Reversing-pulse Electric Birefringence of β-FeOOH Particles Dispersed in Aqueous Media[1]

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(Received September 30, 1994)

The electric properties of colloidal β-FeOOH particles were investigated at a low particle concentration and at various ionic strengths by reversing-pulse electric birefringence. A dip in the electric birefringence signal was observed upon pulse reversal. The electric field orientation of the particles is due mostly to ion-fluctuation dipole moment parallel to the symmetric axis of the prolate ellipsoid.

β-FeOOH (iron(III) oxide hydrate) dispersions were recently used as the model system for studying changes in the surface properties of colloids by the adsorption of polymer and aggregate formation by means of electric light scattering and others experimental techniques.[2,3] Pronounced changes of dipole moments at low frequencies and the appearance of a large permanent dipole moment transverse to the symmetric axis of particle were reported. Since in these investigations the dipole moments of the host β-FeOOH particles are quite important, identification of the exact type and magnitude of these moments (induced and/or permanent) is of considerable scientific interest. The data so far available are controversial. In some cases, a longitudinal (with respect to the particle axis) permanent dipole moment was reported especially at low ionic strengths and particle concentrations,[4] while no such moment was observed by other workers.[2] In order to clarify the type of the electric dipole moment of β-FeOOH particles, reversing-pulse electric birefringence (RPEB) technique is utilized in the present work at a low particle concentration and at various ionic strengths. This is a powerful electro-optic method for determining the electric and hydrodynamic properties of biopolymers, dispersed particles, and colloidal systems.[5-8] In our knowledge this work is the first attempt to apply RPEB techniques for investigation of the electric properties of β-FeOOH.

A sample of β-FeOOH was prepared by slow acid hydrolysis of $FeCl_3$ at a pH of 4 at room temperature for three weeks. The particles are ellipsoidal with an average length of 280 nm and an axial ratio of ca. 4, as determined previously from electron microscopy. Details on the preparation procedure and physicochemical properties were given elsewhere.[2,3] The β-FeOOH dispersion for RPEB measurements was prepared from a single stock solution with a concentration of 0.111 g/dm^3 by successive dilutions with bidistilled water. The stock solution was sonicated in an iced bath for 3 min, at a power level of 100 W and 20 kHz before each dilution, in order to avoid any agregation of the dispersed particles. The ionic strength of β-FeOOH dispersion was varied in the 0.056–2.0 mM range by addition of NaCl. RPEB measurements were performed at 633 nm and 25 ℃ on a previously described instrument.[9] The field strength of applied reversing-pulses was varied to 2.4 kV/cm for high degrees of particle orientation.

Figure 1 shows typical RPEB signals obtained at low fields (the so-called Kerr-law region) and at a low particle concentration (0.01 g/dm^3). The sign of the steady-state electric birefringence expressed in term of the phase retardation δ was always positive. Under consideration that the shape of β-FeOOH particle is a prolate ellipsoid, the optical anisotropy factor (Δg/n) of the particle is positive (the orientation function Φ(E) is also positive). Each RPEB profile of β-FeOOH dispersion shows a monotonic rise in the buildup process, a distinct minimum upon the field reversal, and a decay at the removal of pulse field. The increase in ionic strength or applied field strength affects the depth of the minimum (compare (d) with (f)). The rotational relaxation time τ or the rotary diffusion coefficient Θ_{11} (=1/6τ) for the overall rotational motion of β-FeOOH particle was determined from the decay curve. As shown in Figure 1, values of τ depend on applied electric field strength, reflecting the polydisperse nature of the sample. At infinitely high fields, τ value is 0.23 ms but 1–2 ms in the limiting low field region. Since the increase in ionic strength changes neither the pattern of the field strength dependence of τ nor τ value at limiting high fields, no particle aggregation occurs at the present low particle concentration.

A pronounced and well-reproducible minimum upon field reversal in the RPEB signal (Figure 1) is characterized with two parameters: the depth of the minimum ($1-\Delta_m$) and the time required for the minimum t_m. Figure 2 shows the field-strength dependence of the depth and required time observed in RPEB signals at four different ionic strengths. The distinct depth ($1-\Delta_m$) becomes shallower with increasing field strength for the dispersion at the lowest ionic strength (○), whereas the depths remain shallow or non-existing at higher ionic strengths (■, △, □). The time required for the minimum t_m also shows the same trend as the depth.

