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Viscosity of Solutions of Rigid Rodlike Macromolecules

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ABSTRACT: The steady flow viscosity of solutions of long, monodisperse, rigid, rodlike macromolecules in good solvents is discussed for the entire range of macromolecular concentrations. It is demonstrated that a proper interpretation of viscosity measurements made over an appropriate concentration range provides important information about the formation of anisotropic phases in such solutions. The concentrations which bound the range of biphasic solution behavior and the mean orientation of the macromolecular rods in an anisotropic (strictly nematic) phase can be evaluated for favorable systems. The sharp maximum in a plot of viscosity vs. concentration is characterized, although it is of only marginal interest in discussions of the isotropic–anisotropic phase transition.

An important group of polymers is composed of macromolecules that adopt the shape of long, rigid rods in appropriate solvents. Above a certain concentration these macromolecules spontaneously form an anisotropic phase, i.e., a liquid crystal. This phenomenon has been explained theoretically[1-3] and observed experimentally by many workers in a variety of systems. An important feature of the transition from isotropic to anisotropic behavior is the concentration of macromolecular rods that is required to induce this phase transition. Many attempts have been made to check the predicted[3] value of this critical concentration by steady flow viscosity experiments. Following the initial investigation of Hermans,[4] it has been the usual practice to identify the characteristic, sharp maximum in a plot of viscosity vs. rod concentration as the harbinger of the onset of anisotropic behavior. The investigation which is reported in this paper was undertaken because such an identification is implausible on physical grounds. However, because the rigid rodlike macromolecules are such an important class of materials, this paper will examine the steady flow viscosity of their solutions over the entire range of rod concentration. The principal focus is directed toward an examination of the utility of steady flow viscosity experiments in elucidating the details of the isotropic–anisotropic phase transition, but simple, physical arguments will also be invoked to clarify the physical basis of the viscosity behavior in the range of concentrations remote from those of biphasic stability.

The systems of interest consist of rigid, rodlike macromolecules dispersed in a good solvent of much lower molecular weight. Typical examples are poly(γ-benzyl glutamate) in *m*-cresol, poly(hexyl isocyanate) in chloroform, and poly(*p*-benzamide) in *N*,*N*′-dimethylacetamide (all near 300 K). The properties of these and similar systems will be idealized to the extent that they will be modeled as suspensions of identical, inflexible, impenetrable, noninteracting (except for hydrodynamic and steric interactions), and extremely elongated, uniform, cylindrical rods. The steady flow viscosity of such a monodisperse, idealized suspension will be discussed only in the limit of vanishingly small shear rate.

Much of the subsequent analysis recapitulates or stems directly from earlier work by many authors. In the interest of brevity, only specific theoretical papers and a few illustrative experiments which verify their calculations have been cited. The reader is referred to any of the standard texts and review articles on polymer hydrodynamics for a broader perspective, particularly with regard to the subject treated in the Isotropic Regime section. The span of rod concentrations breaks naturally into three regimes, viz., isotropic, biphasic, and wholly anisotropic solutions. Each is considered in turn.

Isotropic Regime

Let η_{sp} denote the specific viscosity of an isotropic suspension of macromolecules. In general, an equation of the form

$$\eta_{\mathrm{sp}} = \nu_{\mathrm{e}}\varphi + k_1(\nu_{\mathrm{e}}\varphi)^2 + k_2(\nu_{\mathrm{e}}\varphi)^3 + k_3(\nu_{\mathrm{e}}\varphi)^4 + \ldots \qquad (1)$$

is appropriate.[5,6] Here φ is the volume fraction of polymer, ν_{e} is a coefficient which depends on the shape of the macromolecule (the so-called Einstein coefficient), and k_1, k_2, etc., are coefficients which are at most slowly varying functions of molecular shape.[7] For rigid rods k_1 is 0.73 according to Riseman and Ullman[8] and 0.77 according to Simha.[9] An averaged value of 0.75 was verified (approximately) by Hermans.[4] For sufficiently elongated, prolate ellipsoids of revolution ν_{e} will be specifically denoted ν. It is given as[10]

$$\nu = \frac{J^2}{15}\left(\frac{1}{\ln 2J - 1.5} + \frac{3}{\ln 2J - 0.5}\right) + \frac{14}{15} \qquad (2)$$

where J is the axial ratio of the ellipsoid ($J \gtrsim 15$). This well-known expression is applicable to cylindrical rods of length L and diameter d if J is replaced by $(L/d)(2/3)^{1/2}$.[11] Since the sole interest of the subsequent discussion is with such rods, eq 2 is explicitly recast as

$$\nu = \frac{2x^2}{45}\left(\frac{1}{\ln 2x - 1.8} + \frac{3}{\ln 2x - 0.8}\right) + \frac{14}{15} \qquad (2a)$$

where x is the axial ratio of the rods ($x = L/d \gtrsim 19$).

