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Prediction of shear viscosity of a zinc oxide suspension with colloidal aggregation

Danbi Kim and Sangkyun Koo*

Department of Chemical Engineering and Materials Science, Sangmyung University, Seoul 03016, Republic of Korea

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We deal with scaling relations based on fractal theory and rheological properties of a colloidal suspension to determine a structure parameter of colloidal aggregates and thereby predict shear viscosity of the colloidal suspension using an effective-medium model. The parameter denoted by β is $m(3\text{-}d_f)$, where m indicates shear rate (D) dependence of aggregate size R, *i.e.* $R \propto D^{-m}$, and d_f is the fractal dimension for the aggregate. A scaling relation between yield stress and particle volume fraction ϕ is applied to a set of experimental data for colloidal suspensions consisting of 0.13 μm zinc oxide and hydroxyethyl acrylate at ϕ = 0.01-0.055 to determine β. Another scaling relation between intrinsic viscosity and shear rate is used at lower ϕ than the relation for the yield stress. It is found that the estimations of β from the two relations are in a good agreement. The parameter β is utilized in establishing rheological models to predict shear viscosity of aggregated suspension as a function of ϕ and D. An effective-medium (EM) model is employed to take hydrodynamic interaction between aggregates into account. Particle concentration dependence of the suspension viscosity which is given in terms of volume fraction of aggregates ϕ_a instead of ϕ is incorporated to the EM model. It is found that the EM model combined with Quemada's equation is quite successful in predicting shear viscosity of aggregated suspension.

***Keywords*: colloidal aggregate, fractal dimension, yield stress, effective-medium model, zinc oxide**

1. Introduction

Rheological properties of particulate colloidal suspensions have offered useful information to characterize microstructure of the suspensions. The microstructure, *i.e.* spatial distribution of particles in the suspending medium, is primarily affected by interparticle potential among the particles which is obtained by superposition of various particle interactions. The interparticle potential illustrates whether the particles are attractive or repulsive depending on gap distance between the particles. Colloidal particles in Brownian motion diffuse and collide each other in the suspending medium. The particle collision offers chance of aggregation due to interparticle attraction corresponding to primary or secondary minima in the interparticle potential-gap distance curve. The particle aggregation influences rheological behavior of the colloidal suspension even at low volume fractions of the particles. Presence of separate particles itself in suspending fluid increases suspension viscosity due to flow perturbation by the particles. Aggregation of particles causes additional increase of the suspension viscosity as well as non-linear rheological behavior. Description of particle aggregation is not simple. Compactness and shape of aggregates vary with colloidal systems. The state of the particle aggregation can change with particle volume fraction and time. As the particle volume fraction increases, the aggregates tend to cluster to form network structure. This network formation is referred to as colloidal gel or percolation. Colloidal gelation gives steep change in the rheological behavior.

Microstructure of suspension is also affected by externally imposed force. When shear force is applied or mean flow is given, hydrodynamic interaction among the aggregates may play major role in determining the microstructure of the suspension. Many suspensions exhibit shear-dependent behavior related with size reduction of aggregates. The shear dependence is determined by competition between shear force and attractive force between particles in an aggregate.

All these details of the aggregates influence the rheological behavior. Conversely it can be inferred that rheological properties of the suspension would be useful in quantifying the particle aggregation. There have been numerous investigations to find the theoretical relations between the macroscopic rheological properties and the microscopic information of the particulate aggregates (Buscall *et al*., 1988; Eggersdorfer *et al*., 2010; Lee and Koo, 2016; Mewis and Wagner, 2012; Potanin *et al*., 1995; Quemada, 1998; Shih *et al*., 1990; Wessel and Ball, 1992). The microscopic structure of the aggregates can be quantitatively described by adapting fractal concept (Jullien and Botet, 1987; Lin *et al*., 1989; Meakin, 1987) Due to self-similarity of aggregate structure, colloidal aggregates have been considered as of fractal geometry. The average aggregate size is expressed in terms of fractal dimension which is defined in a scaling relation between mass-radius of an aggregate given by Eq. (1). The fractal dimension d_f is a measure for compactness and shape of

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*Corresponding author; E-mail: skkoo@smu.ac.kr

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aggregate. It is also concerned with aggregation rate.

When aggregates are under shear flow, their size decreases as the applied shear force increases. Previous studies have shown that aggregate size has power-law dependence on shear rate (Eggersdorfer *et al*., 2010; Potanin, 1993; Sonntag and Russel, 1986). The power-law dependence is expressed by a scaling relation between aggregate size R and shear rate D, *i.e.* $R \propto D^{-m}$.

These two parameters, d_f and m, are necessarily important in developing scaling theories. Common methods to determine d_f are optical measurement such as static light scattering and small angle X-ray scattering techniques. The exponent m was also measured using a light scattering device specially designed for detecting particles and aggregates in shear flow (Sonntag and Russel, 1986). Computer simulation was performed for two typical cases of aggregation, *i.e.* so-called rigid and soft aggregation (Eggersdorfer *et al*., 2010; Potanin, 1993). Many aggregated colloidal systems lie between the two cases. Generalized formula, however, has not been suggested from the simulation. In practice, scaling theory can be a useful alternative in determining the parameters. In most cases, m and d_f are used in a combined form of $m(d\text{-}d_f)$, where d is the Euclidean dimension. Thus, d is 3 in three dimensional space. For convenience, the parameter $m(3\text{-}d_f)$ is denoted as β.

