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Investigations of the Electro-Optical Birefringence of Polydisperse Bentonite Suspensions

Abstract: Colloidal suspensions of bentonite were observed to undergo a negative electro-optical birefringence at low-voltage fields even in dilute suspensions, a phenomenon not reported earlier. Experimental results do not support a previous theory that the sign of birefringence is reversed because of various particle sizes. Although interaction between particles was found to augment this low-voltage anomalous behavior, we believe that in dilute solutions this behavior is caused by some inherent property of the bentonite micelle. This contention is supported by variation in the relaxation times in negative and positive birefringence regions, thus suggesting orientation on two different axes in the two respective regions.

Introduction

When an electric field is applied to certain anisotropic liquids or gases (e.g., nitrobenzene), they become birefringent. Thus, if a plane-polarized light beam is incident on such fluids at an angle of 45° to the field direction, the emerging light is split into two plane-polarized components with an optical retardation δ between them. (Birefringence is thus defined as the difference between the refractive index of the liquid for the components of the polarized light parallel and perpendicular to the field direction.) The resultant beam is elliptically polarized with the degree of ellipticity dependent on the value of $\delta (0 < \delta < n\pi)$. The relationship between birefringence and the optical retardation δ is

$$\Delta n = n_{\parallel} - n_{\perp} = \delta\lambda_0/2\pi l, \tag{1}$$

where λ_0 is the wavelength of light in vacuo and l is the light path length in the fluid. The magnitude of δ depends on the field strength, and in general, the birefringence increases with increasing field. This phenomenon is known as the Kerr effect.[2] It is exhibited by many liquids and gases as well as by some colloidal suspensions. Examples of some colloids that exhibit Kerr effect are tobacco mosaic virus,[10,13] nucleic acid,[10] poly-γ-benzyl glutamate,[18] and bentonite.[7,15]

In weak fields the birefringence is proportional to the square of the field strength, and a birefringent material is characterized by its Kerr constant K, defined as[11]

$$K = [(\Delta n/n)(1/E^2]_{E\to 0}\,, \tag{2}$$

where n is the mean refractive index of the solution. At higher field strengths the birefringence no longer exhibits linear dependence on E^2, and in very strong fields saturation of birefringence occurs.[12]

Some colloidal suspensions, however, behave in an unexplained manner even in weak fields. O'Konski and Zimm[13] reported a breakdown in Kerr's law for tobacco mosaic virus suspensions of high concentrations. Similarly, Sakmann[15] observed that under ac fields the sign of birefringence was reversed as the concentration of the suspension was increased beyond 0.5%. Since this behavior was reported only in suspensions of high concentrations, it was attributed mainly to interactions between particles. Also as early as 1902, Majorana[9] observed anomalies in the magneto-optical effect of colloidal ferric oxide solutions. Majorana,[9] and later Cotton and Mouton,[3] proposed that birefringence reversal was caused by different particle sizes giving rise to birefringence of opposite signs. In preliminary examinations of the Kerr effect of Wyoming bentonite suspensions in our laboratory, these solutions exhibited anomalous behavior even at low concentrations; these effects depended largely on the preparation of the colloidal solution, even though

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the initial material was identical. The purpose of this study was therefore to examine the anomalous birefringence behavior of bentonite in weak fields.

The experimental study is greatly facilitated if the magnitude as well as the sign of the optical retardation can be evaluated directly. Thus, an experimental assembly was designed to permit such direct measurements of δ. Preliminary experiments established that all our bentonite solutions gave rise to negative birefringence in weak fields. The problem, then, was to study the factors contributing to this phenomenon.

Theory

Born[2] showed that the Kerr effect results from the orientation of molecules in an electric field. The orientation may be the result of a permanent dipole on the molecule or its electrical anisotropy or both. Peterlin and Stuart[14] extended this theory to dilute solutions of macromolecules in a solvent which has negligible birefringence. Furthermore, O'Konski et al.[12] presented a saturation birefringence theory which is valid for strong fields and takes into account the conductivity of the solvent; they also showed that from the birefringence data in strong fields, one can evaluate directly electrical anisotropy of the colloidal macromolecules.

Krause and O'Konski[8] also noted that in conductive colloidal suspensions ion polarization contributes much more than electronic polarization to induced orientation. This was clearly shown by the marked dependence of the birefringence of tobacco mosaic virus on the pH of the solution.

The orientation of macromolecules in a solvent is opposed by Brownian motion, so that in comparison to liquid molecules, colloidal particles exhibit a certain time delay in the establishment and decay of birefringence. Benoit[1] showed that the field-free decay follows a simple exponential law,

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

where D is the rotational diffusion coefficient. For ellipsoids of revolution, D is related to the volume and length of the particles, as well as to the temperature and the viscosity of the solvent. Since D is independent of the electrical properties of the particle and solvent, the birefringence decay measurements have been useful in the determination of particle size. The establishment of birefringence in an instantaneous electric field, however, depends not only on D but also on the dipole moment, the particle anisotropy and the dielectric constants of the particle as well as the solvent.[1]

For polydisperse solutions, i.e., colloidal solutions containing particles of various lengths, the birefringence decay is given by the more general expression[12]

$$\Delta n/\Delta n_0 = \sum_{i}^{j} \theta_i e^{-6D_i t}, \qquad (4)$$

where θ_i is the volume fraction of the component i in the pure macromolecular phase. Thus, when the colloidal system is polydisperse, one cannot easily determine the macromolecular dimensions. At best, it may be possible to determine approximately two diffusion coefficients, if they differ by an order of magnitude, using well-known non-linear estimation techniques.[5] Sosinskii[17] used the general expression (4) in determining the homogeneity of particle sizes while attempting to fractionate some colloidal suspensions.

