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Reversing-pulse Electric Birefringence of Montmorillonite Particles Suspended in Aqueous Media[1)]

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Reversing-pulse electric birefringence of montmorillonite was measured in aqueous media at 25 ℃ and at 633 nm. The counterion for this clay was either Na^+ or Mg^{2+}. The electric field orientation of the disk-shaped particle was due to ion-induced dipole moments but not due to permanent dipole moment.

Montmorillonite is a major constituent of the bentonite clay and easily dispersed in aqueous media. The particle shape is planar and disklike in the dry state, but not well-established in the dispersed state. Using a square-pulse electric birefringence (EB) technique, Shah and his coworkers showed that the clay suspension could be oriented by applied electric fields, and that the sign of the steady-state birefringence at extremely low fields reverses from negative to positive with an increase in field strength E.[2)] Shah explained this orientation behavior in terms of the disklike shape of montmorillonite, proposing that the particle possesses the electric permanent dipole moment μ_3 along the symmetry axis 3, normal to the disk plane, and the field-induced dipole moment $\Delta\alpha E$, where $\Delta\alpha$ $(= \alpha_{33} - \alpha_{11})$ is the electric polarizability anisotropy.[3)]

Recently, Yoshida *et al*. questioned Shah's proposal and suggested the absence of "a permanent dipole moment", by studying the steady-state EB of montmorillonite dispersed at very dilute concentrations.[4)] For elucidation of the contribution of the permanent dipole moment to field orientation of the clay, reversing-pulse electric birefringence (RPEB) is one of the most direct methods.[5-7)] RPEB measurements of montmorillonite particles can shed light on the nature of electric moments and the hydrodynamic size in aqueous media. From the quantitative analysis of observed RPEB profiles, we could verify for the first time that the clay particle should possess no intrinsic permanent dipole moment directed normal to the plane of disklike layers.

A montmorillonite (K10) sample, purchased from Aldrich Chemical Co., was suspended in distilled water and then settled on standing.[8)] The supernatant was recovered and subjected to sonication at 0 ℃ for 40 min at a power level of 200 W, in order to assist homogeneous dispersion in water. The sonicated clay suspension (22.6 $\mu g/cm^3$) was centrifuged for 10000 rpm at 20 min to remove undesired larger particles. The counterion of the clay was converted exclusively either to sodium ion, by dialyzing the suspension against 0.2 M (mol/dm^3) NaCl (3 days) and then distilled or salt-containing water (3 days; totally 6 dm^3), or to magnesium ion (0.2 M $MgCl_2$, additional 9 days). RPEB measurements were performed at 25 ℃ and at 633 nm on a laser RPEB instrument,9) by using a newly constructed reversing-pulse generator. This bipolar double-pulse generator system utilizes two Hitachi K534 FET transistors, the overall time constants being less than 150 ns. The system can deliver a pulse with a variable duration up to ca. 1 s and maximum voltage of ± 300 volts to an ionic solution containing about 0.2 M NaCl.8)

Figure 1 shows some typical RPEB signals of sodium montmorillonite suspension. At very low fields, the sign of the steady-state phase retardation $\delta(\infty)$ is negative (d), but it changes to positive with an increase in field strengths (c and b). Signal (d) shows a dip in the buildup and a second deeper dip in the reverse. This is a peculiar feature that was predicted,5)

