ELSEVIER

Aggregation and gelation kinetics of fumed silica–ethanol suspensions

William E. Smith, Charles F. Zukoski [*]

Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Abstract

The kinetics of aggregation and gelation of fumed silica suspended in ethanol were investigated as a function of volume fraction. At low particle concentrations, gelation is well described by aggregation into a primary minimum arising from hydrogen bonding and dispersion forces. The gelation is extremely slow due to an energetic barrier ($\sim 25kT$) in the interparticle potential associated with solvation forces. The solvation forces also contribute to the formation of a secondary minimum in the interparticle potential. The depth of this minimum ($\sim 3kT$) is sufficient that, at a critical particle concentration, long-range diffusion is arrested due to the short-range attractions and the cooperative nature of particle interactions, as described by mode coupling theory. The presence of the secondary minimum is also observed in the microstructure of the gels studied using X-ray scattering. These observations reinforce the importance of understanding the role of solvent–particle interactions in manipulating suspension properties.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Aggregation kinetics; Colloidal gels; Dynamic light scattering; Fumed silica; Mode coupling theory; Solvation forces

1. Introduction

Fumed silica suspensions are known for their thixotropic behavior, which is associated with the build up of aggregates and gelation [1,2]. Thixotropy in general is a poorly understood phenomenon as it links mechanical properties to changes in microstructure and state of aggregation, typically in dense and strongly interacting systems [3,4]. Here we explore the gelation of fumed silica in ethanol. We present evidence that the pair interaction energy at separations on the order of the solvent diameter leads to two different gelation mechanisms. One mechanism acts at low volume fractions and is related to particles diffusing over a primary maximum in the interparticle potential. This maximum is correlated with solvent molecules that associate with the silica surface and are displaced when the particles fall into a primary attractive minimum. As particles diffuse into the primary minimum, aggregates grow that ultimately span space forming a gel. The primary minimum is sufficiently deep that aggregation is expected at all measurable volume fractions. The second gelation mechanism is

associated with a shallow secondary minimum. Gelation due to this minimum is associated with cooperative phenomena and is only observed when the volume fraction exceeds a critical value.

Fumed silica is composed of primary particles of silica (~ 10 nm) irreversibly fused together to form an open branched particle [1], Fig. 1. Previous studies on the geometrical effects of fumed silica on suspension properties were carried out by eliminating the interparticle forces [5,6]. These "hard" fumed silica particles only experienced volume exclusion interactions and showed rheological properties similar to hard spheres when the particle concentration was scaled with the free volume in the suspension. These studies demonstrated the ability of these branched particles to occupy the same volume as an equivalent sphere but with lower mass. In the study reported here where the unaltered fumed silica particles are suspended in ethanol, we anticipate that the important forces governing the suspension properties will be dispersion and electrostatic forces as well as solvation forces due to the hydrogen bonding of the ethanol to the surface silanol groups [7]. The degree these forces influence the suspension behavior can be shown by a comparison of the results of the hard fumed silica suspensions with particles capable of hydrogen bonding to one another and to the solvent.

* Corresponding author. Fax: +1 217 333 5052.
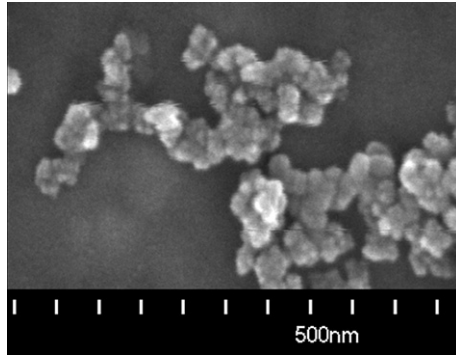 *E-mail address:* czukoski@uiuc.edu (C.F. Zukoski).

Fig. 1. Scanning electron micrograph of fumed silica particles.

These observations are significant in developing methods for manipulating particle interactions to achieve desired mechanical properties and time-dependent behavior. The strength of interaction between particles is one of the key parameters in determination of the state of aggregation and mechanical properties of colloidal suspensions. The particle–particle interaction potential can be manipulated by altering the continuous phase of the suspension, where small changes in temperature, pH, ionic strength, and concentration or molecular weight of polymer can drastically alter the properties of the suspension [8,9]. Changes in the interparticle potential not only change the state of particle aggregation, but the kinetics of transformations as well. In many applications, the time required to achieve a given state is important. This study indicates that with proper manipulation of solvent–surface interactions, one can achieve either slow gelation that continues to stiffen with time due to diffusion into the primary minimum or rapid gelation associated with a shallow secondary minimum.

