

## ELECTRO-OPTIC INVESTIGATION OF THE PERMANENT AND INDUCED DIPOLES OF MONTMORILLONITE AS AFFECTED BY ELECTROLYTE CONCENTRATION

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**Abstract**—An electro-optic birefringence technique was employed to study the orientation mechanism of montmorillonite in an electric field. The instantaneous reversal of the field polarity produced evidence of a low voltage permanent dipole and a high voltage induced dipole. This technique was used to study the effect of electrolyte concentration on the rotational diffusion coefficient, a measure of the rate at which the particles rotate or relax, within the solution, from a preferred orientation. Thus, a measure of the immediate environment of the particles was obtained that is not an average effect for the whole system, yet allows for the full development of the clay-cation-water interactions under the experimental conditions. It was found that particle rotation could be accounted for using the measured particle size and normal water viscosity only when the double layer was fully developed, with no free ions or other perturbations. As soon as perturbations were applied, either by adding salts or applying an electric field, the measured particle size and normal viscosity would not account for the data. Either the rotating moiety has to be larger, that is, be a particle plus a water hull, or the viscosity greater, or in some cases both.

### INTRODUCTION

The electrochemical properties of clay particles and the characteristics of the surrounding ion-water atmosphere are not well understood. Yet their characteristics affect almost all systems in which clays are found. Many studies of clay-associated water have been conducted, but relatively few studies of these studies help elucidate the internal electronic or the exchangeable cation distribution. The orientation and relaxation of clay particles in an electric field, studied by determining the electro-optic birefringence of the particles, may lead to a greater understanding of the clay and clay-ion-water properties.

Clay particles in an aqueous suspension are normally in a random distribution. Upon application of an electric field across parallel electrodes in a clay suspension, the particles will adopt a preferred orientation. If a monochromatic light source is imposed upon the sample, the birefringence will increase upon orientation of the particles and decrease with return to a random state.

The mechanisms responsible for the orientation of the particles are not well known and apparently depend on the type of clay. The relaxation upon removal of the electric field follows the Benoit equation

(Benoit, 1951; Brown, 1971; Jennings *et al.*, 1970; Kahn and Lewis, 1954; Mehta, 1973; O'Konski and Haltner, 1957; O'Konski *et al.*, 1959; Shah, 1963) which relates the birefringence decay with time after initiation of relaxation.

Perrin's formula for oblate spheroids relates particle size and solution viscosity to the rate of relaxation (Kahn and Lewis, 1954; Shah *et al.*, 1963; Laffer and Posner, 1970). The data of Kahn and Lewis (1954) and Shah *et al.* (1963) have been applied in this way by Brown (1971) who determined the viscosity of the water surrounding the particle. These calculated viscosities were considerably different from normal water suggesting the possibility of nonhomogenous clay samples or inaccurate particle size determinations.

The birefringence build-up with particle orientation and subsequent decay with particle relaxation are intimately related and are affected by several factors. The rate of birefringence build-up is largely dependent upon particle size, clay concentration and pulse voltage (Brown, 1971; Kahn and Lewis, 1954; Shah, 1963; Shah *et al.*, 1963; van Olphen and Waxman, 1958). Each of these parameters may have the same net effect on birefringence. Larger particles do so by having a larger refraction differential per particle, while increased clay concentration increases the number of particles and thus birefringence. Increased voltage simply orients the particles faster.

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There appear to be at least two mechanisms responsible for the orientation of the particles. Bentonite suspensions have been extensively studied (Kahn and Lewis, 1954; Mehta, 1973; Shah, 1963; Shah and Hart, 1963; Shah and Thompson, 1963; Shah *et al.*, 1963) and demonstrate a birefringence build-up and orientation at low voltages due to an apparent permanent dipole (O'Konski and Haltner, 1956; Shah *et al.*, 1963). At higher field strengths an induced polarization develops that may cause reorientation of the particles and a subsequent change in the sign of the birefringence (Shah *et al.*, 1963). The relaxation rates are generally faster for the apparent permanent than for the induced dipole. Nontronites also exhibit different relaxation times suggesting that they too may develop induced dipoles (Uhlhorn and Gaddy, 1968).

These two types of polarization may be occurring simultaneously, but at different rates. Thus the polarization depends on the nature and ionic form of the clay, but is further influenced by the frequency, magnitude and duration of the applied field (O'Konski, 1960; O'Konski and Haltner, 1957; Sakmann, 1945; Shah *et al.*, 1963; Uhlhorn and Gaddy, 1968).