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As previously noted, eq 1 is applicable to macromolecules of arbitrary shape. For the specific consideration of rodlike macromolecules its full generality is not needed, and it can be profitably simplfied on physical grounds. Doi[12] has formulated an attractive physical model for moderately concentrated solutions of isotropically oriented, very long, and very thin rods. At concentrations in the range $\varphi \gtrsim 3/2x^2$ each rod is imagined to be held in a "cage" composed of neighboring rods. An individual rod is restrained from rotating primarily by collisions with these neighboring rods. As the rods randomly diffuse (almost entirely in directions parallel to their isotropically oriented major axes), the shape of the cage around any particular rod changes on a time scale that is long compared to that during which the rod reaches equilibrium inside the cage. Thus, a particular rod "rotates" by describing a set of nearly independent, small jumps. Doi asserts that this phenomenon will dominate the rotational relaxation of the system of rods and, hence, will dominate the steady flow viscosity of the solution. Doi deduces from this model that the viscosity depends on L and d according to

$$\eta \propto \eta_0 p^3 L^9/\ln (L/d) \tag{3}$$

where η_0 is the solvent viscosity and p is the number density of rods. In the range of interest $\eta \gg \eta_0$, hence $\eta_{\mathrm{sp}} \equiv (\eta - \eta_0)/\eta_0 \approx \eta/\eta_0$. Converting to volume fraction, one can recast this as

$$\eta_{\mathrm{sp}} \propto x^6 \varphi^3/\ln x \tag{4}$$

In the same limit of very large x, eq 2a can be simplified to

$$\nu \approx 8x^2/45 \ln x \tag{5}$$

With this approximation the cubic term of eq 1 is of almost the same form as eq 4. It is the dominant term in the expression for the viscosity. Thus, when applied to solutions of long rods the series in eq 1 can be truncated at the third term. Moreover, the coefficient k_2 can be identified as

$$k_2 = k_2'(\ln x)^2 \tag{6}$$

with k_2' a numerical constant.

Together with the classical physical interpretations of the linear and quadratic terms in eq 1, this completes a simple and satisfying interpretation of the concentration dependence of η_{sp}. In the limit of infinite dilution, the solution viscosity depends only on the perturbation of the solvent flow (treated as a continuum) by the presence of the individual rods. At *slightly* higher concentrations, hydrodynamic interaction between rods becomes important, and the viscosity increased as $\nu\varphi + 0.75(\nu\varphi)^2$. Then at concentrations in the range $\varphi \gtrsim 3/2x^2$, physical contact between the rods becomes important, and the flow properties are dominated by the rod–rod collisions. The equation which summarizes these physical concepts is

$$\eta_{\mathrm{sp}} = \nu\varphi + 0.75(\nu\varphi)^2 + k_2'(\ln x)^2(\nu\varphi)^3 \tag{7}$$

where ν is given by eq 2a and k_2' should be a universal constant when x is sufficiently large.

It is not easy to obtain k_2' theoretically, but it can be obtained empirically (and eq 7 thereby partially verified) by comparison with experiment. Table I summarizes the results of such a comparison. The cited references invariably report the dependence of η on φ as a curve. Extraction of the ordered pairs which are tabulated in columns 3 and 4 of Table I from such a curve is necessarily imprecise. Consequently, the reasonable concordance of values of k_2' for the tabulated systems is encouraging but not definitive.