In present study we first examine scaling relations to estimate the parameter β. A scaling relation regarding yield stress is introduced to determine β. It is compared with that from another scaling relation for intrinsic viscosity. This scaling relation assumes that volume fraction of aggregates is low so that interaction between the aggregates is negligibly weak. This assumption means that the scaling relation of intrinsic viscosity is adequate at the very dilute regime where yield stress is negligible. Estimations by these two scaling relations are compared. For experimental data we prepare a colloidal suspension consisting of 0.13 μm zinc oxide particles and Newtonian hydroxyethyl acrylate. The particle volume fraction ranges 0.01-0.055. Once the parameter β is obtained, we shall consider an effective-medium model for predicting the suspension viscosity as a function of shear rate and particle volume fraction. In the model, hydrodynamic interaction between the aggregates is considered in an approximate manner. Particle concentration dependence of the suspension viscosity is incorporated with the model to predict shear viscosity for suspension of aggregates. Finally, these theoretical predictions are compared with experimental results.

2. Experimental Procedure

2.1. Sample preparation

Zinc oxide (ZnO) particles are widely used in industry as an ingredient for cosmetics and coloring pigment. We used the zinc oxide particles manufactured by Sukgyung AT Co. in Korea. The grade is SG-ZNO01 with average size of 0.13 μm and density of 5.61. Hydroxyethyl acrylate ($CH_2CHCOOCH_2CH_2OH$, Junsei Chemical Co., Ltd., Japan) with density of 1.10 g/cm^3 is used as suspending medium. It is a Newtonian fluid with viscosity of 4.37 cP at 25°C. Particle volume fraction of this colloidal suspension ranges from 1 to 5.5%.

Preparation of the colloidal suspension starts with wetting zinc oxide particles with hydroxyethyl acrylate. The zinc oxide particles are wetted with 10-20 mL of the acrylate using spatula for about 5 min. Then the remaining acrylate is added to the wetted particles. The mixture is vigorously dispersed by a mechanical homogenizer (Model HG-150, WiseTIS Corporation). This operation lasts for 3 min at 3000 RPM at a time and yields a slurry state of the mixture after three times repetition. The slurry is treated with an ultrasonic treater (SD-100H, Seongdong Co., Korea). The ultrasonic dispersion is performed for 30 min at 280 Watts and 60 Hz. After the operation we obtain a colloidal suspension of the zinc oxide particles.

2.2. Measurement

Shear viscosity of the colloidal suspension is measured. For the measurement a cone-and-plate Brookfield viscometer (Model LVDV-II, AMETEK Brookfield Inc., USA) is used, which is implemented with a cone sensor (Model CPA-52Z) at tilting angle of 4° from a plate plane. The colloidal suspension is pre-sheared at 10 sec^{-1} for 1 min. Then the shear viscosity is measured at the shear rates ranging from 10 sec^{-1} to 100 sec^{-1}. The temperature is kept at 25°C (±0.1°C) by the water circulator with temperature control unit.

Sedimentation behavior is also checked. For the sedimentation test, we use cylindrical tubes of 15 mm diameter and 150 mm height immersed vertically in a water bath maintained at 25°C (±0.1°C). The tube is filled with 20 mL of colloidal suspension. In the sedimentation process, if the aggregated particles begin to settle down leaving clear fluid zone at the top of the suspension in the tube, an interface between clear liquid and settling sediment appears. Evolution of the interface position is measured with time. A circulator with temperature control unit is connected to the water bath to keep the temperature during the sedimentation.

3. Results and Discussion

A scaling relation between yield stress τ_y and particle volume fraction ϕ is considered to estimate the parameter β which is $m(3\text{-}d_f)$. Let us suppose N particles with radii a forming an aggregate with a radius of gyration R and mass M. Then the aggregate follows mass-radius relation

$$N \propto M \propto \left(\frac{R}{a}\right)^{d_f} \tag{1}$$

where d_f is the fractal dimension of the aggregate. When the suspension is under shear flow, the shear dependence of aggregate is expressed by (Buscall *et al.*, 1988; Eggersdorfer *et al.*, 2010; Potanin, 1993)

$$\frac{R}{a} \propto D^{-m} \tag{2}$$

where D is the shear rate and the exponent m indicates shear dependence of aggregate size. It is assumed that all the particles in the suspension reside in equal-sized aggregates. Each aggregate is considered as a sphere with radius R and it contains N particles and suspending medium within a spherical volume of radius R. Then the effective volume fraction of aggregates in the suspension denoted by ϕ_a can be written as

$$\phi_a = \frac{\phi}{N}\left(\frac{R}{a}\right)^3 \propto \phi\left(\frac{R}{a}\right)^{3-d_f}. \tag{3}$$

Just near yield stress point, $\eta_0 D \approx \tau_y$ where η_0 is the viscosity of suspending medium, *i.e.*, fluid. Since the yield stress is considered as onset of gelation in the colloidal suspension, the whole suspension can be approximated as an aggregate. The ϕ_a becomes unity for the state of colloidal gel. Then, from Eqs. (2) and (3) we obtain

$$\tau_y \propto \phi^{1/\beta}. \tag{4}$$

This is consistent with previous work (Buscall *et al.*, 1988; Lee and Koo, 2014; Snabre and Mills, 1996).