As noted earlier, the purpose of this investigation was to examine the factors contributing to the negative birefringence of bentonite suspensions. A series of experiments was performed to test the hypothesis that various particle sizes give rise to birefringence of opposite signs and yield birefringence reversal in polydisperse suspensions. A study of the effects of concentration on the negative birefringence was performed to examine the extent of interactions between particles. Finally, the effect of suspension conductivity on the birefringence properties was studied in view of the importance of ionic polarization in colloidal systems. In the last section a possible explanation is presented to account for the experimental observations in the negative birefringence of bentonite.

Experimentation

Because continuous application of the electric field promotes migration of colloid particles to the electrodes and produces heating of the solution, experiments must be conducted with pulsed fields. Alternating the sign of successive pulses reduces migration further. One may also use ac fields to eliminate migration. Sakmann[15] claims that ac field birefringence leads to more direct information on the contribution of permanent and induced effects. The heating effects under ac fields can be reduced also by utilizing a pulsed rather than a continuous ac field. In the present work we have utilized pulsed dc fields, a necessary prelude to investigations under other types of fields which involve additional complications in orientation mechanisms.

• *Apparatus*

Our experiment arrangement, shown in Fig. 1, is similar in principle to the assembly described for electro-optical birefringence measurements by O'Konski and Haltner,[11] Benoit,[1] and Kahn.[7]

A mercury vapor lamp mounted and enclosed in a cylindrical black box is used as a light source. The light is transmitted through a small hole in the box, and the beam emerging from this source (which approximates a point source) is collimated and passes through a green (λ = 5460 A) filter. The monochromatic collimated beam is then passed through a Glan Thompson polarizing prism mounted on a rotating scale with a vernier having an accuracy of 0.1°.

The polarized light beam is transmitted through the birefringence cell and then to a Babinet Soleil compensator (Gaertner-Scientific). The compensator intro-

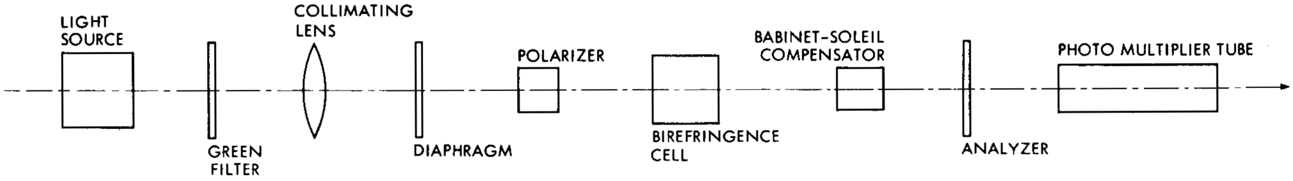


Figure 1 **Experimental arrangement showing optical assembly.**

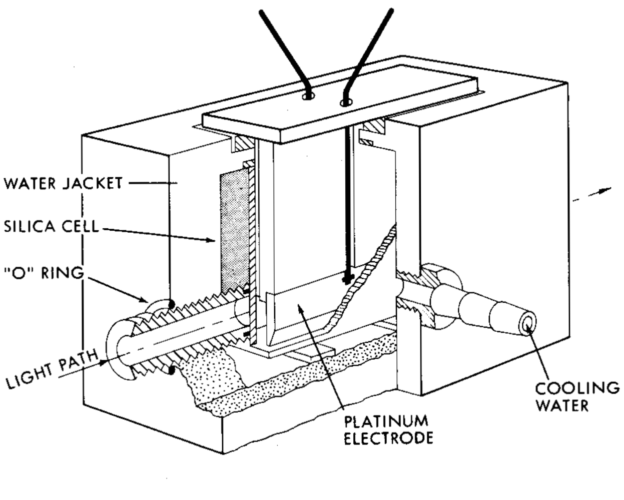
duces an optical retardation δ between the horizontal and vertical components of the plane-polarized beam. This retardation is added to or subtracted from the optical retardation of the emerging light beam. Thus the resultant retardation can be reduced to zero and the emerging light beam converted to plane-polarized light. The beam then passes through an analyzing Glan Thompson prism to a photomultiplier tube (CBS-CL-1008). This optical assembly permits the measurement of the optical retardation to an accuracy of ±1°. The output of the photomultiplier tube is displayed on a dual beam oscilloscope.

- *The birefringence cell*

Three different cells were used in the experiments with the following containers: (1) Beckman fused silica spectrophotometer cell (#46005) with 10 mm light path length; (2) Beckman fused silica spectrophotometer cell (#46029) with 40 mm path length; (3) Quartz cell with $\frac{1}{2}$ inch path length. The quartz container was stress relieved and found to be free of strain within experimental accuracy. On the other hand, spectrophotometer cell (#46005) showed an optical retardation of 3°, and cell (#46029) exhibited a δ of 2° for the mercury line 5460 A.

One cell assembly is shown in Fig. 2. The platinum electrodes were supported on a piece of carefully machined nylon. The removable nylon insert assembly in the cell was provided with two holes: one to remove air, and the other to introduce the sample by means of a hypodermic syringe. The cell container was placed in a water jacket, which permitted the passage of a light beam as shown in Fig. 2. Water was circulated in the jacket from a constant temperature bath. All measurements were performed at 20-22°C.

Figure 2 **Birefringence cell with water jacket.**



- *Electrical assembly*

Cell electrodes were energized by rectangular pulses; alternate pulses were reversed in sign. The width of the positive and negative pulses could be varied separately. Also, the time interval between succeeding pulses could be controlled. The applied pulse, as well as the photomultiplier output, was displayed on the oscilloscope simultaneously. When desired, the oscilloscope could be switched to display the cell current pulse on the screen instead of the applied voltage pulse.