Table I
Empirical Values of k_2'

x	J[a]	φ	η, P	system	$k_2' \times 10^3$
66	54	0.047	20	PBLG[b] in *m*-cresol[27]	3.0
98	80	0.045	70	PBLG in *m*-cresol[4]	1.3
120	98	0.033	150	PBLG in *m*-cresol[4]	4.0
150	122	0.044	500	PBG[b] in *m*-cresol[16]	1.5
153	125	0.033	240	PBLG in *m*-cresol[4]	1.3
157	128	0.048	400	PBLG in dimethylformamide[28]	21[c]
282	230	0.037	500	PBLG in dimethylformamide[28]	1.8
298	243	0.030	500	PBLG in dichloroethane[28]	2.6
364	297	0.018	200	PBLG in dimethylformamide[28]	1.4

[a] The hydrodynamic axial ratio was computed for each sample from the reported molecular weight and the experimental value for the diameter of the molecular rod in the solvent of interest. These diameters for PBLG[b] are 15.4 Å in *m*-cresol, 14.9 Å in dimethylformamide, and 14.1 Å in 1,2-dichloroethane. An extension along the helix axis of 1.5 Å per residue for the α-helix was used in all cases. [b] PBLG is used to abbreviate poly(γ-benzyl L-glutamate) and PBG denotes a mixture of equal amounts of the L and D isomer of this polymer. The former forms cholesteric liquid crystals in the cited solvents, and the latter forms nematic liquid crystals. [c] No reasonable explanation of this anomolous value is apparent.

According to Doi,[12] his analysis will break down when the "jump" lengths approach the magnitude of the rod diameters. It happens to be the case that this begins to occur at approximately the same concentration at which biphasic behavior is predicted to begin in the solution (see the Biphasic Regime section). Therefore, care was exercised during the compilation of the data reported in Table I to avoid the region of the viscosity–concentration curves which bordered the expected onset of biphasic behavior. Doi tentatively suggests that the analysis can be extended to cover the entire range of isotropic concentrations by modifying eq 3 to read

$$\eta \propto \eta_0 p^3 L^9/[\alpha/\alpha^* - p/p^*]^2 \ln (L/d) \tag{8}$$

Here α and α^* are constants and p^* is the critical concentration at which some volume of anisotropic phase will appear.[29] In view of the tentative and ad hoc origin of eq 8, it is reproduced here only for completeness, and no subsequent account will be taken of it. It will suffice to acknowledge that eq 7 may break down over a small range of concentration just prior to the end of the isotropic regime. The effect of this breakdown will be indiscernible in the limit of large x, but for real systems one may anticipate that the viscosity will deviate from a strict dependence on the third power of the concentration.

Biphasic Regime

An isotropic distribution of long rods cannot be maintained above some critical concentration denoted φ^*.[1-3] φ^* is primarily a function of axial ratio and is given approximately by[3]

$$\varphi^* \approx \frac{8}{x}(1 - 2/x) \tag{9}$$

for large x ($x \gtrsim 50$). At concentrations in excess of φ^*, an entropically driven transition occurs to produce an anisotropic (liquid crystalline) phase of concentration given approximately by[13]

$$\varphi^{\mathrm{A}} \approx 11.6/x \tag{10}$$

for large x ($x \gtrsim 100$). The predicted values of φ^* and φ^{A} have been *approximately* verified by experiment,[4,14-16]

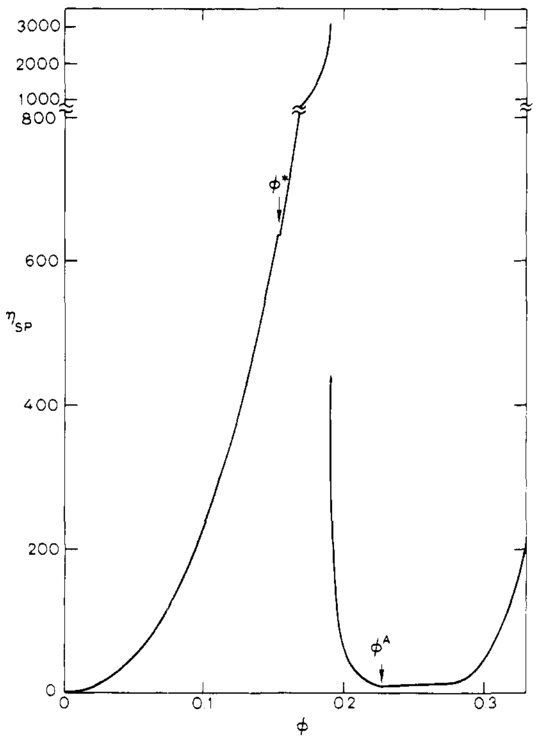

Figure 1. The specific viscosity for a solution of rods with an axial ratio of 50 is plotted vs. the volume fraction of rods. The biphasic regime begins at volume fraction $\varphi^* = 0.1538$ and ends at volume fraction $\varphi^A = 0.2282$. Details of the procedure used to compute this curve are given in the text.

including steady flow viscosity measurements. Therefore, it is of interest to consider the dependence of solution viscosity on rod concentration in the range $\varphi^* \leq \varphi \leq \varphi^A$, i.e., the biphasic regime.

