COMMENTS ON THE CONCENTRATION-DEPENDENCE OF THE VISCOSITY OF SOLUTIONS OF DISCRETE PARTICLES IN A HOMOGENEOUS CONTINUUM

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It has been demonstrated that, for systems containing discrete particles dispersed in a continuum, the mathematical relation between viscosity and concentration is the same over the whole concentration range, provided that certain conditions are fulfilled; those conditions are; *a*) concentration is expressed as the volume fraction of the particles in the solution; *b*) the particles interact only hydrodynamically. This statement is true both for monodisperse solutions, in which the absolute size of particles may vary from one solution to another and for heterodisperse solutions but in the latter case it must be stipulated that all the solutions must contain the same qualitative distribution of shapes and sizes, so that they differ from one another only in the sense that each individual particle is scaled (up or down) relatively to the corresponding particle in another solution by a factor which is constant for all the particles.

The majority of theories which deal with the calculation of the dynamical viscosity of suspensions and solutions of macromolecular compounds are based on the view that these systems consist, on the one hand, of discrete particles of defined character (spheres, ellipsoids, bead necklace, worm-like chain), which model particles of the dissolved compound, and on the other, of a continuum which represents the solvent. The justification offered for this approach is that the size of the solvent molecules can be neglected by comparison with the size of the dissolved particles. We attempt to demonstrate in this paper that, for this type of system (discrete particles in an incompressible continuum, the viscosity of which is η_0), provided that interactions between the dissolved particles are only hydrodynamic, the form of the dependence of the dynamic viscosity of the solution on the concentration, expressed as the volume fraction of the dissolved particles, is the same if all the particles are of the same shape, even if their absolute size is not uniform.

THEORETICAL

The Macroscopic and Microscopic Velocity Gradients in Solution

The expression "velocity gradient in solution" usually implies the "macroscopic gradient".

Let it be imagined that some solution of the above type is subjected to planar shear between two infinite parallel planes (realized to a first approximation between the walls of a Couette vessel. It is clear that in our case the velocity gradient in the liquid phase is a complex function of coordinates and time, depending on the size, shape and concentration of the dispersed particles. Let us call this gradient, which is a tensor quantity, the microscopic gradient $\mathbf{G}_{ij}^{(m)}$. For a system of coordinates (x_1, x_2, x_3), it can be written in the general form

$$\mathbf{G}_{ij}^{(m)} = \mathbf{G}_{ij}^{(m)}(x_1, x_2, x_3, t) = \frac{\partial v_i}{\partial x_j}. \tag{1}$$

It is obvious that the change in the microscopic gradient cannot be examined experimentally and in practice. The macroscopic gradient $\mathbf{G}^{(M)}$ is always used. In the case of planar shear, investigated in this paper, this quantity is governed by the mutual velocity, v, and by the perpendicular separation d, of the infinite parallel walls which set the solution in motion, assuming that the surface liquid layer remains fixed in contact with these walls:

$$\mathbf{G}^{(M)} = v/d. \tag{2}$$

Hence, the gradient $\mathbf{G}^{(M)}$ is a much simpler quantity than $\mathbf{G}_{ij}^{(m)}$, it is experimentally easy to measure and in the selected case of planar shear it is actually a constant, and consequently independent of the spatial coordinates and of time.

Dynamic Viscosity of Solution

In the type of system under consideration the viscosity of the liquid medium is η_0, and the viscosity of the dispersed particles is infinite from the microscopic standpoint. The quantity which is usually discussed is the solution viscosity η, by which is meant the coefficient of proportionality between the macroscopic shear stress $\tau^{(M)}$ and the macroscopic gradient:

$$\tau^{(M)} = \eta \mathbf{G}^{(M)}. \tag{3}$$

Using macroscopic quantities, the dissipation of energy in unit volume within a unit time interval, ε, is given for a planar shear by a simple relation[1]:

$$\varepsilon = \eta(\mathbf{G}^{(M)})^2. \tag{4}$$

For the selected solution model, the dissipation of energy in unit volume within unit time is given (by using Einstein's summation notation) by[1]

$$\varepsilon = \frac{2\eta_0}{x_1^0 x_2^0 x_3^0 t^0} \int_0^{x_1^0} \int_0^{x_2^0} \int_0^{x_3^0} \int_0^{t^0} \mathbf{D}_{ij}^{(m)}(x_1, x_2, x_3, t)\, \mathbf{D}_{ij}^{(m)}(x_1, x_2, x_3, t)\, \mathrm{d}x_1\, \mathrm{d}x_2\, \mathrm{d}x_3\, \mathrm{d}t\,, \tag{5}$$

