Viscosity of Suspensions of Spherical and Other Isodimensional Particles in Liquids

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The viscosity of a suspension is related to the properties of the suspending liquid and the suspended particles by measuring the viscosity of suspensions made up of closely sized materials such as glass spheres, plastic Zeolite spheres, blasting sand, and salt cubes in a wide range of concentrations in liquids of varying properties made up of castor oil, tetrabromoethane and carbon tetrachloride, or corn syrup and water. The measurements were made under carefully controlled conditions by means of a Brookfield viscometer, and the reproducibility of results was demonstrated by repetitive runs.

Equations are derived to describe the viscosities of these various suspensions in terms of the viscosity and density of the suspending liquid and of the shape, size distribution, density, and concentration of solid particles. The range of concentration covered is from infinite dilution to near infinite viscosity.

The results obtained can best be explained by postulating nonuniform distribution of particles in a suspension in a network of tetrahedral and simple cubical packings.

The control of viscosity of suspensions of solid particles in liquids is an important industrial problem. Although the number of factors influencing the viscosity is large, mechanical interference of the suspended particles undoubtedly is of major importance. The ultimate solution of this problem will probably be expedited by first clearing up the problem of mechanical interference. The purpose of this investigation is to throw some light on this phase of the question.

Historic Review

The first piece of fundamental theoretical work on the viscosity of suspensions was done by Einstein (*6*), who obtained the following equation:

$$\mu = (1 + 2.5x_v)\mu_0 \qquad (1)$$

Bingham and Durham (*2*) measured fluidities of various suspensions with concentrations up to 5 to 9%. The fluidity decreased rapidly and linearly as the volume concentration of the solids increased. Drucker and Kassel (*5*) and White (*18*) found that fluidities are normally additive in homogeneous mixtures and fine suspensions. The fact that suspensions of rigid spherical particles exhibited the same anomaly as lyophilic sols, viz., a decrease of viscosity with increasing rate of shear, was explained by McDowell and Usher (*10*) and supported by striking evidence.

Smith, Toote and Busang (*14*) made an interesting investigation of the packing of homogeneous spheres. Although the actual packing of spheres was of a very irregular and distorted pattern, they showed that for statistical purposes the arrangement may be treated as a mixture of close-hexagonal and simple-cubical packings only, in the proportion required to yield the observed porosity. Manegold, Hofmann, and Solf (*11*) calculated voids for packing with spheres of uniform or different sizes.

The shape and surface characteristics of particles naturally affect viscosity. Studies of DeVaney and Shelton (*4*) verified this fact.

Vand (*16*) derived a formula for spheres in liquids,

$$\mu = (1 + 2.5c + 7.17c^2 + 16.2c^3)\mu_0 \quad (2)$$

Robinson (*12*) found that the specific viscosity of the suspension is directly proportional to the volume fraction of the spheres and inversely proportional to the volume fraction of the free liquid in suspension. His data showed that packed-sediment volume appears to be approximately the effective volume of the particles at any concentration. The viscosity showed some decrease as the rate of shear increased, but the suspension was assumed to be Newtonian in his treatment.

MATERIALS AND EXPERIMENTAL METHODS

Solid Particles

Glass spheres, mustard seeds, and Nalcite resin were used as spherical particles. Crystals of common salt and blasting sands were used as cubes and rounded particles, respectively. All samples of particles were sized through standard fourth-root testing sieves. All samples of particles used were free flowing except one sample of glass spheres which was used to illustrate its effect on viscosity.

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In the study of polydisperse suspensions, binary and ternary mixtures of glass spheres were investigated. In the binary mixtures used, the particle-diameter ratios covered the range from 0.59 to 0.85, and the volume ratio of the large particles to the small ones from 0.10 to 10. In the ternary mixtures studied, the diameter ratios of the medium particles to the large ones varied between 0.42 and 0.84, and the diameter of the small particles to the medium ones was 0.84. The volume ratios among the large, medium, and small particles were either 1:4:2 or 3:4:2.

Liquid Media

Dense media blended to match the density of the solids: carbon tetrachloride and *s*-tetrabromoethane; castor oil and tetrabromoethane. Viscous media were castor oil and corn syrup.

