A Frequency-Dependent Surfactant Bridge Model
for the Electrorheological Behaviors of Surfactant-Activated Suspensions

Young Dae Kim[†] **and Moo Sung Lee**

Faculty of Applied Chemistry, Chonnam National University, Yongbong-dong 300, Gwangju 500-757, Korea
(*Received 4 October 2003 • accepted 5 January 2004*)

Abstract−In surfactant-activated electrorheological (ER) suspensions, the ER response shows linear ER behavior ($\tau \propto E_o^2$) at small surfactant concentrations and nonlinear ER behavior ($\tau \propto E_o^n$, n<2) at large surfactant concentrations. A surfactant bridge model was proposed to explain the nonlinear ER behavior at large surfactant concentrations with some assumptions. The proposed model successfully predicted the qualitative nonlinear ER behavior of surfactant-activated ER suspensions at large surfactant concentrations. Here, the surfactant bridge model is expanded to predict the electric field frequency dependent ER behavior of surfactant-activated ER suspensions. The developed surfactant bridge model can predict both the linear ER behavior at small surfactant concentrations and the nonlinear ER behavior at large surfactant concentrations. Furthermore, this model can predict two different types of the electric field frequency dependent ER behaviors of surfactant-activated ER suspensions, which depend on the amount of surfactants.

Key words: Electrorheology, Surfactant Bridge Model, Suspension, Electric Field Frequency, Surfactant

INTRODUCTION

The electrorheological (ER) response is defined as the dramatic change in rheological properties of a suspension of small particles due to the application of a large electric field transverse to the direction of flow. ER suspensions are typically composed of nonconducting or semiconducting particles dispersed in a nonconducting continuous phase. A large ER effect was first reported by Winslow [1949]. Although many ER devices, such as dampers, clutches, and adaptive structures have been brought successfully to the prototype stage [Shulman et al., 1981], and despite much industrial activity in the U.S. and abroad, there are currently no commercially available devices. The main limitation of ER technology development is a lack of effective fluids [Hartsock et al., 1991; Weiss and Carlson, 1993]. Our inability to design effective fluids stems largely from a lack of a fundamental understanding of the mechanisms that control ER behavior. To design effective fluids, surfactants have been added to ER suspensions [Petrzhik et al., 1980; Trapeznikov et al., 1981; Kim and Klingenberg, 1996] or semiconducting polymer particles have been employed to enhance the particle polarizability [Goodwin et al., 1997; Kim and Park, 2002a, b; Kim and Song, 2002]. Also, the yield stress scaling function for ER fluid [Choi et al., 2001] and the effect of two polarizable particles on ER behavior [Kim et al., 1999] were investigated to understand the mechanisms.

Surfactants are added to ER suspensions for a variety of reasons [Winslow, 1949; Petrzhik et al., 1980; Trapeznikov et al., 1981; Deinega and Vinogradov, 1984; Block and Kelly, 1988; Gast and Zukoski, 1989; Jordan and Shaw, 1989; Kim and Klingenberg, 1996; Chin and Park, 2001] and can be used to tailor suspension properties. They are often used to promote colloidal stability, which is necessary to keep particles from irreversibly flocculating, and to control rheological properties in the absence of the electric field. Surfactants are also used to "activate" suspensions. Some suspensions display little or no ER activity unless a small amount of water or surfactant is added, while other suspensions exhibit a significantly enhanced response with activators present [Petrzhik et al., 1980; Trapeznikov et al., 1981; Kim and Klingenberg, 1996]. Enhancing ER activity with surfactants offers advantages over other approaches, such as adding water which severely limits the allowable temperature range of operation, promotes corrosion, and also increases suspension conductivity and power consumption. Furthermore, additional independent variables (*i.e.*, type and amount of surfactants) give flexibility to designing desired properties that is not possible by simply varying the materials of the disperse and continuous phases.

Surfactant influences the ER response in two different ways. At small surfactant concentrations, it enhances the ER response by enhancing the particle polarizability; at large concentrations, the response degrades (nonlinear ER response). The ER enhancement at small surfactant concentrations arises from the enhanced interfacial polarization due to the increased particle surface conductivity by the adsorbed surfactants. For the nonlinear ER response at large surfactant concentrations, it was proposed that the nonlinear ER response arose from the formation of surfactant-rich phase between particles induced by the applied electric field [Kim and Klingenberg, 1996]. A surfactant bridge model was proposed to explain the nonlinear ER behavior at large surfactant concentrations based on the following assumptions: the surfactant adsorbed particles are very conductive and therefore the potential drop in an ER chain occurs mainly in the continuous phase (*i.e.*, the particles were taken to be equipotential) and the continuous phase is an ideal dielectric material [Kim, 2001]. The proposed model successfully predicted the qualitative nonlinear ER behavior of surfactant-activated ER suspensions at large surfactant concentrations. However, the model cannot predict the electric field frequency effect on the ER behavior of surfactant-activated ER suspensions due to the imposed assumptions.

In this paper, we develop a surfactant bridge model by remov-

[†]To whom correspondence should be addressed.
E-mail: youngdae@chonnam.ac.kr

ing the assumptions and expanding to predict both the linear ER behavior at small surfactant concentrations and the nonlinear ER behavior at large surfactant concentrations. The developed surfactant bridge model can predict two different types of the electric field frequency dependent ER behaviors and the ER behaviors over the entire range of surfactant concentrations of surfactant-activated ER suspensions.

MATERIAL AND METHODS

The neutral alumina particles employed (Aldrich, ρ_p=3,970 kg/m^3, average pore diameter=58 Å) were approximately spherical and sieved to obtain diameters in the range of 63-90 μm. Nonionic surfactant investigated was Brij 30 ($C_{12}H_{25}(OCH_2CH_2)_4OH$, Aldrich). The particles were dried for 3 hours under vacuum (−10 psig) at 58 °C ("dried"). Alumina suspensions were prepared by first adding the desired amount of surfactant to silicone oil (General Electric, η_c=0.0968 Pa·s, ρ_c=968 kg/m^3). The particles were then added to the surfactant solution and stored in a desiccator to minimize contact with air. Suspensions were allowed to equilibrate for at least 24 hours before experiments.