Oscilloscope traces of rise and fall of birefringence were photographed on 35 mm film. Photographs were subsequently projected on the screen of a Benson Lehner Analyzer (Model N-2), where the x and y coordinates of a number of desired points were transferred to punched cards. The x coordinate values represented time in milliseconds, and the y coordinate depicted the light intensity. The relationship of light intensity to optical retardation is

$$\delta(t) = 2 \text{ arc } \sin(\sqrt{I/I_0} \sin \delta_0/2), \tag{5}$$

where I_0 is the light intensity before the electric field is cut off and δ_0 is the corresponding value of optical retardation determined by the compensator. Values of δ and t were calculated from x and y coordinates on an IBM 704. Results were obtained from a recorder-translator in the form of δ/δ_0 versus t and log δ/δ_0 versus t plots.

- *Preparation of bentonite suspensions*

The Wyoming bentonite clay used for our investigations was obtained from the Baroid Division of National Lead Company. The particle sizes ranged from $\frac{1}{2}$ micron or less to 50 microns. The clay contained mostly montmorillonite molecules. Each particle generally consisted of layers of montmorillonite molecules, so that the final structure resembled a stack of mica sheets. The montmorillonite structure has been described by Hofmann et al.[6]

Figures 3a and 3b are, respectively, optical micrographs of the sample as received directly from the supplier and after vacuum drying and separation by a

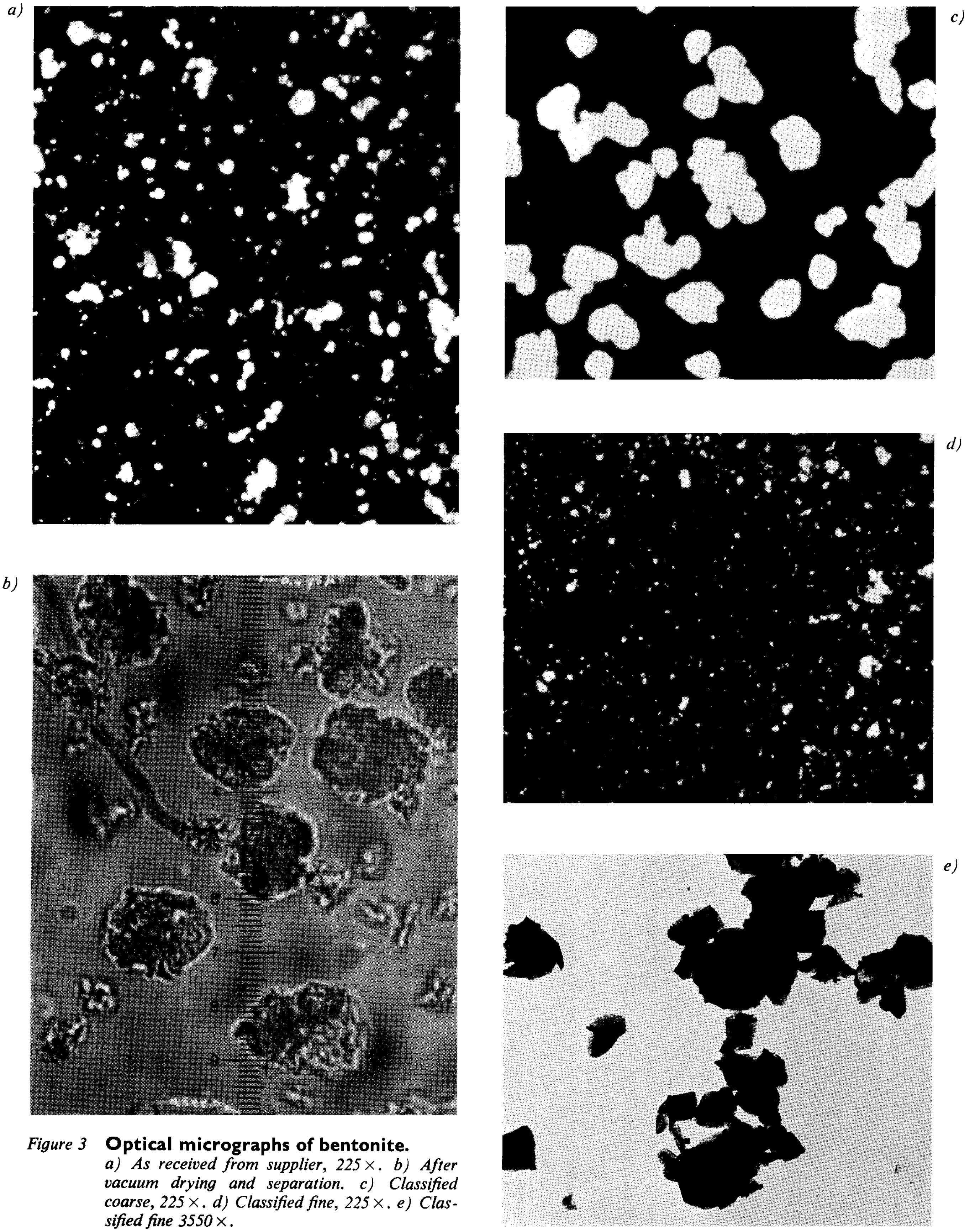
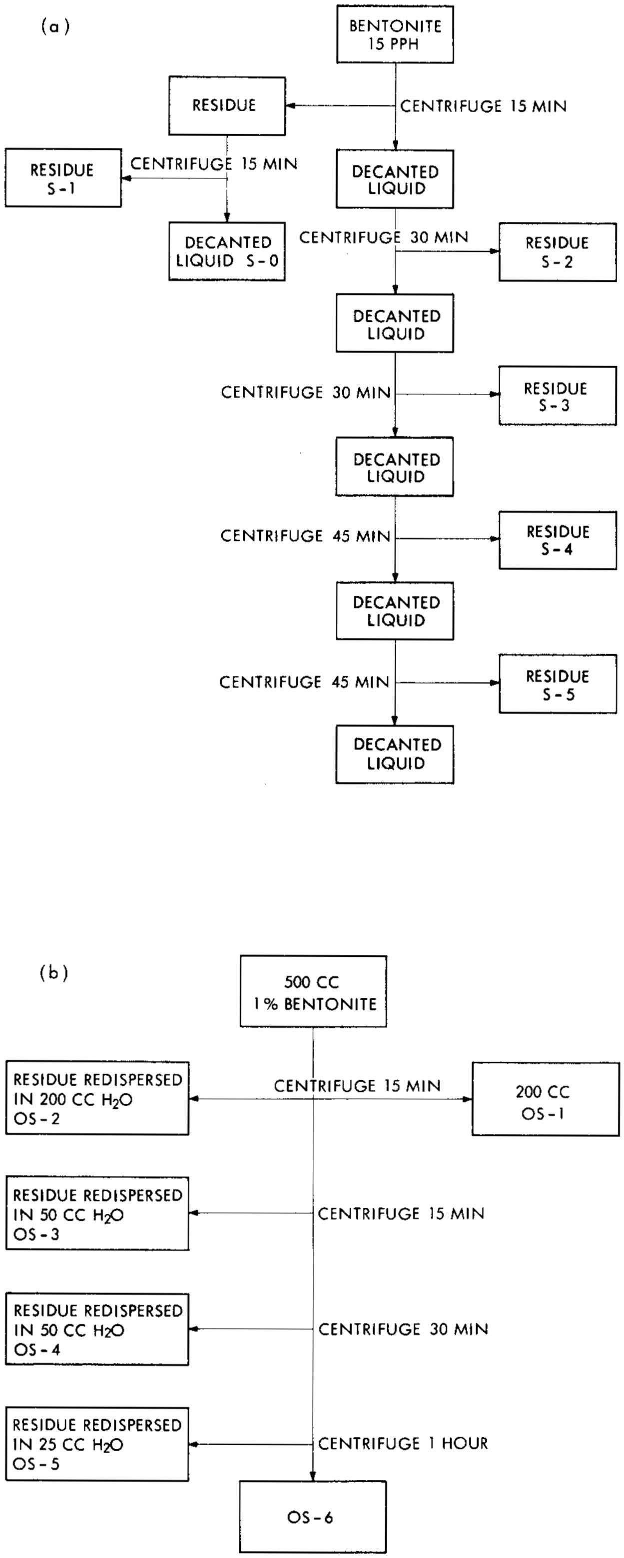


