beef tendon in water, and Küntzel and Doehner[3] found 1.18 kcal. mole^{-1} for hide powder in water.

The tendons used by Wöhlisch and de Rochemont, and those used by Tobolsky and co-workers as well, were not cross linked, apart from cross linkages present in the native tendon or formed adventitiously in the course of the procedure. As noted above, they determined T_s rather than T_m. For these reasons we consider their stress-temperature coefficients to be unsuitable for the application of the thermodynamic equation 1 and the low value of ΔS reported by Tobolsky and co-workers consequently to be in error. The entropies of fusion recorded in the last column of Table V compare favorably with those for other polymers. They are not abnormally low, as claimed by Tobolsky and co-workers.[13]

All of the results cited, in common with those of the present paper, represent enthalpy changes per mole of peptide units present in native collagen rather than per mole of those units which are *crystalline*. To the extent that the native collagen may contain non-crystalline regions, correction is required to obtain the heat of fusion per mole of units which undergo melting. The percentage of crystallinity in collagen is unknown. The physical properties (*e.g.*, elastic modulus) of the native fiber suggest that native collagen is predominantly crystalline, and hence that the mentioned correction is small, if not negligible.

The diluent melting method applied by Garrett[5] to the ethylene glycol–collagen system gives directly the heat of fusion per mole of crystalline polymer. Unfortunately, application of this method to the collagen–water system is fraught with difficulties posed by extensive solvolysis during the long periods of time during which the sample must be subjected to elevated temperatures.[30] For collagen–ethylene glycol, Garrett obtained $\Delta H_u = 2.25$ kcal. mole^{-1}. The smaller value for ΔH_u found by us could conceivably be due to the presence of an appreciable proportion of amorphous material in native collagen. We are inclined to reject this explanation in consideration of the evident high degree of crystallinity of native collagen. We suggest instead that the smaller value of ΔH_u for collagen in water is attributable to an intrinsic difference in solvating effects of the two solvents.

The reduction in the enthalpy of fusion by KCNS is striking. Complexing of collagen with thiocyanate evidently reduces the enthalpy in the amorphous state considerably more than in the native (crystalline) state. This is not surprising in view of the greater accessibility of functional groups in the amorphous (dissolved) state.

It will be observed that whereas 3 M KCNS reduces ΔH_u by a factor of nearly three, it lowers T_m^i only from 333 °K. (in water) to 287 °K. The entropy change ΔS_u accompanying melting, given in the last column of Table V, is reduced proportionately almost as much as ΔH_u. This result is consistent with formation of ionic complexes in the amorphous state, with resultant decrease in entropy.

Finally, we note the somewhat surprising observation of a *decrease* in exothermicity of dilution with addition of KCNS to the medium (see values of κ_1 in Table II). It is as if the protein complex with thiocyanate is *less* hydrophyllic than the hydrate formed with water alone. More effective saturation of polar functional groups by KCNS could conceivably account for this observation.

(30) L. P. Witnauer and J. G. Fee, *J. Polymer Sci.*, **26**, 141 (1957), reported $\Delta H_u = 7.2 - 8.0$ kcal./mole based on the dependence of T_s^i under zero stress on the concentration of water in cross-linked cowhide collagen. Again, the use of T_s^i rather than T_m^i casts doubt on the results.

Non-Newtonian Viscosity and Flow Birefringence of Rigid Particles: Tobacco Mosaic Virus

BY JEN TSI YANG[1]

The non-Newtonian viscosity and flow birefringence of tobacco mosaic virus (TMV) were measured over a three-decade range of shearing stress, τ. The hydrodynamic lengths, L, as determined from the two methods were comparable at high τ (after due consideration of the different averages involved). A striking difference in L, however, was observed as τ approached zero, where the viscosity curve went through a shallow maximum as contrasted with the sharp upward curvature for flow birefringence. The concept of equivalent ellipsoid was found applicable even for "fat" rods like TMV, although its equivalent length could differ by about 15% from the true molecular dimension.

Introduction

The theories of non-Newtonian viscosities of rigid particles developed by Saito[2,3] and by Kirkwood and his co-workers[4] afford a new method for the determination of the rotary diffusion coefficient,

(1) Cardiovascular Research Institute, University of California Medical Center, San Francisco 22, California.

(2) N. Saito, *J. Phys. Soc. Japan*, **6**, 297 (1951).

(3) H. A. Scheraga, *J. Chem. Phys.*, **23**, 1526 (1955).

