Prediction of the Viscosity of Multimodal Suspensions from Unimodal Viscosity Data

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Synopsis

A theoretical treatment of particle-particle interaction is described from which the viscosity-concentration behavior of multimodal suspensions of rigid particles can be related to the viscosity-concentration behavior of the unimodal components. From this theory, the viscosity of multimodal suspensions can be calculated and shows excellent agreement with existing experimental data. Blend ratios that will produce minimum viscosities are simply derived from the theory and agree well with experimental results. Another important feature of this theory is that it predicts and defines a lower limit for the viscosity at any concentration and indicates that this lowest viscosity can be obtained with a variety of solids combinations.

Introduction

Perhaps the most basic work in the rheology of suspensions was due to Einstein, who derived a formula for the relative viscosity of dilute suspensions of uniform-sized spherical particles. Since the publication of his basic analysis, numerous equations have been developed in efforts to extend Einstein's formula to suspensions of higher concentrations. The various resulting formulas, both theoretical and empirical, differ considerably from each other as do experimental data at high concentrations; the experimental data probably differ because of varying latitudes of the particle size distributions of the monodispersed sizes used, thereby changing the maximum possible concentrations in each study.

Attempts to extend this work to understand and predict the behavior of a suspension when two or more monodispersed sizes are blended together has been unsuccessful to date. Geometrically, it

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is easy to understand that through the use of multimodal size distributions the limiting concentrations could be increased, but the blend ratios and size ratios of such systems had to be determined experimentally, always with the question, "Is there another blend that will reduce the viscosity even more?"

This paper does not attempt to describe mathematically the viscosity-concentration behavior of suspensions of particles of unimodal size distribution. Instead it treats the way in which two or more size distributions interact when they are combined in the same suspension. The result of which is a simple means to understand and predict the viscosity of multimodal suspensions from the observed viscosity-concentration behavior of its unimodal components. Through the use of this model, optimum blend ratios for multimodal suspensions can be derived as well as the minimum possible viscosity for any concentration.

Theory

In the literature there are references\textsuperscript{2,6,7} indicating that the finer particles in a bimodal suspension behave essentially as a fluid toward the coarser particles. The most illustrative work was performed by Fidleris and Whitmore who investigated the settling velocity of a large sphere in a 20\% suspension of uniform-sized small spheres. The results of their investigation showed that if the size ratio, \( R_{12} \) (small to large) was \( 1/10 \) or less, then the large sphere encountered the same resistance to motion when passing through a suspension of smaller spheres as when it passed through a pure liquid of the same viscosity and density as the suspension. When the size ratio became greater than \( 1/10 \), the falling sphere appeared to encounter the same resistance but followed a zig-zag random path instead of a linear path. This was true even when the falling sphere was smaller than the suspension spheres.

Using this concept, the viscosity of a multimodal suspension of particles can be calculated from the unimodal viscosity data of each size as long as the relative sizes in question are sufficient to have this condition of zero interaction between coarse and fine, since then the behavior of each size is completely independent of the other. For the purpose of clarity and to minimize the mathematics, a system containing two sizes (bimodal) will be described first followed by the general case of \( N \) sizes.
Consider the two parts of the volume making up a suspension having only very fine particles: \( V_I = \) volume of liquid; \( V_f = \) volume of fine particles. The volume concentration of the fine filler in the liquid is:

\[
\phi_f = \frac{V_f}{V_I + V_f}
\]  

(1)

We know that the liquid is going to be stiffened and viscosity increased by the presence of the filler. This stiffening factor is defined as \( H(\phi) \) and is simply the relative viscosity of a unimodal system to that of the liquid alone. Figure 1 illustrates \( H(\phi) \) versus the concentration \( \phi \) for unimodal rigid spherical particles. From the data it appears that \( H(\phi) \) is independent of size. Therefore from the definition of \( H(\phi) \) we may write

\[
H(\phi_f) = \frac{\eta_f}{\eta_0} = \eta_r
\]  

(2)

where \( \eta_0 = \) viscosity of liquid; \( \eta_r = \) viscosity when filled with fines; \( \phi_f = \frac{V_f}{V_I + V_f}; \eta_r = \) relative viscosity, compared to the pure liquid.

