# Electric Birefringence of Na-Montmorillonite Suspended in Water-Ethanol Mixed Solvent[1]

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In order to clarify the effect of ethanol on the electrooptic and hydrodynamic properties of Na-montmorillonite (Na-M), the transient and steady-state electric birefringence (EB) of Na-M was measured in the water-ethanol mixed solvent system at a low particle concentration and at various ethanol contents. The hydrodynamic size of Na-M was decreased at ca. 10 vol% in EtOH content. This first EB attempt strongly supports the notion that the Na-M layers are delaminated by the adsorption of EtOH molecules onto the Na-M disk.

The montmorillonite particle, a kind of cation-exchangeable inorganic polymer with the stacked layer structure,[2] adsorbs transition-metal ions, cationic organic compounds, and so on.[3] Once intercalated into intralayers of the clay, these adsorbates display various unique reactions and properties, e.g., cyanosilylation of carbonyl compounds, photochemical process, and photochromism.[3] It is well known that these phenomena are affected strongly by the condition of the solution to which the clay particle is dispersed.[4] For example, the effect of higher alcohols (e.g., stearyl alcohol) on the physicochemical properties of clay has been widely studied.[3] The important results of these works are as follows. (1) An orientation of alkylammonium ion on clay plate changes from parallel to perpendicular in the presence of higher alcohols.[3] (2) Higher alcohols are intercalated into clay layers by the charge-dipole interaction between exchangeable cation and the alcohol molecule.[3] Such a detailed study, however, has not been done on the effect of lower alcohols. In order to clarify the effect of solvation on the electrical, optical, and hydrodynamic properties of sodium-montmorillonite (Na-M) in the water-ethanol mixed solvent system, electric birefringence (EB) techniques are now utilized for Na-M suspension in aqueous media at various ethanol contents, [EtOH]. This electrooptical method is powerful for determining the aforementioned properties of biopolymers, dispersed particles, and colloidal systems.[5,6] To our knowledge, the present work is the first attempt to apply the EB techniques to the investigation of the solvation of Na-M particles.

Details on the preparation of the Na-M stock suspension were the same as given elsewhere.[7,8] The average diameter of Na-M particles was determined to be ca. 300 nm by the electron microscopic observation and EB measurements.[7,8] The Na-M samples for the present EB measurement were prepared from a single stock suspension dispersed in water, first by mixing with appropriate amount of distilled EtOH and then by diluting with double-distilled water always to the final particle concentration of 0.029 gdm$^{-3}$. The [EtOH] of Na-M suspension was varied in the 0—90 vol% range. The EB measurement was performed at 633 nm and 25 ℃ by using a single square-pulse instrument, as previously described.[8,9] The applied field strength was varied to 0.8 kVcm$^{-1}$ for the high degree of orientation of particles. The EB measurement had good reproducibility and the error involved in each experimental value was less than 2—3 %.

The steady-state EB ($\Delta n_{st}$) of suspension was expressed as $\Delta n_{st} = 2\pi C_v \Delta g \Phi(E)/n$, where $n$ is the refractive index in the absence of electric field, $C_v$ is the volume fraction of dispersed particles, and $\Delta g$ (= $g_3 - g_1$) is the optical anisotropy factor (the subscripts 3 and 1 denote the symmetry and transverse axes, respectively).[5,6] The orientation function $\Phi(E)$ describes the degree of orientation of the dispersed particles by the applied electric field $E$. Therefore, such electrical parameters as the magnitude and kind of electric dipole moments, can be estimated from the field dependence of $\Delta n_{st}$ with the theoretical orientation function. The optical anisotropy of dispersed particles can also be determined from the $\Delta n_{st}$ value at infinite high fields. In the present work, the theoretical orientation function for disklike particle was used under the assumption that the field orientation is induced by the permanent, saturable, and unsaturable induced dipole (PD-SUSID) moments.[7] The optical phase retardation $\delta_{st}$, detected in EB measurement, is related to $\Delta n_{st}$ by $\Delta n_{st} = \lambda\delta_{st}/2\pi d$,

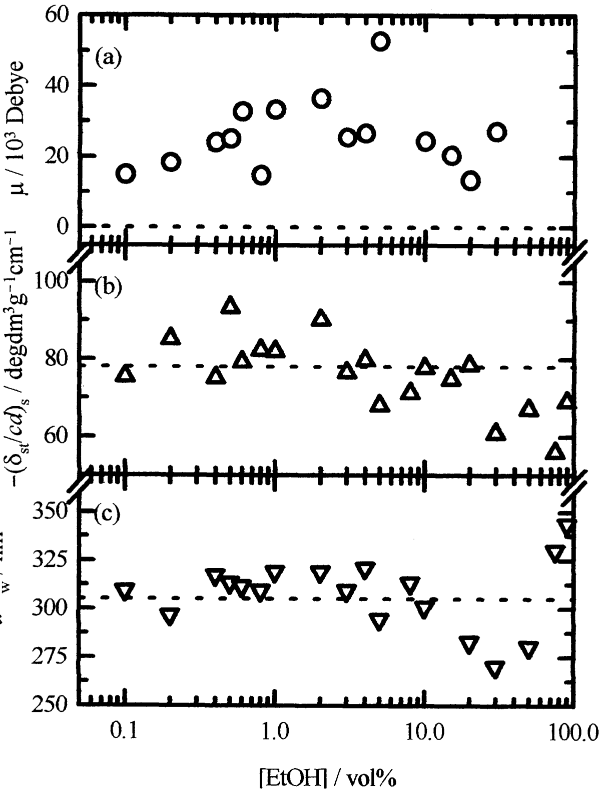

**Figure 1.** Dependence of (a) the permanent dipole moment $\mu$, (b) the intrinsic phase retardation $(\delta_{st}/cd)_s$, and (c) the average diameter $\langle d \rangle_w$ of the Na-M particles on [EtOH] in the water-EtOH mixed system. Broken lines indicate the $\mu$, $(\delta_{st}/cd)_s$, and $\langle d \rangle_w$ values in aqueous media without added EtOH.

where $\lambda$ is the wavelength of incident light, and $d$ is the optical path length of a Kerr cell.