(4) J. G. Kirkwood, *Rec. trav. chim.*, **68**, 649 (1949); J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951); J. G. Kirkwood and R. J. Plock, *ibid.*, **24**, 665 (1956).

θ. The validity of the theories were confirmed experimentally in previous publications.[5] These earlier studies, however, were designed to cover as wide a range of shearing stresses as possible (up to 10^5 dynes cm.$^{-2}$) at the expense of precision. For very elongated or flattened particles this is neither necessary nor practical, and it seems desirable, therefore, to further explore this subject by using

(5) J. T. Yang, *J. Am. Chem. Soc.*, **80**, 1783 (1958); *ibid.*, **81**, 3902 (1959).

Ubbelohde-type viscometers which adequately cover the shear range of interest.

Until recently the flow birefringence technique was the only convenient method for determining the θ of rigid particles. With the development of the viscosity method, it is now possible to study the molecular shapes of rigid particles with either technique. It seems also of interest to compare the effect of polydispersity on these hydrodynamic measurements. In a recent paper[6] it has further been suggested that the intrinsic viscosity at zero shear can be determined by a combination of the two methods without extrapolation of the viscosities to zero shear. Complications due to polydispersity that would be expected to arise have still not been investigated.

It is now generally recognized that the mathematical models used in the hydrodynamic calculations do not necessarily resemble the actual molecules in size and/or shape. A further examination of the extent to which the interpretations of hydrodynamic properties in terms of these models can be trusted seems highly desirable. It is with these objectives in mind that we have made a more detailed study of the non-Newtonian viscosity and flow birefringence of tobacco mosaic virus. The actual characterization of this protein has already been excellently described by Boedtker and Simmons.[7]

Experimental

A. Material.—The tobacco mosaic virus (TMV) solution was obtained through the courtesy of Dr. N. S. Simmons of the Atomic Energy Project, University of California at Los Angeles.

All the chemicals were of reagent grade. The phosphate buffer was made up with 0.008 M Na_2PO_4 and 0.002 M NaH_2PO_4, containing 10^{-3} M Versene (adjusted to pH 7.4). The final pH was 7.2.

B. Viscosity Measurements. (a) Viscometers.—Three Ubbelohde-type viscometers were specially designed to cover a wide range of shearing stresses, τ. One was modified after Hermans and Hermans[8] with a precision-bore tubing attached to the capillary, which constitutes a continuously varying pressure head when filled with the solution. Usually about thirty experimental points were taken for each solution. The other two were multi-gradient viscometers having four and five bulbs, respectively. In Table I are listed the relevant geometrical data of the three

TABLE I

DIMENSIONS OF VISCOMETERS

Type	Capillary Radius, R, cm.	Length, L, cm.	Volume of flow, V, ml.	Range of shearing stress[a] τ, dynes cm.$^{-2}$
Continuously varying pressure head	0.0265_1	$282._0$	0.124_2 per cm.	0.05–1.10
4-bulb	$.0215_6$	25.4_0	(1) 1.00_0	3.13_2
			(2) 1.49_5	6.18_0
			(3) 2.01_8	9.41_6
			(4) 3.00_8	11.8_4
5-bulb	$.0167_0$	3.61_0	(1) 0.99_8	14.9_8
			(2) 1.51_0	24.9_7
			(3) 1.99_6	35.7_8
			(4) 2.50_7	47.1_3
			(5) 3.02_0	58.0_2

[a] Based on water at 25.0°.

(6) J. T. Yang, *J. Phys. Chem.*, **62**, 894 (1958).

(7) H. Boedtker and N. S. Simmons, *J. Am. Chem. Soc.*, **80**, 2550 (1958).

(8) J. Hermans, Jr., and J. J. Hermans, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **B61**, 324 (1958).

instruments which were calibrated with mercury. For the 5-bulb viscometer, where kinetic energy and end effects were no longer negligible, the viscosities were calculated from the equation

$$\eta = \alpha t - \beta / t^2$$

Here α and β are two constants characteristic of the geometrical dimensions of the viscometer and also of the solution used. In all cases the constants, as determined with water at two temperatures, were found in excellent agreement with those calculated from the capillary dimensions.

(b) Calculations.—Details of the calculations of the maximum shearing stresses at the capillary wall and the nominal rates of shear for the multi-gradient viscometers have already been described elsewhere.[5] With the concentrations used in this paper corrections to the rates of shear due to inhomogeneous flow were found to be negligible in all cases. All the intrinsic viscosities at constant shearing stress[5] were calculated according to the Huggins' equation. No corrections due to the density difference between solution and solvent[9] were applied, since they were quite insignificant in this case.

