit length along the cylinder axis as a function of the contour distance s from one end. Let $\mathbf{r}$ be the normal radius vector from the contour point s on the axis to an arbitrary point P which would be just located on the cylinder surface if the cylinder were absent, so that

$$\begin{gathered} |\mathbf{r}| = (1/2)d \\ \mathbf{r} \cdot \mathbf{u}_0 = 0 \end{gathered} \tag{4}$$

with $\mathbf{u}_0$ the unit vector tangential to the axis at the point s, and let $\mathbf{S}(s)$ be the distance from the center of mass to the point s. Then, the unperturbed velocity $\mathbf{v}^0(P)$ of solvent at the point P is given by

$$\mathbf{v}^0(P) = \kappa \mathbf{e}_x \mathbf{e}_y \cdot [\mathbf{S}(s) + \mathbf{r}] \tag{5}$$

and the molecule rotates around the z axis with the angular velocity $\omega = -(1/2)\kappa \mathbf{e}_z$, so that the velocity $\mathbf{U}(P)$ of the point P on the cylinder surface is

$$\mathbf{U}(P) = (1/2)\kappa[\mathbf{S}(s) + \mathbf{r}] \times \mathbf{e}_z \tag{6}$$

We therefore have

$$\mathbf{v}^0(P) - \mathbf{U}(P) = (1/2)\kappa(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x) \cdot [\mathbf{S}(s) + \mathbf{r}] \tag{7}$$

Now, if we consider the velocity perturbation due to the force $\mathbf{f}(s)$, the velocity $\mathbf{v}(P)$ of solvent at the point P relative to the velocity $\mathbf{U}(P)$ for an instantaneous configuration may be expressed as

$$\mathbf{v}(P) = (1/2)\kappa(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x) \cdot [\mathbf{S}(s) + \mathbf{r}] + \int_0^L \mathbf{T}(-\mathbf{R} + \mathbf{r}) \cdot \mathbf{f}(t)\mathrm{d}t \tag{8}$$

where $\mathbf{R}$ is the distance between the contour points s and t, and $\mathbf{T}$ is the Oseen tensor

$$\mathbf{T}(\mathbf{R}) = \frac{1}{8\pi\eta_0 R}[\mathbf{I} + (\mathbf{R}\mathbf{R}/R^2)] \tag{9}$$

with $\mathbf{I}$ the unit tensor. The Oseen-Burgers procedure requires that values of $\mathbf{v}(P)$ averaged over a normal cross section of the cylinder vanish for all values of s ranging from 0 to L; that is

$$\langle \mathbf{v}(P) \rangle_{(\mathbf{r})} = 0 \tag{10}$$

where $\langle\rangle_{(\mathbf{r})}$ designates the average over $\mathbf{r}$, assuming its uniform distribution subject to the conditions given by eq 4. Since $\langle \mathbf{r} \rangle_{(\mathbf{r})} = 0$, we then have, from eq 8 and 10

$$\int_0^L \langle \mathbf{T}(-\mathbf{R} + \mathbf{r}) \rangle_{(\mathbf{r})} \cdot \mathbf{f}(t)\mathrm{d}t = -(1/2)\kappa(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x) \cdot \mathbf{S}(s) \tag{11}$$

for an instantaneous configuration.

Next, we multiply both sides of eq 11 by $\mathbf{e}_x\mathbf{e}_y \cdot \mathbf{S}(s')$ and take the configurational average. In doing this, we preaverage the Oseen tensor as follows

$$\langle \mathbf{T}(-\mathbf{R} + \mathbf{r}) \rangle = (1/6\pi\eta_0)\langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle \mathbf{I} \tag{12}$$

where we have simply designated the two averaging processes by angular brackets. Equation 11 then becomes

$$\int_0^L \langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle \langle [\mathbf{f}(t) \cdot \mathbf{e}_x][\mathbf{S}(s') \cdot \mathbf{e}_y] \rangle \mathrm{d}t = -\pi\eta_0\kappa\langle \mathbf{S}(s) \cdot \mathbf{S}(s') \rangle \tag{13}$$

If we define a function $\varphi(s,s')$ by

$$\eta_0\kappa\varphi(s,s') = -\langle [\mathbf{f}(s) \cdot \mathbf{e}_x][\mathbf{S}(s') \cdot \mathbf{e}_y] \rangle \tag{14}$$

eq 13 becomes

$$\int_0^L \langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle \varphi(t,s')\mathrm{d}t = \pi\langle \mathbf{S}(s) \cdot \mathbf{S}(s') \rangle \tag{15}$$

The intrinsic viscosity $[\eta]$ (reduced with λ^3) may then be written in the form

$$\begin{aligned} [\eta] &= -(N_A/M\eta_0\kappa)\int_0^L \langle [\mathbf{f}(s) \cdot \mathbf{e}_x][\mathbf{S}(s) \cdot \mathbf{e}_y] \rangle \mathrm{d}s \\ &= (N_A/M)\int_0^L \varphi(s,s)\mathrm{d}s \end{aligned} \tag{16}$$

with N_A the Avogadro number.

If we choose the mean reciprocal distance as the kernel

$$\langle |\mathbf{R} - \mathbf{r}|^{-1} \rangle = K(s,t) \tag{17}$$

as before, eq 15 is an integral equation for φ. The average on the right-hand side may be evaluated from

$$\langle \mathbf{S}(s) \cdot \mathbf{S}(s') \rangle = (1/2L)\left[\int_0^L \langle R^2(s,s') \rangle \mathrm{d}s + \int_0^L \langle R^2(s,s') \rangle \mathrm{d}s'\right] - (1/2)\langle R^2(s,s') \rangle - \langle S^2 \rangle \tag{18}$$

with $\mathbf{R}(s,s')$ the distance between the contour points s and s', and S the radius of gyration. The result is

$$\begin{aligned} \langle \mathbf{S}(s) \cdot \mathbf{S}(s') \rangle = {} & (1/2L)(s^2 + s'^2) - (1/2)(s + s') - (1/2)|s - s'| - (1/4)e^{-2|s-s'|} - \\ & (1/8L)[e^{-2s} + e^{-2s'} + e^{-2(L-s)} + e^{-2(L-s')}] + \\ & (1/3)L + (1/4L) + (1/8L^2)(1 - e^{-2L}) \end{aligned} \tag{19}$$