Consider now what would happen when coarse particles are added to the suspension of fines. With the assumption that the fine par-
particles behave as a fluid toward the coarse, the coarse particles can be considered simply as stiffening this already stiffened fluid by an additional factor of $H(\phi_c)$. $H(\phi_c)$ is the ratio of the new viscosity with coarse and fine particles, $\eta_c$, to that of the fluid containing only the fine particles, $\eta_f$.

$$H(\phi_c) = \frac{\eta_c}{\eta_f} = \left(\frac{\eta_c}{\eta_0}\right) \cdot \left(\frac{\eta_0}{\eta_f}\right)$$

$$= \left(\frac{\eta_c}{\eta_0}\right) \cdot [1/H(\phi_f)] = \left[\eta_r/H(\phi_f)\right]$$

(3)

where $\eta_c/\eta_0$ becomes the relative viscosity of this bimodal suspension. Hence

$$\eta_r = H(\phi_f)H(\phi_c)$$

(4)

In eq. (4), $\phi_c$ is the concentration of coarse in the apparent liquid whose volume is now given by $(V_i + V_f)$. Thus,

$$\phi_c = \frac{V_c}{[(V_i + V_f) + V_c]}$$

(5)

where $V_c$ is volume of coarse particles.

Since $H(\phi) = 1$ when $\phi = 0$, eq. (4) is valid for all values of $V_f$ and $V_c$ including zero. Naturally this line of reasoning can be applied again and again to obtain:

$$\eta_r = H(\phi_1)H(\phi_2)H(\phi_3) \ldots H(\phi_N) = \prod_{i=1}^{N} H(\phi_i)$$

(6)

where $\Pi$ denotes product and $\phi_i$ is concentration of each size in apparent liquid.

In this system of notation the sizes are always ordered from smallest to largest as $i$ goes from 1 to $N$. The liquid volume is always designated as $V_0$. Thus $\phi_m$, the concentration of the $m$th value of $i$, is written as

$$\phi_m = \frac{V_m}{(V_0 + V_1 + V_2 \ldots V_{m-1}) + V_m} = \frac{V_m}{\sum_{i=0}^{m-1} V_i}$$

(7)

All that is left now is to describe the total filler concentration, $\phi_T$, in terms of the concentration of each component, $\phi_i$. This total concentration is clearly

$$\phi_T = \frac{V_1 + V_2 + \ldots + V_N}{V_0 + V_1 + V_2 \ldots V_N} = \frac{\sum_{i=1}^{N} V_i}{\sum_{i=0}^{N} V_i}$$

(8)
Recalling that each value of $T_i$ involves the same $V_0$, but not the same value of apparent liquid, e.g., $(V_0 + V_1 + V_2 + \ldots + V_{i-1})$ is the apparent liquid for $V_i$, it is clear that the total concentration is not simply $\Sigma T_i$. The general solution for the total concentration may be expressed as

$$(1 - \phi_T) = \prod_{i=1}^{N} (1 - \phi_i)$$

(9)

Equation (9) is not readily apparent but is simply verified by substitution as follows. From the definition of $\phi_m$ and $\phi_T$ we may write the following two equations,

$$(1 - \phi_m) = 1 - \frac{V_m}{\sum_{i=0}^{m} V_i} = \frac{m-1}{\sum_{i=0}^{m} V_i}$$

(10)

$$(1 - \phi_T) = 1 - \frac{\sum_{i=1}^{N} V_i}{\sum_{i=0}^{N} V_i} = \frac{V_0}{\sum_{i=0}^{N} V_i} = \frac{V_0}{V_0 + V_1 + V_2 \ldots V_N}$$

(11)

substituting eqs. (10) and (11) into eq. (9) term for term we obtain

$$\left(\frac{V_0}{V_0 + V_1 + V_2 \ldots + V_N}\right)$$

$$= \left(\frac{V_0}{V_0 + V_1}\right)\left(\frac{V_0 + V_1}{V_0 + V_1 + V_2}\right)\left(\frac{V_0 + V_1 + V_2}{V_0 + V_1 + V_2 + V_3}\right)$$

$$\cdot \left(\frac{V_0 + V_1 + \ldots + V_N - 1}{V_0 + V_1 + V_2 + V_N}\right)$$

(12)

Careful examination of the right side of eq. (12) reveals that the denominator of each term is cancelled by the numerator of the following term. Hence, all terms cancel except the numerator of the first term, $V_0$, and the denominator of the last term, $V_0 + V_1 + V_2 \ldots V_N$, and the proof is complete.