The type of polarization responsible for the birefringence of Tobacco Mosaic Virus (TMV) has been studied by rapidly reversing the polarity of the applied pulse (O'Konski and Haltner, 1956). It was concluded that the orientation of the TMV is due to an induced polarization since the birefringence remained constant during pulse reversal. Had the orientation been due to a permanent dipole moment, a visible birefringence transition would occur. O'Konski and Haltner (1957) have also studied the effect of pH and salt concentration on the birefringence of TMV, but since they worked with a buffered system their results may not be applicable to clay suspensions.

This induced and permanent polarization of clay particles demonstrates an intrinsic property of the clay that can be more closely examined with the technique of electro-optic birefringence. Studies using this technique to identify and characterize permanent and induced dipoles as affected by ion concentration are reported.

#### THEORETICAL BASIS OF BIREFRINGENCE RELAXATION MEASUREMENTS

The birefringence of certain anisotropic crystalline materials is in response to the double refraction of incident light through uniformly oriented particles. Upon removal of the orienting electric field the birefringence rapidly decays as the particles assume a random orientation. When the incident light strikes crystalline material it is vectorially divided into a parallel component and a perpendicular component with respect to

the optical axis. In the case of isotropic crystals the light passes along the two components at the same speed and thus remains in phase. As the light emerges from the crystal it forms a vector sum of the two components. This resultant light will lie in the same plane as the incident light and give no birefringence. In contrast, anisotropic crystals, such as clay platelets, contain different refractive indices with respect to the optical axis. One component of the light travels through material with a constant refractive index while the other component passes through materials with more than one refractive index. This latter component will travel at a different speed than the former and thus the two components will be out of phase when they reach the end of the crystal. As such, the vector sum of the two components will emerge in a different plane than the incident light.

The anisotropic crystalline properties of clay particles dictate that the incident light must pass through either of the long dimensions of the particle. Light entering the *c*-dimension of the particle will simultaneously pass through materials of the same refractive index and thus would not demonstrate birefringence. In addition the particles must be in a plane other than that of the incident light before birefringence will occur.

Light emerging from a suspension of many clay particles is elliptically polarized with the primary axis rotated at angle  $\delta/2$  to that of the original plane of polarization. If the percent transmittancy (*T*) is known as a function of time, the optical retardation ( $\delta$ ), in degrees, can be determined since

$$\delta = 2 \arcsin T^{\frac{1}{2}} \quad (1)$$

when referenced to the light intensity with parallel Polaroids and no electric field. The  $\delta$  is further related to the birefringence ( $\Delta n$ ) of the optical system by

$$\delta = \frac{\pi d}{\lambda} (\Delta n) \quad (2)$$

where *d* is the pathlength and  $\lambda$  is the wavelength of the incident light. The birefringence ( $\Delta n$ ) represents the difference ( $n_{\text{par}} - n_{\text{per}}$ ) in refractive indices of the crystal in directions parallel and perpendicular to the optical axis respectively. The rotational diffusion coefficient (*D*) in  $\text{sec}^{-1}$  can be determined to a good approximation using the Benoit (1951) equation

$$\Delta n / \Delta n_0 = e^{-6Dt} \quad (3)$$

where  $\Delta n_0$  is the initial birefringence and  $\Delta n$  is the birefringence at time *t*. Since the pathlength and frequency are constant for the system, substitution of equation (2) into (3) gives

$$\delta / \delta_0 = e^{-6Dt} \quad (4)$$

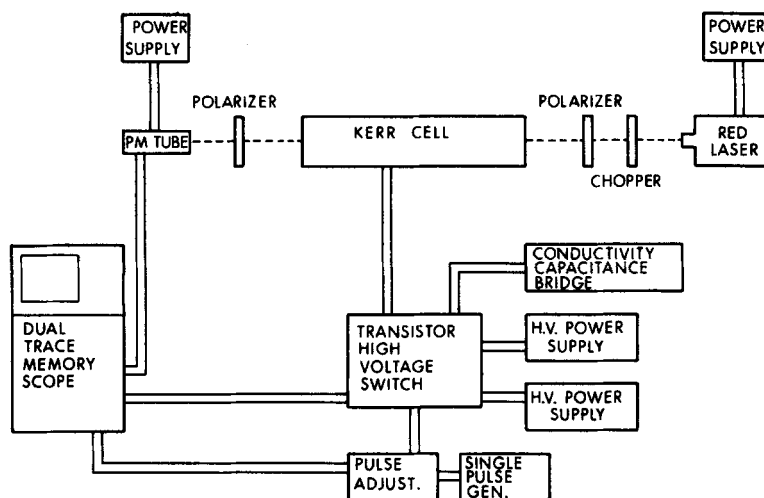


Fig. 1. Diagram of electro-optic birefringence experimental apparatus.

which can be integrated to give

$$\ln \delta/\delta_0 = -6Dt. \quad (5)$$

When  $\ln \delta/\delta_0$  is plotted as a function of time, the slope is given by  $-6D$ .

