Biophysical Chemistry 15 (1982) 205–208
Elsevier Biomedical Press

THE VISCOSITY INCREMENT FOR ELLIPSOIDS OF REVOLUTION

SOME OBSERVATIONS ON THE SIMHA FORMULA

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Received 29th September 1981

Key words: Viscosity; Ellipsoid; Simha formula; Particle rotation

Outstanding uncertainties in the widely employed Simha (J. Phys. Chem. 44 (1940) 25) function for the viscosity increment ν of macromolecules as modelled by axially symmetric ellipsoids are resolved. A simple development of the analysis also reveals an interesting relationship between ν and the translational frictional property of macromolecules.

1. Introduction

Amongst the hydrodynamic shape parameters used for modelling biological macromolecules in solution, the 'viscosity increment' ν for ellipsoids of revolution as derived by Simha has been very widely used. The viscosity increment can be simply related to the experimentally determinable intrinsic viscosity [7] by

$$\nu = \frac{[\eta]}{\bar{V}_s}$$

where $\bar{V}_s$ is the (solvated) specific volume of the particle. The exact definition of ν and of the conditions under which it can be related to measured properties of macromolecular solutions is thus of some importance. In the present work we identify a long-suspected error in Simha's treatment, show that the final result is nonetheless valid because of apparent cancellation of errors, and discuss the importance of the Brownian rotational velocity (ω_i) in distinguishing shear-induced from pure translational motion of solute particles. The value of ν for the apparently hypothetical case of $\omega_i = 0$ is shown to be capable of very simple derivation under consistent assumptions, to yield a value identical with that given by classical hydrodynamics; a result which may fuel future application.

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2. The Simha formula

In his 1940 paper, Simha [1] gave the following formula for relating ν to the axial ratio for ellipsoids of revolution in dominant Brownian motion

$$\nu = \frac{1}{ab^2}\left\{\left(\frac{\alpha_0''}{2b^2\alpha_0'\beta_0''} + \frac{1}{2b^2\alpha_0'} - \frac{2}{\beta_0'(a^2+b^2)}\right)\frac{4}{15} + \frac{1}{3b^2\alpha_0'} + \frac{4}{3\beta_0'(a^2+b^2)}\right\} + \frac{1}{ab^2} \times \left\{\frac{\beta_0'(a^2+b^2)+2\beta_0''}{\beta_0'[2a^2b^2\beta_0' + (a^2+b^2)\beta_0'']} - \frac{2}{\beta_0'(a^2+b^2)}\right\}\frac{2}{5} \quad (1)$$

where a, b and b are the 3 semi-axes of the ellipsoid ($b > a$ for oblate and $b < a$ for prolate) and the α_0' terms, etc., which depend on a and b

0301-4622/82/0000–0000/$02.75

are elliptic integrals defined by Jeffery [2]. This relationship could be evaluated numerically for both cases and a table of values for ν as a function of axial ratio was given by Mehl et al. [3]. Eq. 1 can be simplified after cancellation of terms to:

$$\nu = \frac{1}{ab^2}\left\{\frac{2\alpha_0''}{15b^2\alpha_0'\beta_0'} + \frac{7}{15b^2\alpha_0'} + \frac{2}{5}\left[\frac{\beta_0'(a^2+b^2)+2\beta_0''}{\beta_0'\left[2a^2b^2\beta_0' + (a^2+b^2)\,\beta_0''\right]}\right]\right\} \tag{2}$$

There have remained, however, some uncertainties in the derivation presented by Simha, as first pointed out by Saito [4] in 1951.

In 1922, Jeffrey [2] had calculated the viscosity increment for a suspension of ellipsoids subject to purely hydrodynamic (or 'convective' [5]) forces and torques and no Brownian motion. Simha's paper was an attempt to extend Jeffrey's analysis to the case where Brownian motion was dominant. According to Simha, as a result of the Brownian motion the suspended ellipsoids would have random orientations and have zero angular velocity: '$\omega_i = 0$ in Jeffery's formulae 22, 24 and 26'. Saito [4] later stated that the latter assumption was incorrect, showing in his eqs. 3.7 that the particles should rotate on average with the local angular velocity of the fluid. This can also be proved from Brenner [6]: combining his eqs. 7.36 and 8.36

$$\boldsymbol{\Omega} = \boldsymbol{\omega}$$

where $\boldsymbol{\Omega}$ and $\boldsymbol{\omega}$ are, respectively, the angular velocity pseudo vectors of the particle and the fluid. In Brenner's original paper, eq. 7.36 is misprinted and should read

$$\boldsymbol{\omega} - \boldsymbol{\Omega} = -\tfrac{1}{2}\boldsymbol{B}:\boldsymbol{\Delta} - (\boldsymbol{\Omega}^c + \boldsymbol{\Omega}^B)$$

Surprisingly, however, Saito obtained the same final formula as Simha and this fact led him to suggest that perhaps Simha had made 'some errors in calculation'. In order to explain this inconsistency we outline the method followed by Simha and Jeffery.