Rheological experiments were performed at 23 °C on a Bohlin VOR rheometer fitted with parallel plates, and modified for the application of large electric field. Potential differences were supplied by a function generator (Stanford Research Systems, model DS345) and amplified with a Trek amplifier (model 10/10). Experiments were conducted with an electric field frequency of 500 Hz. Values for the dynamic yield stress were determined by extrapolating the shear stress-shear rate data to zero shear rate, using data over the range of shear rate, $0.01 \, s^{-1} < \dot{\gamma} < 0.1 \, s^{-1}$.

Suspension capacitance and loss were measured with a Fluke impedance analyzer (Fluke 6306A RLC meter), which probes frequencies in the range of 50 Hz to 100 kHz, and operates with potential differences in the range of 0.01-1.0 V (rms). A three-terminal, guarded dielectric cell was employed. The conductivities of suspensions and their supernatants were measured by using a picoammeter (Keithley 485).

The adsorption isotherm of Brij 30 on neutral alumina particles in silicone oil was obtained spectrophotometrically (Beckman DU series 60 Spectrophotometer) at a wavelength of 276 nm.

RESULTS AND DISCUSSIONS

The dependence of the yield stress on Brij 30 concentration is presented in Fig. 1 for 20 wt% neutral alumina suspensions in silicone oil. The yield stress initially increases with surfactant concentration and then passes through a maximum; the surfactant concentration at the maximum is insensitive to the applied electric field strength E_o, especially at large electric field strengths. At small Brij 30 concentrations, the yield stress scales with the electric field strength squared (linear region). However, at larger Brij 30 concentrations (>3 wt%), the yield stress deviates from the field squared dependence, increasing approximately with E_o^n where n<2 (nonlinear region).

In the linear region, the ER enhancement arises from the interfacial polarization. The yield stress increases with surfactant concentration and is proportional to the field strength squared. The electrostatic polarization model [Klingenberg and Zukoski, 1990; Par-
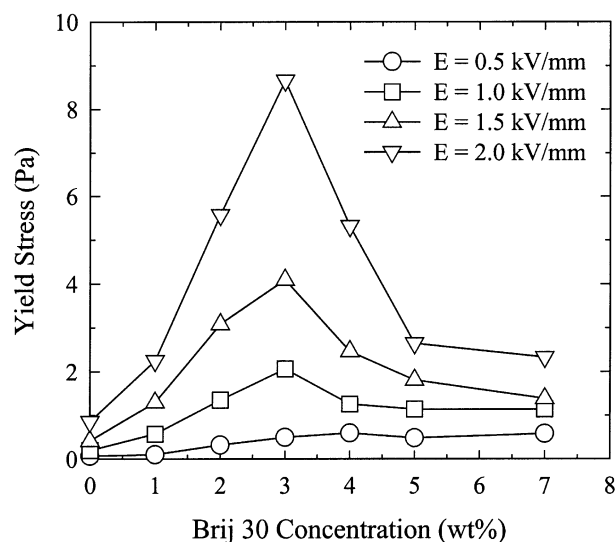

Fig. 1. Yield stress as a function of Brij 30 concentration for 20 wt% neutral alumina particles in silicone oil (f_E=500 Hz).

thasarathy and Klingenberg, 1996] describes the yield stress in terms of the electrostatic force acting between particles, induced by the applied electric field---this force increases quadratically with the particle polarizability for weakly polarizable particles. Surfactants readily adsorb to the particles and, together with adsorbed water, play a role to increase the surface conductivity on the particle [Kim and Klingenberg, 1996]. As a result, interfacial polarization would be enhanced, enhancing the ER response.

At large surfactant concentrations, above the maximum in the yield stress (Fig. 1), the yield stress scales as E_o^n where n<2, a feature that is not captured by enhanced linear interfacial polarization. The nonlinear ER behavior does not arise from dramatic changes in the suspension dielectric properties with surfactant concentration at small electric fields. Dielectric properties of neutral alumina suspensions increase smoothly with surfactant concentration, showing no abnormal behavior. Kim and Klingenberg [1996] proposed that the nonlinear ER behavior arose from the formation of surfactant-rich phase between particles induced by the applied electric field. Also, Choi et al. [2001] proposed a scaling function to explain the transition of linear and nonlinear ER behavior by incorporating both the polarization and conductivity models.

A surfactant bridge model was proposed to explain the nonlinear ER behavior at large surfactant concentrations. The proposed model successfully predicted the qualitative nonlinear ER behavior of surfactant-activated ER suspensions at large surfactant concentrations. However, the model cannot predict the electric field frequency effect on the ER behavior of surfactant-activated ER suspensions due to the imposed assumptions: the surfactant adsorbed particles are very conductive and therefore the potential drop in an ER chain occurs mainly in the continuous phase and the continuous phase is an ideal dielectric material [Kim, 2001]. Here, we develop a surfactant bridge model by removing the assumptions made in the surfactant bridge model and expanding to predict the electric frequency dependent ER behaviors of surfactant-activated ER suspensions.

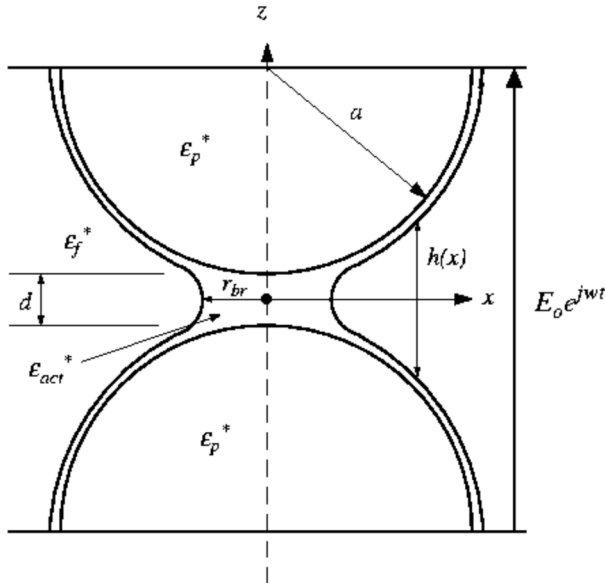Consider two particles adsorbed with surfactants and connected

Fig. 2. The geometry of two particles with a surfactant bridge and surfactant films on the particle surface.

with a surfactant bridge under the AC electric field ($\mathbf{E}_o^*(\mathbf{x}, t) = \mathbf{E}_o^*(\mathbf{x})$ $e^{-j\omega t}$). The system is described in Fig. 2, where ε_p^* ($=\varepsilon_p - j\sigma_p/\omega$) is the complex dielectric constant of the particle which is considered the same as that of the surfactant adsorbed particles (ε_{act}^*) and ε_f^* ($=\varepsilon_f - j\sigma_f/\omega$) is the complex dielectric constant of the continuous phase. In a real system, the assumptions of the equipotential and ideal dielectric particles and continuous phase have limitations.