Viscometer

A Brookfield Synchro-Lectric viscometer was used. For each measurement in this investigation the slowest permissible spindle speed was used and the reading taken as soon as its change began to be slow and steady. Ten to fifteen seconds was normally sufficient to obtain a reading.

Control of Temperature

All the viscosity determinations were made at 20.0° ± 0.1°C.

Experimental Procedure

Liquid was poured into a beaker large enough to eliminate wall and end effects. After the viscosity of the liquid was determined, a known weight of solid particles was added to the liquid. The mixture was stirred to form a "uniform" suspension. Air bubbles introduced into the suspension were removed in a vacuum chamber. After one viscosity test had been completed, more solids were added, and this procedure was repeated until the suspension became so concentrated that the viscosity readings were erratic and not reproducible.

EXPERIMENTAL RESULTS

The complete data on the suspension of various types of isodimensional solid particles in various types of liquids are presented in reference *15*. A representative run for a monodisperse suspension is shown in Table 1. In Figure 6, data from two typical viscosity runs were plotted against the volume fraction of glass spheres for illustration. The rate of change of viscosity with volume fraction increases rapidly until the viscosity is nearly infinite at a volume fraction of 0.5. In order to obtain a linear relationship, all viscosity data were plotted as x_v/μ_{sp} vs. x_v graphs, as shown in Figures 7 and 8. Several conclusions are immediately apparent:

1. The data fall on straight lines. This indicates that the form of the linear relationship is valid over the entire range of concentration tested.

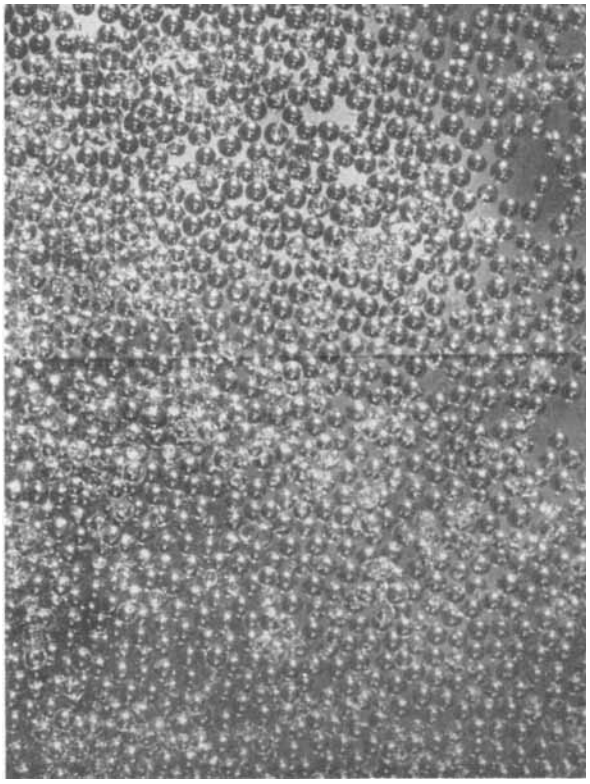

Fig. 1. Glass spheres, 390μ.

TABLE 1

VISCOSITY OF SUSPENSION OF GLASS SPHERES IN HEAVY LIQUID

Run: 6

Spheres: 3M#10, 60/70 mesh, 230μ
Density, 2.47 g./ml.

Liquid: Castor oil and *s*-tetrabromoethane
Density, same as for spheres
Weight, 731.3 g.