The original theory[5] predicts that the appearance of this minimum is associated with the electric permanent dipole moment μ_3 and/or slowly induced ionic moment σ_3E along the major principal axis (the 3 axis) of a prolate ellipsoid, in addition to the moment Δα'E resulting from the fast-induced ionic and/or electronic polarizability anisotropy. For the β, γ-mixed dipole orientation, where $\beta = \mu_3E/kT$ and $\gamma = \Delta\alpha'E^2/2kT$ (k and T are the Boltzmann constant and absolute temperature), the parameters for the minimum are given in the Kerr-law region as[5]

$$1-\Delta_m = (2/\sqrt{3})[Q/(1+Q)], \quad t_m = (3\tau/2)\ \ln 3 \qquad (1)$$

where $Q=\mu_3^2/kT\Delta\alpha'$. In this case, values of t_m should remain constant, even if the depth becomes shallower by the decrease in the electric parameter Q. If the field orientation is due to the moment σ_3E (instead of μ_3) and Δα'E (the slow-induced orientation), the parameters are given as[5,6]

$$1-\Delta_m = [\sigma_3/(\sigma_3+\Delta\alpha')](\tau^\sigma{}_3/\tau)^{[1-(\tau^\sigma{}_3/\tau)]^{-1}},$$
$$t_m = [\tau^\sigma{}_3/((\tau^\sigma{}_3/\tau)-1)]\ \ln\ (\tau^\sigma{}_3/\tau) \qquad (2)$$

In this case, the minimum position may change considerably, depending on values of the relaxation time $\tau_3{}^\sigma$ of counterion mobility and the magnitude of electric moments. Recently, a

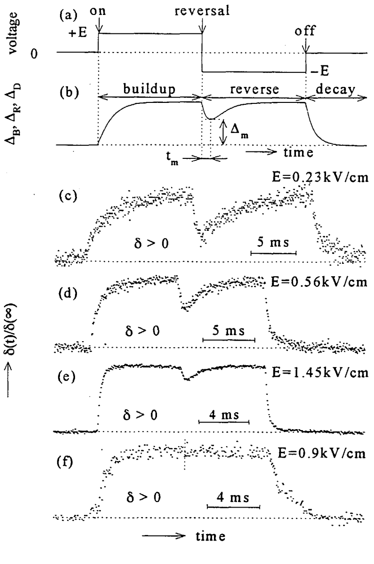

Figure 1. Normalized RPEB signals of β-FeOOH dispersion. A schematic reversing-pulse pattern (a) and a RPEB signal profile (b). RPEB signals measured in the presence of 0.056 mM (c–e) and 2.0 mM NaCl (f). τ in ms: 1.28 (c), 0.61 (d), 0.39 (e), and 2.0 (f). Note the effect of ionic strength on the minimum in the reverse process.

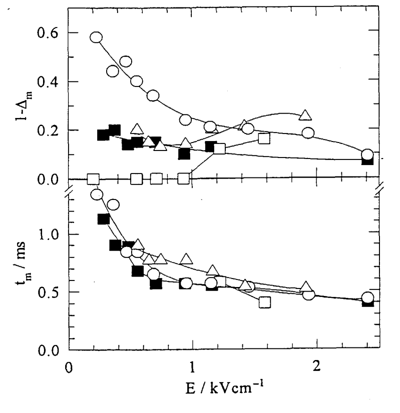

Figure 2. Field-strength dependence of the minimum position (Δ_m and t_m) in RPEB signals of β-FeOOH suspension at four ionic strengths. Concentrations of added NaCl in mM: 0.056 (○), 0.094 (■), 0.76 (△), and 2.0 (□).

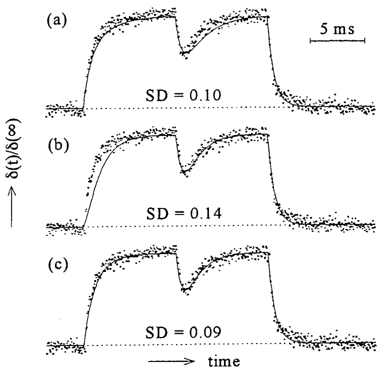

Figure 3. Measured and simulated RPEB signals of β-FeOOH dispersion. Measured signal is (d) in Fig. 1. Simulated curves: (a) τ = 0.61 ms and Q = 0.53 for the mixed orientation (Eq. (1)); (b) $\tau_3{}^{\sigma}$ = 1.2 ms and $\sigma_3/(\sigma_3+\Delta\alpha')$ = 0.8 for slow-induced orientation (Eq. (2)); (c) τ_I = 3.5 ms and q = 0.67 for ion-atmosphere orientation (Eq. (3)). As a measure of discrepancy between observed and simulated curves, the standard deviation $SD^2 = [(\text{obsd.})-(\text{simul.})]^2$ is shown for each signal.

