

A Generalized Model to Predict the Viscosity of Solutions with Suspended Particles. I

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SYNOPSIS

Several suspension equations available in the literature have been found to have a common derivative form. This common derivative was found to be equivalent to a ratio of the intrinsic viscosity, $[\eta]$, and a quantity, V_{Int} , defined as the "relative suspension interaction volume" available for particle flow. V_{Int} was, in general, found to be a relatively simple function of the suspension particle volume fraction, ϕ , the maximum particle packing fraction, ϕ_n , and a new variable, σ , defined as the particle interaction coefficient. Different forms of this common derivative were obtained by modifying V_{Int} with a simple adjustment for the value for the interaction coefficient, σ . Integration of this generalized derivative yielded a generalized suspension viscosity equation that was found to predict the form of many suspension equations that have previously appeared in the literature. For example, by varying the interaction coefficient, σ , the Arrhenius equation resulted when $\sigma = 0$, the Kreiger–Dougherty equation resulted when $\sigma = 1$, and when $\sigma = 2$, the Mooney equation resulted. Fractional values for the particle interaction coefficient were also found to be useful when optimizing the empirical fit of the literature data of Vand and Eiler. Additional insight from such a data fit can also be obtained from the magnitude of both the particle interaction coefficient, σ , and the packing fraction, ϕ_n . © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The prediction of solution viscosities with suspended particles crosses many applications. The prediction of spherical particle suspension viscosities was recognized as an early need in the development of latexes to make synthetic rubber.^{1–4} Paint and coatings latex development^{5,6} has also found a need for this technology. Other diverse suspensions that have utilized this technology have included the food industry to evaluate milk⁷ as well as the coal industry to evaluate bitumen emulsions.⁸ More recently, this technology has also been applied to filled thermoplastics.^{9–11} However, the new emerging thermoplastic particulate-filled thermoset resins of the type recently described by Recker et al.¹² would probably be described as one of the types of materials currently most in need of a better understanding of the

relationship between particle-size distribution and viscosity.

Several recent reviews^{11,13–16} have addressed the current understanding of particle size and particle-size distribution on the rheology of suspensions. Many theoretical efforts have been attempted to develop equations to predict the relationship between the suspension viscosity, η , and the volume fraction of particles, ϕ , in the suspension. An extensive survey of the viscosity–concentration literature was made by Rutgers in 1962.^{17,18} He identified 96 equations from the literature that described the behavior of these viscosity–concentration systems. Comparing the experimental data with the equations, he concluded that these 96 equations could be reduced to five useful ones. From an evaluation of their derivative properties, it has been found that these important equations can be combined into a single generalized viscosity–concentration equation for most applications. This generalized viscosity–concentration equation will be developed in this paper.

VISCOSITY EQUATION DEVELOPMENT

Early in this century, Einstein^{19,20} showed that single isolated particles increased the viscosity of a liquid as a simple function of their volume fraction, φ , according to the formula

$$\eta = \eta_0(1 + 2.5\varphi) \quad (1)$$

where η = suspension viscosity and η_0 = viscosity of suspending medium. The derivative of eq. (1) gives

$$d\eta = \eta_0(5/2)d\varphi \quad (2)$$

More concentrated solutions can be tackled by introducing an averaging of the influence of neighboring particles or alternately to simulate the situation using computer modeling. The averaging technique used by Ball and Richmond²¹ started from an assumption that the effect of all particles in a concentrated suspension is the sum of the effects of particles added sequentially. Using this assumption, Ball and Richmond pointed out that the Einstein equation can be written in differential form as

$$d\eta = \eta(5/2)d\varphi \quad (3)$$

where $d\eta$ is the increment of viscosity on the addition of a small increment of phase volume $d\varphi$ to a suspension of viscosity η . It is interesting that the form of this equation was first described by Arrhenius^{22,23} without the significance identified by Ball and Richmond. The viscosity of the final suspension is then obtained by integrating the phase volume between 0 and φ to give

$$\eta = \eta_0 e \exp[(5/2)\varphi] \quad (4)$$

Ball and Richmond also pointed out that the major limitation of eqs. (3) and (4) is that they omit viscosity effects resulting from the interactions between spheres due to their finite size. This means that when a particle is added to a relatively concentrated suspension it requires more space than does its volume $d\varphi$ due to packing difficulties. When the volume fraction is increased by an amount $d\varphi$, the spheres that were already present suffer a crowding effect. This crowding causes a reduction in the available volume that can effect a change in viscosity by an amount proportional to $(1 - k\varphi)$, where k accounts for the so-called crowding factor. Consequently, $d\varphi$ is replaced with $d\varphi/(1 - k\varphi)$ to give

$$(1 - k\varphi)d\eta = \eta(5/2)d\varphi \quad (5)$$

At this point, consider two of the more widely used equations to describe the viscosity of suspensions as a function of concentration. First, consider the Kreiger–Dougherty equation⁴:

$$\eta = \eta_0(1 - k\varphi)^{-5/(2k)} \quad (6)$$

The derivative of this equation gives

$$\frac{d\eta}{\eta} = (5/2)(1 - k\varphi)^{-1}d\varphi \quad (7)$$

Note that this equation is the same as eq. (5). Likewise, the Mooney¹ equation given as

$$\eta = \eta_0 \exp[(5/2)\varphi/(1 - k\varphi)] \quad (8)$$

has the following derivative:

$$\frac{d\eta}{\eta} = (5/2)(1 - k\varphi)^{-2}d\varphi \quad (9)$$

The derivatives of the Einstein eq. (3), the Kreiger–Dougherty eq. (7), and the Mooney eq. (9) can all be written in the following general form:

$$\frac{d\eta}{\eta} = (5/2)(1 - k\varphi)^{-\sigma}d\varphi \quad (10)$$

Equation (10) can also be rewritten in the following form:

$$(1 - k\varphi)^\sigma \frac{d \ln \eta}{d\varphi} = 5/2 \quad (10a)$$

All the derivatives previously described can be obtained from eq. (10). The Arrhenius equation results when $\sigma = 0$, the Kreiger–Dougherty equation results when $\sigma = 1$, and the Mooney equation results when $\sigma = 2$.