Viscometer spindle: #1

Spheres, g.	x_v	μ, cp., at rev./min.				μ_{sp}	x_v/μ_{sp}
		6	12	30	60		
0	0				29.6		
5.3	0.0072				29.9	0.010	0.719
15.8	0.021				30.8	0.040	0.526
31.4	0.041				32.0	0.080	0.513
40.3	0.052				32.9	0.110	0.472
65.8	0.083				35.2	0.189	0.439
86.6	0.106				37.6	0.270	0.392
103.5	0.124				39.7	0.342	0.362
120.4	0.141				41.8	0.412	0.342
163.5	0.183				47.1	0.591	0.310
184.8	0.202				50.6	0.710	0.285
206.9	0.221				53.5	0.808	0.274
230.8	0.240				57.7	0.950	0.253
261.3	0.263				63.9	1.160	0.227
315.3	0.301				76.9	1.598	0.198
343.4	0.319				89.3	2.02	0.158
384.3	0.345			105.2		2.56	0.135
413.8	0.361			118.3		3.00	0.120
458.7	0.385	150	146	142.0		3.78	0.102
543.9	0.426	218	217			6.32	0.067
614.1	0.456	308	296			9.00	0.051
698.6	0.489	572				18.30	0.027
766.8	0.512	700 →	500	The reading decreased with the time while the spindle was rotating in the suspension.			

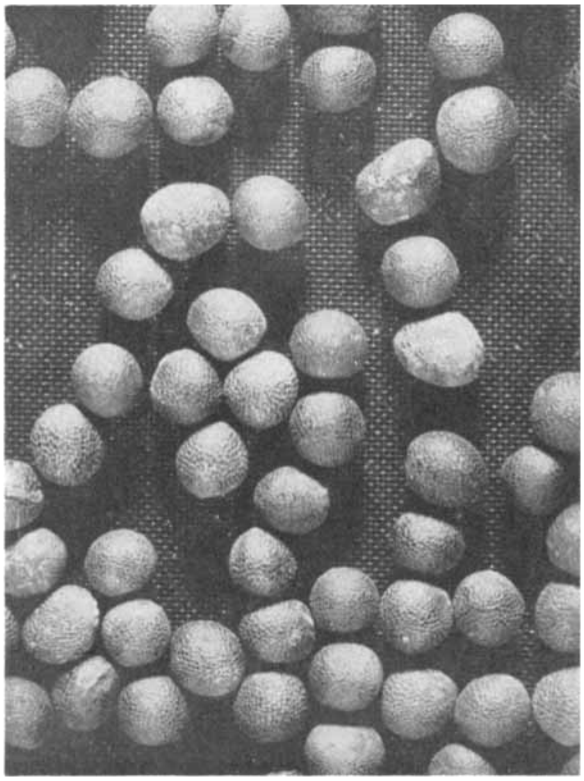

Fig. 2. Mustard seeds, 1,545μ, on 200-mesh screen.

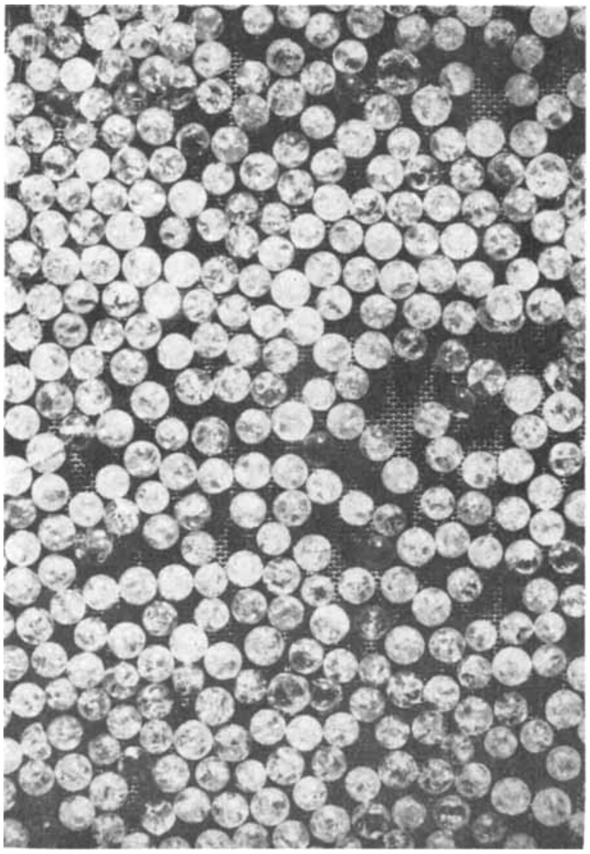

Fig. 3. Nalcite SAR., 920μ, on 200-mesh screen.