3. The flow velocity and pressure

We need to calculate the additional dissipation of energy caused by introducing the particle into a given flow, and we do this by comparing the given flow with the consequent disturbed flow within a suitable sphere, S, of radius R, centred on the particle position. We impose two requirements upon S: firstly, that it is small compared with the scale of spatial variations in the given flow, and thus within it that flow is a linear variation of velocity with position; secondly, that it is large compared with the size of the particle, and thus that the disturbed flow will not appreciably differ from the given flow by the time the surface of S is reached. Naturally, these requirements can only be met when the particle is, as we have assumed, very much smaller than the scale of spatial variations in the velocity field of the given flow.

For our purposes then, the disturbed flow may be taken to be the flow of an incompressible fluid in the region between the rotating ellipsoidal surface of the particle and the concentric spherical surface S. On the inner surface we impose the usual no-slip boundary condition, whilst on S we require the velocity field to be equal to its value in the original flow. We give the velocity components of the two flows with respect to rectangular Cartesian axes fixed in the rotating particle so that its ellipsoidal surface will always be given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$$

The undisturbed flow is given, within S, by

$$u_i^0 = g_{ij} x_j$$

where g_{ij} are the components of the velocity gradient tensor which are, by our assumptions, independent of position within S. In this equation and in subsequent equations, the indices range over the values 1, 2 and 3 and the summation convention is used whereby when an index is repeated within a term a summation is indicated over the three values of that index.

Using ellipsoidal harmonics, Jeffrey was able to give the flow velocity and pressure in the region of S for large but finite R. He gives the result under the assumption that the angular velocity is such that no net hydrodynamic torque acts on it, i.e., hydrodynamic effects alone affect the motion of the particle. In order to consider the Brownian motion we follow Simha in dropping this restric-

Table 1

The relationship between the notation used in this study and that used by Jeffrey [2]

$$(A_{ij})=\begin{bmatrix} A & H & G' \\ H' & B & F \\ G & F' & C \end{bmatrix}$$

$$(a_{ij})=\begin{bmatrix} a & h & g \\ h & b & f \\ g & f & c \end{bmatrix}$$

$$(\xi_{ij})=\begin{bmatrix} 0 & -\zeta & \eta \\ \zeta & 0 & -\xi \\ -\eta & \xi & 0 \end{bmatrix}$$

tion whence the flow near S is found, to leading order, to be

$$u_i = u_i^0 - 4\Phi x_i\left[\frac{1}{r^5}-\frac{1}{R^5}\right]+\frac{5}{}\frac{\partial\Phi}{\partial x_i}\left[\frac{1}{R^3}-\frac{r^2}{R^5}\right]$$

In this equation, $\Phi = A_{ij}x_i x_j$, whilst the A_{ij} terms themselves are coefficients independent of position but dependent on the g_{ij} terms and the components ω_i of the angular velocity of the particle; their explicit values are given by Jeffrey (see table 1 for the relationship between his notation and ours). We consider the values of the A_{ij} below.

On the assumption that terms of second order in the velocity may be neglected and that the particle spins are of the same order as the fluid velocities, the dynamic equation for the fluid reduces to

$$\eta\nabla^2 u = \nabla p$$

from which the pressure, p, can be found. For the disturbed flow we find the pressure on S to be

$$p = p_0 - \frac{50\eta\Phi}{R^5}$$

where p_0 is a constant.

4. The dissipation of energy

Assuming a steady state, we can compare the rates of dissipation of energy within S in the two flows by comparing the corresponding rates for working of the viscous stresses on the surface S. This rate of working, dW/dt, is given by

$$\frac{dW}{dt}=\int_S u_i^0 \sigma_{ij} n_j \, dS$$

where

$$\sigma_{ij} = -p\,\delta_{ij} + \eta\left[\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right]$$

are the components of the stress tensor, and

$$n_j = \frac{x_j}{R}$$

are the components of the unit normal to S.