At this point, a review of the earlier argument of Ball and Richmond of the crowding factor, k , should be considered when comparing eq. (5) and (10a). Based on this comparison, it would be expected that the available unhindered volume that can effect a change in suspension viscosity would be expected to be reduced by an amount proportional to $(1 - k\varphi)^\sigma$ when suspension particles begin to interact. If this quantity can be defined as the “relative suspension interaction volume,” V_{Int} , then

$$V_{\text{Int}} = (1 - k\varphi)^\sigma \quad (11)$$

This relative suspension viscosity volume can be visualized more effectively if it is noted that $(1 - k\varphi) = 0$ when $\varphi = 1/k$. If φ_n is defined as the maximum packing fraction for a given particle-size distribution such that $\varphi_n = 1/k$, then eq. (11) can be rewritten to give

$$V_{\text{Int}} = \left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^\sigma \quad (12)$$

The "total relative unpacked volume," V_{unpacked} , can be defined as

$$V_{\text{unpacked}} = \left(\frac{\varphi_n - \varphi}{\varphi_n} \right) \quad (13)$$

Based on this definition, the relative suspension interaction volume fraction would appear to be related to the influence of particles and solvent on the relative unpacked volume fraction.

Further illustration of the "relative suspension interaction volume," V_{Int} , as a function of both φ and σ is indicated in Figure 1 for an example where $\varphi_n = 0.75$. The results in Figure 1 indicate the "relative suspension interaction volume," V_{Int} , decreases with φ at a faster rate as σ increases. For the case where $\sigma = 0$, then $V_{\text{Int}} = 1$ for all φ and the "relative suspension interaction volume" does not change with an increase in particle volume fraction, φ . For this special case, particles have a negligible interaction with each other as if they were essentially isolated from each other. However, as σ increases, V_{Int} decreases with φ , indicative of a higher concentration, a higher particle interaction, or a greater

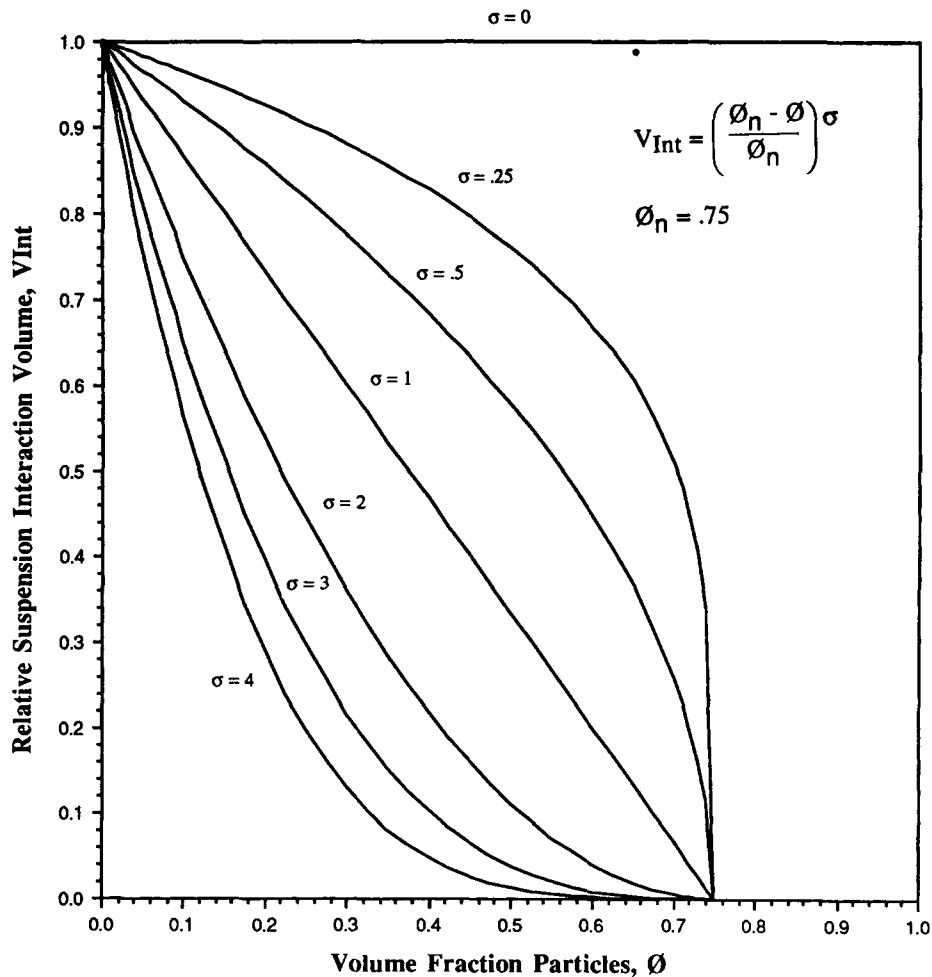


Figure 1 Relative suspension interaction volume, V_{Int} vs. volume fraction particles, φ , as a function of the particle interaction coefficient, σ .

interference of particles with each other. This suggests that σ can be described as a "particle interaction coefficient" since it is apparently a measure of particle interaction.