Figure 3 **Optical micrographs of bentonite.** *a) As received from supplier, 225×. b) After vacuum drying and separation. c) Classified coarse, 225×. d) Classified fine, 225×. e) Classified fine 3550×.*

Figure 4 **Separation of bentonite particle sizes.**
a) Procedure 1.
b) Procedure 2.



Bahco microparticle classifier. The photographs indicate that the particles were flake-shaped and that the distribution of particle size in the original material was rather wide. The classifier brought about some separation; however, the classified samples still exhibited a wide range of particle sizes.

Water dispersions of classified and unclassified clay samples were highly conductive, and therefore were not suitable for birefringence measurements. Also, wide variation in particle sizes made analysis of experimental results quite difficult. A preliminary centrifugation was performed to remove most of the large particles (probably greater than 2 microns). Conductivity of the suspensions was then reduced by dialysis.

• *Separation of particle sizes*

Two procedures were employed to obtain fractionation of particle sizes in the solutions. In both cases an International centrifuge was used which exerted an average centrifugal force of about 2000 g on the solution.

The first method was similar to the procedure described by Sosinskii[17] for the separation of bentonite particles, Fig. 4a. In brief, the settled particles were repeatedly centrifuged and redispersed.

In the second procedure, the fractions of sediments collected over intervals of 15 minutes and 30 minutes of centrifuging were redispersed in distilled water, Fig. 4b. In both procedures it was observed that the largest particles did not form stable suspensions.

Sols prepared from the bentonite clay which were classified on the microparticle classifier were also centrifuged for 1 and 2 hours to remove larger particles not separated in the classifier.

• *Reduction in conductivity*

The high conductivity of bentonite suspensions was mainly due to soluble impurities which were removed by electrodialysis as well as by plain dialysis. However, electrodialyzed samples showed erratic behavior, and consistent results were difficult to obtain. The majority of the samples were therefore dialyzed in a cellulose tube placed in high resistivity water over long periods of time. Water was replaced every 24 hours. After several days, conductivity of the suspension was found to be about two orders of magnitude lower. Most of the dialyzed samples had a specific resistance of 100,000 ohm cm or higher, so that with the available electrical assembly a maximum field of 1500 v/cm could be applied to the cell.

Bentonite micelles possess surface ion-exchange centers; therefore it was desirable to determine if dialysis altered the particle structure. A series of samples of the dialyzed dispersions was dried and examined by electron microscopy and x-ray spectroscopy. Comparison of the electron diffraction patterns and x-ray spectrographs of dialyzed and undialyzed samples showed no morphological difference in the structure of the montmorillonite molecules.

