Vladimír Vand

Theory of viscosity of suspensions and solutions. Effect of small particle size

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Vladimír Vand, Port Sunlight, Cheshire, England.

Theory of viscosity of suspensions is extended to cover molecular particle size range by introducing a correction factor containing the ratio of the volumes of the solvent to the solute molecules. Viscosity formulae are given, in which interactions, collisions and hydration is taken into account, and which can be applied to solutions.

Introduction.

In a previous paper,[1]) the author derived theoretical formulae for the relative viscosity of a suspension of spherical particles, believed to be valid up to second power terms; the formulae were tested on suspensions of glass spheres[2]) and on solutions of sucrose in water.[3]) The object of this paper is to extend the theory for solutions when the size of the molecules of the solvent is of the same order of magnitude as that of the molecules of the solute.

The theory of viscosity of solutions can be attacked in several different ways; laws can be derived on the same lines as for pure liquids, depending on their internal structure and forces between molecules. As, however, the whole subject of the internal structure of liquid is still not completely quantitatively understood, another line of attack can be based on the application of hydrodynamical equations to the streaming of liquid round each suspended, or dissolved, particle. This method of approach is known to yield results when the particles or dissolved molecules are larger than the solvent molecules. The whole theory of viscosity of suspensions will be briefly reviewed, the full derivation of some of the formulae not being given as it can be found in the author's previous papers.

According to Jaeger,[4]) Stokes' resistance law holds for small ions in water, which indicates that the hydrodynamical laws are still valid with fair approximation for molecular dimensions. On the other hand, there must be some limit to the validity of hydrody-

namical laws, when the size of the molecules dissolved approaches closely to the size of the molecules of the solvent as, clearly, in the limiting case of addition of the molecules of solvent to itself, increase of viscosity cannot result. However, as the author's investigation of the viscosity of sucrose solutions in water[3] revealed, the numerical value of the constants appeared to be of the same order of magnitude as for large particles. Sucrose molecules have a volume of 360 Å³, whereas water molecules have volume 30 Å³; it can be said that the laws of hydrodynamics were confirmed as being still approximately valid for particles the volume of which is 12 times larger than that of the solvent molecules. The effects discussed in this paper thus come into play only for solutions in which molecules of the solute are less than ten times larger than those of the solvent.

Theory of viscosity of suspensions.

Viscosity of a homogeneous liquid is defined by the relation between kinetic energy transformed into heat W and the components of the velocities of deformation a_{ik}:

$$\mathrm{d}W/\mathrm{d}t = 2\eta \int \int_V \int a_{ik}a_{ik}\,\mathrm{d}V, \tag{1}$$

where η is the viscosity of the liquid,

$$a_{ik} = \tfrac{1}{2}\,(\partial u_i/\partial x_k + \partial u_k/\partial x_i) \tag{2}$$

are the velocities of deformation, u_i the three components of velocities and the summation performed tensorially over twice occurring indices from 1 to 3. The integral is then taken over the whole of the liquid. Equation (1) can be used for determination of viscosity in any apparatus.

Viscosity of a suspension can then be defined by the same equations, provided the instantaneous components of velocity are replaced by their time averages, so that the fluctuations owing to inhomogeneities are smoothed out. This treatment is possible owing to the fact that the components of averaged velocities of a stationary streaming have the same distribution as in a pure liquid, with the possible exception of streaming in the immediate proximity of walls. The wall effects can, however, be evaluated.

Let us take a rectangular co-ordinate system x_1, x_2, x_3. A streaming, which can be expressed by equations:

$$u_1 = \varkappa x_2, \ u_2 = 0, \ u_3 = 0, \tag{3}$$

will be called Couette streaming, as it corresponds to a sufficient degree of approximation to a streaming between two walls of a Cou-

ette viscometer, when their curvature is neglected and the walls are regarded as parallel and perpendicular to x_2 axis.

Substituting (3) into (1), we obtain an important relation between the shearing stress τ, viscosity η and rate of shear $\varkappa$:

$$\tau = \eta\varkappa. \tag{4}$$

It is convenient to regard the Couette viscometer as being driven with constant force, and not at constant velocity, so that the shearing stress τ remains constant. Then a change of concentration of the suspension by addition of one further particle of the suspension in the viscometer and withdrawal of a corresponding volume of pure liquid would produce disturbance of streaming which would decrease the original value $\varkappa$ of the rate of shear to $\varkappa + \mathrm{d}\varkappa$. It thus follows from (4) that

$$\eta\varkappa = (\eta + \mathrm{d}\eta)\,(\varkappa + \mathrm{d}\varkappa). \tag{5}$$

so that

$$\mathrm{d}\eta/\eta = - \mathrm{d}\varkappa/\varkappa, \tag{6}$$

which represents an important relation between viscosity and rate of shear, valid for idealised Couette streaming.