An increase in σ can also be described in terms of an increase in all directions of a projected "radius of influence" around each particle. This radius of influence per particle could probably be better related to a projected volume increase around each particle as indicated by a new effective size or "sphere of influence." As the sphere of influence for each particle increases, then the "relative suspension interaction volume," V_{Int} , between particles would be expected to decrease. A decrease in the unhindered volume between particles would then be expected to result in an increase in suspension viscosity. For example, electrically charged particles would be expected to significantly affect σ .

It is probable that the relative suspension interaction volume is, in fact, a product of several con-

tributions to the interaction process of both particle and solvent. For this case,

$$V_{Int} = \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{\sigma_S} \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{\sigma_1} \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{\sigma_2} \dots \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{\sigma_{n-1}} \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{\sigma_n} \quad (14)$$

Such that

$$\sigma = \sigma_S + \sigma_1 + \sigma_2 + \dots + \sigma_{n-1} + \sigma_n \quad (15)$$

and

$$\sigma = \sigma_S + \sigma_P \quad (16)$$

where σ = particle interaction coefficient; σ_S = solvent contribution to the particle interaction coeffi-

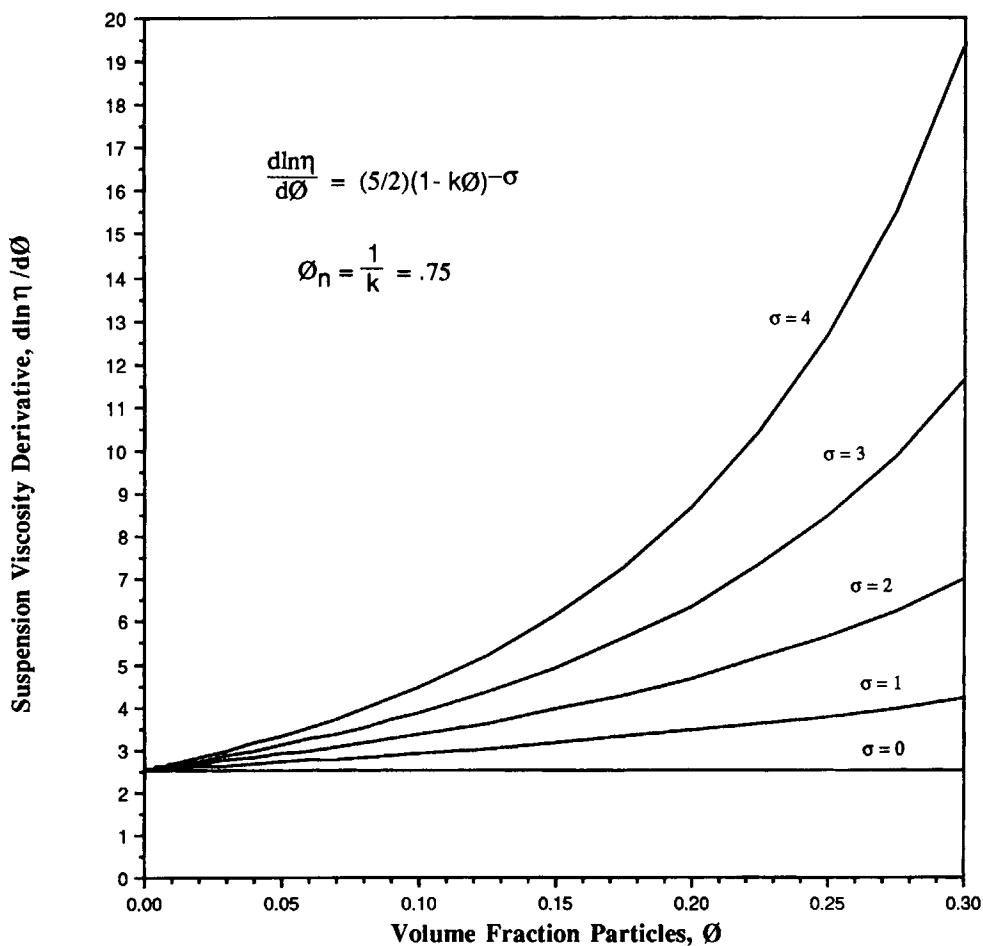


Figure 2 Suspension viscosity derivative $d \ln \eta / d \phi$ vs. volume fraction particles, ϕ , as a function of the particle interaction coefficient, σ .

Table I Generalized Suspension Viscosity Equation for Selected Values of the Particle Interaction Coefficient, σ

Particle Interaction Coefficient, σ	Simplified Form of Generalized Equation	Previous Reference for Equation Derivation
0	$\ln(\eta/\eta_0) = [\eta]\phi$	Arrhenius ^{22,23} (1887, 1917)
0.5	$\ln(\eta/\eta_0) = \left(\frac{2[\eta]}{k}\right)(1 - (1 - k\phi)^{0.5})$	
1	$\ln(\eta/\eta_0) = \left(\frac{-[\eta]}{k}\right)\ln(1 - k\phi)$	Krieger-Dougherty ⁴ (1959)
2	$\ln(\eta/\eta_0) = [\eta]\left\{\frac{\phi}{1 - k\phi}\right\}$	Mooney ¹ (1951)
3	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{2}\right)\left\{\frac{2\phi - k\phi^2}{(1 - k\phi)^2}\right\}$	
4	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{3}\right)\left\{\frac{3\phi - k\phi^2 + k^2\phi^3}{(1 - k\phi)^3}\right\}$	

cient; σ_i = i th particle contribution to the particle interaction coefficient; and σ_P = summation of all of the individual particle contributions to the particle interaction coefficient.