Consider a solution of rods at equilibrium, where the concentration is exactly equal to φ^*. The rod axes are isotropically arranged. To this solution let an infinitesimal volume of additional rods be introduced. The isotropic solution cannot accommodate these additional rods at equilibrium, and an infinitesimal volume of an anisotropic phase will be created. The concentration of rods in the anisotropic phase is φ^A. This second phase, when dispersed in the continuous isotropic phase, will increase the viscosity as would any other occlusion. If the dimensions of the suspended domains of the anisotropic phase are large relative to the size of the rodlike solute, yet smaller than the characteristic dimensions of the experimental apparatus (e.g., capillary tube diameter or plate separation), then the composition of the solution will be exactly that envisioned in the development of eq 1. Hence, an appropriately "rescaled" version of eq 1 is expected to quantitatively describe the viscosity. Addition of more rods will cause an increase in the volume of the anisotropic phase, while the rod concentrations in the isotropic and anisotropic phases remain fixed at φ^* and φ^A, respectively. Hence, the viscosity of the continuous isotropic phase will remain constant, and it can be identified as the viscosity of the "rescaled solvent" (now a binary mixture). Similarly, the quantities ν and φ which appear in eq 1 now apply to the "rescaled particles", i.e., the anisotropic occlusions. Thus, as the concentration of macromolecular rods enters the range $\varphi > \varphi^*$, the slope of the viscosity–concentration curve will exhibit an abrupt change but will remain positive. This is illustrated in Figure 1 which will be more fully described below.

The discussion of the previous paragraph should be compared with the frequently stated belief that *a maximum* in the viscosity concentration profile corresponds to the onset of anisotropic phase formation. There are no grounds to support this belief provided that all of the caveats of the preceding paragraph are observed. It may at first appear that these caveats are so restrictive that no real system can be accommodated within their strictures, viz., the anisotropic phase is required to (initially and for the duration of the experiment) disperse in domains that are characterized by dimensions of the order of 100–0.1 μm. The beautiful photomicrographs published by Robinson[17] and Aharoni[18] demonstrate that this concern is unwarranted. Nevertheless, it is also quite clear that the equilibrium structure of a system in the biphasic regime would have just two domains: one isotropic and one anisotropic. Typically, equilibration of these very viscous solutions requires days or weeks. Therefore, we anticipate that experiments can readily be carried out under conditions (albeit nonequilibrium conditions) where a rescaled version of eq 1 will adequately describe the viscosity–concentration profile of the initial portion of the biphasic regime.

There is a concentration at which the viscosity of a solution of macromolecular rods attains a sharp maximum. It corresponds to the end of the concentration regime over which the rescaled version of eq 1 is applicable, and we now examine its probable meaning in molecular terms. As the concentration of rods continues to increase above φ^*, an increasingly large fraction of the total solution volume becomes occupied by the second (anisotropic) phase. Regardless of whether this second phase is present as dispersed domains (the condition for applicability of the rescaled eq 1) or as a macroscopically distinct portion of the solution, it must prevade the entire volume at φ^A. In either case the viscosity will exhibit a maximum at a concentration that is intermediate between φ^* and φ^A but for quite different reasons in the two cases. If the solution consists of one phase finely dispersed in another everywhere throughout the biphasic regime, then a viscosity maximum will be observed at the concentration at which phase inversion takes place. This is the concentration at which the solution changes over from a continuous isotropic phase (with anisotropic occlusions) to a continuous anisotropic phase (with isotropic occlusions). The identification of the inversion point with a viscosity maximum was first made by Ostwald[19] in connection with the viscosity of hydrophobic colloidal suspensions. On the other hand, if some or all of the minor phase is present in domains that are continuous over distances that are of the scale of the experimental apparatus, then the maximum will occur at some ill-defined point in the range of biphasic stability. Observations on such a "two-fluid" system will be hard to interpret on a molecular basis and will probably be difficult to reproduce with precision. At least it may be supposed that since the anisotropic phase will invariably be less viscous (see the Anisotropic Regime section) than the isotropic phase, the viscosity maximum will correspond to a solution which contains a substantial volume of the isotropic phase.