Assuming that clay particles resemble an oblate spheroid (disk) with a mean geometric semimajor axis  $r$ , the viscosity of the surrounding water can be calculated using Perrin's equation (Shah *et al.*, 1963),

$$r^3 = (3/32)(kT/\eta D) \quad (6)$$

where  $\eta$  is the viscosity of water,  $k$  the Boltzman constant,  $T$  the absolute temperature and  $D$  the rotational diffusion coefficient.

## EXPERIMENTAL

### Electrical

The diagram of the optical bench and associated equipment is shown in Fig. 1. The monochromatic light source was a Metrologic model ML-680 laser with a 1.5 mW output at a wavelength of 6328 Å. Two rotatable Polaroids were positioned on the optical bench at the ends of the Kerr cell. The Polaroids were adjusted so that the plane of incident light was at an angle of 45° to horizontal and would be cancelled by the second Polaroid if there were no birefringence. The main body of the Plexiglas cell was fitted with Pyrex end windows. The gold plated electrodes, 7.0 cm in length and with a vertical dimension of 0.94 cm, were placed lengthwise along the inside of the cell wall. The electrodes were separated by 0.4 cm with Teflon spacers. Pulsed d.c. fields of variable amplitude,

duration, frequency, and polarity were supplied to the electrodes from a pulse generation system. Low amplitude pulses from the Rutherford model B14 pulse generator, used to regulate the pulse duration, which subsequently triggered the transistorized high voltage switch. The high voltage switch regulated the flow of current from the variable high voltage power supplies to the electrodes. This specially fabricated switch and the two high voltage power supplies facilitated the instantaneous reversal of the electrode polarity. The conductivity of the suspension in the cell was monitored between pulses with a Wayne Kerr model B641 autobalance universal bridge. Light transmittance through the optical system was monitored with an RCA 5819 photomultiplier tube powered by a specially constructed high voltage d.c. supply. The light beam was modulated with a chopper to obtain reference transmittance values in the absence of an applied field. Output from the photomultiplier and the applied pulser were simultaneously displayed on a Tektronix type 5103N oscilloscope equipped with a type 5A18N dual trace amplifier and a type D13 dual beam storage component.

The optical bench and associated equipment, except for power supplies and instruments, were isolated from stray light by enclosing them in a plywood box.

### Clay preparation

The  $<2 \mu\text{m}$  fraction of a Wyoming montmorillonite\* was separated by sedimentation. Homoionic  $\text{Na}^+$ -clays were prepared by three rinses with 1 N NaCl followed by four rinses with distilled water in an International model B-20 centrifuge. Size fractionated samples were prepared from the clay stock

\* Wyoming Montmorillonite No. 25, Ward's Natural Science Establishment, Inc., Rochester, New York.

using a progressive centrifugation sequence. The stock clay suspension was placed in 50 ml tubes and spun at 650 *g* for 5 min. The supernatants were transferred to additional tubes for further centrifugation. The resulting sediments were resuspended and subjected to another spin of 650 *g* for 5 min to reduce the possibility of particle entrapment. The supernatant was added to that of the previous spin. The resulting sediments were labeled fraction 3. The combined supernatants were then spun at 1750 *g* for 5 min. The supernatants were removed, the sediments resuspended and again spun at 1750 *g* for 5 min with the remaining sediment being labeled fraction 4. The combined supernatants were taken through the same procedure at 4500 *g* for 5 min, 9000 *g* for 20 min and 17,000 *g* for 20 min giving fractions 5, 6 and 7 respectively. The final supernatant was visually free of colloids. The clay concentration of the various fractions were determined gravimetrically.

The particle size of each clay fraction was determined from micrographs taken with a RCA model EMU-4 electron microscope using a magnification of 14,350 $\times$ .

### Procedures

Birefringence relaxation curves were obtained on the oscilloscope screen for each sample by manually triggering the pulse generation circuit. Values as a function of time after the applied pulse were recorded and committed to computer cards. The computer statistically calculated the rotational diffusion coefficient for each birefringence relaxation trace. The correlation coefficient of the rotational diffusion coefficient was 0.97 or better in all cases.

All the results are for size fraction 6 which had an average particle dia. of  $0.294 \pm 0.018 \mu\text{m}$ . A clay concentration of 0.071 per cent and a pulse duration of 10 msec were used in all experiments unless otherwise noted. Each sample was thoroughly dispersed with a Savant model 500 insonator prior to analysis.