The value of the retardation $\mathrm{d}\varkappa$ due to the presence of the added sphere can then be calculated. The calculation proceeds as follows:

The Couette streaming of liquid given by component velocities u_i^0 must satisfy the equations of continuity in the fluid and at the walls. The addition of a rigid sphere of radius a would not satisfy the conditions of continuity of the original streaming at its surface, as it cannot be subject to a shear as in the case of the liquid, and a new additional field of motion u_i^1 must be formed which, when additively superimposed over the original field $u_i^0 + u_i^1 = u_i$ must restore the conditions of continuity:

$$\partial u_1/\partial x_1 + \partial u_2/\partial x_2 + \partial u_3/\partial x_3 = 0.$$

Such a field is given by an equation, where $r^2 = x_1^2 + x_2^2 + x_3^2$:

$$u_i^1 = - \tfrac{5}{2}\frac{a^3}{r^5}\left(1 - \frac{a^2}{r^2}\right)a_{kl}^0 x_i x_k x_l - \frac{a^5}{r^5}\,a_{il}^0 x_l.$$

This new field, when combined with the original field, represents a rigid rotation at the surface of the sphere,

$$u_1 = \tfrac{1}{2}\varkappa x_2, \quad u_2 = - \tfrac{1}{2}\varkappa x_1, \quad u_3 = 0,$$

so that the sphere rotates with an angular velocity $\tfrac{1}{2}\varkappa$. The additional streaming at great distances is radial with two maxima towards and two maxima away from the sphere. The stream tubes are cones, the velocity falling off with the square of the distance from the sphere. As the area of the cross-sections of the elementary cones

increases with the square of the distance, it follows that the influence of the sphere on the movement of an infinite wall will not vanish even at the greatest distance from the wall. On integration, it appears that the wall is retarded by the presence of the sphere by an amount independent of the position of the sphere, and proportional only to the volume of the sphere. This retardation presents itself by decrease of the rate of shear by an amount $d\varkappa$. If interaction between particles is neglected, then it can be shown that for dN spheres of radius a, added to unit volume,

$$d\varkappa = -\tfrac{10}{3}\pi\varkappa a^3 \, dN. \tag{7}$$

As $\tfrac{4}{3}\pi a^3 \, dN = dc$ is the change of concentration, we can write

$$d\varkappa/\varkappa = -k \, dc \tag{8}$$

where $k = \tfrac{3}{2}$ for rigid spheres.

Applying now relation (6), we obtain

$$d\eta/\eta = k \, dc, \tag{9}$$

which on integration gives the well known Arrhenius formula

$$\log_e (\eta/\eta_0) = kc, \tag{10}$$

where the integration constant η_0 is the viscosity of the pure liquid.

The Arrhenius formula is thus obtained when interactions between particles are neglected. As $\eta/\eta_0 = \eta_r$ is the relative viscosity, on developing (10) into an infinite series we obtain

$$\eta_r = 1 + kc + \frac{1}{2!} \, k^2 c^2 + \ldots \tag{11}$$

On neglecting higher power terms than the first. the Einstein[5] formula is obtained.

Similar considerations apply to viscosities of suspensions of non-spherical particles; the same equation (10) is obtained, but the numerical value of the constant k is different; it increases for ellipsoids and rod-like particles. The values of k then also depend on the amount of Brownian movement; for a more general theory of calculation of the shape factor see, for example, Burgers,[6] Peterlin,[7] etc.

Extension of the theory to small particle size.

A result of the theory of viscosity of suspensions is that, for a given shape of particles, the increase of viscosity on increase of concentration depends for particles of the same shape only on the added total *volume* of the particles of the suspension, and not on their actual *size*. It follows that if the laws of hydrodynamics were equally valid for particles of molecular dimensions as for particles of

large dimensions, addition of particles of the same size and shape as solvent molecules would increase the viscosity by the same amount as would addition of an equal volume of larger particles, which is absurd. The argument can be presented also in the following way:

Addition of large particles into the suspension implies removal of an equal volume of solvent molecules, as the total volume must be kept constant. If the viscosity of a suspension did not depend on the size of the particles, the increase of viscosity due to the insertion of the larger particles would be exactly compensated by the decrease due to withdrawal of the solvent particles, and no change of viscosity would result.