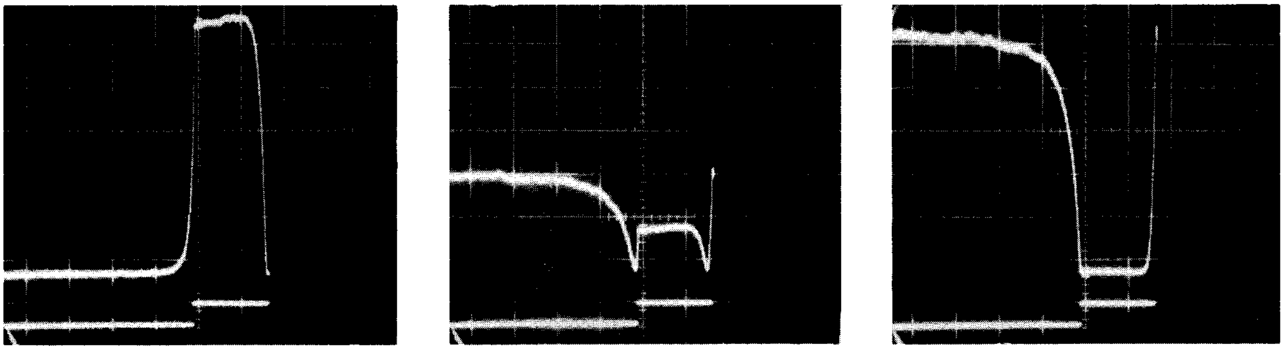


Figure 5 **Photographs of light pulse under dc fields before and after adjustment of the Babinet-Soleil compensator.**
Left: compensation $\delta = 0$. *Center: compensation* $\delta > 0$. *Right: exact compensation.*

The birefringence property and conductivity of the suspensions were checked at every step of the various treatments. Effects of aging on the suspension were also recorded by repeated measurements of electro-optical birefringence at known time intervals.

- *Birefringence measurements*

The optical assembly was aligned, and the light beam adjusted until its diameter was less than 1 mm. About 0.5 cc of the bentonite dispersion sample was added to the cell after it had been rinsed once with the suspension. The polarizing prism was adjusted to an angle of 45° from the field direction. The analyzer prism and the Babinet Soleil Compensator were adjusted until the photomultiplier recorded minimum light output. The compensator reading was then noted.

The alternating pulsed dc field was applied to the cell, and the pulse width was adjusted until the photomultiplier tube indicated that before field cutoff the birefringence had reached saturation. The compensator was then adjusted until the light output on the photomultiplier tube was minimal at birefringence saturation. Figure 5 shows the light output pulse in the two positions; the first photograph indicates the light pulse before adjusting the compensator, and the second photograph represents the pulse after adjustment. The setting on the compensator was noted, and the above measurements were repeated at increasing voltages.

Conductivity of the suspension was evaluated prior to birefringence measurements, and it was checked at intervals during the electro-optical measurements. Heating of the dispersion was avoided by limiting the duration of the pulsed field to between 2 and 4 seconds; when a longer time was necessary for compensator adjustment, the final reading was taken after the solution had cooled to the temperature of the circulating water in the jacket.

The decay of birefringence was displayed on the oscilloscope screen on expanded scale and photographed on 35 mm film. The developed film was then analyzed to obtain δ as a function of t.

Results

The experimental assembly was checked against a tobacco mosaic virus sample obtained from the virus laboratory of the University of California. The length of the particles as calculated from the birefringence decay curve agreed with the electron microscopy measurements obtained from the virus laboratory, and birefringence measurements were in good agreement with the results of O'Konski and Haltner.[11]

Results of δ at various field strengths E for bentonite suspensions prepared by centrifuging a 0.5% and 1.0% bentonite dispersion are shown in Figs. 6 and 7, respectively. An examination of Figs. 6 and 7 reveals that 1) All four suspensions exhibited a reversal in the sign of δ, 2) Conductivity of these suspensions was very high, thus limiting the maximum field voltage, and 3) Birefringence reversal was brought about at approximately the same voltage for A-O and B-O. This also held essentially true for C-O and D-O. It appears that prior to any further treatment there is no essential difference between the samples centrifuged for 15 minutes and two hours.

Birefringence response of samples A, B, C and D, dialyzed for 20 days under identical conditions, is shown in Figs. 8 and 9. For the dialyzed samples, birefringence measurements in the positive region were extended to higher voltages because of their lower conductivities. When δ is plotted versus E^2 for these four samples, the Kerr law ($\delta = K'E^2$ for weak fields) is not obeyed (see Fig. 10). Furthermore, the suspensions reached saturation rapidly in the positive region.

Figures 8 and 9 show that the region of negative optical retardation differed appreciably from one solution to another. Samples centrifuged both for 15 minutes and 2 hours before dialysis (see Figs. 6 and 7) did not show noticeable difference between the birefringence reversal voltages. However, after dialysis, samples which have been centrifuged for a longer time extended the region of negative birefringence to

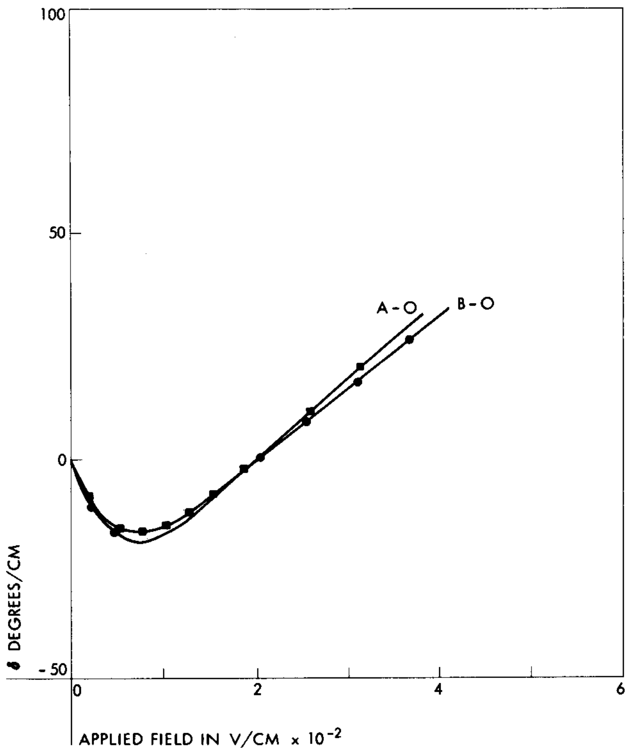


Figure 6 **Birefringence of 0.5% bentonite suspensions.**
Curve A-O: solid content, 0.36%; obtained by centrifuging sample for 15 minutes. Curve B-O: solid content, 0.33%; obtained by centrifuging sample for 2 hours.