It is convenient to change variables as follows

$$\begin{gathered} x = (2s/L) - 1 \\ y = (2s'/L) - 1 \\ \xi = (2t/L) - 1 \\ (1/2)\varphi(s,s') = \psi(x,y) \end{gathered} \tag{20}$$

Then the intrinsic viscosity may be rewritten in the form

$$[\eta] = (N_A L/M)\int_{-1}^{1} \psi(x,x)\mathrm{d}x \tag{21}$$

and the integral equation becomes

$$\int_{-1}^{1} K(x,\xi)\psi(\xi,y)\mathrm{d}\xi = g(x,y) \tag{22}$$

where

$$\begin{aligned} g(x,y) = {} & (\pi/8L^2)[L^2(x^2 + y^2) - 2L^2|x - y| - \\ & 2e^{-L}(\cosh Lx + \cosh Ly) - 2Le^{-L|x-y|} + \\ & (2/3)L^2 + 2 + (1/L)(1 - e^{-2L})] \end{aligned} \tag{23}$$

We adopt the same approximate expression for K as before[7]

$$K(x,y) = \left(\frac{6}{\pi t}\right)^{1/2}\left[1 - \frac{1}{40t}(1 + 5d^2) - \frac{73}{4480t^2}\left(1 - \frac{294d^2}{73} - \frac{63d^4}{73}\right)\right] \quad \text{for } t > \sigma$$

$$= \left(t^2 + \frac{1}{4}d^2\right)^{-1/2}(1 + f_1t + f_2t^2 + f_3t^3) \quad \text{for } t \le \sigma \tag{24}$$

where

$$L|x - y| = 2t$$

$$\sigma = 2.278 \tag{25}$$

and the coefficients f_i as functions of d are given by eq 38 of ref 7.

The integral eq 22 is of the first kind as is the corresponding integral equation for the friction coefficient;[7] it does not contain the exceptional part $\psi(x,y)$. As previously discussed in detail,[7,13] this is the consequence of the application of the Oseen–Burgers procedure to the continuous model, while for discrete bead models, both the Kirkwood and Oseen–Burgers procedures yield the integral equation of the second kind having the exceptional part.

Coil Limit. If we let L and t approach infinity in g and K, respectively, we have

$$\lim_{L\to\infty} g(x,y) \equiv g^*(x,y) = \frac{\pi}{8}\left[x^2 + y^2 - 2|x - y| + \frac{2}{3}\right] \tag{26}$$

$$\lim_{t\to\infty} K(x,y) \equiv K^*(x,y) = \frac{2}{d}\ \mathrm{erf}\left(\frac{3d^2}{8t}\right)^{1/2} \tag{27}$$

where

$$\mathrm{erf}(x) = \frac{2}{\pi^{1/2}}\int_0^x \exp(-t^2)dt \tag{28}$$

The K^* is identical with the K_∞ in the previous paper.[7] We designate the leading term of K or K^* for $t \to \infty$ by K_∞ in the present paper,

$$K_\infty(x,y) = (6/\pi t)^{1/2} \tag{29}$$

The coil limit $[\eta]^*$ of the intrinsic viscosity may then be obtained by the use of g^* and K^*, and the limiting value $[\eta]_\infty$ defined by

$$\lim_{L\to\infty} [\eta]^* \equiv [\eta]_\infty \tag{30}$$

is equal to the Kirkwood–Riseman value for flexible chains in the nondraining limit.[10] $[\eta]^*$ and $[\eta]_\infty$ correspond to Ξ^* and Ξ_∞ in the previous paper, respectively.

Rod Limit. In the limit L, d, $t \to 0$, we have

$$\lim_{L\to 0} g(x,y) \equiv g^{(0)}(x,y) = (\pi L/4)xy \tag{31}$$

$$\lim_{d,t\to 0} K(x,y) \equiv K^{(0)}(x,y) = (t^2 + (1/4)d^2)^{-1/2} \tag{32}$$

The $K^{(0)}$ is identical with the K_0 in the previous paper. We define $[\eta]^{(0)}$ and $[\eta]_0$ by

$$\lim_{\substack{d,L\to 0\\ (\text{const } L/d)}} [\eta] \equiv [\eta]^{(0)} \tag{33}$$

$$\lim_{L/d\to\infty} [\eta]^{(0)} \equiv [\eta]_0 \tag{34}$$

The rod limit $[\eta]^{(0)}$ of the intrinsic viscosity may be obtained by the use of $g^{(0)}$ and $K^{(0)}$, and the limiting value $[\eta]_0$ corresponds to Ξ_0 in the previous paper.

II. Solutions

The analytical solutions may be obtained only for $[\eta]_\infty$ and $[\eta]_0$. The solution for the former has already been found by Auer and Gardner.[14] Now, it is convenient to write

$$[\eta] = \Phi L^{3/2}/M \tag{35}$$

where Φ is a function of L and d. The Auer–Gardner value for Φ_∞ corresponding to $[\eta]_\infty$ is 2.862×10^{23}. We note that Ullman's value 0.875 for his function $G(\infty)$ leads to $\Phi_\infty = 2.82 \times 10^{23}$, which is incorrect since it is based on the erroneous equation $T_A = (11/8)(N_1^2/\sqrt{2}\pi) = 0.28433$ of Auer and Gardner.[15] As in the case of $[\eta]_\infty$, the solution for $[\eta]_0$ may easily be found by a polynomial expansion method, as shown in the Appendix. The result is

$$[\eta]_0 = \frac{\pi N_A L^3}{24M}\,\frac{1}{\ln(L/d) + 2\ln 2 - (7/3)} \tag{36}$$

If we avoid preaveraging the Oseen tensor, the numerical factor 1/24 of eq 36 is replaced by 2/45,[16,17] and the numbers in the second fraction would also be altered.