These considerations lead us thus to a conclusion that the hydrodynamic effects of particles of size and shape equal to that of solvent molecules must be compensated by correction terms of opposite sign.

If we suppose that only one particle of a volume dv is added to one volume unit of suspension, and that a corresponding volume of the solvent is withdrawn in order to keep the total volume constant, then the concentration is changed by $dc = dv$, and it follows from (8) that the rate of shear changes by

$$\frac{d\varkappa}{\varkappa} = - k \, dv. \tag{12}$$

If there were no correction terms, then in the extreme case of adding solvent to itself, the volume of the added particle dv is equal to the volume of one molecule of the solvent dv_0, and the rate of shear would also change by

$$\frac{d\varkappa}{\varkappa} = - k \, dv_0. \tag{13}$$

But from experience it is known that in the latter case

$$\frac{d\varkappa}{\varkappa} = 0. \tag{14}$$

It is apparent that a correct result would be obtained if the theoretical equation (12) is generalised by adding a correction term $k_0 v_0$:

$$\frac{d\varkappa}{\varkappa} = - k \, dv + k_0 \, dv_0, \tag{15}$$

where k_0 is the shape factor of the molecules of the solvent, which represents the simplest assumption as to the form of the correction term. Then equation (15) would become (14) for $k = k_0$ and for $v = v_0$, and would converge to (12) for $v \gg v_0$, i. e. for particles much larger than the molecules of the solvent.

The equation (15) can also be written in the form

$$\frac{d\varkappa}{\varkappa} = -k\left(1 - \frac{k_0 v_0}{kv}\right)dc = -k'\,dc, \tag{16}$$

where

$$k' = k\left(1 - \frac{k_0 v_0}{kv}\right) \tag{17}$$

is the shape factor corrected for the effect of the small particle size.

For $v = v_0$, $k = k_0$, it follows that $k' = 0$, and for $v \gg v$, $k' = k$. As k' does not depend on c, no change of equation form is involved on integration, so that the result is again

$$\log_e \eta_r = k'c \tag{18}$$

when interactions are neglected.

In the simplest case of dissolved particles being of the same shape as the solvent molecules, $k = k_0$ and (17) simplifies into

$$k' = k\left(1 - \frac{v_0}{v}\right).$$

This correction term can be regarded as an empirical extension of the theoretical formulae; in fact, any correction term of a form

$$k' = k\left(1 - \left(\frac{k_0 v_0}{kv}\right)^n\right) \tag{19}$$

with $n > 0$, would fulfil the conditions required, whereas equation (17) is a special case where $n = 1$. If more material were available, it would be possible to determine experimentally the value of the exponent n. In particular, if the correction term depended on the ratio of the radii of the particles rather than on their volumes, $n = \frac{1}{3}$; if on the ratio of their surfaces, $n = \frac{2}{3}$; values of n are thus very unlikely to be smaller than $\frac{1}{3}$ or greater than 1.

It seems to be unlikely that $n = \frac{1}{3}$, as, if this were the case, the correction for sucrose with $v_0/v = 0{,}083$ would amount to $k' = 0{,}565k$, whereas for $n = 1$, the correction would be only $k' = 0{,}917k$. The former value would scarcely escape detection, whereas the latter value would lie within experimental error, so that from this source there is evidence that the correction term depends on volume rather than on the diameter of the particles, and that it is reasonable to assume the validity of (17), unless further experimental evidence indicates otherwise.

Interaction corrections.

The Arrhenius formula (10) was derived under the assumption that the increase of viscosity due to the addition of one particle does

not depend on the presence of other similar particles in the suspension. However, the sphere is subject not only to the streaming field of the liquid as a whole, but also to the additional fields due to its neighbours. If only two spheres are considered, both spheres will develop a series of additional fields, decreasing in intensity, in order to fulfil the conditions of continuity on their surfaces. The resulting interaction is then obtained by integrating over all the positions of the second sphere in the space, i. e. over the whole space except positions nearer than $2a$ from the centre of the first sphere.