To extract β from Eq. (4), yield stress data at each ϕ are required. We apply Casson's equation (Casson, 1959), *i.e.*, Eq. (5), to shear stress-shear rate data at ϕ = 0.01-0.055 in Fig. 1.

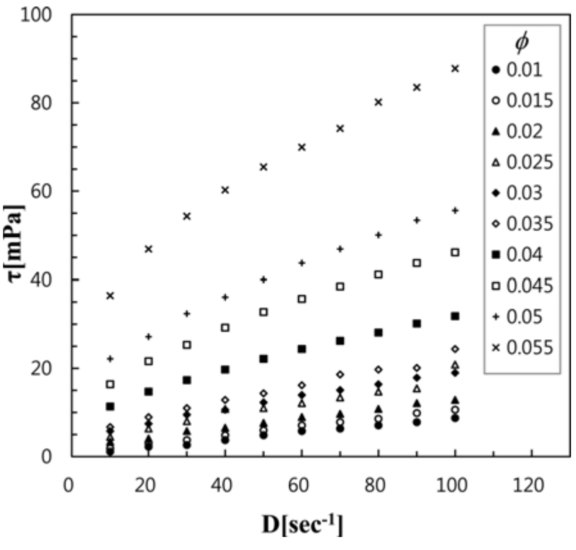


Fig. 1. Shear stress (τ) - shear rate (D) data at various particle volume fractions (ϕ).

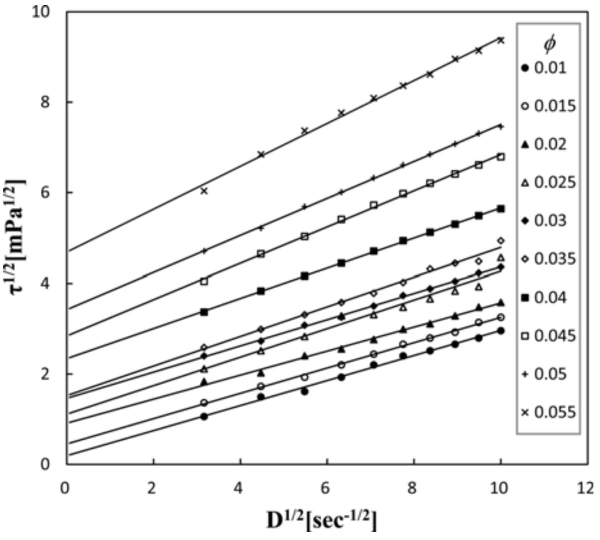


Fig. 2. Casson plot between shear stress$^{1/2}$($\tau^{1/2}$) and shear rate$^{1/2}$($D^{1/2}$).

$$\tau^{1/2} = \tau_y^{1/2} + (\eta_\infty D)^{1/2} \tag{5}$$

where τ is the shear stress at the shear rate D and η_∞ is the suspension viscosity at infinite shear rate. The Casson plot for the yield stress is given in Fig. 2. It is interpreted that the yield stress indicates solid-like behavior and hence it is directly related with onset of colloidal gelation. It is seen that the yield stress begins to appear at $\phi \geq 0.01$ although the magnitude is quite small and rapid increase of the yield stress takes place near ϕ = 0.04. It is, however, somewhat ambiguous to determine gelation threshold by only the appearance of yield stress regardless of its magnitude. To ensure the gelation threshold we check sedimentation behavior. Figure 3 shows the sedimentation

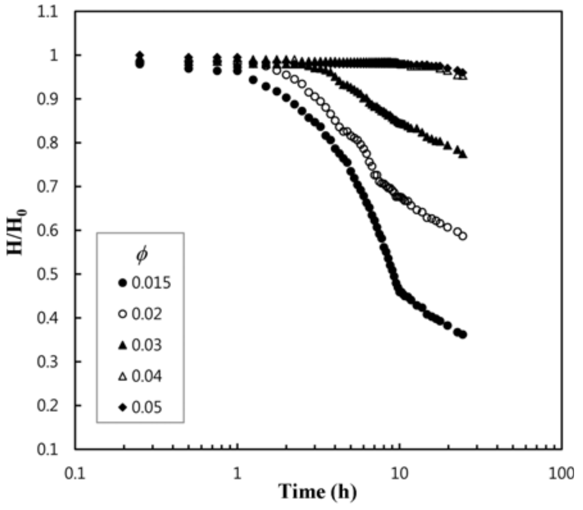


Fig. 3. Evolution of relative sediment height (H/H_0) with time at various ϕ. Here, H_0 is the initial sediment height (100 mm) and H is the sediment height at time t.