Numerical Solutions. In order to obtain the intermediate solution between $[\eta]_\infty$ and $[\eta]_0$, the integral eq 22 has been solved numerically following the procedure of Ullman.[12] The integrals in eq 21 and 22 have been evaluated using n-point Gaussian quadratures with n = 40, 64, 80, and 96 on a FACOM 230-60 digital computer at this University. The values of $[\eta]$ or Φ have been established by extrapolation of the obtained values of the integral in eq 21 to $n^{-1} = 0$. In particular, the value of Φ_∞ thus obtained by the use of g^* and K_∞ is 2.870×10^{23}, and is very close to the exact value cited above. In general, the error of extrapolation is small for large L and small d; *e.g.*, 0.0% for $L = 100$ and $d = 0.25$; 1.6% for $L = 100$ and $d = 0.4$; 0.5% for $L = 10$ and $d = 0.1$; and 3.0% for $L = 10$ and $d = 0.25$. In some cases of large error, the solution has been established in such a way that the extrapolation to $n^{-1} = 0$ coincides with that of the solutions from smaller d. Therefore, the solutions for $L^{1/2}/d \lesssim 30$ may not be regarded as very accurate.

The values of Φ thus obtained for various values of L and d are given in Table I for $L \ge \sigma$ and in Table II for $L < \sigma$. The values of Φ^* as a function of $L^{1/2}/d$ obtained by the use of g^* and K^* are given in Table III, and the values of $[\eta]^{(0)}/[\eta]_0$ as a function of L/d obtained by the use of $g^{(0)}$ and $K^{(0)}$, in Table IV, where $[\eta]_0$ is given by eq 36. No data are given in the region where the error is very large; for instance, for $L \le \sigma$ and $d > 0.1$. However, the data in this region are of no practical use; when $L \le \sigma$, d must be very small. Further, the value of d greater than *ca.* 1.0 will not be realized for real macromolecules.

Approximate Expressions. We can derive semiempirical approximate analytical expressions for $[\eta]$ by a theoretical insight with the use of the numerical solutions.

For $L \ge \sigma$, the dependence of $[\eta]$ on L may well be expressed in the form

$$[\eta] = \frac{\Phi_\infty L^{3/2}}{M}\,\frac{1}{1 - \sum_{i=1}^{4} C_i L^{-i/2}} \quad \text{for } L \ge \sigma \tag{37}$$

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(13) H. Fujita, *J. Polym. Sci., Part A-2*, **11**, 899 (1973).

(14) P. L. Auer and C. S. Gardner, *J. Chem. Phys.*, **23**, 1546 (1955).

(15) The second of eq 7 of ref 14, $T_A = (11/8)(N_1^2/\sqrt{2}\pi) = 0.300$, is incorrect and should be replaced by $T_A = (11/8)(N_1/\sqrt{2}\pi) = 0.29664$.

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(17) R. Ullman, *J. Chem. Phys.*, **40**, 2422 (1964).

Table I
Values of $\Phi \times 10^{-23}$ as a Function of $L(\geq\sigma)$ and d

	d											
L	0.001	0.005	0.01	0.03	0.06	0.10	0.15	0.25	0.4	0.6	0.8	1.0
1,000,000	2.8166	2.8309	2.8371	2.8471	2.8535	2.8584	2.8623	2.8673	2.8721	2.8767	2.8803	2.8834
160,000	2.7437	2.7761	2.7905	2.8141	2.8296	2.8412	2.8507	2.8631	2.8753	2.8867	2.8957	2.9036
25,600	2.5880	2.6547	2.6854	2.7372	2.7720	2.7991	2.8216	2.8517	2.8818	2.9107	2.9341	2.9546
10,000	2.4592	2.5503	2.5933	2.6673	2.7184	2.7589	2.7932	2.8399	2.8876	2.9344	2.9727	3.0066
7,000	2.3997	2.5009	2.5491	2.6329	2.6915	2.7383	2.7782	2.8331	2.8898	2.9459	2.9920	3.0333
4,000	2.2936	2.4113	2.4682	2.5685	2.6400	2.6982	2.7484	2.8185	2.8923	2.9667	3.0289	3.0855
2,000	2.1399	2.2783	2.3464	2.4687	2.5579	2.6319	2.6953	2.7899	2.8903	2.9957	3.0873	3.1728
1,000	1.9632	2.1216	2.2397	2.3460	2.4542	2.5694	2.6272	2.7468	2.8826	3.0329	3.147	3.252
600	1.8193	1.9909	2.0780	2.2394	2.3613	2.4672	2.5596	2.7017	2.8688	3.0634	3.227	3.434
400	1.7134	1.8987	1.9727	2.1465	2.2934	2.3929	2.4983	2.6593	2.8547	3.0932	3.287	3.52
200	1.4906	1.6857	1.7898	1.9843	2.1370	2.2719	2.4012	2.5996	2.8526	3.156	3.418	3.86
100	1.2591	1.4582	1.5664	1.7785	1.9514	2.1100	2.2642	2.5116	2.729	3.225		
70	1.1394	1.3359	1.4440	1.6600	1.8401	2.0082	2.1704	2.4953	2.697			
50	1.0282	1.2199	1.3270	1.5454	1.7321	1.9067	2.0790	2.397	2.658			
20	0.73914	0.90560	1.0061	1.2163	1.4031	1.6354	1.763	2.042	2.53			
10	0.54030	0.67789	0.76473	0.95143	1.1354	1.3179	1.486	1.90	2.43			
7	0.44738	0.56889	0.64470	0.82056	0.97986	1.1700						
5	0.36534	0.47054	0.53837	0.69728	0.85374	1.0312	1.21	1.63	2.22			
2.278	0.20643	0.27475	0.3206	0.4330	0.5638	0.7208						