Expanding eq. (9) for the bimodal and trimodal cases yields:

$$\phi_T(\text{bimodal}) = 1 - (1 - \phi_1)(1 - \phi_2) = \phi_1 + \phi_2 - \phi_1\phi_2$$

(13a)

$$\phi_T(\text{trimodal}) = 1 - (1 - \phi_1)(1 - \phi_2)(1 - \phi_3)$$

$$= \phi_1 + \phi_2 + \phi_3 - \phi_1\phi_2 - \phi_1\phi_3 - \phi_2\phi_3 + \phi_1\phi_2\phi_3$$

(13b)
In both eqs. (6) and (9) the product notation can be eliminated by expressing $\eta_r$ and $\phi_r$ as logarithms as done in eqs. (14) and (15).

\[
\ln \eta_r = \sum_{i=1}^{N} \ln H(\phi_i)
\]  
(14)

\[
\ln (1 - \phi_r) = \sum_{i=1}^{N} \ln (1 - \phi_i)
\]  
(15)

Figure 2 illustrates the excellent agreement between the calculated and measured relative viscosity data for a bimodal system of near zero size ratio (i.e., one filler fraction has very coarse particles compared to the other, or $R_{12} \approx 0$) where this assumption of no interaction should be well justified. Also illustrated in this figure are the measured viscosity data for four other size ratios, the 1:1 corresponding to the monomodal data (also illustrated in Fig. 1) from which the values of $H(\phi_1)$ and $H(\phi_2)$ were obtained. The data in Figure 2 indicate that if the size ratio is 1:10 or less, this assumption of no interaction found for a simple falling sphere by Fidleris and Whitmore, still holds for the blending of two sizes.

Before proceeding further it should be pointed out that the data in Figure 2 correspond to a particular blend situation, namely for a
fixed fraction of fine spheres (based on total volume, not the same as $\phi$). Now using a bimodal blend of $R_{12} = 0$, lines corresponding to $R_{12} = 0.477$ or the other nonzero size ratios in Figure 2 can be calculated, but the corresponding blend ratios will be different. In fact the line for $R_{12} = 0.477$ can be calculated two ways still assuming no interaction. First by having a system of almost all fines or second by having a system of almost all course. Similarly, the curves for $R_{12} = 0.313$ and $R_{12} = 0.138$ can be calculated assuming no interaction by selecting more optimized blends, but again the corresponding blend ratios will be different. In doing so bimodal blends with slightly lower viscosities than illustrated for $R_{12} = 0$ can be found and this will be discussed later.

From the above discussion it appears that all possible lines between monomodal and best bimodal can be calculated assuming no interaction just by changing the blend ratios.

The curve, $H(\phi)$ versus $\phi$, in Figure 1 becomes very steep simply because of the mutual crowding of particles. Since in this method of analysis $H(\phi)$ is used, we are already accounting for mutual crowding in its most severe case, when $R_{12} = 1$. By defining a crowding factor, $f$, the behavior of all size ratios can be accounted for. This crowding factor permits one to find that blend ratio for zero interaction that behaves equivalently to any particular blend ratio with interaction, ($R_{12} > 0.1$). The crowding factor is defined as that fraction of one size that behaves as though it were the other size. Since poorer packing can be obtained by using an excess of the coarse or an excess of the fine fraction if we desire to shift toward poorer packing the crowding factor, $f$, must operate on the size of the filler having the lowest concentration. Logically this factor $f$ varies from 0 to 1 as the size ratio varies from 0 to 1.

The similarities between blend ratios and size ratios are shown in Figure 3 were the calculated viscosity data for different blend ratios assuming $R_{12} = 0$ are illustrated. In a bimodal system one obtains the same viscosity regardless of whether $\phi_1$ and $\phi_2$ are interchanged at any concentration of the two given sizes. There are two blend ratios that will result in the same viscosity, the second being the reciprocal of the first. The equivalence of size ratios and the effect of the crowding factor, $f$, are illustrated in Figure 4 showing the measured viscosity data for different size ratios and the calculated data for different values of $f$. No attempt was made to make the
curves coincide with each other and no data exists to show that \( f \) is independent of the blend ratio. This approach provides a simple, but effective, means of calculating what will result when similar sizes are blended together, however more experimental data are needed so additional correlations can be made.