### RESULTS

Aqueous suspensions of bentonite particles are thought to orient in an electric field due to two mechanisms, a permanent and an induced dipole, whose characteristics can be elucidated by instantaneously reversing the polarity of the applied electric field. The relative extent of birefringence of a sample depends on the particle orientation with respect to the polarized incident light: No birefringence occurs when the particles lie in the same plane as the incident light or when the light passes through the *c*-axis of the particle. Thus, whenever the *a*- or *b*-axis are at an angle

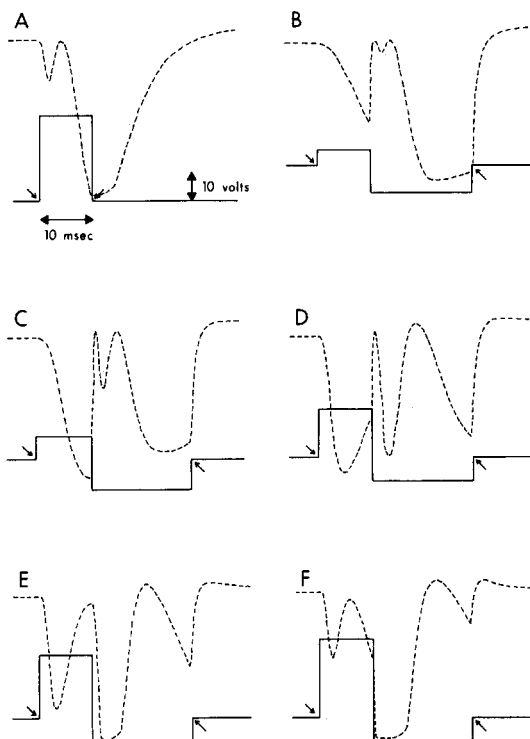


Fig. 2. Electro-optic birefringence traces (---) in response to a positive electric field (—) (A–F) followed by a negative electric field (B–F). The arrows indicate pulse initiation (→) and termination (←). The scale for applied voltage and pulse duration are constant in all cases. A decrease in magnitude of the dashed line shows an increase in birefringence. The initial level of the electric field line indicates no applied field, lines above and below this level represent positive and negative electric fields, respectively. Note the differences in the magnitude of the positive electric field.

of 45° to the plane of incident light there will be birefringence and a signal on the oscilloscope.

Figure 2(A) shows a typical birefringence trace for montmorillonite. Upon application of voltage (30 V in this case) there is some orientation and therefore birefringence. But this is short-lived and is overcome by a second preferred orientation as indicated by the birefringence going to zero. The second orientation quickly predominates giving a birefringence maximum until termination of voltage at which time the particles assume a random state or orientation as shown by the decrease in birefringence.

The effect of reversing the pulse polarity, with low applied voltages, is shown in Fig. 2(B). With a low voltage the particles orient more slowly so there is a slow but steady increase in birefringence until the pulse is reversed. Upon reversal there is an instantaneous loss of birefringence followed by a second orientation and birefringence. Figures 2 (C and D) show that if the voltage is reversed anywhere along the first birefringence

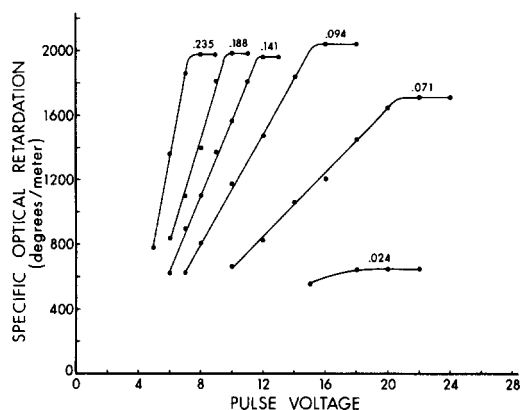


Fig. 3. Specific optical retardation of six concentrations (% clay by weight) of fraction 6 Na-montmorillonite as a function of applied field.

peak there is an instantaneous loss of birefringence followed by two birefringence peaks. The fast reversal of this first peak suggests that this orientation is due to a permanent dipole.

Figures 2 (E and F) demonstrate the effect of voltage reversal during the second peak of Fig. 2(A), that which is believed to be due to an induced dipole. As voltage is increased (Fig. 2E) there is sufficient time for the first mechanism to completely orient the particles before the second mechanism dominates. Now upon voltage reversal, instead of a decrease in birefringence there is an increase, which reaches a maximum. The maximum birefringence does not persist because the reversed voltage is not great enough to hold the particles in that preferred orientation so they relax going through a  $45^\circ$  plane (same plane as the incident light) giving zero birefringence before they are oriented again due to the low voltage mechanisms of Fig. 2(B). Figure 2(B) shows the same events upon pulse reversal at a different stage of voltage application.