For the system, we can write the following equations:

$$\mathbf{E}_f^*(\mathbf{x}, t) h(x) + \mathbf{E}_p^*(\mathbf{x}, t)(2a + d - h(x)) = \mathbf{E}_o^*(\mathbf{x}, t)(2a + d) \tag{1}$$

and

$$\varepsilon_f^* \mathbf{E}_f^*(\mathbf{x}, t) = \varepsilon_p^* \mathbf{E}_p^*(\mathbf{x}, t) \tag{2}$$

where $\mathbf{E}_f^*(\mathbf{x}, t)$ is the complex electric field in the gap between the particles, $\mathbf{E}_p^*(\mathbf{x}, t)$ is the complex electric field in the particles, d is the gap between the particles at x=0, and h(x) is the distance between the two particle film surface at location x. h(x) is given by

$$h(x) = d + 2a\{1 - [1 - (x/a)^2]^{1/2}\}. \tag{3}$$

Therefore, the electric fields in the particles are given by

$$\mathbf{E}_p^*(\mathbf{x}) = \frac{\varepsilon_f^*(2a + d)/h(x)}{\varepsilon_p^* + \varepsilon_f^*(2a + d - h(x))/h(x)} \mathbf{E}_o^*(\mathbf{x}) \tag{4}$$

The force acting between the particles will be composed of the electrostatic force and the force associated with surface free energy. The electrostatic force under the time varying field can be obtained from the electrostatic energy. The time average electrostatic energy under the time varying field is represented by [Jackson, 1975]

$$U_{elec}^{avg} = \frac{1}{4} \int_V \mathrm{Re}(\mathbf{E}^*(\mathbf{x}) \cdot \overline{\mathbf{D}^*}(\mathbf{x})) dV, \tag{5}$$

where $\mathbf{E}^*(\mathbf{x})$ is the time varying electric field and $\overline{\mathbf{D}^*}(\mathbf{x})$ is the conjugate of the time varying displacement ($\mathbf{D}^*(\mathbf{x}) = \varepsilon^* \mathbf{E}^*(\mathbf{x})$).

Force is given by taking the negative gradient of Eq. (5)

$$\mathbf{F}^{elec} = -\frac{1}{4} \int_{V_{particle}} \mathrm{Re}\left\{ \nabla \left[\varepsilon_f \left(1 - \frac{\varepsilon_p^*}{\varepsilon_f^*}\right) \overline{\mathbf{E}_o^*}(\mathbf{x}) \cdot \mathbf{E}_i^*(\mathbf{x}) \right] \right\} dV_{particle} \tag{6}$$

where $\mathbf{E}_i^*(\mathbf{x})$ is the resultant electric field throughout the particles.

Eq. (6) does not agree with Sher [1968] and Phol and Crane [1972] who represent the force as

$$\mathbf{F}^{elec} = -\frac{1}{4} \int_{V_{particle}} \mathrm{Re}\left\{ \nabla \left[\overline{\varepsilon_f^*}\left(1 - \frac{\varepsilon_p^*}{\varepsilon_f^*}\right) \overline{\mathbf{E}_o^*}(\mathbf{x}) \cdot \mathbf{E}_i^*(\mathbf{x}) \right] \right\} dV_{particle} \tag{7}$$

Eq. (6) and Eq. (7) differ in that the complex conjugate dielectric constant in Eq. (7) is replaced by ε_f (dielectric constant). It can be shown that the result for $\mathbf{F}^{elec}$ from Eq. (7) fails to the proper low frequency limit. Jones and Kallio [1979] explained that the failure at low frequency limit results from the application of $\overline{\varepsilon}_f^*$ to the factor of ε_f and the factor, ε_f, comes from Gauss' law and only affects the magnitude (not the phase) of the electric field contribution caused by the effective dipole.

The integration in Eq. (6) is to be performed over the volume of the particle. As Sher [1968], assuming that the media are homogeneous and isotropic, and a particle is a sphere the size of which is sufficiently small so that over its extent the impressed field is uniform to a first approximation, then the internal field is also uniform. Therefore, Eq. (6) can be written

$$\mathbf{F}^{elec} = -\pi a^2 \mathrm{Re}\left\{ \nabla \left[\varepsilon_f \left(1 - \frac{\varepsilon_p^*}{\varepsilon_f^*}\right) \overline{\mathbf{E}_o^*} \cdot \mathbf{E}_i^* \right] \right\} \tag{8}$$

The value of uniform $\mathbf{E}_p^*$ can be taken as that at $x=r_{br}$ and is

$$\mathbf{E}_p^* = \frac{\varepsilon_f^*(2a + d)/h(r_{br})}{\varepsilon_p^* + \varepsilon_f^*(2a + d - h(r_{br}))/h(r_{br})} \mathbf{E}_o^* \tag{9}$$