The viscosities as measured under a continuously varying pressure head were treated according to Hermans and Hermans' equation[8]

$$\frac{1}{\eta} = -\frac{2\,LS}{\pi dgR^4}\left[4\left(\frac{d\ln\Delta h}{dt}\right) + \left(\frac{dt}{d\ln\Delta h}\right)\left(\frac{d^2\ln\Delta h}{dt^2}\right)\right]$$

$$(2)$$

η = viscosity of the solution or solvent
$\Delta h = h_t - h_\infty$ = distance between the meniscus and the equilibrium position
t = flow time
R and L = radius and length of the capillary, respectively
S = cross-section area of the wide precision-bore tubing containing the solution or solvent
d = density of the solution or solvent
g = acceleration of gravity

In most cases, in particular with very dilute solutions, the last term in equation 2 may be omitted without introducing significant errors. Thus we have

$$\frac{\eta\ (\text{solution})}{\eta\ (\text{solvent})} = \frac{(d\ln\Delta h/dt)_{\text{solvent}}}{(d\ln\Delta h/dt)_{\text{solution}}}\qquad (3)$$

at any chosen pressure head, Δh.

The differentials in equation 3 can be determined from a ln Δh *versus* t plot. Or better, the experimental data can be programmed into an equation which assumes the first three terms of a power series

$$t = a_0 + a_1\ln\Delta h + a_2(\ln\Delta h)^2\qquad(4)$$

where a_0, a_1 and a_2 are constants characteristic of the solution used. Thus the d ln $\Delta h/dt$ at any chosen pressure head, Δh, can be computed with great ease. Needless to say, the last term in equation 4 drops out for the solvent viscosity. (Strictly speaking, the solution of equation 4 is by no means unique, but it should be quite adequate for our purposes.)

To use equation 4 one must first know precisely the h values, for example, with a high-precision cathetometer. For solvent alone the equilibrium position, h_∞, at infinite time can be located automatically by the computer so as to give a constant slope of dln$\Delta h/dt$ throughout the entire range of Δh. It turned, however, that the computed h_∞ always differed slightly from the observed h_∞. In the present case h_∞ (computed) $- h_\infty$ (obsd.) $= 0.080$ out of a total pressure head of about 24 cm., presumably due to the surface tension, drainage and other errors. This discrepancy cast some doubt on the calculated viscosities of the solutions, for which the h_∞ could not be computed because of the presence of non-Newtonian viscosity and therefore the value for the solvent was employed for all the calculations. To what extent h_∞ for the solution was different from that for the solvent could not be determined. The error introduced should be negligible so long as Δh is very large, but it certainly can become very serious when Δh reduces to, say, below 5 cm. It is noted that any small error in Δh and, in turn, the relative viscosity could be manifested several times in the final specific viscosities.

C. Flow Birefringence Measurements.—Both the extinction angles and birefringences were measured in a Rao

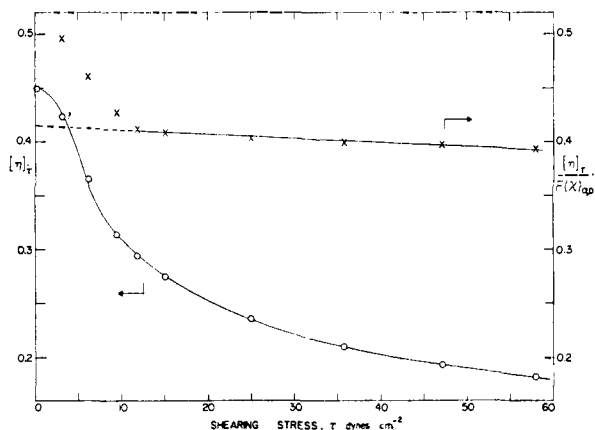(9) C. Tanford, *J. Phys. Chem.*, **59**, 798 (1955).