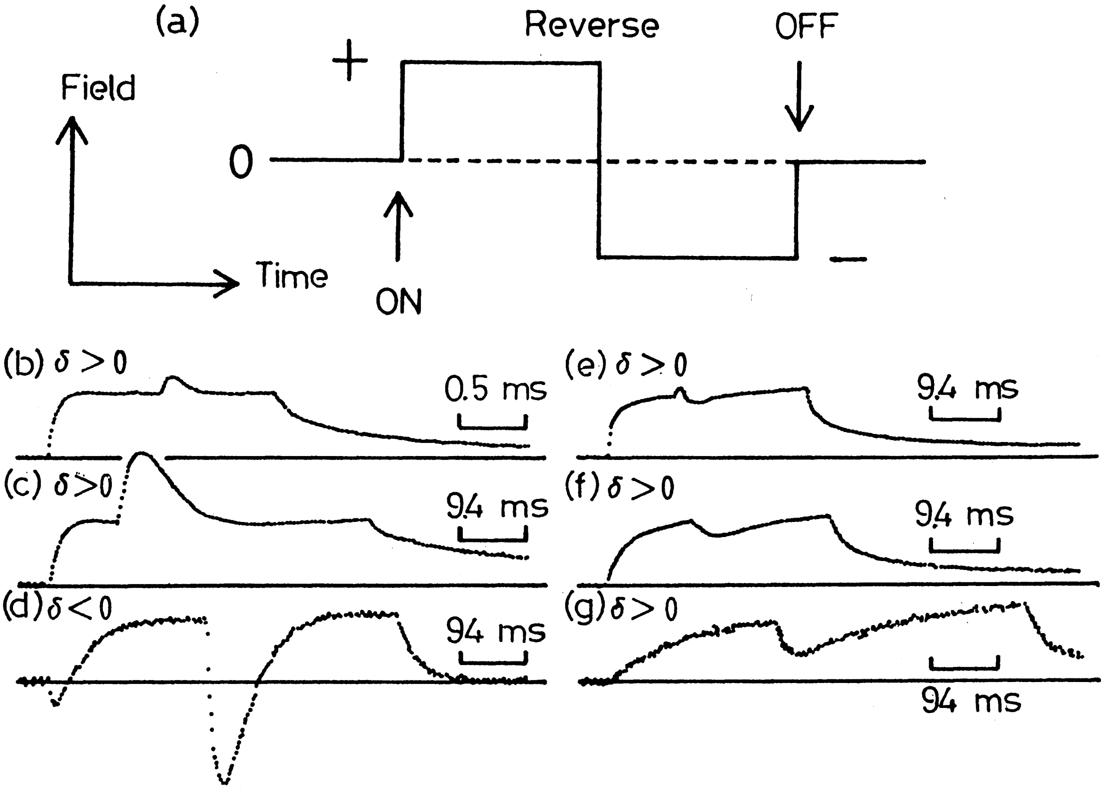

Fig. 1. RPEB signal profiles for montmorillonite particles suspended in aqueous media. (a) : a schematic reversing-pulse pattern. Counterions: Na^+ (b, c, d) and Mg^{2+} (e, f, g) without added salt. E in V/cm: (b) 19300, (c) 247, (d) 27, (e) 437, (f) 219, and (g) 34. Signals were represented in terms of the normalized optical phase retardation $\delta(t)/\delta(\infty)$ with the sign of $\delta(t)$. Arrows indicate the positions of applied pulse.

but has not been observed so far. Signals (c and b) show a hump in the reverse, as reported for a polyelectrolyte.7) The lowest montmorillonite concentration (6.5 μg/cm^3) is *ca.* a hundredth of that used by Shah3) but in the same order of magnitude as employed by Yoshida *et al.*,4) where aggregation is unlikely to occur, as judged from nearly constant relaxation times, $\langle \tau \rangle_{\mathrm{EB}}$, which was evaluated from the decay signal (Fig. 2). An increase in ionic strength does induce the aggregation of disklike particles. The sign reversal of $\delta(\infty)$ occurs at an extremely low field of 40 V/cm for a salt-free suspension but is shifted to a higher field of 120 V/cm in the presence of 0.1 mM NaCl. This sign reversal is due to the change of the direction of field orientation of the disk-shaped particle from the axis normal to the disk plane at very low fields to the plane itself at high fields.3,7) We can now conclude with confidence that the sign reversal is intrinsic to the Na^+-montmorillonite suspension but not merely due to aggregated particles.

The RPEB signal profile of the Mg^{2+}-suspension (e, f, and g) is normal with a monotonic buildup and a minimum in the reverse, as often encountered with some polyelectrolytes.6,7,10) Interestingly, the sign of $\delta(\infty)$ never reverses, remaining always positive regardless of field strengths (e, f, and g) and ionic strengths. The relaxation times for the Mg^{2+}-particle are long as compared with the values for Na^+-particle (Fig. 2), indicating that Mg^{2+}-montmorillonite particles tend to aggregate in suspension. The appearance of the dip or minimum in the reverse of RPEB signals has been attributed to the presence of the permanent dipole moment and/or the slowly induced ionic dipole moment due to counterion displacement along the direction of field orientation.5-7,10) Hence, a quantitative analysis is needed to verify whether or not aggregated Mg^{2+}-particles possess the intrinsic permanent dipole moment.