Combining Eq. (8) with Eq. (9), and note that $\mathbf{E}_i^* = \mathbf{E}_p^*$ and

$$\overline{\mathbf{E}_o^*} \cdot \mathbf{E}_o^* = |\mathbf{E}_o^*|^2 = \mathbf{E}_o^2, \tag{10}$$

the force can be written

$$F_z^{elec} = -\pi a^2 \varepsilon_f E_o^2 \mathrm{Re}\left[\left(1 - \frac{\varepsilon_p^*}{\varepsilon_f^*}\right) \frac{\varepsilon_f^*(2a + d)/h(r_{br})}{\varepsilon_p^* + \varepsilon_f^*(2a + d - h(r_{br}))/h(r_{br})} \right] \tag{11}$$

where E_o is the r.m.s value of electric field strength. The Eq. (11) can be rearranged by substituting $\varepsilon^* = \varepsilon - j\sigma/\omega$ and replacing ε_p^* by ε_{act}^*

$$F_z^{elec} = \pi a^2 \varepsilon_f (1 + G(r_{br})) E_o^2$$
$$\frac{(\varepsilon_{act} - \varepsilon_f)(\varepsilon_{act} + G(r_{br})\varepsilon_f) + (\sigma_{act} - \sigma_f)(\sigma_{act} + G(r_{br})\sigma_f)/\omega^2}{(\varepsilon_{act} + G(r_{br})\varepsilon_f)^2 + (\sigma_{act} + G(r_{br})\sigma_f)^2/\omega^2} \tag{12}$$

where

$$G(r_{br}) = \frac{2a + d - h(r_{br})}{h(r_{br})} \tag{13}$$

$G(r_{br})$ is a geometric factor depending on the size of the surfactant bridge between the particles, the gap between the particles, and the particle radius.

The force acting between the particles is the sum of the electrostatic force and the force associated with surface tension. Mason and Clark [1965] derived the following equation for the cohesive force between the spheres:

$$F_z^{surf} = 2k\pi a \gamma \cos\theta \tag{14}$$

where γ is the surface tension between the surfactant and surrounding liquid, θ is the contact angle between the surfactant and particle, and the coefficient k depends on the volume of surfactants in the bridge. The force is known as insensitive to the size of the bridge and the value of k is between 1 and 0.75.

Therefore, the total force between the particles is given by

$$F_z = \pi a^2 \varepsilon_f (1 + G(r_{br})) E_o^2$$
$$\frac{(\varepsilon_{act} - \varepsilon_f)(\varepsilon_{act} + G(r_{br})\varepsilon_f) + (\sigma_{act} - \sigma_f)(\sigma_{act} + G(r_{br})\sigma_f)/\omega^2}{(\varepsilon_{act} + G(r_{br})\varepsilon_f)^2 + (\sigma_{act} + G(r_{br})\sigma_f)^2/\omega^2}$$
$$+2k\pi a \gamma \cos\theta \tag{15}$$

However, it was noted that the electrostatic force was dominant over the cohesive force between the particles [Kim, 2001] and therefore, Eq. (12) would properly represent the total force between the particles.

In the limit of large frequencies ($\omega \to \infty$), the force reduces to

$$F_z = \pi a^2 \varepsilon_f (1 + G(r_{br})) E_o^2 \frac{\varepsilon_{act} - \varepsilon_f}{\varepsilon_{act} + G(r_{br})\varepsilon_f} + 2k\pi a \gamma \cos\theta, \tag{16}$$

while in the dc limit ($\omega \to 0$)

$$F_z = \pi a^2 \varepsilon_f (1 + G(r_{br})) E_o^2 \frac{\sigma_{act} - \sigma_f}{\sigma_{act} + G(r_{br})\sigma_f} + 2k\pi a \gamma \cos\theta. \tag{17}$$

In the limit of large frequencies, the force can be rearranged by noting that $h(r_{br}) \approx d + r_{br}^2/a$ and written

$$F_z = 2\pi a^4 \varepsilon_f E_o^2 \frac{\varepsilon_{act} - \varepsilon_f}{(ad\varepsilon_{act} + 2a^2 \varepsilon_f) + (\varepsilon_{act} - \varepsilon_f)r_{br}^2} + 2k\pi a \gamma \cos\theta \tag{18}$$

When no surfactant bridge is formed between the particles, i.e., $r_{br}=0$, the force becomes

$$F_z = 2\pi a^3 \varepsilon_f E_o^2 \frac{\varepsilon_{act} - \varepsilon_f}{d\varepsilon_{act} + 2a\varepsilon_f} \tag{19}$$

Therefore, with no surfactant bridge formed between the particles the force is proportional to E_o^2, consistent with the polarization model.

A surfactant bridge will be formed between the particles in surfactant activated ER suspensions, if either the applied electric field strength is greater than $E_{crit}(=\sqrt{2\gamma/\varepsilon_{act}d})$ or W>0. The size of the surfactant bridge is given by [Kim, 2001]

$$r_{br}^2 = k_{br}^2 \frac{\varepsilon_f a d^{3/2} E_o}{\pi \sqrt{2\gamma \varepsilon_{act}}} \left(1 - \sqrt{1 - \frac{\varepsilon_f W \sqrt{2\gamma}}{\varepsilon_{act}^{3/2} a d^{5/2} E_o}}\right) \tag{20}$$

where k_{br} is the proportional constant and W is the adsorbed amount of surfactants on a particle that can contribute to the formation of a surfactant bridge between the particles. As shown in Eq. (20), the size of the surfactant bridge will depend on the surfactant concentration, the electric field strength, the surface tension of surfactants, and the dielectric constant of surfactants, et al. When W=0, no surfactant bridges form between the particles ($r_{br}=0$). When the adsorbed amount of surfactants is large, the size of the surfactant bridge will be saturated and independent of W. Therefore, if W>W_{crit}, r_{br} is given by

$$r_{br}^2 = k_{br}^2 \frac{\varepsilon_f a d^{3/2} E_o}{\pi \sqrt{2\gamma \varepsilon_{act}}} \tag{21}$$

W_{crit} is given by

$$W_{crit} = \frac{\varepsilon_{act}^{3/2} a d^{5/2} E_o}{\varepsilon_f \sqrt{2\gamma}} \tag{22}$$

Since the size of the surfactant bridge is saturated if W>W_{crit}, the proportional constant, k_{br}, can be determined on the approximation that the volume of a saturated surfactant bridge is equal to the critical adsorbed amount of surfactants on a particles, W_{crit},

$$\pi r_{br}^2 d \approx W_{crit} \tag{23}$$

From Eq. (21) using Eq. (22) and Eq. (23), the proportional constant, k_{br}, can be given by

$$k_{br} \approx \left(\frac{\varepsilon_{act}}{\varepsilon_f}\right) \tag{24}$$

As a result, when r_{br} is appreciable, the force (Eq. (15)) cannot be proportional to E_o^2 due to the electric field dependence of r_{br} as represented by Eq. (20) and will scale to E_o^n where n<2.