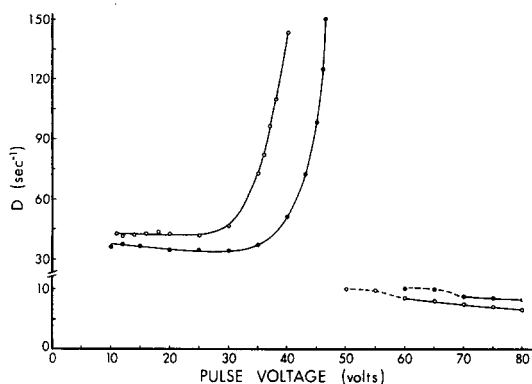


Fig. 4. The rotational diffusion coefficient ( $D$ ) of Na-montmorillonite as a function of pulse voltage with specific conductance 0.04 (●—●) and 0.08 (○—○)  $\text{m}\Omega \text{cm}^{-1}$ .

The optimum clay concentration for birefringence relaxation was chosen to be 0.071 per cent clay by weight (Fig. 3). Above this concentration the photomultiplier tube became saturated before all of the particles were oriented, but at more dilute concentrations the accuracy of the system was reduced. Double layer theory suggests that no particle interaction would be expected at a clay concentration of 0.071 per cent where adjacent particles are in excess of  $3 \mu\text{m}$  apart (van Olphen, 1963).

The rate of birefringence decay or the rotational diffusion coefficient ( $D$ ) at low electrolyte concentration remains nearly constant at low voltages (Fig. 4) while oriented due to the permanent dipole of the particle. At higher voltages the induced dipole begins to overcome the permanent dipole orientation as seen by the increase in  $D$ . Once the particles are completely oriented according to an induced dipole, the rate of relaxation is again nearly constant but at a lower rate than for the permanent dipole orientation. The dashed line represents the rate of relaxation before total preferred orientation is achieved.

The concept of an induced dipole is substantiated by examining  $D$  as a function of pulse duration at constant voltages (Fig. 5). If a threshold voltage were required to initiate induction, the  $D$  should be constant with pulse duration for a given voltage, but this is not the case which suggests a continuous ion redistribution and the development of an induced dipole.

The specific conductivity of various concentrations of NaCl were determined. This relationship was then used to determine the approximate salt concentration of the clay suspension from a measurement of their conductivity.

Since salt concentration has a marked effect on double layer thickness it might be expected to affect  $D$ , the rotational diffusion coefficient. That it does so is shown in Fig. 6. Using the range of  $D$ 's determined in Fig. 6 and assuming a viscosity of 1 cP, Perrin's equation was

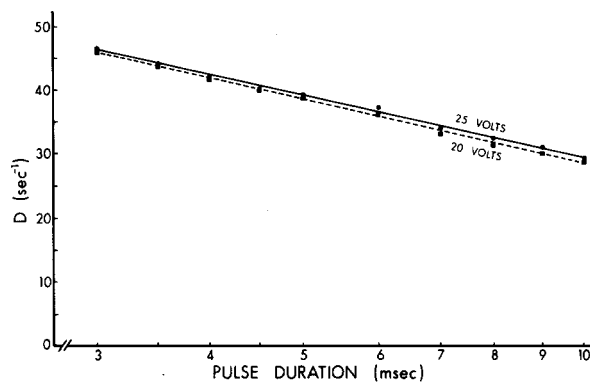


Fig. 5. The rotational diffusion coefficient ( $D$ ) of Na-montmorillonite at two voltages as a function of pulse duration. (Specific conductance = 0.08  $\text{m}\Omega \text{cm}^{-1}$ .)

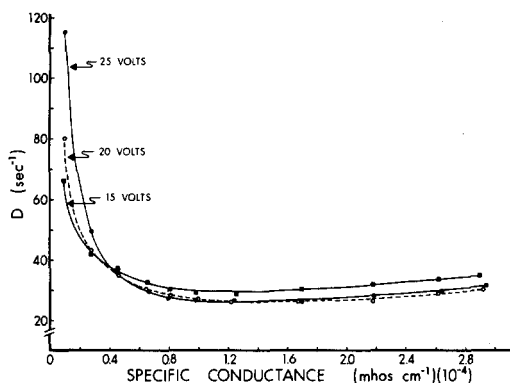


Fig. 6. The rotational diffusion coefficient ( $D$ ) for Na-montmorillonite at three voltages as a function of the specific conductance of the suspension.

used to calculate the particle size necessary to account for the data (Fig. 7). It is seen that the actual particle size will only account for the very high  $D$  of about  $110 \text{ sec}^{-1}$ . All other  $D$ 's would require a larger particle than actually present.