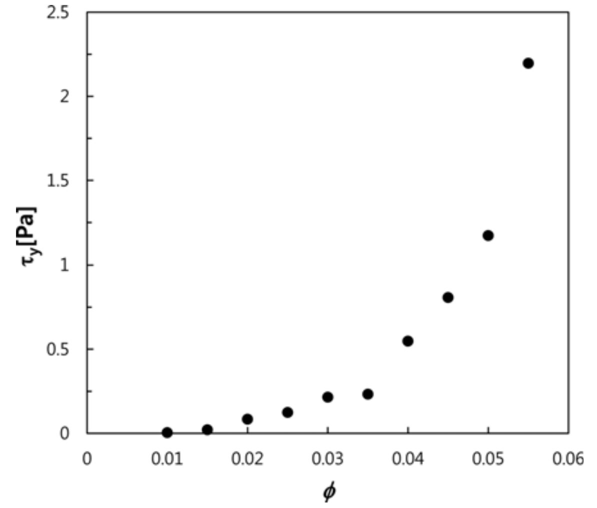


Fig. 4. Yield stress (τ_y) vs. particle volume fraction (ϕ) at $\phi = 0.04\text{-}0.055$.

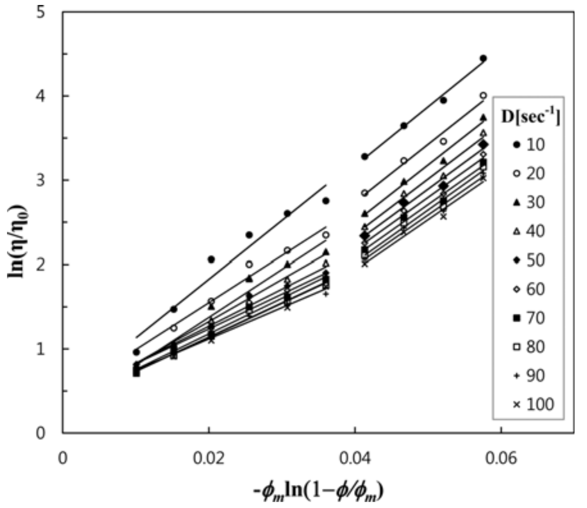


Fig. 5. $\ln(\eta/\eta_0)$ vs. $-\phi_m \ln(1-\phi/\phi_m)$.

behavior. When sedimentation takes place, the suspension is divided into settling sediment and clear fluid in the upper zone. Height of interface between the sediment and clear fluid in test tube form sedimentation is monitored with time. Ratio of the height H at time t to initial height H_0 is plotted with time at $\phi = 0.015\text{-}0.05$. It is seen that sedimentation does not occur near $\phi = 0.05$. In Fig. 2 the yield stress begins to increase steeply at $\phi = 0.04$. Considering both results it is proper to take $\phi \geq 0.04$ for yield stress data. Plot of yield stress data with ϕ in Fig. 4 gives $\beta = 0.26$. It has been previously reported that the parameter m ranges 0.2-0.5 and d_f is 1.6-2.5 in most colloidal suspensions (Meakin 1987; Lin *et al.*, 1989; Mewis and Wagner, 2012). Then β usually lies in the range of 0.1-0.7. Our value for β is within this range.

It is also possible to determine β below gelation threshold. The well-known Einstein's equation (Einstein, 1906) is used to give a useful relation for intrinsic viscosity. When interaction between aggregates is negligible, the intrinsic viscosity $[\eta]$ for an aggregated suspension is given by

$$[\eta] = 2.5/\phi_{pa} \tag{6}$$

where ϕ_{pa} is the particle volume fraction in an aggregate and thus $\phi_{pa} = \phi/\phi_a$ (Smith and Bruce, 1979). The intrinsic viscosity can be estimated from Krieger-Dougherty's equation (Krieger and Dougherty, 1959) given by

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{7}$$

where η is the suspension viscosity and ϕ_m is the maximum random packing density of particles. Generally, ϕ_m is taken to be 0.63 for hard spheres (Russel and Sperry, 1994).

Using Eq. (7), the relative viscosity η/η_0 is plotted as a function of ϕ at each shear rate in Fig. 5. The slope of each fitting line corresponds to the intrinsic viscosity at each shear rate. As the shear rate increases, it is evident that two separate fitting for the experimental data is more suitable near ϕ between 0.035 and 0.04. One fitting line is for $\phi = 0.01\text{-}0.035$ and the other is for $\phi \geq 0.04$. It seems that there's remarkable change near $\phi = 0.04$ in the colloidal suspension. This is consistent with rapid increase of yield stress at $\phi > 0.04$. It is confirmed that gelation among the aggregates seems to take place at $\phi > 0.04$. Since Eq. (6) assumes dilute suspensions where interaction among aggregates is negligible, the data for $\phi = 0.01\text{-}0.035$ in Fig. 5 are used for the intrinsic viscosity.

Incorporating Eqs. (2) and (3) into Eq. (6), we obtain a scaling relation for the intrinsic viscosity in terms of β

$$[\eta] \propto D^{-\beta}. \tag{8}$$

This relation is used to determine the exponent β. It is illustrated in Fig. 6 and β is found to be about 0.24. This value is in reasonable agreement with that from yield stress data. This agreement between two scaling relations has been reported previously for colloidal suspensions of inorganic nanoparticles (Lee and Koo, 2014; Cho and Koo, 2015). This result exhibits that β is constant whether the aggregates form network or not. Hence it is interpreted that the parameters, m and d_f, maintain constant across the gelation threshold.