The forces are estimated in the limit of large frequencies as a function of surfactant concentrations. The dielectric constants of Brij 30 adsorbed alumina particles, ε_{act}, were obtained from the measured dielectric constants of Brij 30 activated suspensions of 20 wt% neutral alumina particles in silicone oil as follows:

$$\varepsilon_{act} = 4.16 + 2.77C_{Br} \tag{25}$$

where C_{Br} is the initial Brij 30 concentration (wt%) in the suspension. It is found that the value of k_{br} calculated from Eq. (24) seems to be underestimated by a factor of 6 and, therefore, a factor of 6 is introduced in Eq. (24). Also, the dielectric constant of the continuous phase changes as Brij 30 concentration in the ER suspension increases. The dielectric constant of the continuous phase as a function of Brij 30 concentration was measured as a function of Brij 30 concentrations and is represented by

$$\varepsilon_f = \varepsilon_{silicon} + 0.13255C_{Br} \tag{26}$$

where $\varepsilon_{silicon}$ is the dielectric constant of silicone oil and 2.74.

Brij 30 adsorption data is required for the estimation of the adsorbed amount of surfactants on a particle. The Brij 30 adsorption on neutral alumina particles in silicone oil was measured and the Brij 30 adsorption isotherm is obtained from data fitting and represented by

$$\Gamma_{adsorb} = 2.02 \times 10^{-4} C_{equil}^{0.9985} \tag{27}$$

where Γ_{adsorb} is the Brij 30 adsorption on the particles (gmole/m²) and C_{equil} is the equilibrium surfactant concentration (gmole/kg) in the continuous phase. The equilibrium surfactant concentration in the continuous phase was measured as a function of initial Brij 30 concentration for 20 wt% neutral alumina suspensions in silicone oil and is represented by

$$C_{equil} = 0.0063 + 0.00389C_{Br} \tag{28}$$

Assuming that the adsorbate area is 46 Å² (reported for Brij 30 adsorption at the air-water interface [Rosen, 1989], monolayer coverage, Γ_{mono}, corresponds to approximately 3.5×10^{-6} gmole/m². The pore volume of the neutral alumina particles is approximately 0.225 cm³/g; the amount of Brij 30 (ρ_{surf}=0.95 g/cm³, MW=362.5) required

to fill the pores is approximately 3.8×10^{-6} gmole/m^2. This result indicates that, in the monolayer coverage, almost all the adsorbed surfactants are present in the particle pores. Therefore, the amount of adsorbed surfactants, Γ, that can contribute to the formation of surfactant bridges between the particles is approximately given by

$$\Gamma = \Gamma_{adsorb} - \Gamma_{mono} \tag{29}$$

As a result, the adsorbed amount of surfactants on a particle that can contribute to the formation of a surfactant bridge between the particles is

$$W = 4\pi a^2 \Gamma \times MW / \rho_{surf} \tag{30}$$

where MW is the molecular weight of Brij 30 and ρ_{surf} is its density.

For the ER suspensions activated with Brij 30 (Fig. 1), a is 38 μm, the surface tension of Brij 30 is 3.2×10^{-4} N/m [Myers, 1991], that of silicon oil is 2.0×10^{-4} N/m, and therefore the resulting surface tension difference $\gamma = 1.2 \times 10^{-4}$ N/m. The electrode gap during the experiment was 1.0 mm. The value of d/a is taken as 5.0×10^{-3} and k and $\cos\theta$ are taken as 1, respectively.

The yield stress of surfactant-activated ER suspensions can be estimated from the total force between the particles. For an electrode gap of l, the yield stress is give by [Klingenberg and Zukoski, 1990]

$$\tau = \frac{3\phi}{2\pi a^2} F_z f_m \left[1 - \frac{(\pi/6)^{1/2}}{(l/a)\tan\theta_m \phi^{1/2}} \right] \tag{31}$$

where f_m and θ_m are the maximum in the dimensionless force and the angle at the maximum, respectively, and are function only of $\alpha(=\varepsilon_{act}/\varepsilon_f)$. For the Brij 30 activated suspensions, $f_m = 0.105$ and $\theta_m = 15.64°$.

The dependence of the estimated yield stress on Brij 30 concentration is presented in Fig. 3 for 20 wt% neutral alumina suspensions in silicone oil. The yield stress initially increases with Brij 30 concentration and then passes through a maximum; the Brij 30 concentration at the maximum is 3 wt% and insensitive to the applied

electric field strength. This result is consistent with the experimental yield stress behavior of 20 wt% neutral alumina suspensions in silicone oil (Fig. 1). Comparison of the estimated and experimental yield stresses shows that the estimated yield stresses are underestimated. It was reported that the yield stress model (Eq. (31)) failed to predict experimental yield stress at low volume fractions ($\phi < 0.2$), and the discrepancy (underestimation) at low volume fractions was attributed to rearrangement of the particle structure after rupture, a phenomenon not captured in the electrostatic polarization model [Klingenberg and Zukoski, 1990]. Therefore, the discrepancy (underestimation) seems to arise from rearrangement of the particle structure after rupture since the volume fraction of 20 wt% neutral alumina suspensions is low ($\phi = 0.1034$). However, it was noted that the polarization model based on the dipole-dipole interaction might be limited for predicting ER behavior and the limitation might be a possible explanation for the underestimation.

The value of r_{br} is 0 up to nearly 3 wt% of Brij 30, increases rapidly from 3 wt% to 4 wt%, and then reaches almost a saturated value at large Brij 30 concentrations (>4 wt%), suggesting that the slower ER response deterioration at large Brij 30 concentrations (>4 wt%) arises from the saturation of surfactant bridges between the particles.