Fig. 1.—Shear dependence of the intrinsic viscosities of tobacco mosaic virus, including the calculated values of $[\eta]_\tau/F(\chi)_{\alpha,p}$. See text for detail.
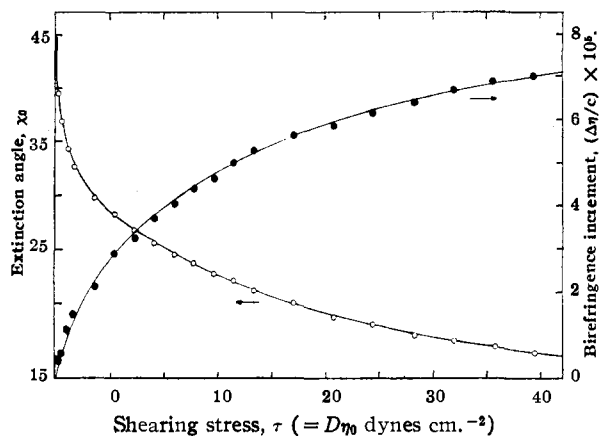

Fig. 2.—Intrinsic extinction angles and birefringence increments of tobacco mosaic virus as a function of shearing stress.

Flow Birefringence Instrument, Model 4-B. The methods of operations have been described elsewhere.[10] The intrinsic extinction angles, χ_0, were calculated from an empirical equation[10]

$$\cot 2\chi = \cot 2\chi_0 + KC \qquad (5)$$

where χ is the extinction angle for concentration, C, at constant rate of shear, D, and K is a constant. For TMV solutions in the concentration range studied (<0.4%) this concentration dependence was rather small but definitely measurable.

D. Calculations of the Hydrodynamic Length.—With the determination of the rotary diffusion constant, θ, from either the non-Newtonian viscosity or the flow birefringence measurements, the hydrodynamic lengths at various shearing stresses were calculated from the Perrin's equation, assuming a prolate ellipsoid of revolution model for the protein[11]

$$\frac{\eta_0 \Theta}{T} = \frac{3k}{16\pi a^3}(2 \ln 2p - 1) \qquad (6)$$

where η_0 is the viscosity of the solvent, T the absolute temperature, k the Boltzmann constant, a the semi-major axis and p the axial ratio of the ellipsoid.

Results and Discussion

A. Intrinsic Viscosities and Flow Birefringence.

—The intrinsic viscosities of tobacco mosaic virus, as determined from the three viscometers,

(10) J. T. Yang, J. Am. Chem. Soc., 80, 5139 (1958).
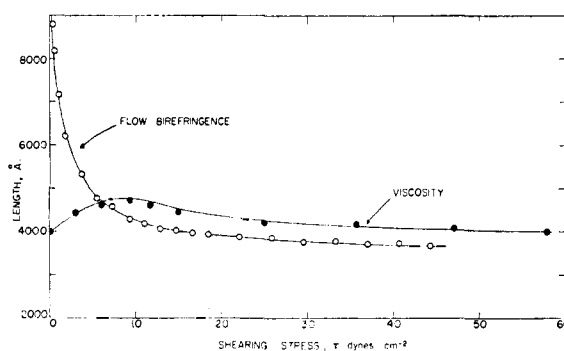(11) F. Perrin, J. phys. radium, [7] 5, 497 (1934).

Fig. 3.—Hydrodynamic lengths of tobacco mosaic virus as calculated from non-Newtonian viscosity (●) and flow birefringence (O).

are summarized in Fig. 1. The marked drop in $[\eta]_\tau$ with increasing shearing stress, τ, was what would have been expected for rigid particles.[5] The intrinsic extinction angles, χ_0, as a function of the τ are shown in Fig. 2, where the smooth curve was made possible by the use of equation 5 which greatly minimized the scattering of the experimental points. Also included in Fig. 2 are the birefringence increments, $\Delta n/C$, at one concentration. The shape of the curve, which appeared to approach saturation at high shear, clearly indicated that TMV is comprised of rigid particles.

B. The Mean Hydrodynamic Lengths.—From the results in Figs. 1 and 2 the α values at various shears can be calculated by using the theoretical tables[3,5,12] and assuming an approximate axial ratio (in this case, $p = 25$). Here α is defined as the ratio of the rate of shear, D, to the rotary diffusion coefficient, Θ, from which the lengths, L $(=2a)$, can be determined by means of equation 6. In Fig. 3 are shown the results from both the viscosity and the flow birefringence methods.