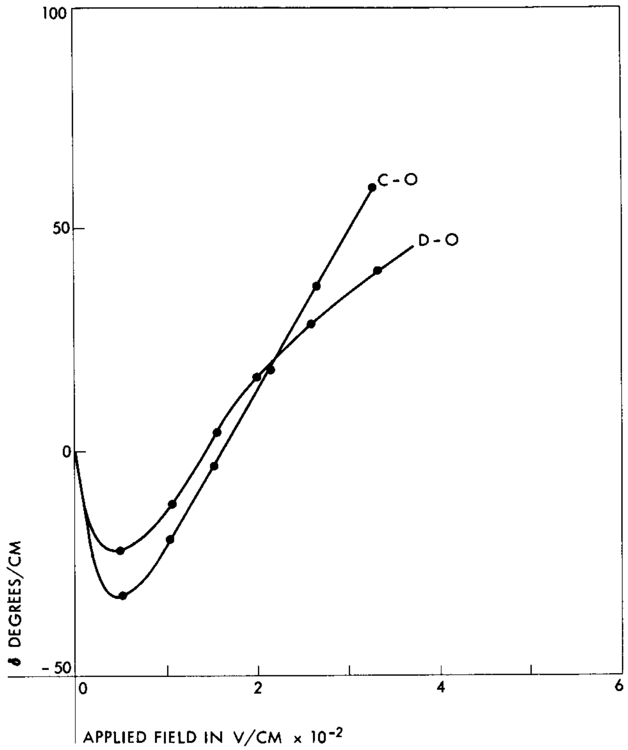


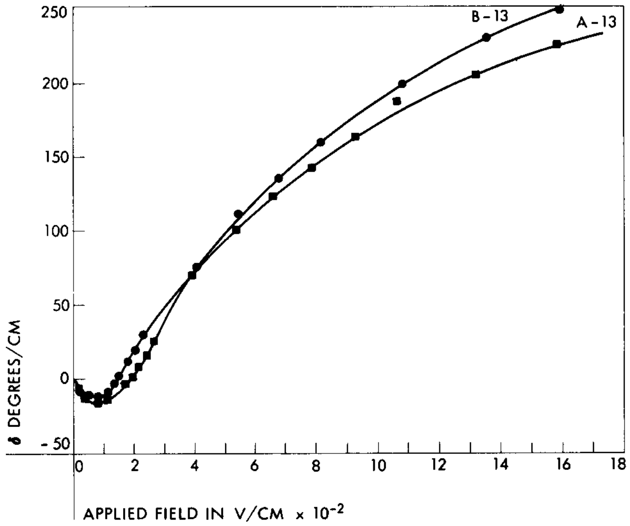
Figure 7 **Birefringence of 1.0% bentonite suspensions.**
Curve C-O: solid content, 0.53% obtained by centrifuging sample for 15 minutes. Curve D-O: solid content, 0.53%; obtained by centrifuging sample for 2 hours.

higher voltages. Since the concentrations of the sols A-O and B-O as well as C-O and D-O were found to be rather close, these results suggest that the difference in the reversal voltage was caused by some shift in the ionic structure around the montmorillonite molecules. Thus although dialysis did not bring about any structural changes in the montmorillonite micelle, it altered the ionic cloud around the particle sufficiently to affect the orientation mechanism responsible for birefringence of the colloids.

- *Particle size variation*

Micrographs of the bentonite powder (Fig. 3) show that our initial material had a wide range of size distribution. Preliminary centrifuging removed large particles to a great extent. However, as shown in Fig. 11 for one sample, the log δ/δ_0 versus t curves were not linear; they indicated the presence of at least two particle sizes. Thus if one were to hypothesize, according to Majorana,[9] that the two sizes give rise to opposing birefringence, the resultant δ can certainly cause a birefringence reversal with increasing voltage, since the saturation of larger particles occurs

Figure 8 **Birefringence of suspensions after dialysis for 20 days.**
A-13: solid content, 0.33%; from dialysis of A-O. Curve B-13: solid content, 0.32%; from dialysis of B-O.



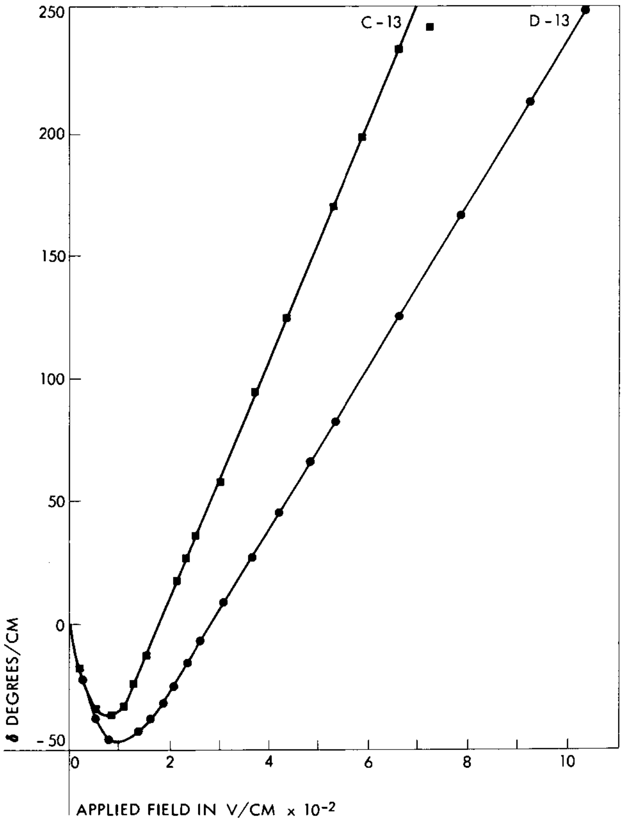


Figure 9 **Birefringence of suspensions after dialysis for 20 days.**
Curve C-13: solid content, 0.530%; from dialysis of C-O. Curve D-13: solid content, 0.536%; from dialysis of D-O.

at lower voltages. A series of experiments of birefringence of various particle sizes of bentonite was performed to investigate the validity of such a model.