Below in Section 2, standard aggregation models are discussed that describe the kinetics of aggregation and gelation when particles diffuse over maxima in interparticle potentials to form essentially irreversible bonds. These models have a venerable history and the work is briefly reviewed to distinguish this approach from more recent models of gelation based on mode coupling theory (MCT), where the strength of attraction is sufficiently weak that gelation is a reversible phenomenon. In Section 3, the experimental system is described, along with the use of dynamic light scattering as a noninvasive technique for investigating the rates of aggregation and gelation. Section 4 contains the results of the study, including slow gelation at low volume fractions and a narrow volume fraction range where the gel times become shorter than can be measured with the experimental techniques. Conclusions are drawn in Section 5.

2. Theoretical background

The typical starting point in investigating particle–particle interactions is through the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, which contributes interparticle attractions to van der Waals dispersion forces and repulsive forces to electrostatic interactions [9]. The DLVO theory is the sum of the two potentials between two spheres as described below. The van der Waals attraction potential Φ_A between spheres of equal radius a at a center-to-center separation r is given by

$$\Phi_A(r) = -\frac{A_H}{6}\left(\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln\frac{r^2 - 4a^2}{r^2}\right) \quad (1)$$

and

$$A_H = \frac{3}{4}kT\left(\frac{\varepsilon_p - \varepsilon_c}{\varepsilon_p + \varepsilon_c}\right)^2 + \frac{3h_P\upsilon_e}{16\sqrt{2}}\frac{(n_p^2 - n_c^2)^2}{(n_p^2 + n_c^2)^{3/2}}, \quad (2)$$

where A_H is the Hamaker coefficient, k is the Boltzmann constant, T is the absolute temperature, ε is the dielectric constant, n is the refractive index, the subscripts p and c correspond to the properties of the particle and continuous phase, respectively, h_P is the Planck constant, and υ_e is the characteristic adsorption frequency.

The potential energy of repulsion Φ_R for spheres following the approximations for superposition of single sphere potentials at a surface separation, $h = r - 2a$, is

$$\Phi_R(r) = 32\pi\varepsilon_c\varepsilon_0 a\left(\frac{kT}{ze}\right)^2 \tanh^2\left(\frac{ez\psi_0}{4kT}\right)\exp(-\kappa h) \quad (3)$$

and

$$\kappa = \left(\frac{e^2\sum_i z_i^2 c_{i0}}{\varepsilon_c\varepsilon_0 kT}\right)^{1/2}, \quad (4)$$

where ε_0 is the vacuum permittivity, z is the valence number of the ion, e is the charge of an electron, ψ_0 is the potential at the interface, κ^{-1} is the Debye length, and c_{i0} is the bulk concentration of ion species i [9]. An approximation of ψ_0 is the zeta potential, which is extractable from measurements of the electrophoretic mobility.

The concepts of the DLVO theory can be used in studying aggregation of colloidal suspensions. In the dilute limit, multibody interactions can be ignored and the flux J of particles coming together is

$$J = \frac{4kT}{3\eta_c a}\frac{\rho^2}{\int_{2a}^{\infty}\frac{\exp(\Phi/kT)}{r^2 G(r)}\,dr}, \quad (5)$$

where ρ is the particle number density, η_c is the continuous phase viscosity, Φ is the interparticle potential, and $G(r)$ is a hydrodynamic correction term approximated as being equal to one [9]. For aggregation without any repulsive forces, Φ can be approximated as being zero. Thus,

$$J_0 = \frac{2\phi kT\rho}{\pi\eta_c a^3}, \quad (6)$$

where ϕ is the particle volume fraction

$$\phi = \rho\frac{4}{3}\pi a^3. \quad (7)$$

The stability ratio is

$$W = \frac{J_0}{J}, \quad (8)$$

leading to the characteristic time for doublet formation t_d, where the number of particles is reduced to half of its original value

$$t_d = \frac{\pi\eta_c a^3 W}{\phi kT}. \quad (9)$$