2. The slopes of the linear graphs are primarily -1 and the intercepts on both axes equal each other for free-flowing monodisperse suspensions, regardless of the particle shape.

3. The intercepts of the linear graphs for spherical particles on the x_v axes ($x_{v,\infty}$, volume fraction of the solids when the viscosity of the suspension would approach infinity) vary with the attraction between particles, the viscosity of the pure liquids, and the relative density of the liquids to the particles. For free-flowing spheres there is no attraction between particles and the value of $x_{v,\infty}$ depends only upon the ratio of the viscosity of the pure liquid to the relative density of the liquid with respect to the solids, μ_0/R as shown in Figure 9. For cubes and grains with rounded corners, $x_{v,\infty}$ does not vary with the function μ_0/R but seems to remain constant regardless of the liquids used.

4. When the concentration of the solids became very high and close to the infinite-viscosity concentration, the viscometer readings decreased with continued shearing owing to the rotation of the viscometer bob, regardless of the shearing rate. The viscosity returned to its original value upon standing for a certain length of time. Therefore, structural thixotropy was definitely indicated. However, its effect was not obvious until the solids concentration was very high, as shown in Table 1.

For these thixotropic suspensions the first or second reading was taken as the viscosity at zero time. Only those viscometers which permit very rapid readings can be relied on for the reproducible results with suspensions. Continued shearing results in a change in viscosity. If the measurements were continued for a suspension of 0.5 solids fraction, the viscosity readings often decreased by as much as 30% in one hour with no evidence of a minimum value being reached even then.

CORRELATION

Derivation of Equation

If fluidity is additive and there is no interference between the liquid and the solids in a suspension, and as the fluidity of rigid solids is zero, the fluidity of the suspension would be

$$\phi = (1 - x_v)\phi_0 \qquad (3)$$

where ϕ_0 is the fluidity of the liquid and x_v the volume fraction of the solids in the suspension. However, solids suspended in liquid media do not form uniform suspensions but "clusters," or a certain type of packings, even though they are inert and free flowing before being put into the liquids. The authors believe that only the portion of liquid which is not occluded can move freely. Therefore the preceding equation does not represent the true picture, and the actual fluidity of a suspension should be that of the free liquid only; i.e.,

$$\phi = (1 - x_{v,eff})\phi_0 \qquad (4)$$

where $x_{v,eff}$ is the effective volume fraction of the solids, i.e., the sum of the actual volume fraction of the solids plus the volume fraction of the occluded liquid. When solids concentration becomes so high as to form a complete ramifying aggregate or network of some rigidity, all the liquid is occluded in the particle packing and is no longer free. Under such conditions $x_{v,eff}$ equals unity, fluidity equals zero, viscosity approaches infinity, and x_v equals $x_{v,\infty}$, the volume fraction when the viscosity would equal infinity. Since $x_{v,eff}$ is proportional to x_v, $x_{v,eff}$ must equal $x_v/x_{v,\infty}$.

In terms of viscosity, Equation (4) becomes

$$\mu = \frac{\mu_0}{1 - \dfrac{x_v}{x_{v,\infty}}} = \frac{x_{v,\infty}}{x_{v,\infty} - x_v}\mu_0 \qquad (5)$$

where μ and μ_0 are viscosities of the suspension and the liquid, respectively.

To simplify the equation and make it more convenient to use, one may express it in terms of specific viscosity,

$$\mu_{sp} = \frac{\mu - \mu_0}{\mu_0} = \frac{x_v}{x_{v,\infty} - x_v} \qquad (6)$$

and

$$\frac{x_v}{\mu_{sp}} = x_{v,\infty} - x_v \qquad (7)$$

When x_v/μ_{sp} is plotted against x_v, a line with a slope of -1 should be obtained. If the viscosity of a particular solids concentration is available, $x_{v,\infty}$ can be calculated by means of Equation (7) and viscosities for the complete concentration range can be predicted without further experiments. If no viscosity data are available, a correlation between $x_{v,\infty}$ and physical properties of the liquid-solids system will be very helpful for the prediction of viscosities of the suspension without any experiment.