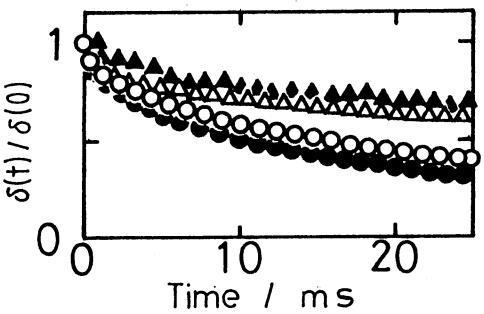

Fig. 2. Normalized decay signals, $\delta(t)/\delta(0)$, for montmorillonite suspensions with Na^+ (○, ●) and Mg^{2+} (△, ▲) at ionic strengths of 0 (○, △) and 0.0001 (●, ▲). $\langle \tau \rangle_{\mathrm{EB}}$ values in ms:6,9) 35 (○); 30 (●); 44 (△); 86 (▲).

Tinoco and Yamaoka derived an RPEB theory for the field orientation of ionic polymers with the permanent dipole moment and the electronic or ion-induced dipole moment, i.e., the β, γ-mixed dipole orientation, where $\beta^2 \fallingdotseq (\mu_3 E/kT)^2$ and $\gamma = \Delta\alpha E^2/2kT$ (and k and T have usual meaning).5)

Buildup: $$\Delta_{\mathrm{B}}(t) = \left(\frac{\delta(t)}{\delta(\infty)}\right)_{\mathrm{B}} = 1 - \frac{3}{2}\left(\frac{1}{Q+1}\right)\mathrm{e}^{-2\Theta t} + \frac{1}{2}\left(\frac{Q-2}{Q+1}\right)\mathrm{e}^{-6\Theta t} \qquad (1)$$

Reverse: $$\Delta_{\mathrm{R}}(t) = \left(\frac{\delta(t)}{\delta(\infty)}\right)_{\mathrm{R}} = 1 - \left(\frac{3Q}{Q+1}\right)\left(\mathrm{e}^{-2\Theta t} - \mathrm{e}^{-6\Theta t}\right) \qquad (2)$$

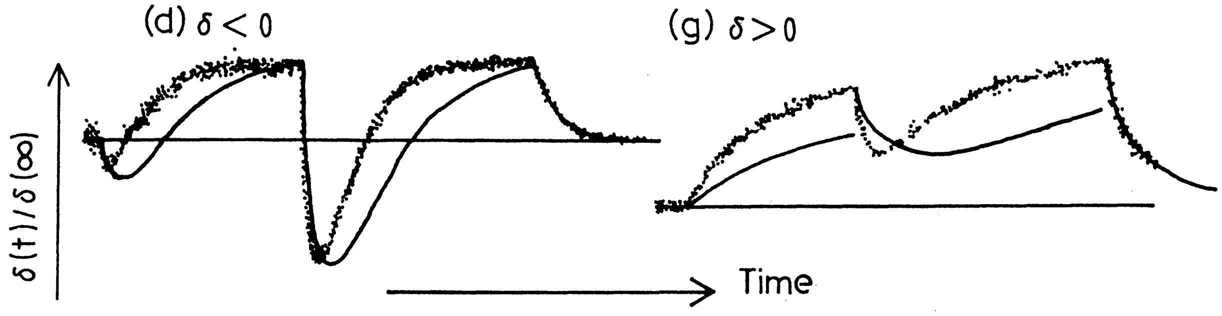

Fig. 3. Comparison of theoretical curves (solid lines) with normalized RPEB signals (dots) at very low fields (d and g), as shown in Fig. 1.

where $Q = \beta^2/2\gamma$ and Θ is the rotary diffusion constant of the whole particle about the symmetry axis. By substituting the Θ ($= 1/6\tau$) values to Eqs. 1 and 2 and by selecting the best values for the parameter Q (-1.95 for d and $+1.37$ for g in Fig. 1), the buildup and reverse signals were simulated.

Figure 3 shows the result of fitting of theoretical RPEB curves to observed signals (d) and (g) for Na^+- and Mg^{2+}-montmorillonite at very weak fields. The negative Q value indicates that the $\Delta\alpha$ value is negative, specifying in turn a disklike shape for dispersed particles. Indeed, these calculated RPEB curves completely fail to reproduce the observed buildup and reverse processes, no matter how adjusted Q values may be. It is now clear that Eqs. 1 and 2 cannot represent the field-on RPEB behavior of montmorillonite particles in aqueous media. We, therefore, conclude that these Na^+- and Mg^{2+}-particles should possess no intrinsic permanent dipole moment against the original proposition by Shah.3) We were able to demonstrate in this Letter the usefulness of RPEB techniques in colloidal dispersions to elucidate the electric and hydrodynamic properties.

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