The prevalent feature of surfactant-activated ER suspensions is that below the maximum, the yield stress, τ, increases quadratically with the field strength, E_o, while above the maximum, yield stress increases slower than E_o^2. The dependence of the calculated power of electric field ($\tau \propto E_o^n$), n, on Brij 30 concentration is presented in Fig. 4. The value of n is 2.0 when no surfactant is added and remains 2.0 up to the Brij 30 concentration of 2 wt%. At Brij 30 concentrations around 3 wt%, n starts to slightly decrease from 2.0 and reaches 1.5 at large Brij 30 concentrations (>4 wt%). As represented by Eq. (20), when r_{br} is appreciable, the force scales to E_o^n where n<2 and n decreases with Brij 30 concentrations.

The yield stresses are estimated as a function of the electric field frequency from the total force (Eq. (15)). The yield stress of surfactant-activated ER suspensions shows two different frequency depen-
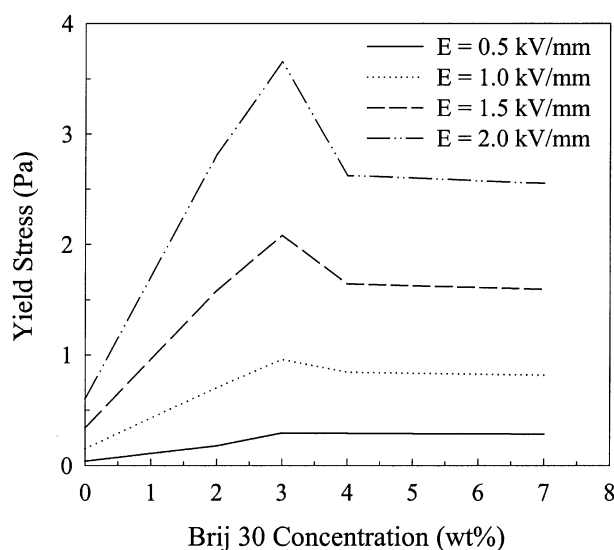

Fig. 3. Calculated yield stress as a function of Brij 30 concentration for 20 wt% neutral alumina suspensions in silicone oil.
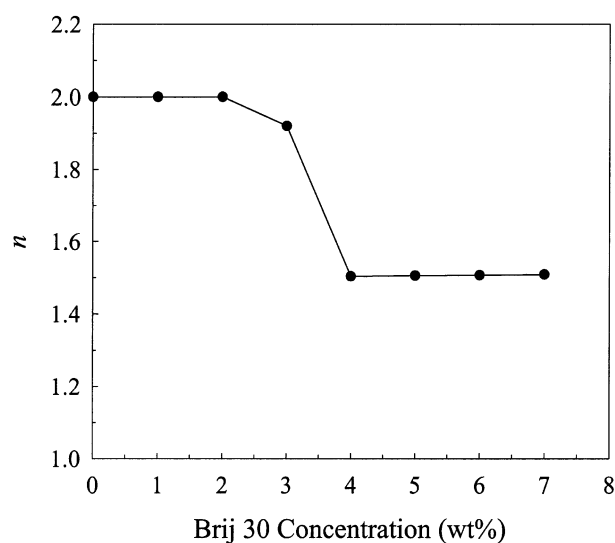

Fig. 4. Calculated value of n as a function of Brij 30 concentration for 20 wt% neutral alumina suspensions in silicone oil.

dent ER behaviors depending on the amount of surfactants (*i.e.*, on the formation of surfactant bridges between the particles). For frequency dependent yield stress calculations, dc conductivities of suspensions and their supernatants were measured for 20 wt% neutral alumina suspensions activated with various amounts of Brij 30. The suspension conductivities are 4.5×10^{-11}, 5.4×10^{-10}, and 7.3×10^{-9} mho/m for 0 wt%, 3 wt%, and 7 wt% Brij 30 concentrations, respectively. Also, the corresponding supernatant conductivities are 1.0×10^{-11}, 3.1×10^{-10}, and 6.3×10^{-9} mho/m for 0 wt%, 3 wt%, and 7 wt% Brij 30 concentrations, respectively. Accordingly, the particles conductivities are obtained as 3.48×10^{-10}, 2.55×10^{-9}, and 1.59×10^{-8} mho/m for 0 wt%, 3 wt%, and 7 wt% Brij 30 concentrations, respectively.

The dependence of the yield stress on electric field frequency is presented in Fig. 5 for 20 wt% neutral alumina suspension. Fig. 5(a) represents the experimental data and Fig. 5(b) represents the estimated values at $E_o = 1.0$ and 1.5 kV/mm, respectively. For both experimental and estimated cases, the yield stress decreases with the electric field frequency, showing good agreement between the experimental and estimated ER behaviors. However, the estimated values are underestimated compared with the experimental data, due to rearrangement of the particle structure after rupture at low
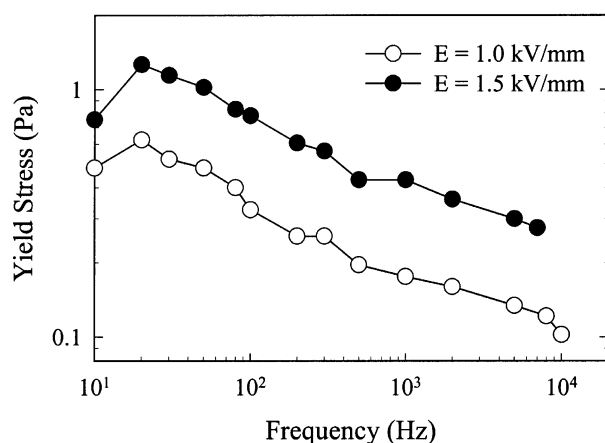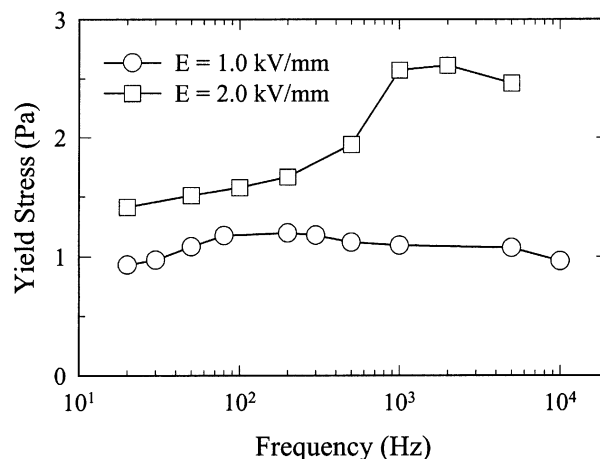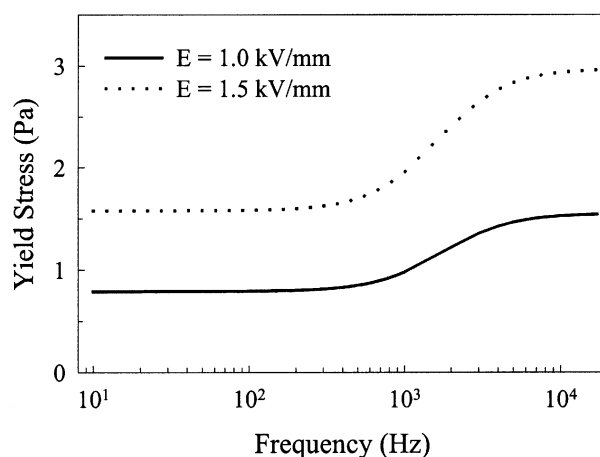