The viscosity-average length at zero shear was estimated in the following way: By definition the intrinsic viscosity is

$$[\eta] = NV_e \nu/100 \, M \qquad (7a)$$

or, for a prolate ellipsoid

$$[\eta]M = (4\pi N/300) (a^3) (\nu/p^2) \qquad (7b)$$

where V_e is the effective hydrodynamic volume of the particle,[13] M its molecular weight, a its semi-major axis, p its axial ratio, N the Avogadro number and ν Simha's viscosity increment.[14] For large p values the term (ν/p^2) is very insensitive to the variations in p, thus providing a simple method of estimation of the length of the equivalent ellipsoid. This method has been shown to be as good as the commonly-used flow birefringence method.[15] By using the relationship $[\eta] = KM^{1.7}$ for rigid particles we have estimated, together with Boedtker and Simmons' data,[7] a molecular weight of about 44×10^6 for our sample. Thus according to equation 7b the length at zero

(12) H. A. Scheraga, J. T. Edsall and J. O. Gadd, Jr., J. Chem. Phys., 19, 1101 (1951).
(13) H. A. Scheraga and L. Mandelkern, J. Am. Chem. Soc., 75, 179 (1951).
(14) R. Simha, J. Phys. Chem., 44, 25 (1940).
(15) J. T. Yang, to be published.

shear was about 4100 Å. if p was taken as 25 (or 4000 Å. for $p = 20$).

The most striking feature in Fig. 3 was the variation of the lengths with the shears. This was due to the different averages obtained from the two methods, even though both obey the same orientation distribution function. The flow birefringence average is quite complicated and still not well understood. Goldstein and Reichmann[16] have shown that as the shear approaches zero $a_{FBR} = (<a^6>/<a^3>)^{1/3}$, which is more heavily weighted by the longer particles than the weight-average value. They have also suggested a number-average, $a_{FBR} = 1/<a^{-1}>$ when the shear becomes infinite. The situation is somewhat less complicated for the viscosity method. It is generally recognized that the viscosity-average at zero shear is closer to the weight-average. At any finite shear the mean lengths would be weighted by the longer particles more than a weight-average and the reason for the appearance of a maximum at low shear has been discussed previously.[5] Once all the particles are oriented parallel to the stream lines (as the shear approaches infinity) there will be no further drop in viscosity and all the particles would again be expected to contribute to the solution viscosity in the same proportion as at zero shear, thus probably approaching the same average as in the latter case. The cross-over of the two curves in Fig. 3 may be explainable by a similar line of reasoning. The foregoing data also show that flow birefringence results are extremely sensitive to the degree of polydispersity, much more so than viscosity. Both curves in Fig. 3, however, appeared to level off gradually at high shear. This merely confirms the fact that the apparently constant length in any narrow range of shear could easily be misleading unless a wide range of shear is covered.

C. Combination of Viscosity and Flow Birefringence.—In a previous paper[6] it has been suggested that the intrinsic viscosity of rigid particles at zero shear can be determined by a combination of non-Newtonian viscosity and flow birefringence. This is made possible by the relation

$$[\eta]_\tau/[\eta]_{\tau=0} = F(X)_{\alpha,p} \tag{8a}$$

or

$$[\eta]_\tau/F(X)_{\alpha,p} = [\eta]_{\tau=0} \tag{8b}$$

where the $F(X)_{\alpha,p}$ values can be read from a calibration curve[6] (the effect of p being insignificant for highly asymmetric particles). For monodisperse systems this method offers an independent check for the intrinsic viscosity values as determined by direct extrapolation to zero shear. Of more interest is the fact that it provides a convenient way to determine which model, prolate or oblate, fits better with the actual molecules. Complications would certainly arise if the particles are polydisperse. This was clearly shown from the $[\eta]_\tau/F(X)_{\alpha,p}$ curve in Fig. 1. The over- and under-correction at low and high shears could again be explained by the different averages of the two methods in the said ranges of shear. Suffice it to say, the evaluation of $[\eta]_{\tau=0}$ by this

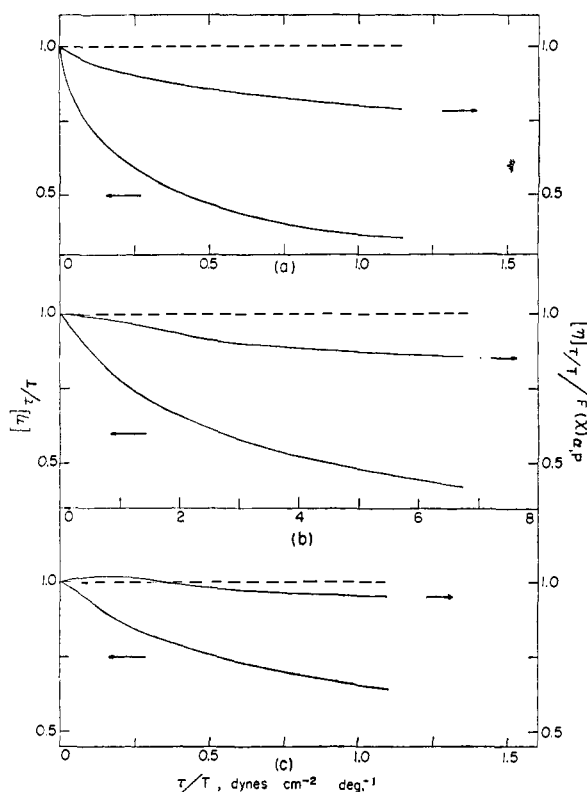(16) M. Goldstein and M. E. Reichmann, *J. Am. Chem. Soc.*, **76**, 3357 (1954).