For the disturbed flow we find

$$\frac{dW}{dt}=\frac{8}{3}\pi\eta a_{ij}a_{ij}R^3 + \frac{32}{3}\pi\eta A_{ij}g_{ij}$$

where the $a_{ij} = \frac{1}{2}(g_{ij}+g_{ji})$ terms are the components of the local distortion in the undisturbed flow. On the other hand, the well-known formula of Stokes gives, for the undisturbed flow

$$\frac{dW}{dt}=\frac{8}{3}\pi\eta a_{ij}a_{ij}R^3$$

We thus obtain an expression for Δ, the extra dissipation of energy when the particle is present, namely

$$\Delta = \tfrac{32}{3}\pi\eta A_{ij}g_{ij}$$

If we split g_{ij} into its symmetric and skew-symmetric parts, we have

$$\Delta = \tfrac{32}{3}\pi\eta(A_{ij}a_{ij} + A_{ij}\xi_{ij})$$

where $\xi_{ij} = \frac{1}{2}(g_{ij} - g_{ji})$. Jeffrey, as a consequence of the dynamic assumption mentioned above, was working with symmetrical A_{ij}, and so naturally obtained only the first term in our expression for Δ; and it appears that Simha, although he removed the restriction on A, failed to find the second term: Using Jeffrey's notation (table 1)

$$A_{ij}a_{ij} = (Aa+Bb+Cc)+(F+F')f+(G+G')g + (H+H')h$$

$$A_{ij}\xi_{ij} = (F'-F)\xi + (G'-G)\eta + (H'-H)\zeta$$

whilst the values of, for example, F and F' are

$$F=\frac{\beta_0 f - c^2\alpha_0'(\xi-\omega_1)}{2\alpha_0'(b^2\beta_0+c^2\gamma_0)}$$

$$F'=\frac{\gamma_0 f + b^2\alpha_0'(\xi-\omega_1)}{2\alpha_0'(b^2\beta_0+c^2\gamma_0)}$$

In Jeffrey's paper, the α_0' terms, etc., in the numerators of the above expressions are misprinted as α_0, etc.

We can thus deduce that

$$(F+F')f=\frac{\frac{2\alpha_0''}{\alpha_0'}f^2+(b^2+c^2)f^2+(b^2-c^2)(\xi-\omega_1)f}{2(b^2\beta_0+c^2\gamma_0)}$$

$$(F'-F)\xi=\frac{(b^2-c^2)f\xi+(b^2+c^2)(\xi-\omega_1)}{2(b^2\beta_0+c^2\gamma_0)}$$

where we have utilised the various relationships between α_0, β_0, etc., that are given by Jeffrey.

Now Simha apparently did not find the $A_{ij}\xi_{ij}$ term (it is missing from his eq. 5) and thus would not have had terms like $(F'-F)$ in his calculation. We can see, however, that taking $\omega_1=0$, as he apparently did, in the $(F+F')f$ term gives the same final result as taking $\omega_1=\xi$ in the sum of the $(F+F')f$ and the $(F'-F)$ terms. Since the same argument applies to the other terms we conclude that Simha's formula (eq. 1), although incorrect for $\omega_i=0$ on account of the omission of the term $A_{ij}\xi_{ij}$, is, by a fortunate coincidence, actually correct if $\omega_1=\xi$, $\omega_2=\eta$, $\omega_3=\zeta$.

It is worth noting that if one does take $\omega_i=0$ and includes the $A_{ij}\xi_{ij}$ term, one obtains for spherical particles $\nu=4$, in contrast to Einstein's [7–9] value of 2.5. The result $\nu=4$ for $\omega_i=0$ agrees with that previously found by Brenner [10]. The conditions are physically equivalent to the particles being randomly orientated but having zero angular velocity, i.e., being rigid with respect to the local angular velocity of the fluid. This is appropriate to particles undergoing translation only (e.g., in sedimentation) but not shear. It is of some interest to note therefore that a very simple derivation of ν, based upon the translational properties of uncharged solute particles, can be devised which gives precisely the same value ($\nu=4$). The derivation is as follows:

The effective volume flux associated with the translation of a solute volume $c\bar{V}_s$ ($c=$ mass concentration, $\bar{V}_s=$ specific volume of the particle) is in the limit $c\to 0$ equal to $4c\bar{V}_s$ [11]. The effective free solvent volume fraction, $(1-4c\bar{V}_s)/1$, will be precisely equal to the area fraction occupied by free solvent in any given plane, by standard stereological principles. Assuming zero slip across the area corresponding to effective solute volume, and the pure solvent viscosity coefficient to be otherwise applicable, it follows at once from the basic definition of viscosity (force/area) that the solution viscosity will be incremented by $(1-4c\bar{V}_s)^{-1}$, and hence that in the limit as $c\to 0$, ν (as defined earlier) $\to 4$. The case considered is of course hypothetical, though it could be of potential interest in describing solutions in which the particles were constrained in some manner and hence unable to rotate. It is of value, however, to see that consistent assumptions lead to a consistent result, even using very different theoretical approaches.

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