Evaluation of $x_{v,\infty}$

Although the packing of spherical particles in suspension is very irregular and distorted, the authors suggest that it may be considered statistically as consisting only of the two most open types: the simple cubical and the tetrahedral packings, wherein there are six and four spheres, respectively, in contact with each sphere in consideration. The

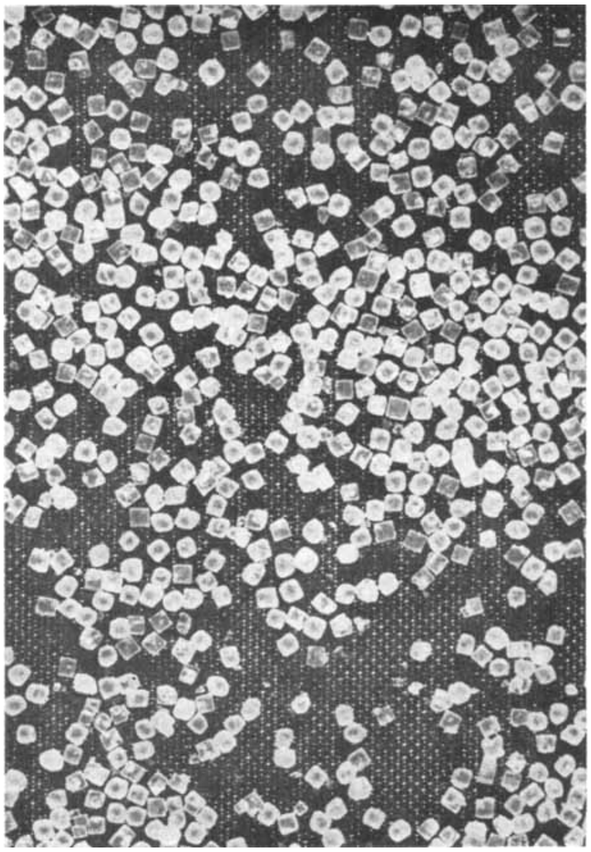

Fig. 4. Salt cubes, 385μ, on 200-mesh screen.

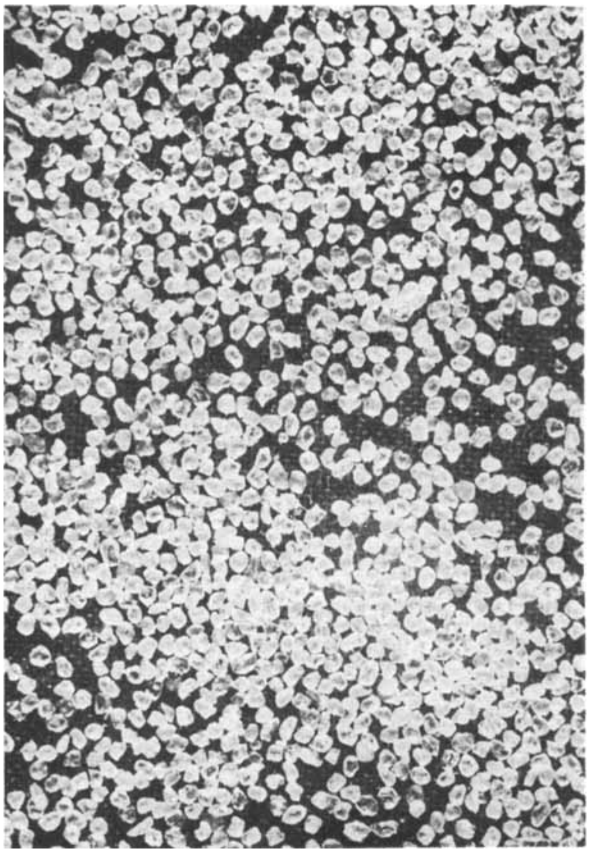

Fig. 5. Blasting sand, 274μ, on 200-mesh screen.

volume fractions of the solids are 0.524 and 0.34, respectively, for these two types of packings.