For this definition of the particle interaction coefficient, the interaction of each particle influences the relative unpacked volume. The interactive volume fraction or the remaining fraction of free vol-

ume between particles is then elucidated from the product of particle influences on the unpacked volume fraction. The solvent would also be expected to have a similar contribution on the unpacked volume fraction.

One formulation of the individual particle contributions to the overall particle interaction coefficient could be described as

Table II Vand's Observed Data Compared with Results Calculated Using the Generalized Suspension Viscosity Equation

Concentration by Volume	Vand's Observed with Stirring (η/η_0)	Calculated with Stirring (η/η_0)	Vand's Observed without Stirring (η/η_0)	Calculated without Stirring (η/η_0)
0.00	1.000	1.000	1.000	1.000
0.05	1.145	1.144	1.145	1.144
0.10	1.342	1.338	1.342	1.340
0.15	1.621	1.612	1.621	1.613
0.20	2.024	2.018	2.024	2.013
0.25	2.632	2.665	2.632	2.627
0.30	3.636	3.798	3.636	3.636
0.35	5.556	6.082	5.556	5.435
0.40	11.770	11.793	10.530	9.015
0.45	33.330	32.610	18.180	17.264
0.50	200.000	200.267	33.330	40.557
Intrinsic viscosity, $[\eta]$ (Einstein value assumed)		2.500		2.500
Particle interaction coefficient		1.700		2.900
Maximum packing fraction		0.602		0.982
Minimum average absolute % error		1.713		4.063

Table III Eiler's Observed Data Compared With Results Calculated Using the Generalized Suspension Viscosity Equation

Concentration by volume	Eiler's Observed (η/η_0)	Calculated (η/η_0)
0.00	1.000	1.000
0.10	1.250	1.307
0.20	1.840	1.783
0.30	2.550	2.581
0.40	4.000	4.078
0.50	7.600	7.430
0.60	18.000	17.784
0.65	34.000	34.010
0.70	90.000	90.689

Intrinsic viscosity, $[\eta]$ (Einstein value assumed)	2.500
Particle interaction coefficient	1.000
Maximum packing fraction	0.776
Minimum average absolute % error	1.158

$$\sigma_P = \sum_{i=1}^n \sigma_i = \sigma_{PC} \sum_{i=1}^n \left(\frac{N_i}{\sum_{i=1}^n N_i \mathcal{D}_i} \right) \quad (17)$$

where σ_{PC} = particle contribution constant assumed to be identical for all particles in a suspension; N_i = number of particles with the i th size diameter; and \mathcal{D}_i = diameter of i th particle size.

For this characterization, the individual contribution to the overall particle interaction coefficient is assumed to be directly proportional to the number of particles of a given size, N_i , and inversely proportional to the product sum of the numbers of particles and their respective diameters. Further simplification can be obtained by noting that

$$D_1 = \left(\frac{\sum_{i=1}^n N_i \mathcal{D}_i}{\sum_{i=1}^n N_i} \right) \quad (18)$$

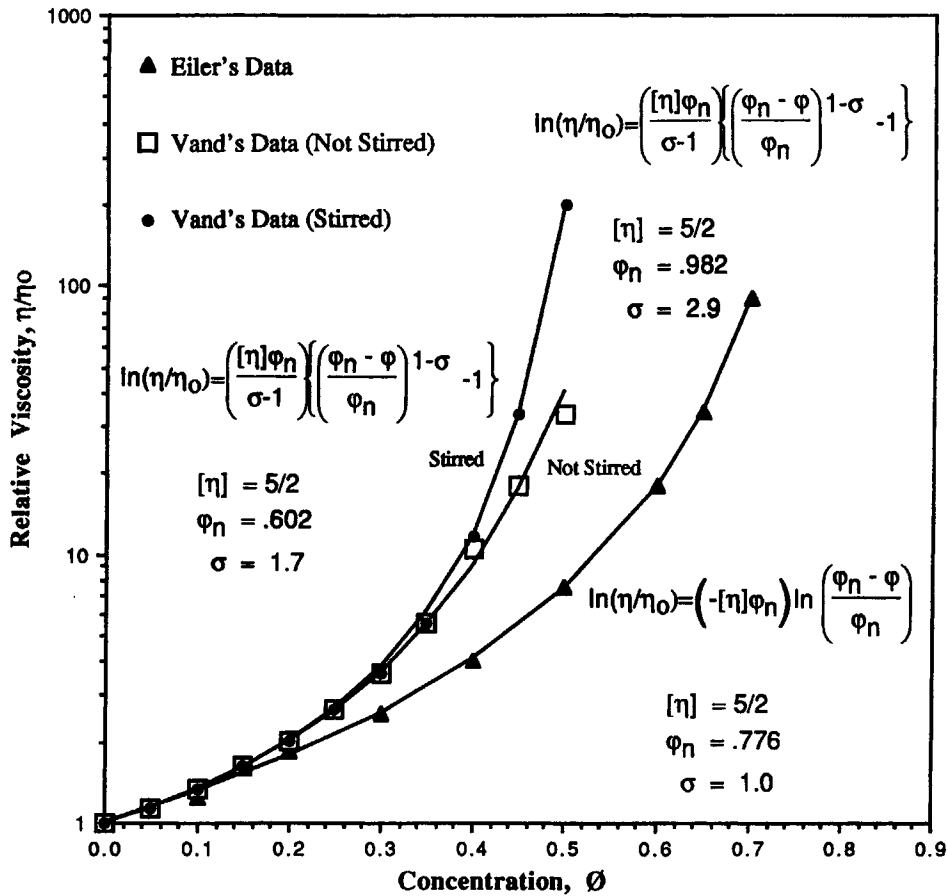


Figure 3 Measured relative viscosity data of Vand and Eiler compared with generalized suspension equation calculations