Fig. 4.—Effect of polydispersity on the $[\eta]_\tau/F(X)_{\alpha,p}$ values for systems having hypothetic molecular-weight distributions: (a) a most probable distribution, D.P. $= 1200$ and $I_w = 1800$ Å.; (b) 3:1 mixture of prolate ellipsoids having $2a = 900$ and 1800 Å.; (c) 3:1 mixture of oblate ellipsoids having $2b = 900$ and 1800 Å. The upper and lower curves in each case represent the use of correct and incorrect models, see text for explanation.

method could involve several per cent. errors under these conditions. To further illustrate this point we have plotted in Fig. 4 the results of three hypothetical molecular-weight distributions[17]: (a) a most probable distribution for rods having a weight-average degree of polymerization of 1200 and length of 1800 Å., (b) a 3:1 mixture of two prolate ellipsoids having lengths of 900 and 1800 Å. and (c) a similar mixture for oblate ellipsoids. In each case the upper curve represented the use of $F(X)_{\alpha,p}$ for the right model and the lower one for the wrong model. As can be seen the extrapolated $[\eta]_{\tau/\tau=0}$ values from high shear differed by less than 10% from its true value. Recently Reichmann has reached essentially the same conclusion.[18]

As expected, the hydrodynamic properties of TMV agree better with a prolate than an oblate ellipsoid, since the $[\eta]_\tau/F(X)_{\alpha,p}$ values based on the latter model (not shown in Fig. 1) would have deviated further from the required horizontal line. It can be said that the substitution of an oblate model for a prolate always results in a downward deviation, whereas the wrong choice of a prolate instead of an oblate becomes overcorrected.[6] Some uncertainty might arise when by

(17) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, Chapter VIII.
(18) M. E. Reichmann, *J. Phys. Chem.*, **63**, 638 (1959).

shear coincidence the $[\eta]_r/F(\chi)_{\alpha,p}$ values of a very polydisperse system of oblate ellipsoids might show little or no deviations from the horizontal line. This complication, however, can easily be resolved by taking into consideration the variations of the calculated lengths based on the chosen model with the applied shear.

D. Equivalent Hydrodynamic Ellipsoids.—It has been a common practice to assume that proteins can be treated as ellipsoids of revolution. By so doing it automatically implies that the hydrodynamic measurements of a protein can only yield information concerning an equivalent ellipsoid which gives the same intrinsic viscosity, sedimentation coefficient and translational and rotational diffusion coefficients as the actual molecule, although the latter does not exactly fit any simple mathematical model. (This idea of an equivalent hydrodynamic ellipsoid was first proposed by Sadron as early as in 1942[19] and lately discussed in detail by Scheraga and Mandelkern.[13]) Very recently question has been raised as to the applicability of the hydrodynamic equations, such as Perrin's (equation 6), to models other than those employed in the theoretical treatments. Boedtker and Simmons[7] reported that the flow-birefringence length of TMV was about 15% higher than that from the light scattering study, a fact seemingly indicative of the failure of Perrin's equation for rodlike particles. Subsequently Haltner and Zimm[20] made a careful study of the rotary frictional coefficient (kT/Θ) of model rods and prolate ellipsoids. These rigid brass models were carefully machined, each having an over-all length of 10.16 cm. and an axial ratio of 20. The latter was chosen to approximate the ratio found for TMV, thus allowing a direct comparison between their data and those for the protein. According to these authors the reciprocal of the rotary diffusion coefficient for the rod (square ends), $1/\Theta_r$, was 40% greater than that calculated on the basis of Burger's approximation for rods[21] and the ratio of the coefficients between the ellipsoid and rod was $\Theta_e/\Theta_r = 1.56$. The latter finding seemed to confirm the inadequacy of Perrin's equation for rodlike particles. It is noted that the two models used in these experiments differed in volumes, although they had the same length and axial ratio. If one adopts a not unreasonable assumption that the volume of the equivalent ellipsoid is identical with that of the rigid, unsolvated rod, then a hypothetic equivalent ellipsoid which retains the same axial ratio of 20 yields some very interesting results. Letting a and b be the semimajor and -minor axes of the ellipsoid and the subscript ee be the equivalent ellipsoid, we then have $(2/3)\, a_{ee}\, b_{ee}^2 = a_r b_r^2$ and $a_{ee}/a_r = b_{ee}/b_r = 1.145$. Now by comparing the rotary diffusion coefficient of this equivalent ellipsoid with that of the previous ellipsoid having a smaller volume, one finds that $\Theta_e/\Theta_{ee} = 1.50$, which indeed agrees very well with Haltner and Zimm's experimental