Figure 1 depicts a viscosity–concentration plot for a system of the idealized rods under consideration which have an axial ratio of 50. The smooth curve in the isotropic regime ($\varphi \leq \varphi^*$) was calculated according to eq 7 with k_2' set equal to 2×10^{-3}. The biphasic regime in Figure 1 ($\varphi^* < \varphi < \varphi^A$) is spanned by a discontinuous curve with specific features that strongly depend on certain idealizations and assumptions. First, it has been assumed that the phase which is the minor constituent of the solution is occluded as colloidal, spherical domains so that a rescaled version of eq 1 is applicable. The Einstein coefficient appropriate for colloidal spheres of one fluid dispersed in another was computed by Taylor[20] to be

$$\nu_0 = 2.5\left(\frac{\eta' + 0.4\eta}{\eta' + \eta}\right) \tag{11}$$

where η' is the internal viscosity of the spherulites, η is the viscosity of the continuous fluid phase, and the subscript 0 denotes the relation of ν_0 to the occlusions. Second, it has been assumed that phase inversion occurs at the midpoint of the biphasic regime. Thus, the rescaled eq 1, viz.,

$$\eta_{sp}{}^{\dagger} = \nu_0\varphi_0 + k_1(\nu_0\varphi_0)^2 + k_2(\nu_0\varphi_0)^3 + k_3(\nu_0\varphi_0)^4 + \ldots \tag{12}$$

is applicable everywhere in the biphasic regime, where φ_0 denotes the volume fraction of anisotropic occlusions before the midpoint and the volume fraction of isotropic occlusions for concentrations between the midpoint and φ^A. Of course, as noted earlier in this section, the solvent viscosity (included implicitly in $\eta_{sp}{}^{\dagger}$) in eq 12 is that of the appropriate, continuous phase (a binary mixture) and not that of the small molecular weight solvent alone. Thus, the value of $\eta_{sp}{}^{\dagger}$ which arises in eq 12 has been used to compute the specific viscosity relative to the viscosity of the small molecular weight solvent; it is the latter specific viscosity η_{sp} which is plotted in Figure 1. The third assumption made for the purposes of constructing the biphasic portion of Figure 1 is that the viscosity in the spherical occlusions is the same as that in the corresponding bulk phase. Thus, η' for isotropic occlusions is given by eq 7 ($\varphi = \varphi^*$) and for anisotropic occlusions it is given by eq 22 ($\varphi = \varphi^A$) which is derived in the next section. The fourth, and final, assumption that has been made is that the coefficients k_1, k_2, etc., are collectively those deduced by Mooney[21] for suspensions of spherical particles. With this assumption, eq 12 can be written more compactly as

$$\eta_{sp} + 1 = \exp[\nu_0\varphi_0/(1 - \varphi_0/\varphi_c)] \tag{12a}$$

where φ_c is a constant. For the idealized system under consideration, φ_c is equal to the maximum volume that can be filled by close-packed, identical spheres, 0.74.

In concluding this discussion of the viscosity throughout the biphasic regime, a few remarks on the discontinuity at the concentration of maximum viscosity and the set of four assumptions which lead to its calculation are in order. The assumption of spherical, colloidal domains is a natural one because of its simplicity, the general tendency toward minimal surface area expected from dispersed systems, and the few experimental observations[17,18] that are available. The expectation of a trend toward minimal surface area also motivates the postulate that phase inversion will occur at the midpoint of the biphasic regime. Also, once the assumption of spherically shaped domains has been made, it is not unreasonable to invoke Mooney's equation[21] (eq 12a), since it is simple, it has some theoretical justification, and it has been successfully applied to a few concentrated solutions of spherical particles.[21,22] Even if another choice of a set of values for the k_i coefficients in eq 12 had been made, the discontinuity at the phase transition will persist unless the viscosities of the conjugate isotropic and anisotropic phases are equal. Thus, in the absence of evidence to the contrary, the assumptions made in this section are defensible except for the equating of the viscosities of the occluded domains and the bulk phases. Clearly, the presence of the curved interface between the occluded and continuous phases will play some role in affecting the rod orientations and their contributions to the viscosity. Equation 11 shows that the relative magnitude of η and η', rather than the absolute value of η', is the important quantity for determining ν_0, and the dependence of ν_0 on η'/η is not very strong. Thus, little error is expected to result from a moderately inaccurate estimate for η'. Furthermore, unless η' is equal to η the discontinuity will persist. It is to be concluded then that a discontinuity at the maximum in the viscosity–concentration profile can be reasonably expected for a system which can be maintained in a sufficiently dispersed biphasic form. Failure of any of the specific assumptions which have led to the precise shape of the biphasic portion of Figure 1 will not change its qualitative features. Even so, the precise position and magnitude of the maximum and its continuous or discontinuous shape are of only marginal interest as parameters of the isotropic–anisotropic transition. At the very least they apply to a nonequilibrium state and will be difficult to observe with precision. The change in slope which marks φ^* is of more fundamental interest. A similar change of slope will mark φ^A, and its precise characterization is the major focus of the following section.