(a)
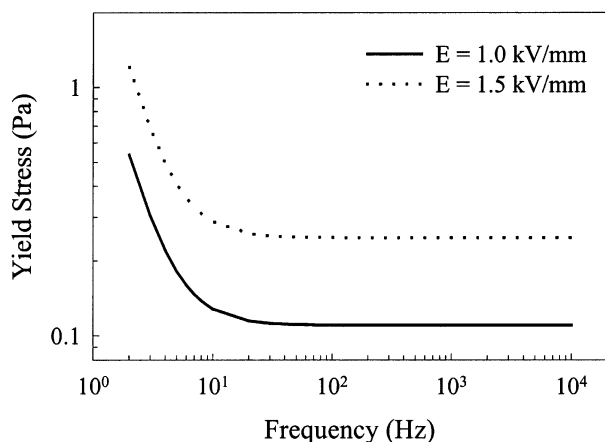
(b)

Fig. 5. Yield stress as a function of electric field frequency for 20 wt% neutral alumina suspension in silicone oil: (a) experimental data and (b) calculated yield stress.

(a)

(b)

Fig. 6. Yield stress as a function of electric field frequency for 20 wt% neutral alumina suspension in silicone oil activated with 7 wt% Brij 30: (a) experimental data and (b) calculated yield stress.

volume fractions. Similar electric field frequency dependent ER behavior was also observed for 20 wt% neutral alumina suspension activated with 3 wt% Brij 30. The agreement between the experimental and estimated yield stress behavior is reasonable, though the estimated one is a little underestimated.

The dependence of the yield stress on electric field frequency is presented in Fig. 6 for 20 wt% neutral alumina suspension activated with 7 wt% Brij 30. Here, the electric field frequency dependence of the yield stress is quite different compared to that of Fig. 5, where there is no appreciable surfactant bridges formed between the particles. For both experimental and estimated cases, the yield stress increases with the electric field frequency, showing good agreement between the experimental data and estimated values. Also, the ER behavior of the surfactant activated ER suspension with 7 wt% Brij 30 is not greatly enhanced compared to that of the ER suspension without Brij 30, which arises from the nonlinear conduction due to the surfactant bridge formation at large surfactant concentrations. It is notable that surfactant bridges form between the particles if suspensions are activated with more than 3 wt% of

Brij 30. Therefore, surfactant-activated ER suspensions show two different electric field frequency dependent ER behaviors, depending on the amount of surfactants. At small surfactant concentrations, the ER response decreases with the electric field frequency. Whereas, at large surfactant concentrations, the ER response increases with the electric field frequency. Also, the estimated values are fairly comparable with the experimental data. Compared with the yield stress underestimation of the suspensions activated with 0 wt%, the relatively good agreement of the experimental and estimated values seems to arise from the suppression of rearrangement of the structure after rupture due to the formation of surfactant bridges between the particles.

The two different electric field frequency dependent yield stress behaviors can be explained from the Eq. (16) and Eq. (17), which represent the force in the limit of large frequencies and in the dc limit, respectively. Eq. (16) and Eq. (17) can be rewritten as follows since the force due to surface tension is negligible to the electrostatic force:

$$F_{n,\infty} = \frac{F_{z,\omega\to\infty}}{\pi a^2 \varepsilon_f (1+G(r_{br}))E_o^2} = \frac{\varepsilon_{act}/\varepsilon_f - 1}{\varepsilon_{act}/\varepsilon_f + G(r_{br})}, \tag{32}$$

and

$$F_{n,0} = \frac{F_{z,\omega\to 0}}{\pi a^2 \varepsilon_f (1+G(r_{br}))E_o^2} = \frac{\sigma_{act}/\sigma_f - 1}{\sigma_{act}/\sigma_f + G(r_{br})}. \tag{33}$$

Therefore, at a given surfactant concentration and electric field strength, the yield stress depends on ω, $\varepsilon_{act}/\varepsilon_f$, and σ_{act}/σ_f. If $F_{n,0} > F_{n,\infty}$ (or $\sigma_{act}/\sigma_f > \varepsilon_{act}/\varepsilon_f$), the yield stress will decrease from $F_{n,0}$ to $F_{n,\infty}$ as the electric field frequency increases. On the other hand, if $F_{n,0} < F_{n,\infty}$ (or $\sigma_{act}/\sigma_f < \varepsilon_{act}/\varepsilon_f$), the yield stress will increase from $F_{n,0}$ to $F_{n,\infty}$ as the electric field frequency increases. The values of $\varepsilon_{act}/\varepsilon_f$ are 1.34, 4.10, and 7.06 for 20 wt% neutral alumina suspensions activated with 0, 3, and 7 wt% Brij 30, respectively. Also, the values of σ_{act}/σ_f are 34.8, 8.3, and 2.5 for 20 wt% neutral alumina suspensions activated with 0, 3, and 7 wt% Brij 30, respectively. As a result, the yield stress decreases with the electric field frequency for 20 wt% neutral alumina suspensions activated with up to 3 wt% Brij 30 since $\sigma_{act}/\sigma_f > \varepsilon_{act}/\varepsilon_f$, as shown in Fig. 5 and Fig. 7. While the yield stress of 20 wt% neutral alumina suspension activated with 7 wt% Brij 30 increases with the electric field frequency since $\sigma_{act}/\sigma_f < \varepsilon_{act}/\varepsilon_f$, as shown in Fig. 7.