By using the specific conductance values and the data of Fig. 6 approximate concentrations were determined. These were then used to calculate a double layer thickness as a function of salt concentration (Fig. 8). From Fig. 6 experimental  $D$ 's at various salt concentration for 25 V, were chosen. These  $D$ 's were then applied to Fig. 7 to obtain a particle dimension. The difference between the true particle size ( $0.294 \mu\text{m}$ ) and that needed to account for the  $D$ 's were plotted in

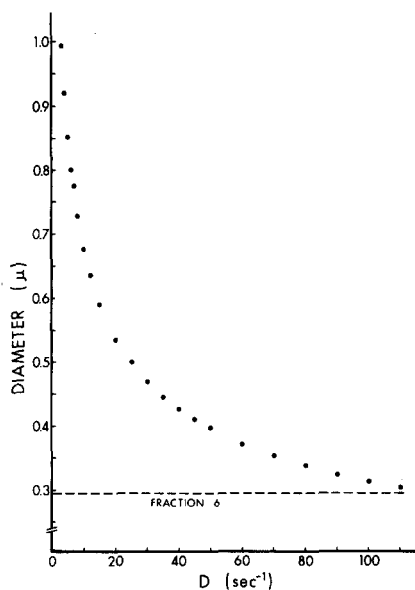


Fig. 7. The relationship between particle size and  $D$  as determined from the Perrin equation. Measured  $D$ 's were used, a viscosity of 1 cP was assumed and the particle size determined.

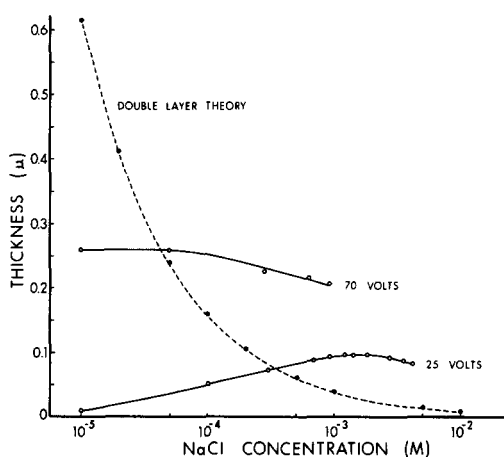


Fig. 8. The theoretical double layer thickness as a function of salt concentration (----) and the additional particle size needed to account for the experimentally determined  $D$ 's (Fig. 7) assuming a viscosity of 1 cP (—). The double layer thickness  $x$ , was calculated using

$$\psi = \frac{4\pi\sigma}{DK} e^{-Kx}$$

where  $\psi$  is approaching zero, the surface charge density ( $\sigma$ ) =  $3.62 \times 10^4 \text{ e.s.u. cm}^{-2}$  (Davidtz, 1968)  $D$  is the dielectric and  $K$  is the Debye-Huckel constant.

Fig. 8. Similar calculations were made for 70 V which is in the induced dipole range.

Since the cation-water shell would not be expected to exceed that predicted by the double layer theory, the viscosity assumed in Perrin's equation must be greater than that of normal water at salt concentration above  $4 \times 10^{-4} \text{ M}$  (Fig. 8). Substitution of the measured particle size plus the theoretical double layer thickness and the  $D$ 's (Fig. 6) into Perrin's equation shows the viscosity as a function of salt concentration (Table 1).

Table 1. The calculated viscosity from Perrin's equation as a function of salt concentration assuming the theoretical double layer thickness ( $x$ ) and the measured rotational diffusion coefficient ( $D$ )

NaCl concentration (M)	$D$ ( $\text{sec}^{-1}$ )	$x$ ( $\text{\AA}$ )	$\eta$ (cP)
$3.7 \times 10^{-4}$	36.5	725	0.999
$4.60 \times 10^{-4}$	34.5	634	1.200
$6.25 \times 10^{-4}$	31.0	525	1.566
$7.80 \times 10^{-4}$	28.8	458	1.868
$9.50 \times 10^{-4}$	27.4	405	2.134
$1.25 \times 10^{-3}$	26.5	341	2.449
$1.58 \times 10^{-3}$	26.5	294	2.650
$2.23 \times 10^{-3}$	26.5	237	2.925
$2.87 \times 10^{-3}$	27.5	201	3.004
$3.51 \times 10^{-3}$	29.0	176	2.980
$4.15 \times 10^{-3}$	30.9	158	2.891

## DISCUSSION

The rotational diffusion coefficient has units of reciprocal time, and is thus a measure of the rate at which the particles return to random orientation. Or, it can be thought of as the rate at which particles rotate, the larger the numerical value of  $D$  the faster the rotation. Thus  $D$  and its use in Perrin's equation should be indicative of the particle's environment.