The fraction of each type of packing for any suspension of spherical particles is related to the value of the $x_{v,\infty}$ according to the following equation:

$$F_4 = \frac{0.524 - x_{v,\infty}}{0.524 - 0.34} = \frac{0.524 - x_{v,\infty}}{0.184} \qquad (8)$$

where F_4 is the fraction of the tetrahedral packing. Thus

$$x_{v,\infty} = 0.524 - 0.184F_4 \qquad (9)$$

For packing consisting of tetrahedral type only, $F_4 = 1$ and $x_{v,\infty} = 0.34$. For packing consisting of simple cubical type only, $F_4 = 0$ and $x_{v,\infty} = 0.524$.

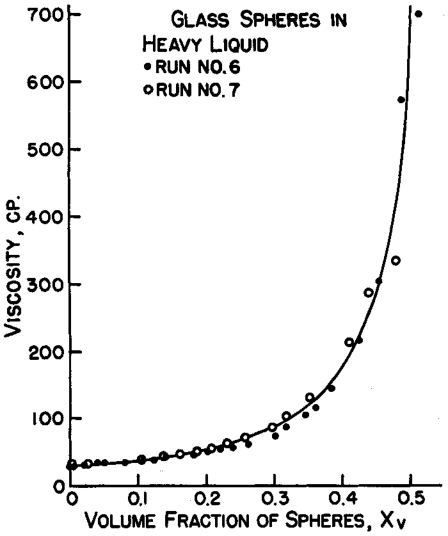

Fig. 6. Viscosity of suspensions of glass spheres in heavy liquid.

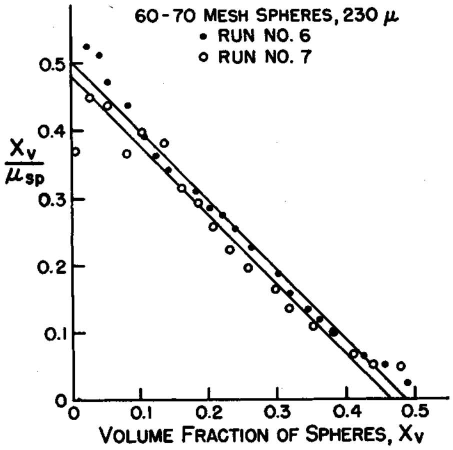

Fig. 7. Viscosity of suspensions of glass spheres in heavy liquid; 60- to 70-mesh spheres, 230μ.

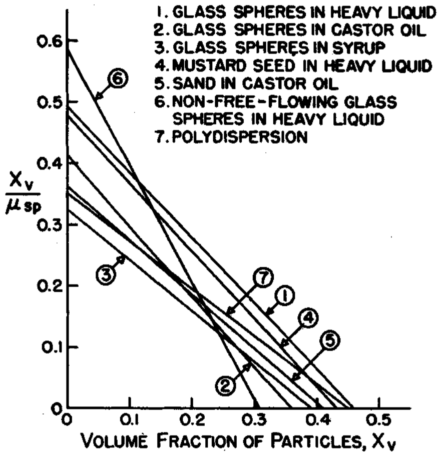

Fig. 8. Typical curves of mono- and polydispersed suspensions.

Evaluation of F_4

If the spherical particles are free-flowing, have negligible attraction among themselves, and are inert to the liquid, the distribution of the two types of packing should be determined by the interaction of the force causing closer packing and the resistance to movement. The force may be represented by R, the relative density of the liquid to the solids, and the resistance may be represented by μ_0. A log-log plot of F_4, the fraction of tetrahedral packing, against μ_0/R, the ratio of the viscosity of the pure liquid to the relative density, results in a slightly curved line, Figure 9. The relationship is given by the following equation:

$$F_4 = 8.59\times10^{-3}\left(\frac{\mu_0}{R}\right)^{0.469} + 0.350 \qquad (10)$$

where μ_0 is expressed in centipoises. The average deviation from Equation (10) is 7.4% and the maximum 22%.