which yields a particle interaction coefficient of

$$\sigma = \frac{\sigma_{PC}}{D_1} + \sigma_S \quad (19)$$

Note that the D_1 particle-size average, often called the number-average particle-size diameter, generally gives greater weight to smaller particles than to larger particles. This means that the particle interaction coefficient would be expected to increase as the number of smaller particles in the suspension mixture increases. Further discussion of the relationship between particle-size distribution and the particle interaction coefficient will be described in a later paper.²⁸

The calculation of V_{Int} utilizes the maximum packing fraction, φ_n , which is expected to depend on both the number of different classes of particle diameters, n , and the polydispersity of the particle-

size distribution. Several attempts have been made in the literature²⁴⁻²⁶ to predict the correct value for φ_n based on particle-size distribution. A new analysis approach that generates unique insight into the calculation of φ_n has been described by this author.²⁷ This paper shows that the packing fraction, φ_n , can be defined as a function of the following particle-size distribution variables:

$$\varphi_n = F[n, \varphi_m, (D_5/D_1)] \quad (20)$$

where φ_m = monodisperse loose random packing fraction; n = number of classes of particles with different particle diameters; and D_5/D_1 = ratio of specific average particle diameters. Since particle-size distribution is not of primary concern here; additional detailed considerations of particle-size distribution will not be addressed further in this paper.

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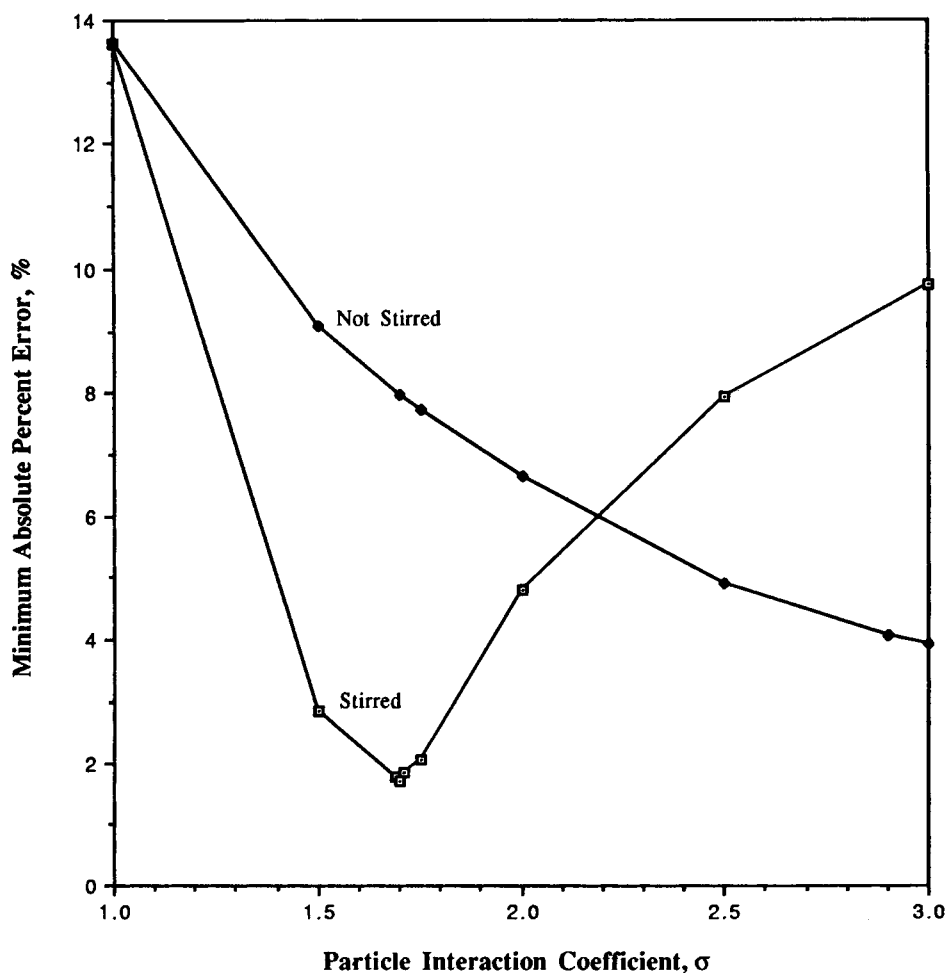


Figure 4 Minimum absolute percent error vs. particle interaction coefficient for Vand's data.

all $\sigma \geq 0$ can then be obtained by integrating eq. (10) to give

$$\int_{\eta_0}^{\eta} \frac{d\eta}{\eta} = (5/2) \int_0^{\varphi} (1 - k\varphi)^{-\sigma} d\varphi \quad (21)$$

When $\sigma = 1$, then eq. (21) integrates to give the Kreiger–Dougherty equation. However, when $\sigma \neq 1$, then eq. (21) integrates to give

$$\ln(\eta/\eta_0) = \left(\frac{5}{2k}\right) \left(\frac{1}{\sigma - 1}\right) \left[\frac{1 - (1 - k\varphi)^{\sigma-1}}{(1 - k\varphi)^{\sigma-1}}\right] \quad (22)$$

Again, the Arrhenius equation results from eq. (22) when $\sigma = 0$ and the Mooney equation results when $\sigma = 2$.