**Figure 3.**

**Figure 4.**
Optimization of Multimodal System

In order to optimize the blend ratios in a multimodal system (assuming no or equal interaction) all that is necessary is to determine the minimum value of the product of the values of $H(\phi_i)$. This can be achieved by differentiating $\eta_r$ or $\ln \eta_r$ with respect to $\phi_i$ and setting the differential equal to zero. The solution of the minimum minima can be obtained as follows:

$$\ln \eta_r = \sum_{i=1}^{N} \ln H(\phi_i) \quad \text{definition from theory} \quad (14)$$

$$\ln (1 - \phi_T) = \sum_{i=1}^{N} \ln (1 - \phi_i) \quad \text{definition from theory} \quad (15)$$

From the definition of a total derivative we may write

$$d \ln \eta_r = \frac{\partial \ln \eta_r}{\partial \phi_1} d\phi_1 + \frac{\partial \ln \eta_r}{\partial \phi_2} d\phi_2 + \ldots + \frac{\partial \ln \eta_r}{\partial \phi_N} d\phi_N$$

$$= \sum_{i=1}^{N} \frac{\partial \ln \eta_r}{\partial \phi_i} d\phi_i \quad (16)$$

The partial derivatives in eq. (16) can be obtained from eq. (14). Doing this and setting eq. (16) equal to zero we obtain

$$0 = \sum_{i=1}^{N} \frac{\partial \ln H(\phi_i)}{\partial \phi_i} d\phi_i \quad (17)$$

The values of $d\phi_i$ can be obtained by differentiating eq. (15) for constant $\phi_T$

$$d \ln (1 - \phi_T) = \sum_{i=1}^{N} d \ln (1 - \phi_i) = \sum_{i=1}^{N} \frac{-d\phi_i}{1 - \phi_i} = 0 \quad (18)$$

since $\ln (1 - \phi_T)$ is constant. Solving eq. (18) for $d\phi_N$ we obtain

$$d\phi_N = -(1 - \phi_N) \sum_{i=1}^{N-1} \frac{d\phi_i}{1 - \phi_i} \quad (19)$$

Substituting this into the last term of eq. (17) yields

$$0 = \sum_{i=1}^{N-1} \left[ \frac{\partial \ln H(\phi_i)}{\partial \phi_i} - \left( \frac{1 - \phi_N}{1 - \phi_i} \right) \frac{\partial \ln H(\phi_N)}{\partial \phi_N} \right] d\phi_i \quad (20)$$
There are many solutions to eq. (20), but all of these solutions but one are for secondary minima. The primary solution is for the blends that will produce the lowest possible relative viscosity for any concentration and that occurs when each term in the series is zero. This occurs when

\[ \phi_1 = \phi_2 = \phi_3 = \phi_4 \ldots = \phi_N \text{ providing } H(\phi_1) = H(\phi_2) \ldots = H(\phi_N) \]

Figure 5 illustrates the relative viscosity of the best multimodal suspensions using the above solution. It is interesting to note that there is a lower limit to the viscosity of a suspension and that this lower limit can be achieved with only one component at low concentrations. The equation being independent of the concentration of each size, \( \phi_i \).

The functional form of this lower limit may therefore be found by treating each term in eq. (20) as the differential equation

\[
\frac{\partial \ln H(\phi_i)}{\partial \phi_i} - \left( \frac{1 - \phi_n}{1 - \phi_i} \right) \frac{\partial \ln H(\phi_n)}{\partial \phi_n} = 0
\]

and since \( \phi_i \) is independent of \( \phi_n \) we have

\[
\frac{(1 - \phi_i) \frac{\partial \ln H(\phi_i)}{\partial \phi_i}}{1 - \phi_i} = \frac{(1 - \phi_n) \frac{\partial \ln H(\phi_n)}{\partial \phi_n}}{1 - \phi_n} = \text{constant} = K
\]

and one arrives at the solution

\[
H(\phi_i) = (1 - \phi_i)^{-K} \text{ when } \phi_i \leq 0.25
\]

and for all values of \( \phi_i \) the following inequality can be demonstrated

\[
H(\phi_i) \geq (1 - \phi_i)^{-K}
\]

applying eq. (24) to eq. (6) yields

\[
\eta_r \geq (1 - \phi_1)^{-K}(1 - \phi_2)^K \ldots = (1 - \phi_T)^K
\]