Table II
Values of $\Phi \times 10^{-22}$ as a Function of $L(<\sigma)$ and d

	$d \times 10^2$										
L	0.0005	0.001	0.005	0.01	0.05	0.10	0.50	1.0	3.0	6.0	10.0
2.0	1.0108	1.0743	1.2584	1.3588	1.6693	1.8468	2.4800	2.9155	3.9863	5.248	6.768
1.0	0.49951	0.53297	0.63127	0.68578	0.85682	0.96420	1.3491	1.6304	2.4211	3.339	4.639
0.6	0.27702	0.29652	0.35460	0.38710	0.49380	0.56008	0.81538	1.0139	1.6402		
0.4	0.16817	0.18053	0.21768	0.23870	0.30928	0.35379	0.53712	0.6932	1.221		
0.2	0.068705	0.074158	0.090830	0.10059	0.13493	0.15796	0.2637	0.3627			
0.1	0.027277	0.029603	0.037004	0.041548	0.058048	0.070147	0.1327				
0.06	0.013661	0.014886	0.019015	0.021528	0.031392	0.039017					
0.04	0.007902	0.008673	0.01123	0.01280	0.01947	0.02505					
0.01	0.002203	0.002451									

Table III
Values of $\Phi^* \times 10^{-23}$ as a Function of $L^{1/2}/d$

$L^{1/2}/d$	$\Phi^* \times 10^{-23}$	$L^{1/2}/d$	$\Phi^* \times 10^{-23}$
20	3.704	200	2.9430
30	3.408	400	2.9057
40	3.229	1000	2.8839
62	3.125	2000	2.8768
100	3.0216		

with $\Phi_\infty = 2.870 \times 10^{23}$. The coefficients C_i are independent of L but dependent on d, and may be determined as functions of d from the numerical solutions by the method of least squares. The results are

$$C_1 = 3.230981 - 143.7458d - 1906.263d^2 + (2.463404 - 1422.067d^2) \ln d$$

$$C_2 = -22.46149 + 1347.079d + 19387.400d^2 + (-5.318869 + 13868.57d^2) \ln d$$

$$C_3 = 54.81690 - 3235.401d - 49357.06d^2 + (15.41744 - 34447.63d^2) \ln d$$

$$C_4 = -32.91952 + 2306.793d + 36732.64d^2 + (-8.516339 + 25198.11d^2) \ln d \quad \text{for } d \le 0.1 \quad (38)$$

and

$$C_1 = 0.120367 + 0.220714d + 4.36037d^2 - 6.99899d^3 + 7.94714d^4 + (2.16769 - 12.5326d^2 - 0.293796d^4) \ln d$$

$$C_2 = 1.30917 + 129.550d + 96.9912d^2 - 435.952d^3 + 126.457d^4 - (3.92040 - 413.189d^2 - 4.94474d^4) \ln d$$

$$C_3 = 161.109 - 4926.443d - 4398.88d^2 + 78765.85d^3 - 29296.43d^4 + (40.1861 - 31548.53d^2 - 38.3938d^4) \ln d$$

$$C_4 = -582.038 + 16873.42d + 159994.7d^2 - 273427.7d^3 + 85028.34d^4 - (102.876 - 113150.7d^2 - 88.8684d^4) \ln d \quad \text{for } 0.1 < d < 1.0 \quad (39)$$

For $L < \sigma$, $[\eta]$ may well be approximated by

$$[\eta] = \frac{\pi N_A L^3}{24M \ln (L/d)} \frac{f(L)}{1 + \sum_{i=1}^{4} A_i [\ln (d/L)]^{-i}} \quad \text{for } L < \sigma \quad (40)$$

where

$$f(L) = (3/2L^4)(e^{-2L} - 1 + 2L - 2L^2 + (4/3)L^3) \quad (41)$$

and A_i are constants independent of L and d. The values of A_i determined for $d \le 0.1$ from the numerical solutions by the method of least squares are

$$\begin{aligned} A_1 &= 1.839459 \\ A_2 &= 8.240617 \\ A_3 &= 32.86282 \\ A_4 &= 41.10448 \end{aligned} \quad (42)$$

The error in the value of $[\eta]$ calculated from eq 37 and 40 (compared with the numerical solution) does not exceed 1.5% for $d \le 0.1$ and 2% for $0.1 < d < 1.0$ as far as $L^{1/2}/d \lesssim 30$.

The values of $[\eta]/[\eta]_\infty = \Phi/\Phi_\infty$ are plotted against the logarithm of $L^{1/2}/d$ for various values of d in Figure 1. The numbers attached to the curves indicate the values of d, and the broken curve represents the coil limiting values $[\eta]^*/[\eta]_\infty$. The dotted curves for $d \ge 0.4$ and $L^{1/2}/d \lesssim 30$ indicate that the numerical solutions scatter there slightly. It is important to note that the ratio $[\eta]^*/[\eta]_\infty$ decreases with increasing L, while the corresponding ratio predicted by the Kirkwood-Riseman theory[10] increases with L. The behavior of $[\eta]^*/[\eta]_\infty$ is analogous to that of the Kirkwood-Riseman theory result modified by Yamakawa[18] for flexible touched-bead models, and also of the Zimm theory[19] modified similarly by Osaki.[20] The values of $[\eta]/[\eta]_0$ are plotted against the logarithm of L/d for various values of d in Figure 2. The numbers attached to the curves indicate the values of d; the case of $d = 0$ corresponds to the rod limit $[\eta]^{(0)}/[\eta]_0$.

Table IV
Values of $[\eta]^{(0)}/[\eta]_0$ as a Function of L/d

L/d	$[\eta]^{(0)}/[\eta]_0$	L/d	$[\eta]^{(0)}/[\eta]_0$
10^2	1.0646	2×10^4	1.0183
2×10^2	1.0529	5×10^4	1.0160
5×10^2	1.0380	10^5	1.0149
10^3	1.0327	2×10^5	1.0134
2×10^3	1.0282	5×10^5	1.0121
5×10^3	1.0237	10^6	1.0112
10^4	1.0207		

The values of $M_L[\eta]/\lambda\Phi_\infty$ are plotted against $L^{1/2}$ in Figure 3, and the double-logarithmic plots of $M_L[\eta]/\lambda\Phi_\infty$ against L are shown in Figure 4. The numbers attached to the curves indicate the values of d. Figure 3 corresponds to experimental plots of $[\eta]$ against $M^{1/2}$, and the curves are seen to be concave upward or linear (not concave downward) for typical stiff chains. Figure 4 corresponds to experimental double-logarithmic plots of $[\eta]$ against M, and the curves are seen to be concave downward or linear.