The parameter β is quite useful in predicting shear viscosity of suspension with fractal aggregates. Commonly used is effective volume concept for the aggregates. The aggregates are considered as spheres. It is assumed that particles exist in each aggregate of radius R and R depends on shear rate D, as mentioned earlier. Fractal dimension and spherical shape of aggregates are also assumed invariant. According to these assumptions, particle concentra-

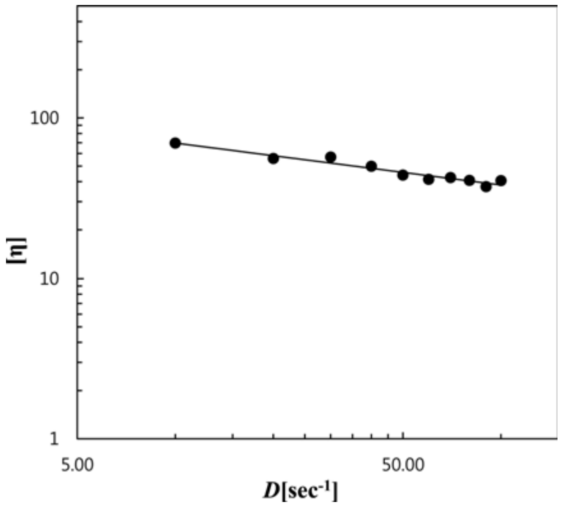
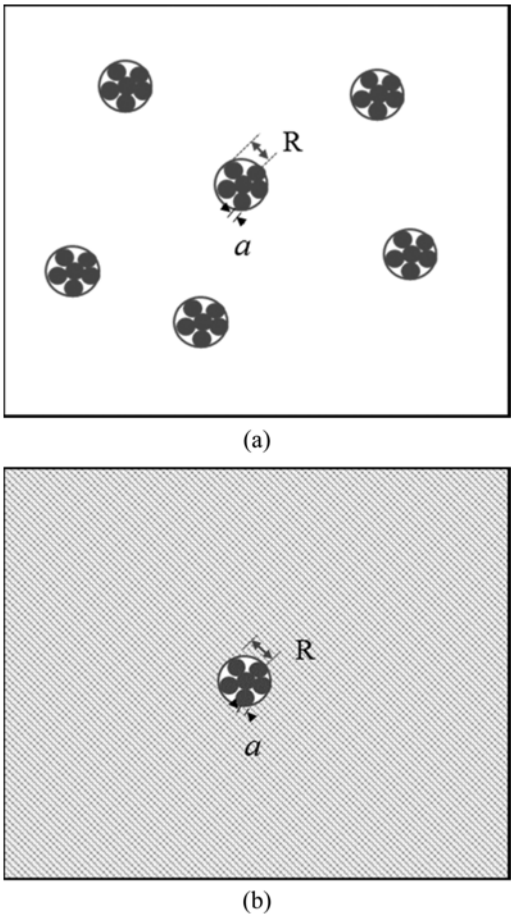


Fig. 6. Intrinsic viscosity ([η]) vs. shear rate (D).



(a)

(b)

Fig. 7. Schematic diagram for (a) suspension of aggregates and (b) effective-medium (EM) model.

tion dependence of suspension viscosity is written in terms of ϕ_a, volume fraction of aggregates, not ϕ. We make use of a viscosity-particle concentration relation proposed by Quemada (1977)

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi_a}{\phi_m}\right)^{-2} . \tag{9}$$

Note that ϕ is replaced by ϕ_a. Instead of Eq. (9), we may choose another viscosity equation such as Batchelor's equation given below for semi-dilute regime (Batchelor and Green, 1972)

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi_a + 5.2\phi_a^2 . \tag{10}$$

Incorporating Eqs. (2) and (3) into ϕ_a in either of the Eqs. (9) and (10), we obtain shear viscosity equation as functions of ϕ and D for given β and material constant σ_m. This scheme, however, does not include hydrodynamic interaction among the aggregates in the relation between aggregate size and shear stress. According to Eq. (2), the aggregate size inversely scales with shear stress, *i.e.* the product of shear rate and fluid velocity, to the power of the exponent m. One way to consider the hydrodynamic interaction in the shear dependence of aggregate size, is to take the shear stress term as the product of shear rate and suspension viscosity, not the fluid viscosity. This change in shear stress term can be well explained by employing an effective-medium model (Quemada, 1998; Patel and Russel, 1988; Potanin, 1992). Figure 7 shows schematic diagram for suspension (a) and effective-medium model (b). In this model, it is supposed that suspension consist of test aggregate at origin and the surrounding effective-medium with suspension viscosity η. The effective medium reflects hydrodynamic interaction due to presence of many aggregates except test aggregate in an approximate manner. According to this model, Eq. (2) should be written in terms of η and D

$$\frac{R}{a} = C\left(\frac{\eta}{\eta_0}\Gamma\right)^{-m} , \quad \Gamma = \frac{\eta_0 D}{\sigma_m} \tag{11}$$