This is due to the fact that the centres of two spheres cannot approach nearer than $2a$. Addition of an infinite series of terms, odd ones of which are all zero owing to the symmetry of the streaming, gives for rigid spheres a result that, at concentration c of rigid spheres in a liquid, every sphere of the suspension develops an additional streaming as if subjected to a field

$$\frac{Qc}{1 - Qc}$$

in addition to the actual field, where $Q = \frac{39}{64} = 0{,}60937$.

The differential formula which includes interactions is thus instead of (9):

$$\frac{\mathrm{d}\varkappa}{\varkappa} = - k \, \mathrm{d}c - \frac{kQc \, \mathrm{d}c}{1 - Qc} - kc \frac{\mathrm{d}}{\mathrm{d}c}\left(\frac{Qc}{1 - Qc}\right) \mathrm{d}c, \qquad (20)$$

where the first term on the right side corresponds to the Arrhenius term without interactions, the second term represents the effect of interactions on the field increase of the particles added to the suspension, whereas the third term represents the effect of the change of concentration on the fields of the particles already present in the suspension.

By integrating (20), we obtain

$$\log_e \eta_r = \frac{kc}{1 - Qc} \qquad (21)$$

where $\eta_r = \eta/\eta_0$.

Another effect to be taken into consideration is the effect of collisions of the particles, as during the collisions the particles would touch each other and, owing to mutual friction, their movement would be altered. Spheres in different strata move under the shearing motion of the liquid with unequal velocity, so that the particles overtake each other and collisions occur, during which the spheres are rolling round each other, till disengagement through further shear takes place. The fraction of time T spent in collisions is quite considerable and for rigid spheres it amounts to $T = 4c$. This time would be modified for non-spherical particles, and also lengthened

by any attractive forces, shortened by strong Brownian movement and repulsive forces.

In a suspension, there is thus present a concentration c_1 of single spheres, c_2 of „doublets", c_3 of „triplets" etc., even if there are no forces between spheres. It is thus

$$c = c_1 + c_2 + c_3 + \dots \tag{22}$$
$$c_2 = r_2 c_1^2,$$
$$c_3 = r_2 r_3 c_1^3, \quad \text{etc.}$$

where $r_2 = 4$, etc. are the collision time constants. Singlets, doublets, triplets etc. will have different shape factors $k_1, k_2, k_3, \dots$ so that the resulting mean shape factor of the mixture will be

$$\bar{k} = \frac{k_1 c_1 + k_2 c_2 + k_3 c_3 + \dots}{c}, \tag{23}$$

or, using (22),

$$\bar{k} = k_1 + r_2 (k_2 - k_1) c + \dots \tag{24}$$

The values of the shape factors of the doublets, triplets etc. cannot be calculated accurately, but an estimate of the „bound" liquid round the point of contact of the spheres gives an approximate value of $k_2 = 3{,}175$ for rigid spheres. Similar considerations give $k_3 = 3{,}34$, etc.

Substituting the value of $\bar{k}$ given by (24), in the viscosity formula (21), we obtain

$$\log_e \eta_r = \frac{k_1 c + r_2 (k_2 - k_1) c^2 + \dots}{1 - Qc}.$$

This formula can now be extended for small particles and solutions by using relation (17). We obtain then a new expression by replacing k_1 and k_2 by corrected shape factors k_1' and k_2':

$$\log_e \eta_r = \frac{k_1' c + r_2 (k_2' - k_1') c + \dots}{1 - Qc} \tag{25}$$

where

$$k_1' = k_1 \left(1 - \frac{k_0 v_0}{k_1 v_1}\right), \tag{26}$$

$$k_2' = k_2 \left(1 - \frac{k_0 v_0}{k_2 v_2}\right). \tag{27}$$

In these equations, k_0 is the shape-factor which would have the solvent molecules according to hydrodynamic theory, v_0 is the volume of a solvent molecule, v_1, v_2, etc. are volumes of the suspended or dissolved single particles, doublets, etc. c is the volume concentration of the solute or particles of the suspension, and from the theory

for rigid spheres without mutual forces and without Brownian movement:

Shape factor of single spheres .... $k_1 = 2,5$
Shape factor of collision doublets .... $k_2 = 3,175$
Collision time constant .... $r_2 = 4$
Hydrodynamic interaction constant......... $Q = 0,609$

Theory of hydration.

The above considerations assume that the particles do not disturb by their presence the structure of the solvent. However, there is ample evidence that disturbances in the immediate vicinity of the particles occur. Here belongs the phenomenon of the solvation or hydration; for example substances containing hydrophilic groups, dissolved in water, attach more or less firmly water molecules to those groups, building thus a so-called solvation or hydration envelope.