The orientation of montmorillonite particles as demonstrated in Fig. 2 is due to a low voltage mechanism attributed to the permanent dipole characteristics of the particle. At higher voltages a second mechanism overcomes the first and orients the particles perpendicular to the preferred low voltage orientation. The immediate loss of birefringence upon pulse reversal at low voltages suggests that the charge in the clay which results in orientation is relatively fixed and for the particle to realign in the reversed field it has to rotate  $180^\circ$ . This is in contrast to the effects of pulse reversal at higher voltages. Here the orientation is enhanced indicating that a redistribution of ions and/or electrons is the cause of the dipole and that this is faster than the time of pulse reversal.

If the above interpretation is correct, results presented by Schepers *et al.* (1974) suggest that the permanent dipole is related to octahedral iron content. The induced dipole is likely related to a redistribution of the exchangeable cations resulting in a skew of cations with an increase in cation content at the clay edge closest to the negative electrode leaving a greater effective net negative charge on the other end. This explanation does not involve redistribution of the internal clay electrons but this effect can not be ruled out. The literature suggests (O'Konski, 1960) that an induced dipole will most likely form across the longest axis. Although the particles used in this study were uniform in dimension (i.e. disk-shaped and approximately monodisperse), this fact is probably of importance for rod-shaped particles.

The orientation mechanism also governed the rate of particle relaxation (Fig. 4). At low voltages  $D$  was nearly constant until the induced dipole began to predominate as seen by the rapid rise in  $D$ . When the particles had reached the preferred induced orientation  $D$  was again nearly constant but had a lower value. Perrin's equation would attribute this difference to a change in particle size or viscosity. An increase in salt concentration did not alter the shape of the curves, but caused a decrease in  $D$  at low voltages and an increase at high voltages. This suggests that at low voltages and low salt concentration the particles can turn within their skew of cations, but at higher salt concentration the skew of cations is compressed increasing the clay-

cation interactions to such an extent that both the clay and the cations rotate, increasing the effective particle size and reducing  $D$ . The solid lines in Fig. 8 support this idea. At the lowest salt concentration used (Fig. 8, 25 V) the actual particle size accounted for the determined  $D$ . At salt concentration of about  $4 \times 10^{-4}$  M, the double layer size accounted for the measured  $D$ . Up to this point the double layer size was much greater than the rotating moiety suggesting particle rotation within the double layer. Beyond  $4 \times 10^{-4}$  M the double layer size is too small indicating a pronounced increase in viscosity. This increase in viscosity (Table 1) reaches a plateau at about  $2 \times 10^{-3}$  M NaCl beyond which the increased double layer suppression and clay-cation interactions no longer appreciably alter the viscosity. If the induced dipole is due to a rearrangement of the double layer cations it may alter the effective size of the rotating moiety. If it is assumed that the double layer ions maintain the same volume after movement as before, then approximate calculations can be made as to the shift needed to account for  $D$ . At a salt concentration of  $10^{-3}$  M, the theoretical cation-water double layer would have to undergo about a 40 per cent volume shift to account for the observed cation-water hull predicted by Perrin's equation (Fig. 8). This change may not be unreasonable but at higher salt concentration an even greater volume shift would be required which suggests the clay-associated cation-water environment may also be undergoing a viscosity change.

Similar arguments can be presented for the 70 V data; however, the higher voltages probably cause a greater cation-skew, increasing the effective particle size which may account for the generally lower  $D$ 's of the induced orientation mechanism. Upon removal of the electric pulse, the perturbed cations would be expected to rapidly distribute themselves around the particles in a uniform manner before the beginning of particle relaxation. If the relaxation rate was not affected by the 'dumb bell' shaped cation distribution, it would suggest that the viscosity must be greater than that of normal water unless the increased voltage has sufficiently perturbed the cations such that particle interactions now exist. These interactions could reduce the rate at which the cations return to a uniform distribution and account for the short term steady state birefringence of Fig. 2(F) before the low voltage permanent dipole mechanism begins to reorient the particles.

The effect of pulse duration on  $D$  (Fig. 5) demonstrates that even low voltages are capable of affecting the cation distribution by lowering  $D$  and thus increasing the effective particle size. Only at the shortest pulse duration does particle size plus double layer account for  $D$ .