where C is the numerical constant, Γ is the dimensionless shear rate, and σ_m is the material constant related with attractive force between particles. Specifically, the parameter σ_m directly related with attractive force f_c between particles is given by

$$\sigma_m = \frac{f_c}{\pi a^2} , \quad f_c = \frac{A_H a}{12 h^2} \tag{12}$$

where A_H is the Hamaker constant and h is the gap distance between particles (Potanin, 1992). The Hamaker constant A_H equals $(A_{H1}^{1/2}\text{-}A_{H2}^{1/2})^2$ where A_{H1} and A_{H2} are the Hamaker constants for particles and fluid, respectively. Since A_{H2} and h are not available in the literature, we need another approximation for σ_m. It is to make use of yield stress data at the maximum particle volume fraction ϕ_m. It was found that rough estimation of σ_m with $A_H \equiv A_{H1}$ and h = 0.4 nm as typical value is on the same order of magnitude as the yield stress at ϕ_m.

It is also necessary to write Eq. (3) in a closed form

$$\phi_a = \frac{\phi}{\phi_m}\left(\frac{R}{a}\right)^{3-d_f}. \tag{13}$$

This is obtained from the relation that as d_f goes to 3 then ϕ becomes ϕ_m and ϕ_a equals unity. Substituting Eqs. (11) and (13) into Eq. (9), we obtain

$$\left(\frac{\eta_0}{\eta}\right)^2 + 2\psi\left(\frac{\eta_0}{\eta}\right)^{\beta} - 1 = 0 \tag{14}$$

where the parameter ψ is given by

$$\psi = \frac{\phi}{2\phi_m^2}\left(\frac{C^*}{\Gamma}\right)^{\beta}. \tag{15}$$

Here, C^* equals $C^{1/m}$. The parameter ψ contains all the variables including ϕ and D to determine the suspension viscosity. The numerical constant C is 2.5^{-m} for so-called rigid aggregates to which applied stress is fully transmitted. Hence the C^* is 0.4 for rigid aggregates. The C^* is expected to be larger than 0.4 for soft aggregates which partially transmit imposed stress and corresponds to secondary energy minimum in interparticle potential curve. It can be inferred that C^* for many colloidal suspensions lie between rigid and soft aggregates. In our analysis C^* is properly chosen to make comparison with experiment.

Instead of Eq. (9) we may choose Eq. (10). From Eqs. (11), (13), and (10), we obtain

$$24\phi_m^2\psi^2\left(\frac{\eta_0}{\eta}\right)^{2\beta} + 5\phi_m\psi\left(\frac{\eta_0}{\eta}\right)^{\beta} + 1 - \left(\frac{\eta_0}{\eta}\right)^{-1} = 0. \tag{16}$$

These formulas, *i.e.*, Eqs. (14) and (16), are used to calculate the suspension viscosity. Figure 8 shows the relative viscosity of aggregated suspension estimated from the model based on Eqs. (14) and (16) as a function of D at $\phi = 0.01$, 0.03, and 0.055. In Fig. 9, the relative viscosity is plotted as a function of ϕ at $D = 10$-100 sec^{-1}. These are compared with experimental data. A simple model without considering hydrodynamic interaction is also included for comparison. In this model, viscosity ratio term in Eq. (11) is not necessary and thus the equation becomes

$$\frac{R}{a} = C\Gamma^{-m}. \tag{17}$$

Then the suspension viscosity based on Eq. (9) reduces to

$$\frac{\eta_0}{\eta} - (1-2\psi)^2 = 0. \tag{18}$$

In Eq. (18) the inverse of relative viscosity becomes zero when $\psi = 0.5$, which means that the suspension vis-

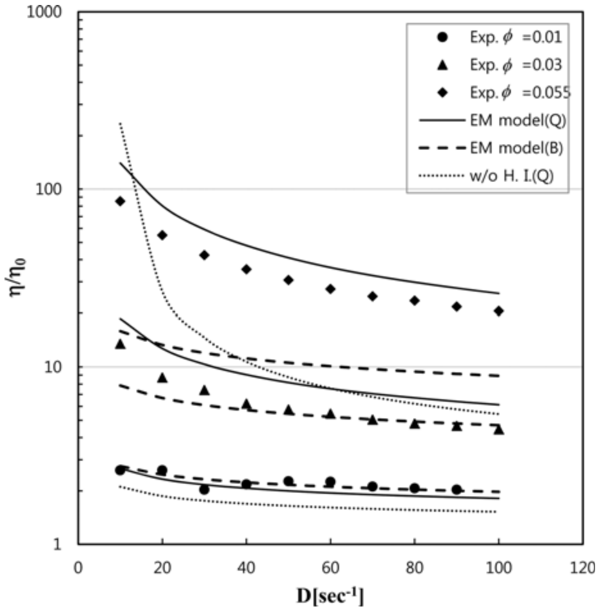


Fig. 8. Relative viscosity (η/η_0) vs. shear rate (D) at $\phi = 0.01$, 0.03, 0.055. Marks indicate experimental result. Solid lines correspond to the EM model with Quemada's equation (Eq. (9)). Dashed lines are for the EM model with Batchelor's equation (Eq. (10)). Dotted lines indicate the model without hydrodynamic interaction between aggregates (the line at $\phi = 0.055$ is not shown here) Lower lines for each model correspond to lower ϕ. The letters Q and B in the parenthesis of legend stand for Quemada's and Batchelor's equations, respectively.

