Journal of Industrial and Engineering Chemistry 27 (2015) 218–222

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Characterization of particle aggregation in a colloidal suspension of magnetite particles

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ARTICLE INFO

Article history:
Received 22 November 2014
Received in revised form 24 December 2014
Accepted 30 December 2014
Available online 8 January 2015

Keywords:
Fractal dimension
Particle aggregates
Sedimentation
Intrinsic viscosity
Yield stress

ABSTRACT

We investigate relation between hydrodynamic transport properties of a colloidal suspension of magnetite particles and aggregation of the particles. The magnetite particles are of 0.3 μm in diameter and are dispersed in Newtonian ethylene glycol. The volume fraction of the particles in the suspension ranges from 0.003 to 0.04. Shear viscosity and average sedimentation velocity of the suspension are measured as a function of the particle volume fraction. To predict the aggregation of the suspended particles particle-scale analysis of sedimentation and viscosity behavior of the suspension is correlated with scaling theories for fractal aggregates. The sedimentation velocity as a function of particle concentration gives the fractal dimension of 1.91 for the magnetite aggregates in the suspension. Shear dependence of the aggregate size which is expressed by a power law is determined from intrinsic viscosity for the aggregates and yield stress of the suspension, respectively. It is found that the shear dependence from intrinsic viscosity is in good agreement with that from yield stress.

Introduction

Colloidal suspensions of magnetite particles have been used in various applications [1–4]. These applications commonly require unwanted aggregation of the suspended particles. Hence it is necessary to estimate degree of aggregation in accurate and convenient manner. One way for the estimation is to make use of macroscopic transport properties since microstructure and macroscopic properties of the suspension are correlated. Rheological properties have been representatively utilized to analyze microstructure of suspensions. In particular, particle-scale rheological studies can be directly correlated with scaling theories on structure of aggregates. In the early studies it is noticeable to deduce that intrinsic viscosity for suspended particle or aggregate is given in terms of particle volume fraction in an aggregate for dilute suspensions [5]. The intrinsic viscosity determined from macroscopic viscosity at various particle volume fractions was shown to provide microscopic information on number of particles in an aggregate when there is no interaction among the aggregates. More remarkable analysis is to directly measure the number of particles in an aggregate, radius of gyration, and its shear dependence. This was done by Sonntag and Russel [6]. They measured the number of particles in an aggregate and its variation with shear rate for polystyrene particles under shear flow using a light scattering technique. Their relations among the number of particles in an aggregate, the radius of gyration and the shear rate have much contributed to developing scaling theories on fractal aggregates. Their study was followed by many investigations on microrheological analysis in the process of particle aggregation and breakup of aggregates [7–12]. Although there have been numerous studies on microscopic analysis on fractal aggregates and their structural change, it is hardly found to make comparison between scaling relations for the aggregates.

The present study is concerned with estimating microstructure of particle aggregates from multiple macroscopic properties including the comparison of two ways of the estimation. Specifically this study is aimed at obtaining fractal dimension and shear dependence of aggregates for a colloidal suspension from sedimentation and rheological properties such as intrinsic viscosity and yield stress. In particular, estimation of aggregate parameters from intrinsic viscosity for the suspended aggregates at low particle concentrations without interaction between aggregates are compared with that from yield stress as a function of particle volume fraction above percolation threshold. This comparison have been recently carried out for a titania colloidal suspension, showing excellent agreement between the estimations from the intrinsic viscosity and the yield stress in a previous work [13]. In the work, prediction of fractal dimension for

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http://dx.doi.org/10.1016/j.jiec.2014.12.038
1226-086X/

aggregates is, however, too rough and is lack of generality due to limitation to a special case that the fractal dimension is not influenced by shear force. Present study employs sedimentation velocity as a function of particle concentration to determine the fractal dimension of aggregates.

From the aspect of materials, ferric oxide particles including magnetite have drawn interest due to unique property change under magnetic field. Since the particles are handled in the state of colloidal suspension, microstructure of the suspended particles becomes important regardless of external magnetic field. There have been many reports on rheological and sedimentation behavior of the colloidal suspension of ferric oxide particles [5,14–18]. However, microscopic analysis to relate aggregation of ferric oxides particles to fractal concept is scarcely found. It is hoped that this study provide a useful tool in understanding aggregation of magnetite particles in a colloidal suspension and characterizing the fractal aggregates.

Materials and methods

We use commercialized magnetite particles manufactured by Cosmo AM&T Company (grade SMT-01S) in Korea. The average diameter of the particles is about 0.3 μm. The specific surface area and magnetic saturation are 8.5 m^2/g and 85 emu/g, respectively. The viscosity of ethylene glycol is around 16.7 cps at 25 °C. The magnetite particles are dispersed in ethylene glycol through mechanical treatment. Mechanical dispersion of the magnetite particles starts with wetting of the particles with ethylene glycol. We take a gram of magnetite particles depending on the particle concentrations ranging from 0.3 to 4 volumetric percent. The magnetite particles are first wetted with 10–15 ml of acrylic liquid with spatula for about 5 min. Then the wetted particles are mixed with remaining ethylene glycol and vigorously stirred with a mechanical homogenizer (Model HG-150, WiseTIS Corporation). The stirring operation lasts for 3 min at 8000 RPM to yield a slurry state of the mixture. Then this slurry is treated with a ball mill (Model Wisemix BML, Daihan Company) equipped with motor, rotating shafts and a cylindrical high-density polyethylene bottle (*D* 60 mm and *H* 130 mm). This bottle is filled with the magnetite slurry and zirconia beads of 3 mm diameter. The volumes of the magnetite slurry and the zirconia beads are fitted to be nearly equal and the rotating speed of the shaft is 300 RPM. After 3 h milling, we finally obtain a colloidal suspension of magnetite particles.