where $\mathbf{D}_{ij}^{(m)}$ is the tensor of the rate of deformation $\left(\mathbf{D}_{ij}^{(m)} = \frac{1}{2}\left(\frac{v_i}{x_j} + \frac{v_j}{x_i}\right)\right)$ and the integration is carried out through a suitably chosen volume of a substantial part of solution, sufficiently large to make the result generally valid for the whole solution. By combining relations (*4*) and (*5*), one obtains for the solution viscosity η

$$\eta = \eta_0 \frac{\dfrac{2}{x_1^0 x_2^0 x_3^0 t^0} \displaystyle\int_0^{x_1^0} \int_0^{x_2^0} \int_0^{x_3^0} \int_0^{t^0} \mathbf{D}_{ij}^{(m)}(x_1, x_2, x_3, t)\, \mathbf{D}_{ij}^{(m)}(x_1, x_2, x_3, t)\, \mathrm{d}x_1\, \mathrm{d}x_2\, \mathrm{d}x_3\, \mathrm{d}t}{(\mathbf{G}^{(M)})^2} \tag{6}$$

Eq. (*6*) demonstrates the important fact that the solution viscosity, η may be expressed by means of the solvent viscosity, macroscopic gradient and the tensor of the rate of deformation.

Dynamic Viscosity of Similar Solutions

We regard as similar such solutions for which it is possible, by using linear isometrical transformation of the space coordinates ($x_i' = kx_i$) at selected times, to transform dimensions, mutual positions and distances of discrete particles contained in a certain volume V_0 of one solution into dimensions, positions and distances between particles in the corresponding volume $V_0' = k^3 V_0$ of another solution, the solvent in both solutions being a continuum with viscosity η_0.

Let us now imagine two similar solutions subjected to planar shear, so that for both the same macroscopic gradient, $\mathbf{G}^{(M)} = \mathbf{G}^{(M)'}$ can be selected so as to be so low that in neither case could non-Newtonian behaviour of dissolved particles become apparent. Such a restriction is important, because non-Newtonian behaviour is exerted to different extent with particles of different sizes. If the conditions mentioned above are conserved, it follows that flows in both cases must be similar. This means that the microscopic gradients at corresponding points in the two solutions are the same. This is determined by the fact that, at the same macroscopic gradient, the rates in similar solutions are transformed in the same way as the space coordinates, *i.e.* $v_j' = kv_j$. Since components of the gradient are derivatives of the rate components with respect to the space coordinates, it follows in such a case that $\partial v_j/\partial x_i = \partial v'_j/\partial x'_i$, which means that, in general

$$\mathbf{D}_{ij}^{(m)'}(x_1, x_2, x_3, t) = \mathbf{D}_{ij}^{(m)}(x_1/k, x_2/k, x_3/k, t)\,. \tag{7}$$

Let us now examine the magnitude of the viscosity η in these two similar systems the measurements are carried out in the system (x_1, x_2, x_3, t). For one solution the viscosity is given directly by (*6*) and for the other (the quantities of which are indicated by primes) the viscosity is given by an equation analogous to Eq. (*6*):

$$\eta = \eta_0 \cdot \frac{\dfrac{2}{k^3 x_1^0 x_2^0 x_3^0 t^0} \displaystyle\int_0^{kx_1^0}\int_0^{kx_2^0}\int_0^{kx_3^0}\int_0^{t^0} \mathbf{D}_{ij}^{(m)'}(x_1, x_2, x_3, t)\, \mathbf{D}_{ij}^{(m)'}(x_1, x_2, x_3, t)\, \mathrm{d}x_1\, \mathrm{d}x_2\, \mathrm{d}x_3\, \mathrm{d}t}{(\mathbf{G}^{(M)})^2}\,. \tag{8}$$

If $\mathbf{D}_{ij}^{(m)'}(x_1, x_2, x_3, t)$ from Eq. (*7*) is substituted into (*8*) and the integral in the numerator is modified by the substitution $x_i/k = y_i$, with the corresponding change of boundaries, we obtain:

$$\eta = \eta_0 \frac{\dfrac{2}{x_1^0 x_2^0 x_3^0 t^0} \displaystyle\int_0^{x_1^0}\int_0^{x_2^0}\int_0^{x_3^0}\int_0^{t^0} \mathbf{D}_{ij}^{(m)}(y_1, y_2, y_3, t)\, \mathbf{D}_{ij}^{(m)}(y_1, y_2, y_3, t)\, \mathrm{d}y_1\, \mathrm{d}y_2\, \mathrm{d}y_3\, \mathrm{d}t}{(\mathbf{G}^{(M)})^2} \tag{9}$$

identical with Eq. (*6*).