Anisotropic Regime

If a solution of long rods is prepared such that the rod concentration exceeds φ^A, then the equilibrium structure of the solution will be that of a liquid crystal. All of the rods will be preferentially oriented toward a particular direction. In a steady flow viscosity experiment the preferred direction will be parallel to the direction of flow.[30] The extent of the orientation depends on the concentration and axial ratio of the rods.[3,13] Let ψ denote the angle formed by the rod axis and the preferred direction of aligned rods. The equilibrium value of ψ and the related disorientation parameter $\bar{y}$ are fixed by the relations[13]

$$(4/\pi)\langle\sin\psi\rangle = \bar{y}/x \tag{13}$$

and

$$\exp(-2/\bar{y}) = 1 - \varphi(1 - \bar{y}/x) \tag{14}$$

The lower solution of eq 14 is the physically meaningful one. Calculations[3,13] show that as x becomes very large, the ratio $\bar{y}/x$ rapidly approaches a limiting value of about 0.2 for $\varphi = \varphi^A$. For concentrations in excess of φ^A, $\bar{y}$ decreases monotonically according to eq 14. A minimum value of $\bar{y} = 1$ is required for strict adherence to the lattice model from which eq 13 and 14 are derived, but no mathematical inconsistencies appear for fractional but still positive values of $\bar{y}$. The lattice model is an idealization. Moreover, all the equations pertaining to solution viscosity which are cited in this paper arise from models of a solvent continuum. Thus, strict adherence to the lattice model will be sacrificed in subsequent discussions, and all nonnegative values of $\bar{y}$ will be permitted.

No adequate theory is available for describing the viscosity behavior of anisotropic solutions such as those contemplated in the preceding paragraph. The problem is formidable. Fortunately, a complete understanding is not required in order to discuss the viscosity in the neighborhood of φ^A, which is the one of dominant interest. The classical theory of the viscosity of dilute isotropic suspensions is a well-developed and quantitatively successful discipline. Equation 1 is a useful product of this classical theory and it is natural to contemplate its physical content in order to obtain a guide for examining these concentrated, anisotropic solutions.

The form of eq 1 implies that the viscosity of a suspension can be analyzed as the result of addition of the perturbations in the flow of the solvent continuum arising from individual particles. Each particle experiences the flow of a solvent with an "effective viscosity" of $\eta_0[1 + k_1(\nu_e\varphi) + k_2(\nu_e\varphi)^2 + ...]$, and the net effect of all particles is given by the product of the effective viscosity, the Einstein coefficient, and the volume fraction of particles. In order to make this evident, eq 1 can be rewritten with the use of the definition of the specific viscosity in the form

$$\eta - \eta_0 = \eta_0[1 + k_1(\nu_e\varphi) + ...]\nu_e\varphi \qquad (15)$$

or, in an obvious notation

$$\eta_{sp} = \left(\frac{\eta_{eff}}{\eta_0}\right)\nu_e\varphi \qquad (16)$$

Anticipating that an equation of this same form will apply to an anisotropic solution of long rods, it is then required to evaluate the coefficients ν_e (ν for rods) and η_{eff}.

The viscosity of an infinitely dilute suspension of long, rigid rods with a particular distribution of rod orientations has been computed by Burgers.[23] In the limit of vanishingly small shear rate, large x, and predominant orientation parallel to the direction of flow, the result is

$$\eta_{sp} = \left[\frac{2x^2\langle g\rangle}{3(\ln 2x - 1.80)} + 2\right]\varphi \qquad (17)$$

where g is the goniometerical expression in eq 10.13 of Burgers' paper. In the present notation

$$\langle g\rangle = \langle\cos^2\psi\,\sin^2\psi\,\sin^2\beta\rangle \qquad (18)$$

where ψ is the azimuthal angle previously defined and β is the transverse angle which together specify the rod direction with respect to the preferred axis of the anisotropic solution. The mean value of g can be computed with the use of the method of asymptotic approximation of Flory and Ronca.[13] Neglecting terms of higher order, the resulting expression is