CONCLUSIONS

A surfactant bridge model was proposed to explain the nonlinear ER behavior of surfactant-activated ER suspensions at large surfactant concentrations. The proposed model successfully predicted the qualitative nonlinear ER behavior of the surfactant-activated ER suspensions at large surfactant concentrations. However, this model has limitations such as not predicting the electric field frequency dependent ER behaviors of surfactant-activated ER suspensions. Here, we develop a surfactant bridge model by removing the assumptions made in the surfactant bridge model and expanding to predict the electric field frequency dependent ER behavior of surfactant-activated ER suspensions. The developed surfactant bridge model can predict both the linear ER behavior at small surfactant concentrations and the nonlinear ER behavior at large sur-

factant concentrations. Furthermore, this model can predict two different types of the electric field frequency dependent ER behaviors of the surfactant-activated ER suspensions, which depend on the amount of surfactants.

REFERENCES

Block, H. and Kelly, J. P., "Electro-rheology," *J. Phys. D: Appl. Phys.*, **21**, 1661 (1988).

Chin, B. D. and Park, O. O., "Electrorheological Response of Particulate Suspensions and Emulsions in a Small-strain Shear Flow: Viscoelasticity and Yield Phenomena," *Korean J. Chem. Eng.*, **18**, 54 (2001).

Choi, H. J., Cho, M. S., Kim, J. W., Kim, C. A. and Jhon, M. S., "A Yield stress Scaling Function for Electrorheological Fluids," *Appl. Phys. Lett.*, **78**, 3806 (2001).

Deinega, Y. F. and Vinogradov, G. V., "Electric Fields in the Rheological Disperse System," *Rheol. Acta*, **23**, 636 (1984).

Gast, A. P. and Zukoski, C. F., "Electrorheological Fluids as Colloidal Suspensions," *Adv. Coll. Int. Sci.*, **30**, 153 (1989).

Goodwin, J. W., Markham, G. M. and Vincent, B., "Studies on Model Electrorheological Fluids," *J. Phys. Chem. B*, **101**, 1961 (1997).

Jackson, J. D., "Electrodynamics," 2nd ed. John Wiley and Sons, Inc. (1975).

Jones, T. B. and Kallio, G. A., "Dielectrophoretic Levitation of Spheres and Shells," *J. Electrostatics*, **6**, 207 (1979).

Jordan, T. C. and Shaw, M. T., "Electrorheology," *IEEE Trans. Elect. Insul.*, **24**, 849 (1989).

Kim, Y. D. and Klingenberg, D. J., "Two Roles of Nonionic Surfactants on the Electrorheological Response," *J. Colloid Interface Sci.*, **183**, 568 (1996).

Kim, Y. D., "A surfactant Bridge Model for the Nonlinear Electrorheological Effects of Surfactant- Activated ER Suspensions," *J. Colloid Interface Sci.*, **236**, 225 (2001).

Kim, Y. D. and Park, D. H., "The Electrorheological Responses of Suspensions of Polypyrrole-coated Polyethylene Particles," *Coll. Pol. Sci.*, **280**, 828 (2002a).

Kim, Y. D. and Park, D. H., "The Electrorheological and Dielectric Behaviors of Conducting Polymercoated Poly(ethyl mathacrylate) Suspensions," *Macromolecular Research*, **10**, 215 (2002b).

Kim, Y. D., Choi, G. J., Sim, S. J. and Cho, Y. S., "Electrorheological Suspensions of Two Polarizable Particles," *Korean J. Chem. Eng.*, **16**, 338 (1999).

Kim, Y. D. and Song, I. C., "Electrorheological and Dielectric Properties of Polypyrrole Dispersions," *J. Materials Sci.*, **37**, 5051 (2002).

Klingenberg, D. J. and Zukoski, C. F., "Studies on the Steady-shear Behavior of Electrorheological Suspensions," *Langmuir*, **6**, 15 (1990).

Mason, G. and Clark, W. C., "Liquid Bridges between Spheres," *Chem. Eng. Sci.*, **20**, 859 (1965).

Myers, D., "Surfaces, Interfaces, and Colloids: Principles and Applications," VCH Pub. Weinheim (1991).

Parthasarathy, M. and Klingenberg, D. J., "Electrorheology: Mecha-

nisms and Models," *Mater. Sci. and Eng. Rep.*, **R17**, 57 (1996).

Petrzhik, G. G., Chertkova, O. A. and Trapeznikov, A. A., "Electrorheological Effect in Nonaqueous Dispersions of Various Compositions in Relation to the Electric Field Parameters," *Dokl. Akad. Nauk SSSR*, **253**, 173 (1980).

Pohl, H. A. and Crane, J. S., "Dielectrophoretic Force," *J. Theor. Biol.*, **37**, 1 (1972).

Rosen, M. J., "Surfactants and Interfacial Phenomena," 2nd. ed. Wiley, New York (1989).

Sher, L. D., "Dielectrophoresis in Lossy Dielectric Media," *Nature*, **220**, 695 (1968).

Shulman, Z. P., Gorodkin, R. G., Korobko, E. V. and Gleb, V. K., "The Electrorheological Effects and Its Possible Uses," *J. Non-Newt. Fluid Mech.*, **8**, 29 (1981).

Trapeznikov, A. A., Petrzhik, G. G. and Chertkova, O. A., "Electrorheological Properties of Nonaqueous Dispersions of Titanium Dioxide and Silicone Dioxide in Relation to Concentration and Moisture Content of Filler," *Koll. Zhurn.*, **43**, 1134 (1981).

Weiss, K. D. and Carlson, J. D., "Material Aspects of Electrorheological Systems," *J. Intell. Sys. and Struct.*, **4**, 13 (1993).

Winslow, W. M., "Induced Fibration of Suspensions," *J. Appl. Phys.*, **20**, 1137 (1949).