Monodisperse Suspensions

The viscosity of a monodisperse spherical suspension can be calculated from the physical constants of the solids and liquid. From Equations (9) and (10),

$$x_{v,\infty} = 0.460 - 1.58\times10^{-3}\left(\frac{\mu_0}{R}\right)^{0.469} \qquad (11)$$

The average deviation from Equation (11) is 1.90% and the maximum 8.3%. Combining Equations (5) and (11) gives

$$\mu = \frac{\mu_0}{1 - \dfrac{x_v}{0.460 - 1.58\times10^{-3}\left(\dfrac{\mu_0}{R}\right)^{0.469}}} \qquad (12)$$

where the viscosities are in centipoises. For a solids fraction of 0.1, the average deviation from Equation (12) is 0.63% and the maximum 3.5%. For solids fraction of 0.3, the average deviation is 6.9% and the maximum 59%.

For cubes and grains with rounded corners, value of the $x_{v,\infty}$ for the monodisperse suspensions is not appreciably affected by the liquid viscosity and remains almost constant at 0.403. From Equation (5)

$$\mu = \frac{0.403}{0.403 - x_v}\mu_0 \qquad (13)$$

Polydisperse Suspensions

If the particles are all of the same size, no more particles can enter into the network without changing the type of packing and consequently the viscosity. However, smaller particles can fill into the voids without changing the type of the primary packing. These additional smaller particles make the $x_{v,\infty}$ of a polydisperse suspension higher than that of a monodisperse suspension. This was found experimentally to be true.

The intercepts on the x_v/μ_{sp} axes for polydisperse suspensions of spherical particles were found to be the same as the intercepts on the x_v/μ_{sp} axes for monodisperse suspensions. The intercepts on the x_v axis were found to be 1.26 times higher, and the slopes 1/1.26, or 0.79, times lower. Therefore, Equation (7) for monodisperse systems may be adapted to polydisperse systems simply by changing the coefficient of x_v,

$$x/\mu_{sp} = (x_{v,\infty})_m - 0.79x_v \qquad (14)$$

where $(x_{v,\infty})_m$ is the $x_{v,\infty}$ for the corresponding monodisperse system as calculated from Equation (11).

DISCUSSION

If the Einstein equation is expressed in terms of specific viscosity, it becomes

$$\frac{\mu - \mu_0}{\mu_0} = \mu_{sp} = kx_v$$

or

$$\frac{x_v}{\mu_{sp}} = \frac{1}{k}$$

where k is a constant independent of the concentration of the solids. As the suspension concentration approached zero, Equation (7), the relationship proposed by the authors, approaches the Einstein equation:

$$\frac{x_v}{\mu_{sp}} = x_{v,\infty}$$

Since $x_{v,\infty}$ is constant for any given system, $k = 1/x_{v,\infty}$. From Figure 7, the value of $1/x_{v,\infty}$ (or μ_{sp}/x_v when x_v approaches zero) is seen to be 2.0, against the Einstein shape factor of 2.5 for the spheres.

Vand and Robinson did not use glass spheres of a uniform size, but a wide distribution of size. As it was found that the size distribution did affect the two intercepts on the viscosity graphs, their conclusion would be good only for polydispersions and inaccurate for monodispersions.

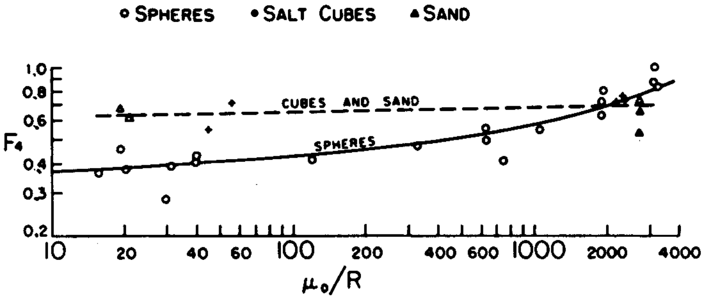

Fig. 9. Relation between the fraction of tetrahedral packing, $F4$, and the ratio of liquid viscosity to the relative density, μ_0/R, for monodisperse suspensions.