$$\langle g\rangle = \frac{3\pi^2}{64}(\bar{y}/x)^2 \qquad (19)$$

Combination of eq 17 and 19 yields

$$\eta_{sp} = \left[\frac{\pi^2\bar{y}^2}{32(\ln 2x - 1.80)} + 2\right]\varphi \qquad (20)$$

where the term in square brackets is identifiable as the Einstein coefficient, denoted as ν_a to signify its significance for an anisotropic solution. It can be seen that in the limit of perfect orientation ($\bar{y} = 0$), $\nu_a = 2$ in agreement with the result of Jeffrey.[24]

In order to obtain an expression for η_{eff} in eq 16, recourse can be taken again to qualitative, physical arguments. There are many conceivable ways in which one rod in anisotropic solution could influence the properties of the solvent that is flowing in the vicinity of another rod. Some of these (e.g., direct shielding of one rod by another in front of it and parallel to both it and the direction of flow) will decrease the frictional forces experienced by a particular rod, and others (e.g., hydrodynamic interactions such as those contemplated in the evaluation of k_1[8,9] for isotropic solutions) will increase those frictional forces. In a first approximation, let us suppose that the negative hydrodynamic interactions cancel out the positive ones, so that only direct steric interactions between the rods need to be considered. Certainly, this assumption that steric interactions dominate the viscosity of anisotropic solutions of rods is encouraged by the success of the same assumption in describing the viscosity of isotropic solutions of rods[12] and in describing the isotropic–anisotropic phase transition.[3] Thus, we suppose that the presence of many neighboring rods in anisotropic solution will influence the properties of the solvent around any particular rod mostly by direct crowding. If φ_m is the maximum volume fraction that can be filled by rods of a particular shape and packing geometry, then this can be expressed as

$$\eta_{eff} = \frac{\eta_0}{1 - \varphi/\varphi_m} \qquad (21)$$

If the diameters of the small molecular weight solvent molecules are negligible with respect to the rod diameters, then φ_m can be readily computed from simple geometrical considerations. For example, very long cylindrical rods can fill the fraction 0.907 of total space when close packed in an hexagonal array. However, if the diameters of solvent and solute are comparable φ_m can be much less than 0.907. This is because when solute particles approach one another so closely as to exclude solvent, they appear to occupy a greater volume than the sums of their individual volumes. The formation of such clusters is expected to profoundly increase the viscosity of an isotropic solution,[7] and a similar effect is obviously expected here. Moreover, the continuum approximation for the effective solvent (necessary for eq 21 and for a meaningful interpretation of ν_a) becomes untenable if the average distance between rod surfaces is less than a few molecular diameters (of the small solvent molecules). A reasonable upper limit for φ_m is, therefore, the volume fraction at which the surfaces of neighboring rods approach to within one solvent molecule diameter for perfectly parallel, hexagonally packed rods. For a system with isodiametrical rods and solvent species, $\varphi_m = 0.227$.

Thus, eq 16, 20, and 21 can be combined to yield

$$\eta_{sp} = \left[\frac{\pi^2\bar{y}^2}{32[\ln 2x - 1.80]} + 2\right]\frac{\varphi}{1 - \varphi/\varphi_m} \qquad (22)$$

as an approximate expression for the viscosity of a spontaneously anisotropic solution of long rods in the limit of vanishingly small shear rates. For sufficiently large x, eq 22 can be expected to apply at φ^A and higher concentrations (approaching φ_m) over a reasonable range of the anisotropic regime.

The portion of the curve in Figure 1 which lies above φ^A was computed with the aid of eq 14 and 22. It was assumed that the diameter of the rods was slightly greater than the diameter of the small molecular weight solvent. The ratio of the two was set equal to 1.5. The qualitative features of this portion of the curve are observed in experiments on anisotropic solutions of rigid rods.[4,16] For these choices of x and φ_m the viscosity at φ^A is a minimum (see Figure 1). However, this will not be the case in general, and only a discontinuity in a uniformly decreasing curve will mark φ^A. The change of slope that is expected to mark the concentration φ^A (where the viscosity–concentration curves described by eq 12a and 22 meet one another) has not yet been reported. Careful experiments to observe this predicted discontinuity in the slope of the viscosity–concentration profile are to be hoped for in the near future.