III. Application to DNA

In the previous paper,[7] we have applied our theory of the sedimentation coefficient s to DNA to estimate its λ^{-1} and d. Now, we attempt to make a similar analysis of the intrinsic viscosity data for DNA. In what follows, it is convenient to use the unreduced intrinsic viscosity, which may be written as

$$[\eta] = \Phi L^{3/2}/\lambda^3 M \quad (43)$$

with L the reduced contour length

$$L = \lambda M/M_L \quad (44)$$

It is known that $M_L = 195$ daltons/Å for DNA.

Figure 5 shows double-logarithmic plots of $[\eta] + 5.0$ (in dl/g) against M, following Hays, Magar, and Zimm.[21] It includes not only the data[22-25] displayed in the figure of ref 21 but also the very recent data of Massa (highest point).[26] The curve of the figure represents the theoretical values for $\lambda^{-1} = 1100$ Å and $d = 24$ Å, and is a best fit to the data. It is interesting to observe that the deviation of the curve from linearity is not negligible in the range displayed. The present estimates of λ^{-1} and d are to be compared with the previous estimates, $\lambda^{-1} = 1300$ Å and $d = 25$ Å, obtained from the sedimentation coefficients.[7] More definite estimates may be obtained from a combination of

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(18) H. Yamakawa, *J. Chem. Phys.*, **53**, 436 (1970).

(19) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

(20) K. Osaki, *Macromolecules*, **5**, 141 (1972).

(21) J. B. Hays, M. E. Magar, and B. H. Zimm, *Biopolymers*, **8**, 531 (1969).

(22) Y. Kawade and I. Watanabe, *Biochim. Biophys. Acta*, **19**, 513 (1956).

(23) K. Iso and I. Watanabe, *Nippon Kagaku Zasshi*, **78**, 1268 (1957).

(24) P. Doty, B. McGill, and S. Rice, *Proc. Nat. Acad. Sci. U. S.*, **44**, 432 (1958).

(25) D. M. Crothers and B. H. Zimm, *J. Mol. Biol.*, **12**, 525 (1965).

(26) D. J. Massa, *Biopolymers*, **12**, 1071 (1973).

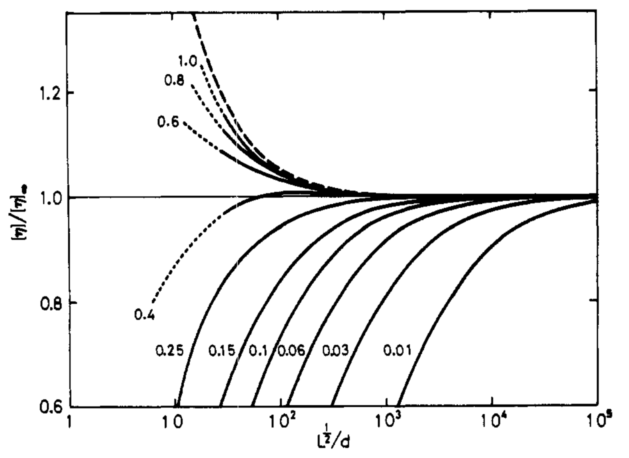

Figure 1. The ratio $[\eta]/[\eta]_\infty = \Phi/\Phi_\infty$ plotted against the logarithm of $L^{1/2}/d$. The numbers attached to the curves indicate the values of d. The broken curve represents the coil limiting values $[\eta]^*/[\eta]$.

the intrinsic viscosity and sedimentation coefficient data, as seen in section IV.

IV. Treatments of Data in Conjunction with *s*

In the case of DNA, M_L is known, and therefore we have been able to estimate λ^{-1} and d either from the data for $[\eta]$ alone or from the data for s alone. Now, we consider the problem of determining M_L, λ^{-1}, and d for the case in which M_L is unknown. The unreduced intrinsic viscosity $[\eta]$ (in dl/g) and the unreduced sedimentation coefficient s (in Svedbergs) may be written in the form

$$\log([\eta]M^{-1/2}) = -\gamma - \Gamma_1(L,d) \qquad (45)$$

$$\log\left[C\left(\frac{1-\bar{v}\rho}{\eta_0}\right)^3 s^{-3}M^{3/2}\right] = -\gamma - \Gamma_2(L,d) \qquad (46)$$

where

$$C = 9.8262 \times 10^{-14} \qquad (47)$$

$$\gamma = (3/2)\log(\lambda M_L) - 21.4579 \qquad (48)$$

and $\bar{v}$ is the partial specific volume of the polymer, ρ is the density of the solvent, and η_0 is expressed in Poises. The functions Γ_1 and Γ_2 of the reduced lengths L and d are defined by [27]

$$\Gamma_1(L,d) = \log(\Phi_\infty/\Phi) \qquad (49)$$

$$\Gamma_2(L,d) = 3\log(3\pi\eta_0 L^{1/2}/A_1\Xi) \qquad (50)$$

where $A_1 = 1.843$ and Ξ is the reduced translational friction coefficient.[7]

Equation 45 suggests that a curve of $-\Gamma_1$ plotted against $\log L$ for a proper d may be displaced by δ

$$\delta = \log(M_L/\lambda) \qquad (51)$$

in the abscissa direction and by γ in the ordinate direction to fit experimental plots of the quantity on the left of eq 45 against $\log M$ on the same scale. Similarly, a curve of $-\Gamma_2$ plotted against $\log L$ for a proper d may be displaced by δ in the abscissa direction and by γ in the ordinate direction to fit experimental plots of the quantity on the left of eq 46 against $\log M$ on the same scale. Thus, d, δ, and γ may be determined in such a way that for the same d, the displacement (δ,γ) of Γ_1 coincides with the displacement (δ,γ) of Γ_2. We may then estimate M_L and λ from eq 48 and 51, and also the unreduced d. Such plots for DNA are shown in Figure 6, where the data for $[\eta]$ are the same as those in Figure 5, and the data for s are those of the same workers[22-25] and also taken from the table of Schmid, Rinehart, and Hearst.[28] The curves of Figure 6 are those of $-\Gamma_1$ and $-\Gamma_2$ with $d = 0.022$, $\delta = 5.34$, and $\gamma = 1.40$. The values of the molecular parameters thus esti-