Equation (25) may also be arrived at by recognizing that the viscosity decreases as the number of components increases for optimized systems. For a fixed value of \( \phi_T \) the lowest viscosity will therefore occur in the limit as the number of components becomes infinitely large.
Taking the optimized case \( \phi_1 = \phi_2 = \phi \ldots = \phi \), and using eqs. (6) and (15) we have

\[
\phi = -\frac{1}{N} \ln (1 - \phi_T) \text{ as } N \to \infty
\]  

and

\[
\eta_r (\text{Minimum}) = \lim_{N \to \infty} \left[ H(\phi) \right]^N = \lim_{N \to \infty} \left[ H \left( -\frac{1}{N} \ln (1 - \phi_T) \right) \right]^N
\]

since \( \phi \to 0 \) as \( N \to \infty \) only first-order terms need be considered and linear approximation for \( H(\phi) \) is appropriate [i.e., \( H(\phi) = 1 + K\phi \) as \( \phi \to 0 \)], substituting this into eq. (27) yields

\[
\eta_r (\text{Minimum}) = \lim_{N \to \infty} \left[ 1 - \left( \frac{K}{N} \right) \ln (1 - \phi_T) \right]^N
\]

\[
= e^{-K \ln (1 - \phi_T)} = (1 - \phi_T)^{-K}
\]

and for the general case one may write the inequality

\[
\eta_r \geq (1 - \phi_T)^{-K}
\]
Choosing $K = 3$, this equation fits exactly the behavior of all the data in Figure 5 at low filler concentrations, and the data at high filler concentrations approach this function as $N$ increases. These data point out that, for all practical purposes, this lowest viscosity can be obtained with very few components even for quite high loadings. Also since the only variable in eq. (29) is the constant $K$, and the viscosity at low concentrations must be included in the solution, $K$ must be a function of particle shape since the viscosity for any concentration is a function of particle shape.

Table I gives the blend ratios for the best bimodal, trimodal, and tetramodal systems. These best blend ratios are dependent upon filler concentration. The values in Table I are mathematical solutions of the equations. At low filler concentrations, however, it would be difficult if not impossible to observe any difference in the viscosity experimentally while at very high filler concentrations, suspensions can only be made if highly optimized systems are used. Figure 6 illustrates the relative viscosities for bimodal systems versus blend ratio for a number of concentrations. As discussed above,
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<th>Total volume % solids</th>
<th>Bimodal by volume</th>
<th>Trimodal by volume</th>
<th>Tetramodal by volume</th>
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</thead>
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<td>Coarse, %</td>
<td>Fine, %</td>
</tr>
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TABLE I
Optimum Multimodal Blend Ratios for Conditions of Zero Interaction
the behavior at low concentrations is practically independent of the blend ratio while at high concentrations marked decreases in viscosity can be made by using proper blends. The unimodal data from which Figure 6 was obtained are in Figure 1. If these unimodal systems contained a greater latitude of particle size distribution, the values calculated at the higher concentrations would be lower.

Figures 7 and 8 illustrate iso-relative-viscosity lines for trimodal systems at 65% and 75% total solids by volume. In Figure 7 the gradient is quite weak and it is apparent that any of the optimum bimodal systems (the minimum occurring along any of the axes) is about as good as the best trimodal blend. This is not the case, however, in Figure 8 where the total solids is higher and the gradient very strong. In each case the location of the minimum is predicted well by the solution of eq. (20).
Another point of interest in these figures is that in a trimodal system, if the per cent of the total solids that is the finest or coarsest is held fixed while the other two are adjusted, the odds are no change in viscosity will occur since, in Figures 7 and 8, the axes and the iso-viscosity lines are apt to be parallel. This is not true when the extreme sizes are adjusted while holding the midsize fixed. Hence, changing the blend ratio and observing no change in viscosity is not an indication that better combinations of those same sizes do not exist.