Results of the suspensions fractionated by the first separation method (see Fig. 4a) are shown in Fig. 12. The data are in the form of light output versus voltage, and the light output is related to the optical retardation by[4]

$$I/I_m = \sin^2 \delta/2\,, \tag{6}$$

where I_m is the intensity of light with the polarizing and analyzing prisms in parallel. Except for S-1, all samples showed a negative birefringence. However, S-1 (as is obvious from Fig. 12) contained all the largest sized particles.

Birefringence response of the suspensions with particle size separated by the second procedure (starting with 1% bentonite dispersion, see Fig. 4b) is presented in Fig. 13. The separation procedure is in some respects similar to the first method, and therefore it is not surprising that the response of the first fraction of particles collected over 15 minutes (viz. OS-2) showed no negative birefringence, since this sample corresponded to S-1. In view of the high degree of polydispersity of S-1, the absence of negative birefringence in the sample contradicted the hypothesis presented for the explanation of negative birefringence. The other fractions exhibited appreciable

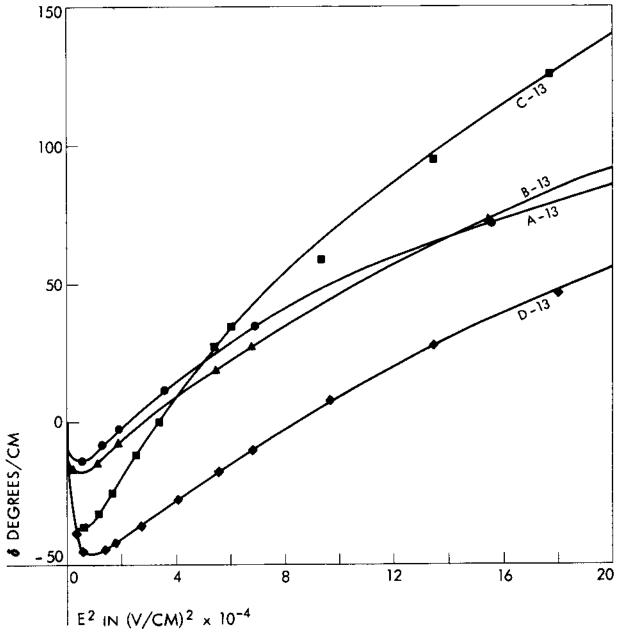


Figure 10 **Comparison of birefringence of dialyzed bentonite samples and their deviation from Kerr's law, $\delta = KE^2$.**
A-13: 0.5% sample; centrifuged 15 minutes; solid content, 0.33%.
B-13: 0.5% sample; centrifuged 2 hours; solid content 0.32%.
C-13: 1.0% sample; centrifuged 15 minutes; solid content 0.53%.
D-15: 1.0% sample; centrifuged 2 hours; solid content, 0.536%.

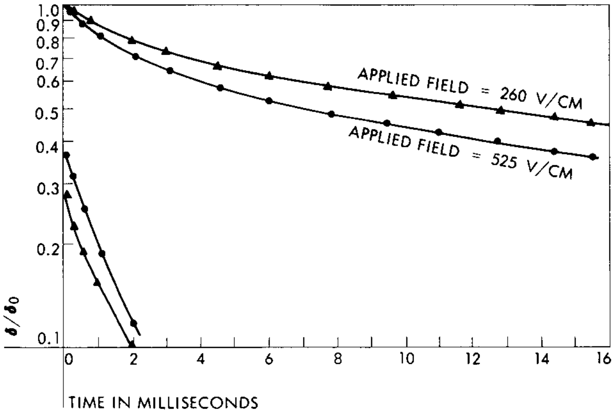


Figure 11 **Relaxation curves for the dialyzed sample A-13 in the positive δ region.**
Curves at lower left obtained by subtracting the contribution of smaller particles.

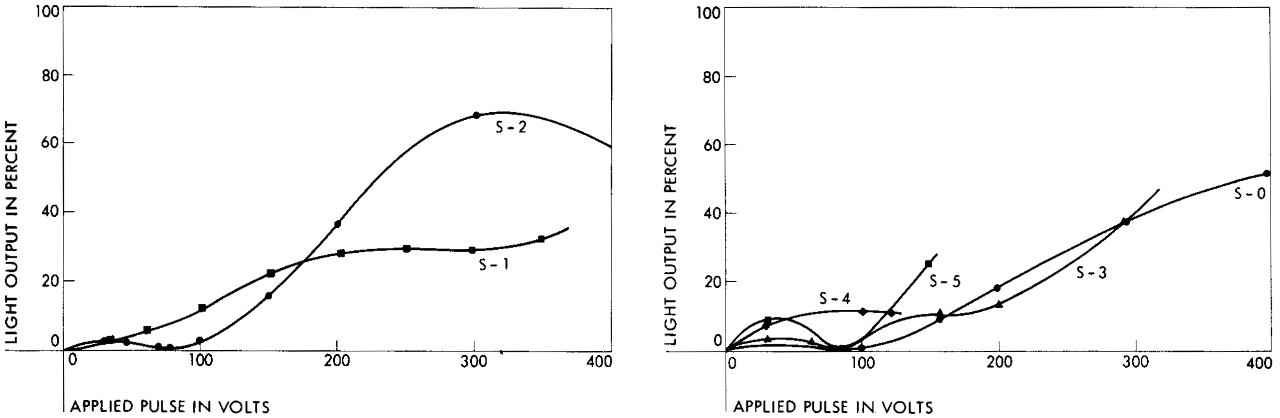


Figure 12 **Light output response for suspensions prepared with various bentonite particle sizes, according to Procedure 1.**