Conclusions

The concentration dependence of the specific viscosity of an idealized solution of rigid rods is given by the system of equations

$$\eta_{sp} = \nu\varphi + 0.75(\nu\varphi)^2 + k_2'(\ln x)^2(\nu\varphi)^3 \qquad \varphi \leq \varphi^* \qquad (23a)$$

$$\eta_{sp}^{\dagger} = -1 + \exp[\nu_0\varphi_0/(1 - \varphi_0/\varphi_c)] \qquad \varphi^* < \varphi < \varphi^A \qquad (23b)$$

$$\eta_{sp} = \left[\frac{\pi^2\bar{y}^2}{32[\ln 2x - 1.80]} + 2\right]\frac{\varphi}{1 - \varphi/\varphi_m} \qquad \varphi^A \leq \varphi < \varphi_m \qquad (23c)$$

In eq 23 the coefficients ν, ν_0, φ_c, and φ_m are all fixed by the dimensions of the macromolecular rods and the solvent. The volume fraction of occlusions, φ_0, in the biphasic regime can be estimated from the predicted[13] values φ^* and φ^A, although the concentration at which phase inversion occurs cannot be predicted in general with much certainty at this time. It has been tentatively assumed in this paper that it occurs at the mean of φ^* and φ^A.

There are three important details of the isotropic–anisotropic phase transition which appear in eq 23, viz., φ^*, φ^A, and $\bar{y}$. Steady flow viscosity measurements can be used to investigate all three. The concentrations φ^* and φ^A which bound the biphasic regime will be marked by discontinuities in the slope of a plot of η_{sp} (or η) vs. the concentration of rods. Of course, in practice the discontinuities will be difficult to observe and shoulders or anomolous scattering of the experimental data may be the only detectable indications of the boundaries of the biphasic regime. In favorable systems where $\varphi^A \ll \varphi_m$, the disorientation parameter $\bar{y}$ can also be measured by steady flow viscosity. It will be proportional to the slope of the curve of η_{sp} vs. φ according to eq 20 and will change with concentration according to eq 14. If φ_m is accurately known, then eq 22 can be used to estimate $\bar{y}$ over a wider range of concentration within the anisotropic regime. However, it is unfortunately clear that most earlier studies have obtained rather sparse data which are not very useful for precisely determining any of the parameters of the isotropic–anisotropic phase transition.

There are some recent indications in the literature that the qualitative features of eq 23 are, in fact, correct. "Anomalous" shoulders have been reported in viscosity vs. concentration measurements,[16,18,25,26] typically at concentrations slightly lower than those at which the maximum viscosity is observed. One study[25] has even reported that the appearance of an anisotropic phase precedes the viscosity maximum, in contrast to the generally accepted interpretation, but in agreement with the view of this paper.

Quantitative verification of eq 23 will have to await additional experiments, and such measurements are now under way in this laboratory. In this regard, it should be mentioned that the changes in slope at φ^* and φ^A may very likely be more pronounced than those indicated in Figure 1. Figure 1 was constructed to lend concreteness to the discussion of the qualitative appearance of the viscosity–concentration profile in its simplest physically acceptable form. The specific assumptions (see the Biphasic Regime section) which were made in the calculations for solutions in the biphasic regime are plausible, but artificial in the sense that no real system may conform to all of them. In particular, if a distribution of sizes is permitted for the occlusions, or if the internal viscosity of the occlusions is considerably different from the corresponding bulk phases, then the change in slope at φ^* will be accentuated. The change in slope near φ^A is most strongly dependent on x and φ_m. Such potential mitigating conditions cannot be treated in a general fashion. Moreover, the barely discernible changes in slope at φ^* and φ^A in Figure 1 do dramatically emphasize the need for great care in experimental studies which attempt to characterize the phase transitions of rodlike macromolecules by steady flow viscosity.

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(29) Doi does not attempt to compute either α or α^*, but we point out here that for large x, $\alpha^* = 32/\pi$. This follows from eq 9 and the requirement[12] that $p^* = \alpha^*/dL^2$.
(30) For simplicity, the discussion in this section will implicitly assume that the anisotropic structure is nematic. The results may be anticipated to also apply reasonably exactly to cholesteric structures such as those of the lyotropic polypeptide anisotropic phases. Additional effects which would arise from the influence of impressed electric or magnetic fields will be ignored. All of these situations involve changes in the direction of the preferred (local) axis, and could be described by correctly accounting for the changes in the value of ν_a (see eq 20).