The identity between relations (*6*) and (*9*) for similar solutions having a similar flow at a sufficiently low $\mathbf{G}^{(M)}$ means that the dynamic viscosity η in the limit $\mathbf{G}^{(M)} \to 0$ is similar for similar solutions.

It follows from Eq. (*6*) or (*9*), that η as a function of $\mathbf{G}^{(M)}$ is a constant which characterizes the solution as long as $\mathbf{G}_{ij}^{(m)}/\mathbf{G}^{(M)}$ is independent of $\mathbf{G}^{(M)}$ for all components of the tensor of the rate of deformation throughout the solution. Deviations from the constancy of this ratio are due to the non-Newtonian behaviour; and they appear at a lower $\mathbf{G}^{(M)}$ values in systems with larger particles.

Strictly speaking, the equality between (*6*) and (*8*) holds only for similar solutions with similar flow characteristics, *i.e.* with the same configuration of particles in relevant volume and time ranges. Since, however, η is an average statistical quantity, independent of solution volume and time, when a sufficiently high number of particles is present, η must be the same throughout the solution under investigation and at all times, and must thus be independent of the configuration of the particles in solution.

It can be said in general, therefore. that if two solutions are to possess the same viscosity, it is sufficient if one can assign to each particle in the chosen volume of one solution a particle of identical shape in the corresponding volume of the other solution; the ratio of particle volumes for all corresponding pairs should be the same and equal to the ratio of the volumes of those parts of the two solutions taken for comparison. This means in practice that the volume fractions of the dissolved particles are the same for both solutions, $\varphi_2' = \varphi_2$, and that the distribution of the shapes of the dissolved particles in the two solutions is also the same. From now onwards, the term "similar solutions" will be used just in this sense.

The Concentration-Dependence of Viscosity of Similar Solutions

The above conclusions allow us to derive some important conclusions with respect to the concentration-dependences of the dynamic viscosity of similar solutions. Let it be assumed that for a certain solution of discrete particles in the continuum, which interact only hydrodynamically, the concentration-dependence of dynamic viscosity takes the form

$$\eta = \mathrm{f}(\varphi_2)\,, \tag{10}$$

where φ_2 is the volume fraction of the particles in solution. Eq. (*10*) describes the concentration-dependence of the viscosity of all solutions which contain particles with the same distribution of shapes as the original solution, even though they differ in the absolute size of the particles. For a solution of monodisperse particles, this means, that the η *vs* φ_2 relation is the same for spheres of an arbitrary radius, for rotational ellipsoids of an arbitrary size having a certain ratio of semi-axes, *etc.* but in the case of systems with heterodisperse particles, the situation is more complicated. Here one should be aware of the fact that a system of heterodisperse particles exists even in the relatively simple case in which a solution contains spheres of various sizes. For such systems the η *vs* φ_2 relation is no longer described by the equation which is valid for a solution of uniform spheres, as suggested by *e.g.* the results of calculations of Peeters and Staverman for the Huggins constant of solutions of heterodisperse molecules[2]. Moreover, in solutions of heterodisperse particles, the dissolved particles may differ also in their shape (*e.g.*, mixtures of spheres and rotational ellipsoids with different ratios of semi-axes, *etc.*). The same η *vs* φ_2 relation is observed with such solutions of heterodisperse particles, which contain corresponding particles in the same distribution. The corresponding particles must have the same shape and the ratio of their sizes must be the same for all of them.

These general conclusions regarding the uniform concentration dependence of the viscosity of similar solutions are in agreement with some specific calculations of the concentration-dependence of the viscosities of dilute solutions.

For a solution of monodisperse spheres, Einstein found that[3]

$$\eta = \eta_0(1 + 2\cdot5\varphi_2)\,, \tag{11}$$

which clearly demonstrates that the viscosity of such solutions depends only on η_0 and φ_2, and not on the size of the spheres.

For a solution of monodisperse solid rotational ellipsoids for a small macroscopic gradient (*i.e.* if the orientation of ellipsoids can be neglected)[4], we have

$$\eta = \eta_0(1 + z(p)\,\varphi_2)\,, \tag{12}$$

where $z(p)$ is a function dependent on the ratio of the semiaxes of the ellipsoid p (characterizing the shape of the ellipsoids), but independent of the size of the ellipsoid.

Let it also be stressed that if the concentration-dependences of the viscosity are to be compared for similar solutions differing in the viscosity of the solvent, it is better to compare the η/η_0 *vs* φ_2 relations because this ratio is independent of η_0, as can be seen from the general equation (*6*) and also from Eqs (*11*) and (*12*).

For polymer solutions, the results obtained in this work are suitable insofar as the polymer molecules or whole polymer coils, including the immobilized solvent (in the case of non-draining coils), can be regarded as discrete particles in the continuum, interacting with each other only hydrodynamically.

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