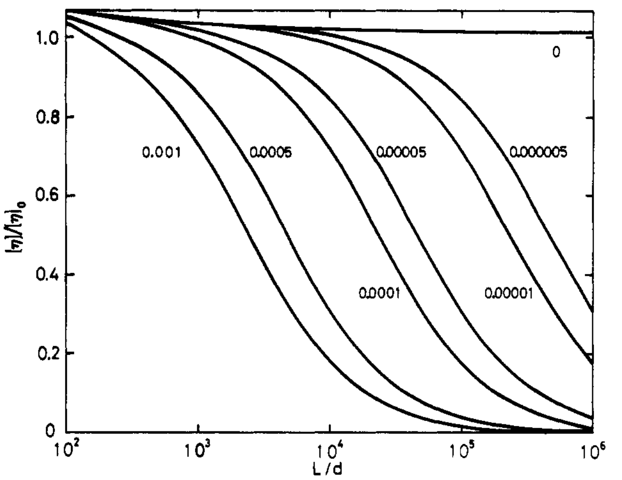

Figure 2. The ratio $[\eta]/[\eta]_0$ plotted against the logarithm of L/d. The numbers attached to the curves indicate the values of d.

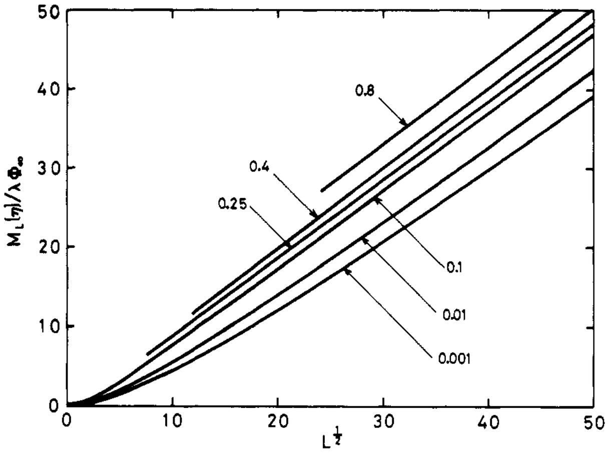

Figure 3. $M_L[\eta]/\lambda\Phi_\infty$ plotted against $L^{1/2}$. The numbers attached to the curves indicate the values of d.

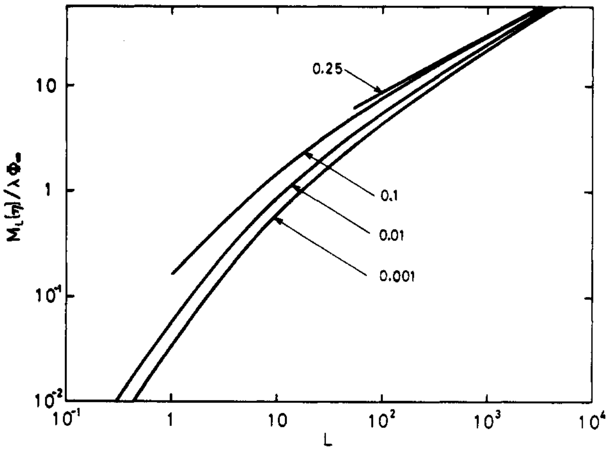

Figure 4. Double-logarithmic plots of $M_L[\eta]/\lambda\Phi_\infty$ against L. The numbers attached to the curves indicate the values of d.

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(27) The detailed numerical tables of Γ_1 and Γ_2 are available from H. Yamakawa on request. The leading term $A_1L^{-1/2}$ on the right of eq 49 of ref 7 should be replaced by $A_1L^{1/2}$.

(28) C. W. Schmid, F. P. Rinehart, and J. E. Hearst, *Biopolymers*, **10**, 883 (1971).

Table V
Values of the Molecular Parameters of Stiff Chains Estimated by the Proposed Method

Polymer	Solvent	M_L (Daltons/Å)	λ^{-1} (Å)	d (Å)
DNA[a]	0.2 *M* NaCl	195	1130	25
Poly(*n*-butyl isocyanate)[b]	CCl$_4$ (20°)	44.2	750	6.0
Cellulose nitrate[c]	Acetone (20°)	52.4	330	4.0

[a] See ref 22–25, 26, and 28. [b] See ref 29. [c] See ref 30.

Table VI
Crystallographic Data for Poly(*n*-butyl isocyanate) and Cellulose Nitrate

Polymer	Conformation	h (Å)	M_L (Daltons/Å)	d (Å)
Poly(*n*-butyl isocyanate)	Trans	2.27[a]	43.6	5.8–7.0
	Cis	1.95[a]	50.7	1.8–13.9
	Helical	1.94[b]	51.0	13.0
Cellulose nitrate	Trans	5.17[c]	56.1	2.7–8.6

[a] See ref 31. [b] See ref 32. [c] See ref 33.

mated are given in Table V. The value of M_L thus determined is seen to be in excellent agreement with the known value 195.

Figures 7 and 8 show similar analyses of the data obtained by Tsvetkov *et al.*[29] for poly(*n*-butyl isocyanate) in CCl$_4$ at 20° and of the data obtained by Meyerhoff[30] for cellulose nitrate in acetone at 20°, respectively, ignoring the excluded volume effect. The curves of Figure 7 are those of $-\Gamma_1$ and $-\Gamma_2$ with $d = 0.008$, $\delta = 4.52$, and $\gamma = 0.70$, and the curves of Figure 8 with $d = 0.012$, $\delta = 4.24$, and $\gamma = 1.34$. The values of M_L, λ^{-1}, and d determined from these displacements are also given in Table V. Now it is interesting to compare these values of M_L and d with those calculated from the crystallographic data. In Table VI are summarized the crystallographic data for the trans, cis, and helical (8 units in 3 turns) conformations of poly(*n*-butyl isocyanate)[31,32] and for the trans conformation of cellulose nitrate.[33] The values of the monomeric projection h on the chain axis are given in the third column, and the corresponding values of M_L in the fourth column. There is some ambiguity in the values of the diameter d calculated from the crystallographic data,[32,33] since the molecular cross section is not a complete circle. From a comparison of Tables V and VI, it is seen that the value of M_L determined by the present method is close to that corresponding to the all-trans conformation. It is interesting to note that this is consistent with the conclusion derived by Maeda *et al.*[3] from a comparison of the broken and wormlike chains. In the case of poly(*n*-butyl isocyanate), our conclusion does not necessarily mean that the cis and helical conformations are not actually existent in solution at all; the situation is similar to that for the broken chain.[3] However, we cannot conclude that the chain of this polymer takes the all-helical conformation in CCl$_4$, considering the difference between the values of M_L, 44.2 and 51.0, in Tables V and VI. Further, our estimates of λ^{-1} for this polymer seems reasonable compared with that for DNA; the earlier estimates[5,29] are much greater than ours.