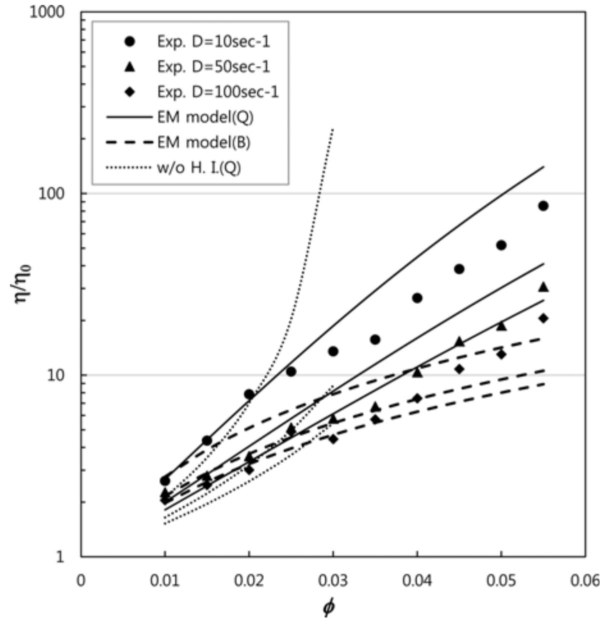


Fig. 9. Relative viscosity (η/η_0) vs. volume fraction (ϕ) at D = 10, 50, 100 sec^{-1}. Marks indicate experimental result. Dotted lines indicate the model without hydrodynamic interaction between aggregates. Solid lines correspond to the EM model with Quemada's equation (Eq. (9)). Dashed lines are for the EM model with Batchelor's equation (Eq. (10)). Lower lines for each model correspond to higher D. The letters Q and B in the parenthesis of legend stand for Quemada's and Batchelor's equations, respectively.

cosity goes to infinity. To avoid ψ of 0.5, the numerical constant C^* can be adjusted. Then the suspension viscosity estimated by this model becomes unreasonably higher than the experimental results. Otherwise, due to limitation of ψ, we are not able to get finite value of the suspension viscosity beyond $\phi = 0.03$. Figure 8 shows the relative viscosity by this model at $\phi = 0.01$ and 0.03 only although variation of ψ is still restricted. It is confirmed more clearly in Fig. 9. This result explains importance of considering hydrodynamic interaction.

The effective-medium (EM) model which takes hydrodynamic interaction into account is coupled with a viscosity equation such as either Quemada's equation, *i.e.* Eq. (9), or Batchelor's equation, *i.e.* Eq. (10), to estimate viscosity of aggregated suspension. It is found that the EM model with Eq. (9) is in a good agreement with the experimental results. On the other hand, the EM model with Eq. (10) shows agreement with the experiment only at $\phi <$ 0.02. It is shown that the EM-model with Batchelor's equation gives considerable discrepancy from the experimental data as ϕ increases. Although ϕ range for the experiment is 0.01-0.055 at which Batchelor's equation may be suitable as dilute concentration, the discrepancy is attributed to the fact that Eq. (10) is based on ϕ_a which is basically larger than ϕ. For this reason, the EM model with Eq. (10) gives limited agreement with experiment for lower ϕ than Eq. (10) for non-aggregated suspension. Conclusively it is found that the EM model coupled with Quemada's equation is suitable for predicting shear viscosity of aggregated suspension as functions of shear rate and particle volume fraction.

4. Conclusion

We determined the structure parameter β for colloidal aggregates using scaling relations regarding rheological properties of a colloidal suspension consisting of 0.13 μm zinc oxide and hydroxyethyl acrylate. The particle volume fraction ϕ is in the range of 0.01-0.055. The parameter β is given by $m(3-d_f)$, where m indicates shear dependence of aggregate size and d_f is the fractal dimension for the aggregate. Two scaling relations were used to determine β. One is to make use of yield stress as a function of ϕ, which is available in the regime that aggregates form network structure. The other is intrinsic viscosity as a function of shear rate D, which is valid for dilute regime where interaction between the aggregates is negligible. Experimental data for $\phi \geq 0.04$ was used for the scaling relation of the yield stress. The scaling relation for the intrinsic viscosity was used for data at $\phi = 0.01$-0.035. The parameter β is 0.24 with the yield stress and 0.26 from the intrinsic viscosity. It is found that estimations of β with the two scaling relations are in good agreement. This implies that shear dependence of aggregate size and fractal dimension keep constant regardless of gelation.