It is interesting that the class of suspension viscosity relationships described by derivative eq. (10a)

used as the basis for the integral in eq. (21) yields a common limit:

$$\text{as } \varphi \rightarrow 0, \text{ then } \frac{d \ln \eta}{d\varphi} \rightarrow 5/2 \text{ for all } \sigma \geq 0$$

This later limit is illustrated graphically in Figure 2 where $\phi_n = 1/k = 0.75$. It is also important to note in Figure 2 that a decrease in the relative suspension interaction volume, V_{Int} , in Figure 1 is translated into a significant increase in the slope of the viscosity curve as the solution volume fraction of particles, φ , increases from 0 toward the maximum packing fraction, φ_n .

Occasionally, the Einstein limiting slope of 5/2 is not obtained as $\varphi \rightarrow 0$. For these cases, this limiting slope is referred to as the intrinsic viscosity, $[\eta]$. For this case, eq. (10a) yields the following result:

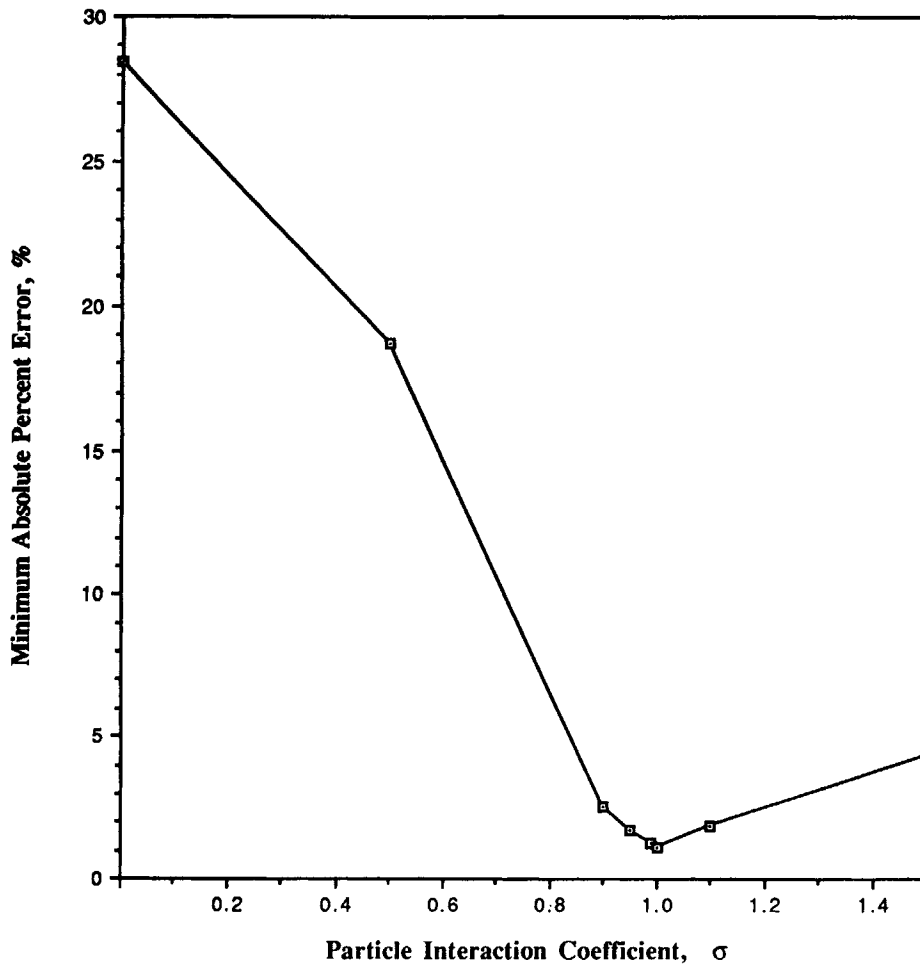


Figure 5 Minimum percent absolute error vs. particle interaction coefficient for Eiler's data.

as $\varphi \rightarrow 0$ then $\frac{d \ln \eta}{d\varphi} \rightarrow [\eta]$ for all $\sigma \geq 0$

It is apparent that this same intrinsic viscosity, $[\eta]$, would be applicable to all equations described by eq. (10) including the Arrhenius, the Mooney, and the Kreiger–Dougherty equations. In addition, eq. (22) would also be rewritten for the more general case as

$$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{k}\right)\left(\frac{1}{\sigma-1}\right)[(1-k\varphi)^{1-\sigma} - 1]$$

for $\sigma \neq 1$ (23)

where $k = 1/\varphi_n$; η = suspension viscosity; η_0 = viscosity of suspending medium; $[\eta]$ = intrinsic viscosity; σ = particle interaction coefficient; k = “crowding factor”; φ = suspension particle volume fraction; and φ_n = particle packing fraction. For the

case where $\sigma = 1$, the general form of the Kreiger–Dougherty eq. (6) would also be written using the intrinsic viscosity, $[\eta]$, to replace the Einstein 5/2 term.