The field-strength dependence of steady-state EB was analyzed by the curve-fitting method with the PD-SUSID orientation function for the disklike particle.[7] Figure 1 shows the dependence of the electrooptic and hydrodynamic parameters on [EtOH]. Surprisingly, the permanent dipole moment $\mu$ appears in the water-EtOH mixed solvent system and increases with the addition of EtOH by less than ca. 10 vol%, as shown in Figure 1a. Since the Na-M particle as such possesses no permanent dipole moment in aqueous media, the field orientation is solely due to the saturable and unsaturable induced dipole moments in the absence of EtOH.[7,8] The appearance and increase of the contribution of $\mu$ should, therefor, be taken as evidence that polar EtOH molecules are adsorbed mostly by orienting the long axis perpendicular to the Na-M plane and layers in an ordered manner. Then, the $\mu$ value seems to decrease with a further increase of [EtOH] (≥ ca. 10 vol%). This result suggests that EtOH molecules are irregularly adsorbed onto Na-M at higher [EtOH] values.

The intrinsic quantity, $(\delta_{st}/cd)_s$, is related to the limiting specific phase retardation per path length at infinitely high electric fields, $(\delta_{st}/cd)_\infty$, where $c$ is the mass concentration, by $(\delta_{st}/cd)_s = (\delta_{st}/cd)_\infty \times (1/\Phi(\infty))$, where $\Phi(\infty)$ is the orientation function at infinitely high fields and equal to $-1/2$ for disklike particle.[7] The value of $(\delta_{st}/cd)_s$ represents the magnitude of the optical anisotropy of dispersed particles. As shown in Figure 1b, the absolute magnitude of $(\delta_{st}/cd)_s$ seems to be constant at ca. 78 $\mathrm{degdm^3g^{-1}cm^{-1}}$ up to ca. 20 vol%, which is close to that in aqueous media without added EtOH. This result indicates that the optical anisotropy of clay particle does not vary with adsorbed EtOH (≤ ca. 20 vol%), because the optical anisotropy of EtOH molecule is very small. At [EtOH] ≥ ca. 20—30 vol%, the $|(\delta_{st}/cd)_s|$ value decreases and becomes smaller than that in EtOH-free suspension, suggesting that the Na-M particles form random aggregates.

The field-off EB decay signal yields information on the hydrodynamic size of dispersed particle. Details on the analysis of the decay signal were given elsewhere.[8] The weight-average diameter $\langle d\rangle_w$ of a very thin oblate ellipsoid particle was calculated with the expressions, $\langle d\rangle_w = [9kT\tau_w/2\pi\eta_0]^{1/3}$, where $\eta_0$ is the viscosity of solvent, $k$ is the Boltzmann coefficient, and $T$ is the absolute temperature.[8] The weight-average rotational relaxation time $\tau_w$ was evaluated from the area of decay signal at infinitely high fields.[5,6,8] Figure 1c shows the dependence of $\langle d\rangle_w$ on [EtOH], together with broken line for the $\langle d\rangle_w$ value without added EtOH. In the low [EtOH] range (≤ ca. 10 vol%), $\langle d\rangle_w$ values are close to that in aqueous media without added EtOH ($\langle d\rangle_w$ = ca. 305 nm). This result suggests that EtOH molecules may be adsorbed onto the surface of clay layers, but not intercalated into the clay layers. Values of $\langle d\rangle_w$ rapidly decreases in the vicinity of 10 vol%, where the $\mu$ value starts decreasing and the optical anisotropy becomes comparable to that in EtOH-free media. This decrease in $\langle d\rangle_w$ suggests that the Na-M layers are delaminated by the adsorption of EtOH molecules onto the Na-M disk. In the high [EtOH] range (≥ ca. 70 vol%), values of $\langle d\rangle_w$ again increase and become larger than the $\langle d\rangle_w$ in aqueous media. This result implies that the Na-M aggregation occurs by the adsorption of excess EtOH molecules onto Na-M particle, since the surface becomes more hydrophobic. The aggregated Na-M particles formed in high [EtOH] region are probably unable to have a regular structure, i.e., the *card-house structure*, as judged from the decrease in optical anisotropy in this [EtOH] range.

This preliminary study presents the possibility that EtOH molecules are not intercalated into clay layers, but adsorbed in parallel orientation to the surface of clay disk, and that the clay layers are delaminated by adding EtOH, as a result of the adsorption of EtOH onto the clay disk. These results suggest that the structural and functional characteristics of clay minerals can be controlled by the addition of a lower alcohol. EB techniques can be applied successfully to study the swelling and aggregation behavior of such clay systems.

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