Next, we examined rheological models to predict shear viscosity of aggregated suspension as a function of ϕ and D. In the models it is assumed that the colloidal aggregates are considered as spheres of radii R depending on D and d_f is invariant. Each sphere includes particles and fluid inside. Then viscosity equation can be written in terms of volume fraction of the spheres, ϕ_a. An effective-medium (EM) model was used to take hydrodynamic interaction between the spheres into account. Simple model without hydrodynamic interaction was also compared. The effective-medium model incorporated with Quemada's equation (Eq. (9)) was shown to reconcile well with experimental results. No solution was found beyond $\phi > 0.03$ for the case of no hydrodynamic interaction. Besides Quemada's equation, Batchelor's equation (Eq. (10)) was adapted. It is found that Batchelor's equation combined with EM model agrees with experimental results at $\phi = 0.01$ but as ϕ increases, it shows large discrepancy from the experimental results. This is attributed to that Batchelor's equation is given in terms of ϕ_a instead of ϕ and ϕ_a is always larger than ϕ for aggregated suspensions. In conclusion, it is found that the EM model with Quemada's equation is the most suitable to estimate shear viscosity of colloidal suspension with aggregates as a function of ϕ and D.

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References

Batchelor, G.K. and J.T. Green, 1972, The determination of the bulk stress in a suspension of spherical particles to order c^2, *J. Fluid Mech.* **56**, 401-427.

Buscall, R., P.D. Mills, J.W. Goodwin, and D. Lawson, 1988, Scaling behaviour of the rheology of aggregate networks formed from colloidal particles, *J. Chem. Soc., Faraday Trans. 1* **84**, 4249-4260.

Casson, N., 1959, A flow equation for pigment-oil suspensions of the printing ink type, In: Mill, C.C., eds., *Rheology of Disperse Systems*, Pergamon Press, Oxford, 84-104.

Cho, J. and S. Koo, 2015, Characterization of particle aggregation in a colloidal suspension of magnetite particles, *J. Ind. Eng. Chem.* **27**, 218-222.

Eggersdorfer, M.I., D. Kadau, H.J. Herrmann, and S.E. Pratsinis, 2010, Fragmentation and restructuring of soft-agglomerates under shear, *J. Colloid Interface Sci.* **342**, 261-268.

Einstein, A., 1906, A new determination of the molecular dimensions, *Ann. Phys.* **19**, 289-306.

Jullien, R. and R. Botet, 1987, *Aggregation and Fractal Aggregates*, World Scientific, Singapore.

Krieger, I.M. and T.J. Dougherty, 1959, A mechanism for non-

Newtonian flow in suspensions of rigid spheres, *Trans. Soc. Rheol.* **3**, 137-152.

Lee, B. and S. Koo, 2014, Estimation of microstructure of titania particulate dispersion through viscosity measurement, *Powder Technol.* **266**, 16-21.

Lee, H. and S. Koo, 2016, Analysis of fractal aggregates in a colloidal suspension of carbon black from its sedimentation and viscosity, *Korea-Aust. Rheol. J.* **28**, 267-273.

Lin, M.Y., H.M. Lindsay, D.A. Weitz, R.C. Ball, R. Klein, and P. Meakin, 1989, Universality in colloid aggregation, *Nature* **339**, 360-362.

Meakin, P., 1987, Fractal aggregates, *Adv. Colloid Interface Sci.* **28**, 249-331.

Mewis, J. and N.J. Wagner, 2012, *Colloidal Suspension Rheology*, Cambridge Press, Cambridge.

Patel, P.D. and W.B. Russel, 1988, A mean field theory for the rheology of phase separated or flocculated dispersions, *Colloid Surf.* **31**, 355-383.

Potanin, A.A., 1992, On the model of colloid aggregates and aggregating colloids, *J. Chem. Phys.* **96**, 9191-9200.

Potanin, A.A., 1993, On the computer simulation of the deformation and breakup of colloidal aggregates in shear flow, *J. Colloid Interface Sci.* **157**, 399-410.

Potanin, A.A., R. De Rooij, D. van den Ende, and J. Mellema, 1995, Microrheological modeling of weakly aggregated dispersions, *J. Chem. Phys*. **102**, 5845-5853.

Quemada, D., 1977, Rheology of concentrated disperse systems and minimum energy dissipation principle: 1. Viscosity-concentration relationship, *Rheol. Acta* **16**, 82-94.

Quemada, D., 1998, Rheological modelling of complex fluids. I. The concept of effective volume fraction revisited, *Eur. Phys. J. Appl. Phys.* **1**, 119-127.

Russel, W.B. and P.R. Sperry, 1994, Effect of microstructure on the viscosity of hard sphere dispersions and modulus of composites, *Prog. Org. Coat.* **23**, 305-324.

Shih, W.H., W.Y. Shih, S.I. Kim, J. Liu, and I.A. Aksay, 1990, Scaling behavior of the elastic properties of colloidal gels, *Phys. Rev. A.* **42**, 4772-4779.

Smith, T.L. and C.A. Bruce, 1979, Intrinsic viscosities and other rheological properties of flocculated suspensions of nonmagnetic and magnetic ferric oxides, *J. Colloid Interface Sci.* **72**, 13-26.

Snabre, P. and P. Mills, 1996, I. Rheology of weakly flocculated suspensions of rigid particles, *J. Phys. III France* **6**, 1811-1834.

Sonntag, R.C. and W.B. Russel, 1986, Structure and breakup of flocs subjected to fluid stresses: I. Shear experiments, *J. Colloid Interface Sci.* **113**, 399-413.

Wessel, R. and R.C. Ball, 1992, Fractal aggregates and gels in shear flow, *Phys. Rev. A.* **46**, R3008-R3011.