Some optional forms for this generalized suspension viscosity equation for several values of the particle interaction coefficient, σ , are summarized in Table I. Also included in Table I are the authors who first referenced some of these specific forms. Note that fractional values of the particle interaction coefficient, σ , are perfectly acceptable in the viscosity formulation methodology presented in this paper.

Series Expansion of the Generalized Equation

Further insight into the characteristics of the interaction parameter, σ , and the packing fraction, φ_n , can be obtained from the series expansion of the

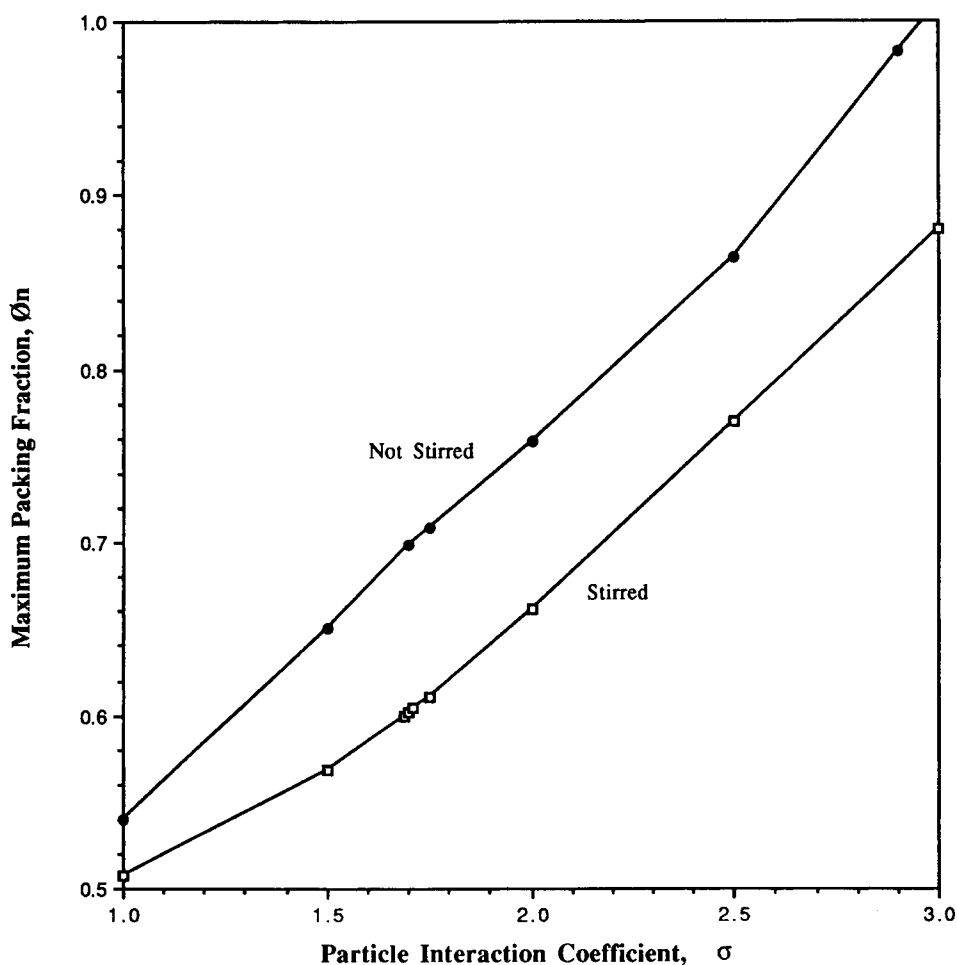


Figure 6 Maximum packing fraction, ϕ_n , vs. particle interaction coefficient for Vand's data.

generalized suspension equation. Using a MacLaurin series expansion for Eq. (23) gives

$$\eta = \eta_0 \left(1 + [\eta] \varphi + \left(\frac{[\eta]}{2} \right) \left\{ [\eta] + \left(\frac{\sigma}{\varphi_n} \right) \right\} \varphi^2 + \left(\frac{[\eta]}{6} \right) \left\{ [\eta]^2 + 3 \left(\frac{\sigma}{\varphi_n} \right) [\eta] + \left(\frac{\sigma}{\varphi_n} \right) \left(\frac{\sigma + 1}{\varphi_n} \right) \right\} \varphi^3 + \dots \right) \quad (24)$$

It is apparent that the first two terms are the Einstein limiting terms for all possible values for the particle interaction coefficient, σ , and the packing fraction, φ_n . It has also been found that σ and φ_n always occur as a paired ratio for second-order and higher expansion terms. If σ increases, it is easy to see that the viscosity, η , will increase. Likewise,

if the packing fraction, φ_n , increases, then the viscosity will decrease for the same particle interaction σ . Since these two parameters are paired in second-order and higher terms, if $\sigma = 0.0$, then the packing fraction does not enter into the viscosity calculation. This again suggests that when the particle interaction coefficient is zero the particle packing is not important and the particles have minimum interference with each other. In later papers,^{27,28} it will be shown that both the particle interaction coefficient, σ , and the packing fraction, φ_n , can be a function of both the number of different classes of particle diameters, n , and the particle-size distribution.