new RPEB theory was developed on the basis of ion-fluctuation mechanism.[8] In this theory, two electric moments are considered: one is the ion-atmosphere polarization α_3 with a relaxation time τ_I along the longitudinal axis and the other is the instantaneously induced polarizability anisotropy $\Delta\alpha'$. The parameters for the minimum in the reverse process are given as[8]

$$1-\Delta_m = [2q/(q+1)][3\tau^*/(\tau^*+3)]^{-(\tau^*+3)/(2\tau^*-3)},$$
$$t_m' = [3\tau^*/(2\tau^*-3)] \ln [3\tau^*/(\tau^*+3)] \qquad (3)$$

where $q = \alpha_3/\Delta\alpha' = \langle m^2\rangle/kT\Delta\alpha'$, $t_m' = t_m/\tau$ and $\tau^* = \tau_I/\tau$. In this case, the depth and time for the minimum change with the ratio of two relaxation times (τ_I and τ), even if the electric parameter q remains constant (Figure 3 of Ref. 8).

By using both the rotational relaxation time τ, evaluated from the decay curve (cf. Figure 1), and the observed depth and time for the minimum in Figure 2, the ionic relaxation time $\tau_3{}^{\sigma}$ or τ_I can be calculated from Eq. (2) or (3); hence, the electric parameter Q, $\sigma_3/(\sigma_3+\Delta\alpha')$, or q can also be estimated from Eq. (1), (2), or (3). With the electric and relaxational parameters, normalized RPEB signals of β-FeOOH dispersion, measured at low field strengths, can be simulated. Figure 3 shows three theoretical RPEB curves (solid lines) fitted to a low-field RPEB profile. The result indicates that the agreement between experimental and simulated signals is best for the ion-fluctuation theory under the consideration of the standard deviation given in Figure 3. Thus, the field orientation behavior of β-FeOOH particles may be best described with an ion-fluctuation model, in which the ion-fluctuation over the interface of particle is considerably slower than the overall particle rotation (τ_I value of 3.5 ms is larger than τ value of 0.61 ms). Both $1-\Delta_m$ and t_m values diminish with increasing ionic strength (Figure 2), though Eq. (1) requires that t_m should remain constant for the β, γ-orientation. Hence, the β-FeOOH particle is unlikely to possess the permanent dipole moment μ_3.

For more rigorous comparisons between existing theories and the measured RPEB data, the test sample must be closely monodisperse. A fractionated β-FeOOH sample is now being prepared. From experimental results reported in this Letter, it is clear that RPEB techniques can be applied successfully for elucidation of the surface electric properties of optically complicated oxide dispersion systems.[10]

This work was in part supported by Grant-in-Aid for Developmental Scientific Research (B) 06554031 (K. Y.) and by the Monbusho's Grant-in-Aid for JSPS Fellows 94062 (V. P.) from the Ministry of Education, Science and Culture. We thank the Japan Society for the Promotion of Science for the JSPS Postdoctoral Fellowship for Foreign Researchers in Japan awarded to Viktor Peikov.

References and Notes

1 Electro-Optics of Dispersed System Part 3. Part 2 of this series is Ref. 9.
2 Ts. Radeva, I. Petkanchin, and R. Varoqui, "Colloid and Molecular Electro-Optics 1991," ed by B. R. Jennings and S. P. Stoylov, IOP Publ. Ltd., Bristol (1992), pp. 111–114.
3 K. Starchev, V. Peikov, S. P. Stoylov, and I. Petkanchin, *J. Coll. Interface Sci.*, **162**, 81 (1994).
4 V. Peikov, I. Petkanchin, and S. P. Stoylov, *Commun. Depart. Chem. Bulg. Acad. Sci.*, **24**, 536 (1991)
5 I. Tinoco, Jr., and K. Yamaoka, *J. Phys. Chem.*, **63**, 423 (1959).
6 K. Yamaoka and K. Matsuda, *J. Phys. Chem.*, **89**, 2779 (1985).
7 K. Yamaoka, R. Sasai, and N. Ikuta, *Chem. Lett.*, **1994**, 563.
8 K. Yamaoka, M. Tanigawa and R. Sasai, *J. Chem. Phys.*, **101**, 1625 (1994).
9 K. Yamaoka, K. Fukudome, S. Matsumoto, and Y. Hino, *J. Coll. Interface Sci.*, **168**, 349 (1994).
10 S. P. Stoylov, "Colloid Electro-Optics," Academic Press, New York (1991).