value of 1.56. Thus Perrin's equation (for prolate ellipsoid) appears to be equally applicable to these "fat" rods, although the major and minor axes of the equivalent ellipsoid in this particular case were 14.5% higher than the length and diameter of the rod. This hypothetic model is by no means unique, but it at least gives us a self-consistent approximate relationship between a "fat" rod and its equivalent hydrodynamic ellipsoid.

Now let us reconsider Boedtker and Simmons' data on TMV in the light of the above discussion. (Their preparation was essentially uniform, thus providing a better test for the theoretical equations than the sample used in this paper.) With the reported $[\eta]_{r=0} = 0.367$ and $M = 39 \times 10^6$ and by assuming $p = 20$, one finds from Equation 7b a viscosity-average length of 3,610 Å. Or, one can estimate the hydrodynamic length from the Svedberg equation for sedimentation which for large p values can be approximated as

$$a = [M\,(1 - \bar{V}\rho)/6\pi\eta_0 NS]\,\ln 2p \qquad (9)$$

where $\bar{V}$ is the partial specific volume of the solute, ρ and η_0 are the density and viscosity of the solvent and s is the sedimentation coefficient. Given $s = 188S$, $\bar{V} = 0.73$ and $M = 39 \times 10^6$, the calculated length $(=2a)$ of TMV turned out to be 3,630 Å. if p was again taken as 20. Boedtker and Simmons' flow birefringence-average length at moderately high shear was about 3,500 Å. Thus all three hydrodynamic methods gave consistent results for an equivalent length of about 3,600 Å. (The choice of $p = 20$ seems reasonable from our present knowledge of TMV. Boedtker and Simmons' calculation was presumably based on a p value of 23.8, and their reported length would have been approximately 3,300 Å. if the same $p = 20$ were used instead. It is noted that the flow birefringence-average length of a polydisperse system becomes smaller at higher shear (see Fig. 3).) On account of the earlier discussion the length of the rodlike particle as deduced from the hydrodynamic measurements would have been 3,600/1.145 or about 3,100 Å. which was in perfect agreement with the reported light scattering result of 3,200 ± 160 Å. Thus there seems to exist a certain relationship between a fairly simple rodlike particle and its equivalent hydrodynamic ellipsoid. Such an agreement may sound rather speculative, but one certainly should not disregard it as shear coincidence unless more experiments of this type indicate otherwise.

Although the length of the equivalent ellipsoid can be estimated with less ambiguity from hydrodynamic properties (due to insensitivity toward variations in p), determination of the diameter or minor axis $(2b)$ and volume is very uncertain without knowing the exact p value. In principle one can calculate both volume and axial ratio from the β- and δ-functions of Scheraga and Mandelkern.[13] The same data of Boedtker and Simmons gave $\beta = 2.61 \times 10^6$ (from $[\eta]$ and s) and $\delta = 1.06$ (from $[\eta]$ and Θ). The former corresponded to a p value of 18.5. If experimental errors were considered to be about $\pm 2\%$, the p values would vary from 16 to 21, which fell into the range ob-

(19) C. Sadron, *Cahiers Phys.*, **12**, 26 (1942); *J. Chem. Phys.*, **44**, 22 (1947); *Progress Biophys. Chem.*, **3**, 237 (1953).

(20) A. J. Haltner, and B. H. Zimm, *Nature*, **184**, 265 (1959).

(21) J. M. Burgers, "Second Report on Viscosity and Plasticity of the Amsterdam Academy of Science," Nordemann, New York, 1938.

served from the X-ray and electron microscope studies. The δ value corresponded to a p of only 8. By assuming a $\pm 15\%$ error (about three times that for Θ) the calculated p varied from 5 to 20. Thus all one can say from the data is that the minor axis of the equivalent ellipsoid for TMV is probably around 180 Å. No attempt will be made to estimate the effective volume of the equivalent ellipsoid since the uncertainty involved is even greater than that for the length and thickness.