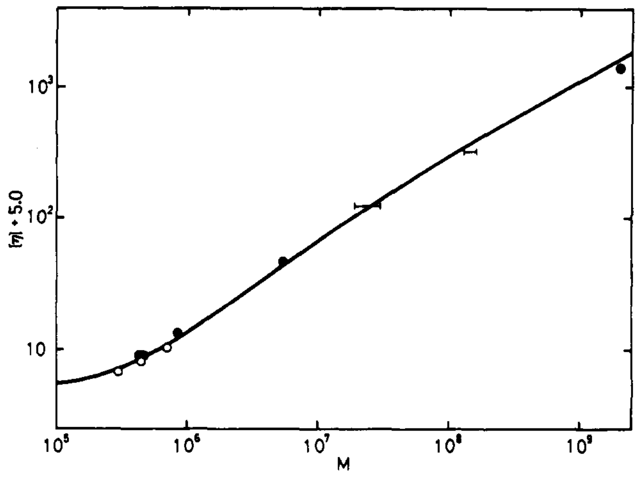

Figure 5. Double-logarithmic plots of $[\eta] + 5.0$ against M; (●) data of Kawade and Watanabe[22] and Iso and Watanabe;[23] (○) data of Doty, McGill, and Rice;[24] (⊢⊣) data of Crothers and Zimm;[25] (◉) data of Massa.[26] The curve represents the theoretical values calculated with $\lambda^{-1} = 1100$ Å and $d = 24$ Å.

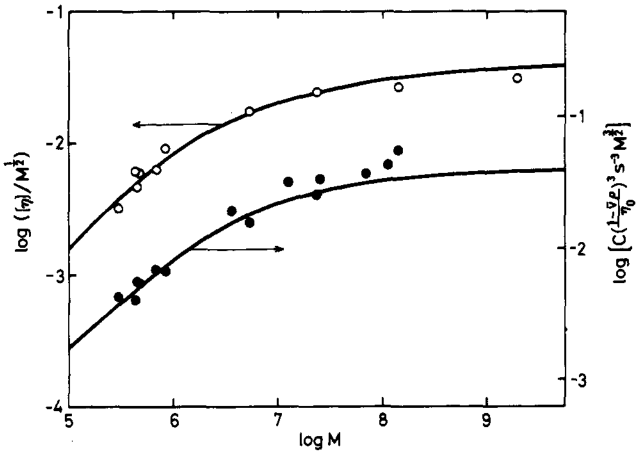

Figure 6. Analysis of the data for $[\eta]$ and s of DNA[22-25,26,28] according to eq 45 and 46. The curves with $d = 0.022$ are displaced by $\delta = 5.34$ and $\gamma = 1.40$.

Although we have also made similar analyses of the data obtained by Burchard[34] for poly(*n*-butyl isocyanate) in tetrahydrofuran at 20° and of the data obtained by Tsvetkov *et al.*[35,36] for three kinds of ladder polymers, we have not been able to select a pair of the curves Γ_1 and Γ_2 which in each case fit the data for the same d. In other words, these samples may not be represented by the wormlike chain in the sense that the data or $[\eta]$ and s cannot be explained theoretically at the same time.

The present method requires some comments. Fortunately, values of M_L and λ^{-1} determined from the displacements of the curves Γ_1 and Γ_2 are rather insensitive to the way of selection of a pair of Γ_1 and Γ_2, *i.e.*, to the change in d. Therefore, the present method leads to rather accurate estimates of M_L and λ^{-1}, while the estimate of d is less accurate. Of course, the accuracy of these estimates depends on that of given data. Further, it is clear that the present method breaks down when one or both of the

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(29) V. N. Tsvetkov, I. N. Shtennikova, E. I. Rjumtsev, and Yu. P. Getmanchuk, *Eur. Polym. J.*, **7**, 767 (1971).

(30) G. Meyerhoff, *J. Polym. Sci.*, **29**, 399 (1958).

(31) N. S. Schneider, S. Furusaki, and R. W. Lenz, *J. Polym. Sci., Part A*, **3**, 933 (1965).

(32) U. Shmueli, W. Traub, and K. Rosenheck, *J. Polym. Sci., Part A-2*, **7**, 515 (1969).

(33) D. W. Jones, *J. Polym. Sci.*, **32**, 371 (1958).

(34) V. W. Burchard, *Makromol. Chem.*, **67**, 182 (1963).

(35) V. N. Tsvetkov, K. A. Andrianov, G. I. Okhrimenko, and M. G. Vitovskaya, *Eur. Polym. J.*, **7**, 1215 (1971).

(36) V. N. Tsvetkov, K. A. Andrianov, M. G. Vitovskaya, N. N. Makarova, S. V. Bushin, E. N. Zakharova, A. A. Gorbunov, and P. N. Lavrenko, *Vysokomol. Soedin., Ser. A*, **15**, 872 (1973).