**Points of Special Interest**

The theory of optimized systems described above indicates that besides having optimized blend ratios at each concentration, the viscosity of some highly concentrated suspensions can be reduced
markedly by adding more filler to the existing suspension thereby actually increasing the total filler concentration, \( \phi_T \). At first this may seem impossible, but it is predicted analytically from this theory and has been verified experimentally. The physical reason for this may be explained as follows. Consider a concentrated monodispersed suspension of coarse particles. For the purpose of simplicity this monodispersed suspension of coarse particles shall be a bimodal suspension with the concentration of fines, \( \phi_1 \), equal to zero (i.e., \( \phi_1 = 0 \)).

From the definition of concentration of each size we have

\[
\phi_1 = \frac{V_1}{V_0 + V_1} \tag{30}
\]
\[
\phi_2 = \frac{V_2}{V_0 + V_1 + V_2} \tag{31}
\]

and the total concentration \( \phi_T \), may be expressed as

\[
\phi_T = \phi_1 + \phi_2 - \phi_1 \phi_2 = \phi_2 \text{ if } \phi_1 = 0 \tag{32}
\]

and the relative viscosity of this suspension is

\[
\eta_r = H(\phi_1)H(\phi_2) = H(\phi_2) \text{ since } H(\phi_1) = 1 \text{ if } \phi_1 = 0 \tag{33}
\]

From eqs. (30) and (31) it is evident that adding fine particles to this concentrated suspension of coarse particles increases \( \phi_1 \) and hence \( H(\phi_1) \) while it decreases \( \phi_2 \) [because \( V_1 \) appears in the denominator of eq. (24)] and therefore decreases \( H(\phi_2) \). If \( \eta_r \) was originally quite high it is possible to decrease \( H(\phi_2) \) much more than \( H(\phi_1) \) was increased, the net result being a decrease of viscosity.

**Example.** Take a suspension made up of 45 cc of liquid and 55 cc of a coarse spherical particles. Hence \( \phi_2 = 55/(45 + 55) = 0.55 \) and from Figure 1 we determine that \( H(0.55) \) which is the same as \( \eta_r \) is 50. Now if 12 cc of fine particles are added to this suspension the various parameters would change as follows:

\[
\phi_1' = \frac{12}{(45 + 12)} = 0.21
\]
\[
\phi_2' = \frac{55}{(45 + 12 + 55)} = 0.493
\]
\[
\phi_T' = \frac{(12 + 55)}{(45 + 12 + 55)} = 0.600 = \phi_1' + \phi_2' - \phi_1' \phi_2'
\]
\[
\eta_r' = H(\phi_1')H(\phi_2') = H(0.21)H(0.493) - 2 \times 14 = 28
\]

and we see that the relative viscosity of this original suspension is decreased by nearly 50\% while the total concentration of solids was increased about 10\%. 

Figure 9 illustrates the relative viscosity of a suspension of 55 vol-% coarse particles when fine particles are added to the original suspension, and when liquid in the original suspension is replaced with fine particles. The one curve on the far right is for a suspension of 65 vol-% coarse particles which remains full of voids because there is not enough liquid to fill the interstices until a sufficient volume of fine particles has been added to decrease the concentration of coarse until there was enough material (liquid + fines) to fill the interstices and free up the close-packed monodispersed system.

The data in Figure 10 is presented as additional proof of this softening by increasing the concentration of fines in some systems. Instead of viscosity we see the stress–strain data on two filled elastomers, the second differing from the first only by the addition of fine particles. The original material was 60 vol-% filler which was then raised to 65 vol-% by the addition of fines. Here we see that the modulus of elasticity was decreased by adding fines. The dilation data presented is a measure of the microstructural failure which is caused by high internal stresses. These data also indicate there was an increase in the internal freedom after the fines were
added. Figure 11 illustrates the viscosity-concentration behavior of a suspension of fines when coarser particles are added. According to the theory, best processing and least particle attrition will be obtained for multimodal systems when the fillers are preblended, or added in stages, fines first, then the next size, etc. The coarsest particles should always be added last. Poor processing can result (until the fines are added) if the coarser particles are added first, even though the total solids combination may process quite well.