The Dependence of Ionic Mobility on the Dielectric Constant of the Solvent

BY DONALD S. BERNS[1] AND RAYMOND M. FUOSS

The conductance of tetrabutylammonium and of tetramethylammonium nitrates in acetonitrile–carbon tetrachloride mixtures was measured over the range $11 < D < 36$ at 25°. Using these data and previous results for the corresponding tetraphenylborides, a comparison was made between the directly observed limiting conductance of $Me_4N \cdot NO_3$ in the various mixtures, and the calculated values obtained by using data for the other three salts and a form of Walden's rule modified to account for electrostatic ion-solvent interaction. Agreement was within about 1%.

Knowledge of the limiting equivalent conductance Λ_0 is necessary for the calculation of the various coefficients which appear in the theoretical conductance equation. This information is readily available for solvents of dielectric constant greater than about 10, but as the dielectric constant decreases, only the quotient K_A/Λ_0^2 can be determined with any precision, regardless of how good the data are, due to the long extrapolation involved when the association constant K_A becomes large. Until recently, the only means for estimating limiting conductances in solvents of lower dielectric constant was Walden's rule, which is known to vary systematically with solvent composition.[2] The use of tetrabutylammonium tetraphenylboride to determine single ion conductances in non-aqueous solvents[3] without recourse to transference data, when combined with the equation

$$R = R_\infty + s/D \tag{1}$$

which relates the Stokes radius R of an ion to the dielectric constant D of the solvent,[4] permits in principle the evaluation of the limiting conductance Λ_0 of any electrolyte in any given solvent of known dielectric constant. The purpose of this paper is to present a test of this working hypothesis. By measuring the conductance of tetra*butyl*ammonium nitrate in mixtures of acetonitrile and carbon tetrachloride and combining the results with previous data for tetrabutylammonium and tetramethylammonium tetraphenylborides in the same solvent system, the limiting conductance of tetra*methyl*ammonium nitrate in these mixtures can be predicted. Comparison of the calculated values with the experimentally determined conductances of tetramethylammonium nitrate shows agreement within about 1% over the approximate

range $11 \leqslant D \leqslant 36$, which is much better than could have been achieved by application of Walden's rule in its original form.

Experimental

Tetramethylammonium nitrate was a sample prepared by Dr. O. V. Brody several years ago from tetramethylammonium bromide by passing a solution through a column packed with Amberlite XE75 (Cl) which had been charged with nitrate ion. The effluent (halogen free) was slightly yellow; it was decolorized with charcoal. The solution was evaporated to dryness under vacuum, and the residue was twice recrystallized from conductance grade methanol; density, 1.25 at 25°. Tetrabutylammonium nitrate was prepared from pure tetrabutylammonium bromide and silver nitrate solutions; after separation of silver bromide and vacuum evaporation of the water, the salt was recrystallized from benzene (15 g./100 ml.); m.p. 119°; density, 0.909 at 25°. Acetonitrile and carbon tetrachloride were purified as described in an earlier paper.[5] Solutions were made up by weight. Two conductance cells were used; they were calibrated using aqueous potassium chloride solutions[6] and have constants 0.073993 ± 0.000006 and 0.39099 ± 0.00004. All measurements were made at $25 \pm 0.002°$. Dielectric constants (1 megacycle), viscosities and densities were determined for all solvent mixtures used; the physical constants are summarized in Table I. The conductance data

TABLE I
PROPERTIES OF SOLVENTS

No.	CCl₄, wt. %	D	100 η	ρ
1	0.00	36.01	3.449	0.7768
2	63.20	18.91	4.796	1.1478
3	63.85	18.45	4.822	1.1527
4	68.46	16.99	5.076	1.1944
5	68.71	17.02	5.078	1.1975
6	74.54	14.65	5.429	1.2547
7	75.81	13.93	5.551	1.2676
8	78.84	12.29	5.800	1.3000
9	80.80	11.35	5.961	1.3226

are summarized in Tables II and III where the solvents are identified by the code numbers of Table I.

(1) California Research Corporation Postdoctoral Fellow, Yale University, 1959–1960.

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(6) J. E. Lind, Jr., J. J. Zwolenik and R. M. Fuoss, *ibid.*, **81**, 1557 (1959).