If in our formulae c is the volume concentration of the suspended particles, then on solvation the volume of the solvation or hydration envelopes is to be included in c. Thus we may write

$$c = hs, \qquad (28)$$

where s is the concentration by volume of the solute without hydration envelopes and h is the hydration constant, which is $h = 1$ when no hydration occurs. If there is hydration, $h > 1$ and it generally decreases to unity when the temperature is increased, and also depends on concentration.

It is important to realise that, except in rare instances, the true volume concentration of the suspensions or of the solute is not directly accessible to measurement. All that is usually directly measurable is the weight concentration W of the solute, the density D of the solution and the density D_o of the pure solvent. If there is a hydration envelope, it would generally have density D_H different from D_0, so that there is change of volume on mixing.

Let us use a new variable x, which is expressible by measurable quantities:

$$x = DW. \qquad (29)$$

Then the following relations are valid:

$$D_s s = x, \qquad (30)$$

$$D_0 + (h - 1)(D_0 - D_H) = D_s\left(1 - \frac{D - D_0}{x}\right), \qquad (31)$$

where D_s is the density of each particle of the solute, the hydration envelope being excluded. This can be regarded as independent of W.

Considering that the number of molecules entering the hydra-tion envelope would be proportional to its area, to the concentra-tion of the free solvent, which is $1 - hs$, and to the velocity of in-coming molecules, and that the number of molecules leaving would be proportional to their number in the hydration envelope and to a term $\exp(-E/kT)$, one obtains a relation between the hydration constant h, the concentration s and absolute temperature T:

$$h^{2/3}(1 - hs)\, T^{\bar{m}} = K\,(h - 1)\exp(-E/kT), \qquad (32)$$

where K is a proportionality constant and m depends on the law according to which is governed the velocity of the incoming mole-cules. Using relation (30) and developing in series, we can write

$$c = \frac{h_0}{D_s}\, x - \frac{3h_0^2\,(h_0 - 1)}{D_s^2\,(h_0 + 2)}\, x^2 + \ldots \qquad (33)$$

which can be used in the viscosity formula (26).

For practical calculations it is convenient to use the following form for viscosity

$$\frac{x}{\log_e \eta_r} = q_0 + q_1 x + q_2 x^2 + \ldots \qquad (34)$$

as a plot of $x/\log_e \eta_r$ against x usually gives a nearly straight line, or a line which can be expressed within experimental error by an equation of the second order, so that determination of the terms q_0, q_1, q_2 can proceed with accuracy and without difficulties. By substituting and solving, one obtains for the terms the following values:

$$q_0 = \frac{D_s}{h_0 k_1''}, \qquad (35)$$

$$k_1' q_1 = \frac{3\,(h_0 - 1)}{h_0\,(h_0 + 2)} - \frac{r_2\,(k_2' - k_1')}{k_1'} - Q, \qquad (36)$$

etc., where k_1', k_2' are given by (26) and (27).

The numerical values of the terms so obtained can then be compared with theory on similar lines as has been done in the case of sucrose.[3]

The shape of the particles or molecules is usually known from other sources, so that k_0, k_1, k_2 can be assumed to be known. The variation of the hydrodynamical interaction constant Q with par-ticle shape is not known, but for particles which are not very far from spherical shape, the variation of Q would cause errors only in the second power terms. The density of the solute particles, D_s, can also be regarded as known, or it can be extrapolated from the den-sity measurements. The first step is thus to calculate the hydration

constant h_0 from (35), and study its variation with temperature; it should decrease to a value $h_0 = 1$, as the temperature is increased.

The next step is to calculate the value of the collision time constant r_2 from (36). The interpretation of this constant for particles of molecular size would, however, be different than for large particles; owing to the strong Brownian motion and the possible existence of strong forces between molecules, theory requires further expansion. This, however, can be profitably undertaken only when sufficient experimental material becomes available on the subject.

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Theorie viskosity suspensí a roztoků. Vliv malých rozměrů částic.

(Obsah předchozího článku.)

Theorie viskosity suspensí je rozšířena tak, aby zahrnovala částice molekulárních rozměrů. Toho je dosaženo zavedením korekce, jež je funkcí poměru objemů molekul rozpustidla a rozpuštěné látky. Diskutovány jsou výrazy pro viskositu roztoků, v nichž byly vzaty v úvahu interakce, srážky a hydrace.