To characterize the magnetite suspension we measure the shear viscosity and the average sedimentation velocity. A cone-and-plate type viscometer (Model LVDV-II, Brookfield Co.) is used to measure the viscosity. The viscometer is implemented with the cone sensor (Model CP-40 and CP-52) with a tilting angle of 4° from the plate plane. The shear rate ranges from 5 s^{-1} to 100 s^{-1}. The temperature is controlled to keep at 25 °C (±0.1 °C) by water bath with heating and cooling unit. The viscosity is measured after pre-shearing at 5 s^{-1} for 60 s.

The sedimentation behavior is analyzed using a cylindrical tube filled with colloidal suspension at 25 °C. As time elapses, the magnetite particles and their aggregates begin to settle down forming clear fluid zone at the top of the suspension in the tube. An interface between clear liquid and settling sediment appears and moves downwards with time. We measure the position of the interface as a function of time. This device is designed to keep the temperature at 25 °C (±0.1 °C) while sedimentation process.

Results and discussion

Macroscopic properties such as viscosity and sedimentation velocity of suspension are affected by not only particle volume fraction but also configuration of particles. When attractive interparticle interaction is dominant, the suspended particles easily aggregate and the suspension viscosity increases. The particle aggregates can be broken into the smaller ones by external shear force, resulting in reduction of the suspension viscosity with the shear force. Our magnetite suspension shows a typical shear thinning behavior as shown in Fig. 1. As the particle volume fraction ϕ increases, the shear thinning effect becomes large. Degree of particle aggregation can be roughly understood in comparison with the case of non-colloidal suspension. Fig. 2 shows the relative viscosity of the suspension to the suspending medium at two shear rates as a function of ϕ. Predictions by the Einstein's equation ($\eta/\eta_0 = 1 + 2.5\phi$,$\eta$ and η_0 are the viscosity of the suspension and the suspending medium) corresponds to the case of non-colloidal hard spheres without aggregation and are also compared in the figure. We see that the colloidal suspension of magnetite particles shows quite higher viscosity than non-colloidal suspension does. The difference increases with ϕ and roughly exhibits the degree of particle aggregation. More quantitative way of estimating aggregate size can be intrinsic viscosity for the suspended particles. For the intrinsic viscosity, we use the Krieger–Dougherty equation [19]

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

where $[\eta]$ is the intrinsic viscosity and ϕ_m is the maximum particle volume fraction. We take $\phi_m = 0.63$ for random packing of hard spheres. Fig. 3 shows the plot of $\ln(\eta/\eta_0)$ and $-\phi_m \ln(1 - \phi/\phi_m)$. The slope between two quantities gives the intrinsic viscosity. It is noted that there exist two slopes for each shear rate condition depending on ϕ range. The slope for $\phi = 0.03$–0.04 is larger than that for $\phi = 0.003$–0.02. This slope change is interpreted as a microstructural change in the suspension. Similar behavior is observed in yield stress data. The yield stress is obtained from Casson's equation [20]

$$\tau^{1/2} = \tau_y{}^{1/2} + (\eta_\infty \dot{\gamma})^{1/2}, \qquad (2)$$

where τ is the shear stress, τ_y is the yield stress, η_∞ is the suspension viscosity at infinite shear rate, and $\dot{\gamma}$ is the shear rate. Fig. 4(a) shows the Casson plot and the yield stress is replotted as a

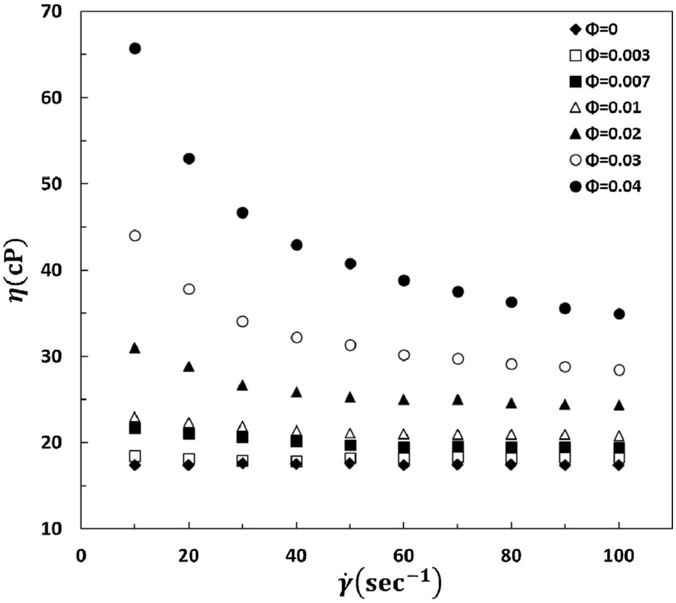

Fig. 1. Viscosity (η) vs. shear rate ($\dot{\gamma}$) at various particle volume fractions.