**Remarks**

It should be pointed out that the first apparent systematic study dealing with the viscosity of solutions and suspensions was done by Arrhenius in 1887. His experimental data indicated there was little difference between dilute suspensions of rigid particles and dilute solutions.

In 1906 Einstein published a theoretical analysis dealing with the viscosity of dilute solutions as part of a paper titled "A New Determination of Molecular Dimensions." In this paper he showed how the size of solute molecules in an undissociated dilute solution could be found from the viscosity of the solution and of the pure solvent, and from the rate of diffusion of the solute into the solvent when the volume of a molecule of the solute is large compared with the volume...
of a molecule of the solvent. He stated such solute molecules would behave approximately, with respect to their mobility in the solvent, and in respect to their influence on the viscosity of the latter, as solid bodies suspended in the solvent which for he chose the spherical form. He then derived the appropriate hydrodynamic equations which satisfied such a problem and calculated the energy, $W^*$, (per unit volume of solution per unit of time) which was transformed into heat during a flow process.

Ignoring higher-order terms, he concluded that

$$W^* = 2\delta^2 k (1 + \phi/2 + \ldots )$$  \hspace{1cm} (34)

where $k$ = viscosity of pure solvent; $\phi$ = volume fraction of solute in the solvent.

$$\delta^2 = (\partial V_x/\partial x)^2 + (\partial V_y/\partial y)^2 + (\partial V_z/\partial z)^2$$

The velocity gradients in eq. (34) are the velocity gradients that would exist if the spherical particles were not present.
He then treated the solution as a homogeneous liquid with viscosity, \( k^* \), and expressed \( W^* \) as being

\[
W^* = 2\delta^{*2}k^*
\]  

(35)

Again ignoring higher-order effects, he proved that for dilute solutions

\[
(\partial V_\perp/\partial x)^* = (\partial V_\perp/\partial x)(1 - \phi)
\]

\[
(\partial V_\parallel/\partial y)^* = (\partial V_\parallel/\partial y)(1 - \phi)
\]

\[
(\partial V_\perp/\partial z)^* = (\partial V_\perp/\partial z)(1 - \phi)
\]

(36)

since

\[
\delta^{*2} = (\partial V_\perp/\partial x)^2 + (\partial V_\parallel/\partial y)^2 + (\partial V_\perp/\partial z)^2
\]

(37)

is followed that

\[
\delta^{*2} = \delta^2(1 - \phi)^2.
\]

(38)

The above-mentioned point is of interest since even today there is still considerable controversy as to the increase of the microscopic strain or shearing rate due to the presence of filler. Einstein’s mathematics on this point provides verification that the line fraction, area fraction, and volume fraction of solids in dilute suspensions are on the average equal.

Substituting eq. (38) into eq. (35), Einstein obtained

\[
W^* = 2\delta^{*2}k^*(1 - \phi)^2.
\]

(39)

Equation (39) together with eq. (34) yields

\[
k^*/k = (1 + \phi/2 + \ldots)/(1 - \phi)^2
\]

(40)

Since Einstein was only interested in dilute solutions, he simplified this to

\[
k^*/k = 1 + 2.5\phi.
\]

(41)

His main assumption in solving the hydrodynamic equations was that there be no interaction between the suspension particles which is similar to the assumption made in this text. Einstein’s relation must therefore satisfy the lowest possible viscosity for any concentration as well as being the analytical solution for dilute suspensions since one analytical solution must be contained in the other. If all
the higher-order effects were accounted for, one would expect Einstein's equation to become

\[ \frac{k^*}{k} = (1 - \phi)^{-2.5} \]  \hspace{1cm} (42)

This equation known as the Brinkman-Roscoe\textsuperscript{12,13} equation, deviates little from eq. (40) which Einstein derived in 1911 and satisfies the functional form required by this text for the equation of the lower bound for the viscosity at any concentration.

The experimental data used in Figures 1 and 2 of this paper were taken by J. S. Chong when he was at Aerojet. His fine report "The Rheology of Suspensions" (Aerojet Technical Memorandum 251 SRP 1964) and his Ph.D. Thesis "Rheology of Concentrated Suspensions" (University of Utah, 1962) provide a fine accumulation of facts pertinent to this subject.

References


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