According to the authors' hypothesis of the most open particle packing in suspension, $x_{v,\infty}$ varies between 0.34 and 0.524 and hence $1/x_{v,\infty}$ varies between 1.9 and 2.9. This figure agrees with the work of Bancelin (*1*), 2.9; of Einstein, 2.5; of Eirich, Bunzl, and Margaretha (*7*), 2.5; of Broughton and Windebank (*3*), 2.5; and of Robinson (*12*), 2.4. It also accounts well for the discrepancies among these investigators. Therefore, the authors' equation is not only equivalent to the well-established Einstein's equation at negligible concentrations, but offers a useful expression and prediction for the viscosity of suspensions ranging from infinite dilution to infinite viscosity.

Few workers in this field have emphasized the effect of the size distribution of the solid particles on the viscosity of a suspension. This is probably due to the fact found by Einstein and supported by many others, that the viscosity of a monodisperse suspension is independent of the size of the particles. However, it does not follow that viscosity is independent of size distribution. The effect of particle-size distribution has not been seriously considered until recently (*13*, *17*).

The linear relationship between x_v/μ_{sp} and x_v also holds for the monodisperse suspension of isodimensional particles of other than spherical shape. However, owing to the complexity introduced by their shapes, their packing would be entirely different from that of the spherical particles. Up to the present time there is no satisfactory method of describing their packing.

All these correlations, however, can be applied only to free-flowing particles. With nonfree-flowing particles the attraction between particles becomes a controlling factor and the value of $x_{v,\infty}$ becomes much less than predicted by the suggested method. This accounts for the high $1/x_{v,\infty}$ values found by Harrison (*8*), 4.75, during investigation of aqueous suspensions of starch granules. Other seeming disagreement in values given in the literature may be explained by the fact that the effect of a wide size distribution of the particles on the value of $x_{v,\infty}$ might have been counteracted by nonfree-flowing properties.

It has always been difficult to obtain steady viscometer readings when the solid concentration became extremely high. Owing to the gradual change of the pattern of packing of the solids by the rotation of the viscometer, it would not be surprising to see the viscosity decreased with time during measurements. This thixotropic phenomenon of decreasing viscosity with continued shearing can be clearly explained by the authors' hypothesis of particle packing.

SUMMARY

A hypothesis for describing the viscosity behavior of suspensions of spherical particles is proposed—the hypothesis of the most open particle packing in suspensions.

The authors are of the opinion that solid spherical particles suspended in liquids do not form uniform suspensions, even though they are inert to the liquids and there is negligible attraction between particles. Instead, they form a network consisting of tetrahedral and simple cubical packings. The extent of each type of packing depends on a function of the viscosity of the pure liquid and the relative density of the liquid to that of the solids.

The extent to which each type of packing occurs determines the porosity of the suspension at the yield point and the concentration of the solids at infinite viscosity.

An equation describing the viscosities of suspensions of spherical particles was derived. The concentration range covered by this equation is from infinite dilution to infinite viscosity. The same equation may be used for polydisperse spherical suspensions if a proper coefficient is used. An equation describing the viscosities of monodisperse suspensions of other isodimensional particles is also given.

NOTATION

c = concentration of solids in a suspension, the ratio of the volume of the particles to that of the liquid
k = an empirical constant
R = ratio of the liquid density to the solid density in a suspension (or the reciprocal if the liquid is heavier)
x_v = volume fraction of solids in a suspension
$x_{v,\infty}$ = volume fraction of solids in a suspension when its viscosity would reach infinity if plastic flow did not come into play
$(x_{v,\infty})_m$ = $x_{v,\infty}$ for monodisperse suspension
μ = viscosity of a suspension, centipoise, cp.
μ_0 = viscosity of the pure liquid making up a suspension, cp.
μ_{sp} = specific viscosity, the ratio of the increase in viscosity of the suspension over that of the liquid to that of the liquid, $(\mu - \mu_0)/\mu_0$
ϕ = fluidity of a suspension, $1/\mu$, cp.$^{-1}$
ϕ_0 = fluidity of pure liquid, $1/\mu_0$, cp.$^{-1}$
F_4 = fraction of the tetrahedral packing

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