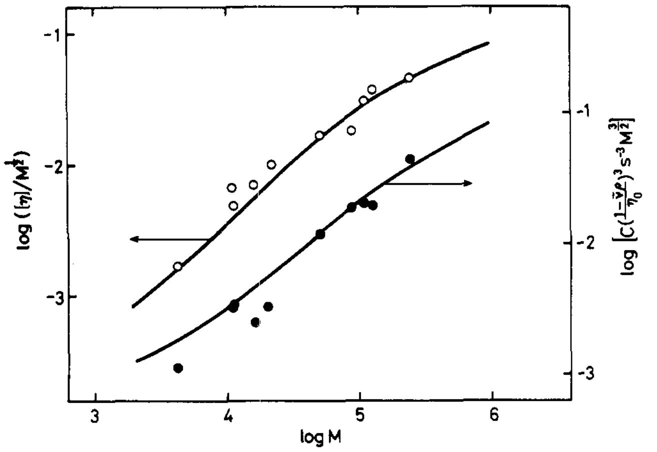

Figure 7. Analysis of the data for [η] and s of poly(n-butyl isocyanate) in carbon tetrachloride at 20°[29] according to eq 45 and 46. The curves with $d = 0.008$ are displaced by $\delta = 4.52$ and $\gamma = 0.70$.

quantities on the left-hand sides of eq 45 and 46 are independent of M. It will be useful in the determination of M_L for typical stiff-chain macromolecules, and also in the judgement of whether a given sample may or may not be represented by the wormlike chain.

In conclusion, it must be emphasized that within the framework of classical hydrodynamics the transport properties of a continuous body should be expressed in terms of only dimensional parameters and η_0. This is the case in our theory, while Ullman's theory includes an additional parameter (friction constant per unit contour length) because of its improper limiting process. Therefore, the application of the latter makes it difficult to analyze experimental data, especially to determine the shift factor. Hearst, Beals, and Harris[37] have also evaluated the intrinsic viscosity for wormlike touched-bead models with and without excluded volume. As argued earlier, cylinder models and touched-bead models must lead to equivalent results. In fact, the theory of Hearst *et al.* includes no additional parameter, and its numerical results without excluded volume are similar to ours. However, they have not obtained complete numerical results, and it is of little practical use.

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Appendix

We derive the solution for $[\eta]_0$ in the long-rod limit. We start from the integral eq 22 with $g = g^{(0)}$ and $K = K^{(0)}$, where $g^{(0)}$ and $K^{(0)}$ are given by eq 31 and 32, respectively. To solve this integral equation, we expand the solution $\psi(x,y)$ in terms of the Legendre polynomials $P_l(x)$,

$$\psi(x,y) = \sum_{l=0}^{\infty} b_l(y) P_l(x) \qquad \text{(A1)}$$

so that the integral equation becomes

$$\sum_{l=0}^{\infty} b_l(y) \int_{-1}^{1} K^{(0)}(x,\xi) P_l(\xi) \mathrm{d}\xi = g^{(0)}(x,y) \qquad \text{(A2)}$$

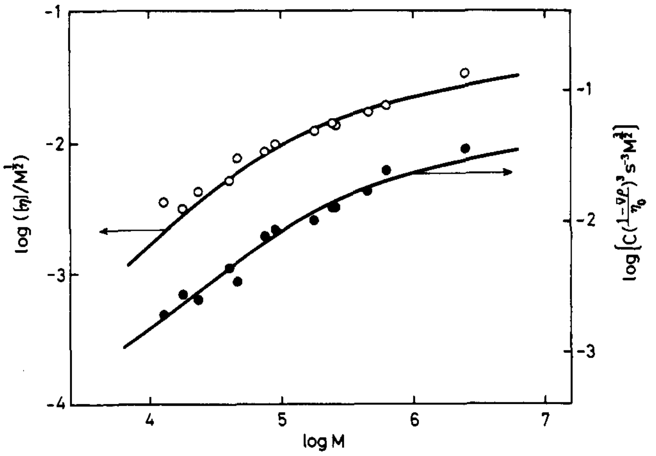

Figure 8. Analysis of the data for [η] and s of cellulose nitrate in acetone at 20° according to eq 45 and 46. The curves with $d = 0.012$ are displaced by $\delta = 4.24$ and $\gamma = 1.34$.

We multiply both sides by $P_k(x)$ and integrate to obtain

$$\sum_{l=0}^{\infty} a_{kl} b_l(y) = c_k(y) \qquad (k = 0, 1, 2, \cdots) \qquad \text{(A3)}$$

where

$$a_{kl} = a_{lk} = \int_{-1}^{1}\int_{-1}^{1} K^{(0)}(x,\xi) P_k(x) P_l(\xi) \mathrm{d}x \mathrm{d}\xi \qquad \text{(A4)}$$

$$c_k(y) = \int_{-1}^{1} g^{(0)}(x,y) P_k(x) \mathrm{d}x \qquad \text{(A5)}$$

The solution of the linear simultaneous eq A3 is

$$b_l(y) = \sum_{k=0}^{\infty} c_k(y) A^{-1} A^{kl} \qquad \text{(A6)}$$

where A is the determinant whose elements are a_{kl}, and A^{kl} is the cofactor of a_{kl}. From eq 21, A1, and A6, the rod limit $[\eta]^{(0)}$ of the intrinsic viscosity is then found to be

$$[\eta]^{(0)} = \frac{N_A L}{M} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} A^{-1} A^{kl} c_{kl} \qquad \text{(A7)}$$

where

$$c_{kl} = \int_{-1}^{1} c_l(x) P_k(x) \mathrm{d}x$$
$$= (\pi L/9) \delta_{kl} \delta_{l1} \qquad \text{(A8)}$$

with δ_{kl} the Kronecker delta. Therefore, eq A7 reduces to

$$[\eta]^{(0)} = (\pi N_A L^2/9M)(A^{11}/A) \qquad \text{(A9)}$$

We now let L/d approach infinity, and retain only the leading term of the expansion of A^{11}/A, *i.e.*, a_{11}^{-1}, where

$$a_{11} = \frac{8}{3L}\left[\ln (L/d) + 2 \ln 2 - \frac{7}{3} + 0(L/d)\right] \qquad \text{(A10)}$$

It can be shown that the neglected terms of the expansion of A^{11}/A are of the order of magnitude smaller than the retained terms of a_{11}^{-1}. Thus, from eq A9 and A10, we obtain eq 36.

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(37) J. E. Hearst, E. Beals, and R. A. Harris, *J. Chem. Phys.*, **48**, 5371 (1968).