Evaluation of Literature Data Using Generalized Equation

To illustrate the application of the generalized suspension equation, a procedure was developed to ob-

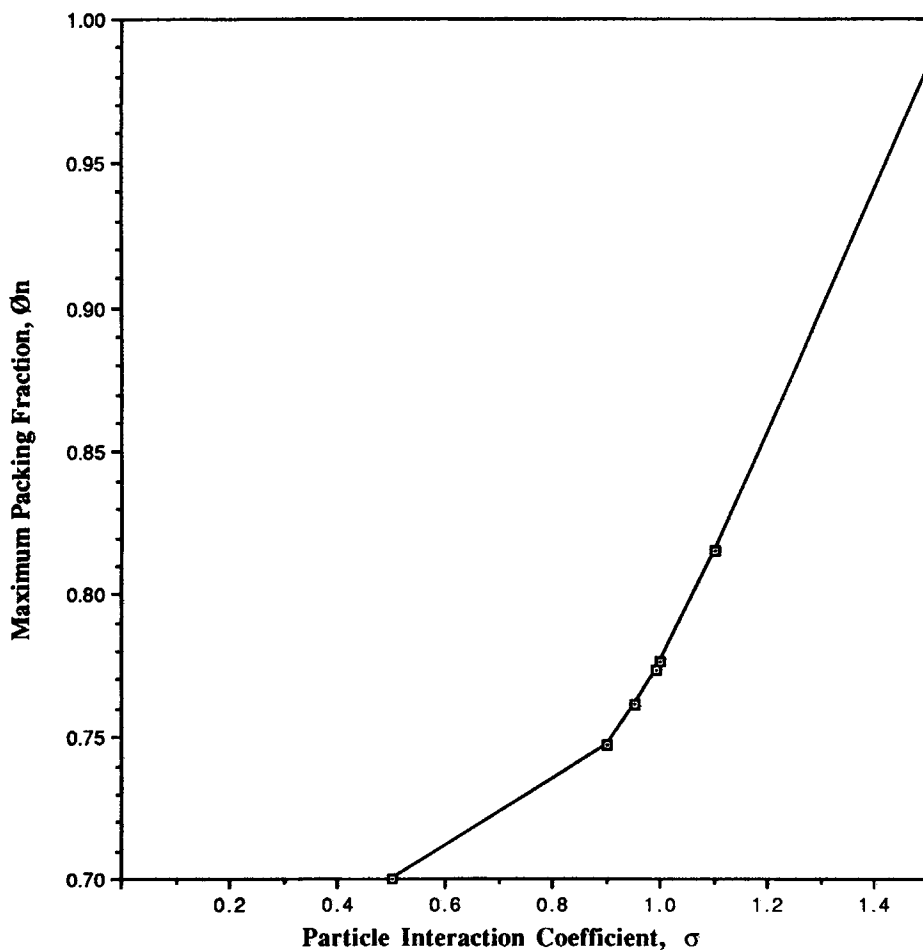


Figure 7 Maximum packing fraction, ϕ_n , vs. particle interaction coefficient for Euler's data.

tain the best fit of the suspension viscosity data of Vand²⁹ and Eiler⁸ summarized in Tables II and III. These observed and calculated results are illustrated in Figure 3. A minimum absolute error was obtained for each of these sets of data at a very distinct value for the particle interaction coefficient, σ , as shown in Figures 4 and 5. The packing fractions, φ_n , required to give the minimum absolute error at each particle interaction coefficient, σ , are shown in Figures 6 and 7.

These data illustrate several points. First, for each set of suspension viscosity data, there appears to be only one preferred particle interaction coefficient that gives the best fit of the data. The significance of this result should be related to the particle interaction within the suspension. Since the best fit for Vand's stirred suspension viscosity results was obtained with a particle interaction coefficient of 1.7, it is also apparent that it is not necessary for the particle interaction coefficient, σ , to be a whole number. However, the best fit of Eiler's data did occur for a whole number at $\sigma = 1.0$.

The trend of the data in Figures 6 and 7 is also interesting in that the packing fraction, φ_n , at the minimum average absolute error for each data set appears to increase as the value of the particle interaction coefficient, σ , increases. This observation can be used to save some time in finding optimum values for σ and φ_n .

Note that the minimum error for Vand's unstirred data occurred at a particle interaction coefficient greater than $\sigma = 3.0$ and at a packing fraction, φ_n , greater than 1.0. This would suggest that the parameters obtained for the unstirred data do not necessarily have reasonable physical significance. However, for Vand's stirred data, the packing fraction of $\varphi_n = 0.602$ at a particle interaction coefficient of $\sigma = 1.7$ does seem reasonable. This is especially true since the minimum average absolute error for this stirred data was less than half the value for the unstirred data.

CONCLUSIONS

Several suspension equations available in the literature have been found to have a common derivative form. This common derivative was found to be equivalent to a ratio of the intrinsic viscosity, $[\eta]$, and a quantity, V_{Int} , defined as the "relative suspension interaction volume" available for particle flow. V_{Int} was, in general, found to be a relatively simple function of the suspension particle volume

fraction, φ , the maximum particle packing fraction, φ_n , and a new variable, σ , defined as the particle interaction coefficient. Different forms of this common derivative were obtained by modifying V_{Int} with a simple adjustment for the value for the interaction coefficient, σ . Integration of this generalized derivative yielded a generalized suspension viscosity equation that was found to predict the form of many suspension equations that have previously appeared in the literature. For example, by varying the interaction coefficient, σ , the Arrhenius equation resulted when $\sigma = 0$, the Kreiger-Dougherty equation resulted when $\sigma = 1$, and when $\sigma = 2$, the Mooney equation resulted. Fractional values for the particle interaction coefficient were also found to be useful when optimizing the empirical fit of the literature data of Vand and Eiler. Additional insight from such a data fit was also obtained from the magnitude of both the particle interaction coefficient, σ , and the packing fraction, φ_n .

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