The data indicate that this montmorillonite has a permanent dipole and that at higher voltages an additional dipole can be induced. If the clay-ion-water environment surrounding the particle is not disrupted by ions or an applied force field the measured particle size accounts for the determined  $D$  when Perrin's equation is used, suggesting that with a fully developed double layer the water is normal. As soon as the double layer is perturbed by adding salts or applying a field, there are interactions between the clay and the cations which are great enough that the particles now rotate with a shell. As the perturbations are increased, the interactions continue to increase and there appears to be an increase in viscosity as well as clay-ion interactions. Thus, viscosity changes would appear to be due to clay-cation interactions.

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**Résumé**—Une technique de biréfringence électro-optique a été utilisée pour étudier les mécanismes d'orientation de la montmorillonite dans un champ électrique. L'inversion instantanée de la polarité du champ fournit la preuve de l'existence d'un dipole permanent à basse tension, et d'un dipole induit à haute tension. Cette technique a été utilisée pour étudier l'effet de la concentration en électrolyte sur le coefficient de diffusion rotationnel, qui est une mesure de la vitesse de la rotation ou de la relaxation des particules, dans une solution, à partir d'une orientation privilégiée. Ainsi, a été obtenue une mesure de l'environnement immédiat des particules, qui n'est pas un effet moyen sur l'ensemble du système, mais qui tient compte pourtant du développement complet des interactions argile-cation-eau, dans les conditions expérimentales choisies. On a trouvé que la rotation des particules pouvait être expliquée en utilisant la taille expérimentale des particules et la viscosité normale de l'eau seulement lorsque la double couche était entièrement développée, sans ions libres ni aucune autre perturbation. Dès que des perturbations étaient introduites, soit en ajoutant des sels, soit en appliquant un champ électrique, la taille expérimentale des particules et la viscosité normale ne pouvaient plus rendre compte des résultats. Ou bien l'entité en rotation doit être plus grande, c'est-à-dire que ce doit être une particule plus une enveloppe d'eau, ou bien la viscosité doit être plus grande, ou bien encore, dans certains cas, les deux effets doivent intervenir.



**Kurzreferat**—Eine elektrooptische Doppelbrechungsmethode wurde zur Untersuchung des Orientierungsmechanismus von Montmorillonit in einem elektrischen Feld eingesetzt. Die unvermittelte Umkehrung der Polarität des Feldes lieferte den Nachweis eines permanenten Dipols bei niedriger Spannung und eines induzierten Dipols bei hoher Spannung. Diese Technik wurde benutzt, um den Einfluß der Elektrolytkonzentration auf den Rotationsdiffusionskoeffizienten zu untersuchen, der ein Maß für die Geschwindigkeit darstellt, mit der die Teilchen innerhalb der Lösung aus bevorzugter Orientierung heraus rotieren oder sich entspannen. Auf diese Weise wurde ein Maß für die unmittelbare Umgebung der Teilchen erhalten, das keine Durchschnittswirkung für das Gesamtsystem darstellt, sondern der vollen Entwicklung der Ton-Kation-Wasser-Wechselwirkungen unter den gegebenen experimentellen Bedingungen Rechnung trägt. Es wurde gefunden, daß bei Benutzung der gemessenen Teilchengröße und der normalen Viskosität des Wassers die Teilchenrotation nur dann erklärt werden konnte, wenn die Doppelschicht voll ausgebildet war und keine freien Ionen oder andere Störungen enthielt. Sobald Störungen hervorgerufen wurden, sei es durch Salzzugabe oder durch Anlegen eines elektrischen Feldes, konnten die Ergebnisse nicht aus den gemessenen Teilchengrößen und der normalen Viskosität des Wassers erklärt werden. Entweder hat der rotierende Anteil größer zu sein, das heißt aus einem Teilchen und einer Wasserhülle zu bestehen, oder die Viskosität hat größer zu sein oder in einigen Fällen beides.

**Резюме** — Механизм ориентации монтмориллонита в электрическом поле изучался техникой электрооптического двойного лучепреломления. Немедленная перемена полярности поля свидетельствует о постоянном диполе низкого напряжения и о индуктированном диполе высокого напряжения. При помощи этой техники изучали действие концентрации электролита на коэффициент вращательной диффузии и меру скорости при которой частицы вращаются или релаксируют в растворе. Таким образом, получили меру непосредственных окружающих условий для частиц, которая не является действительной для всей системы, но позволяет развитие взаимодействия между глиной-катионами-водой в экспериментальных условиях. Вращение частиц объяснимо, если частицы определенного размера и вода нормальной вязкостью только при условии образования полного двойного слоя и при отсутствии свободных ионов или других возмущений. Как только начинают возмущение добавлением соли, или приложением электрического поля, определенный размер частиц и нормальная вязкость воды не объясняют данных. Одно из двух, либо вращение должно быть повышено, либо вязкость, а в некоторых случаях оба параметра.