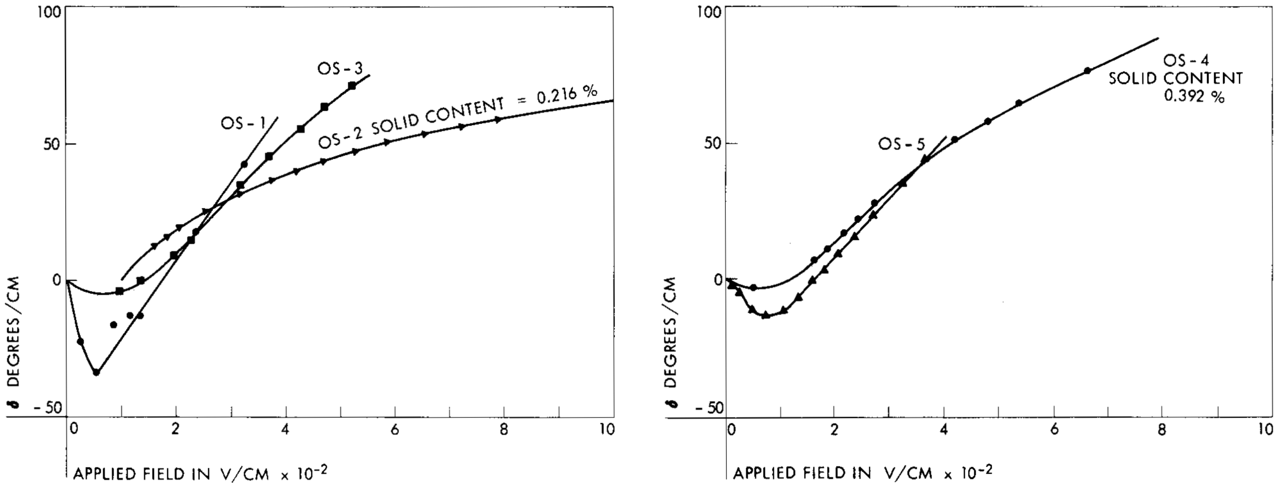


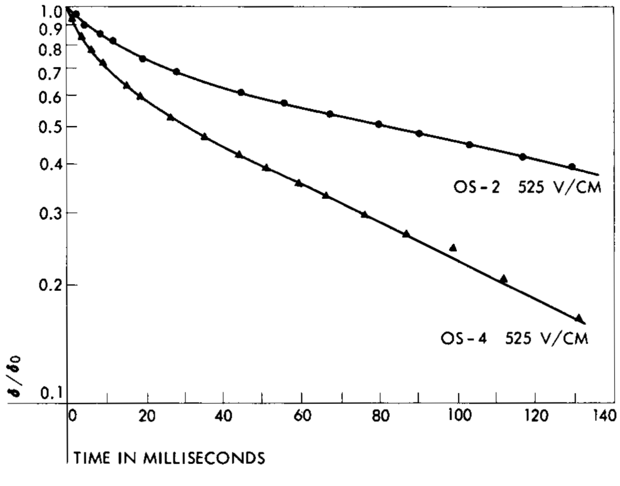
Figure 13 **Birefringence of bentonite suspensions as produced by Procedure 2.**

negative δ except OS-4, which indicated only a value of $-1.4°$ for δ at 25 v/cm when measured with the 40 mm cell. Also in Fig. 14, we have plotted the decay curves for two samples, OS-2 and OS-4. Although these curves are not as linear as would be desirable, a comparison between them suggests that a good degree of separation was achieved in the fractionation procedure.

In another procedure, bentonite powder was dried at room temperature under a high vacuum and separated by the Bahco microparticle classifier into three categories: coarse, medium and fine. A 0.5% suspension of the coarse and fine fractions was centrifuged and dialyzed for 20 days. Birefringence results for these suspensions are shown in Fig. 15. Despite the separation treatments, negative birefringence for the bentonite suspension did not disappear. The concentration of these suspensions was close to that of the B-13 samples, which were prepared in the same manner from the original bentonite powder. Figures 8

Figure 14 **Relaxation curves for separated bentonite particles.**

Curve OS-2 or (S-1) for larger particles. Curve OS-4 indicates smaller particles.



and 15 indicate that the negative birefringence region and the reversal voltage for classified and unclassified samples are comparable. On the other hand, a comparison of birefringence of coarse and fine suspensions in Fig. 7 indicates that separation by the particle classifier reduced the magnitude of the negative δ for the fine suspension (B-13 fine), without affecting the reversal voltage significantly. This behavior may very well have been caused by the reduced particle size because as indicated by the log δ/δ_0 versus time curve for this suspension (Fig. 16), the diffusion coefficient was larger for B-13 fine.

It was observed that relaxation curves for the suspensions fractionated by the first two procedures (Fig. 7) tended to deviate from the simple exponential relationship of Eq. (3), indicating that size separation procedures did not produce complete homogeneity in particle sizes. However, as shown in Fig. 14, relaxation times for various suspensions were indeed widely different, indicating a good separation of particle sizes, although complete homogeneity was not attained.

It can be concluded then that birefringence reversal cannot be explained by the hypothesis that various particle sizes give rise to birefringence of opposite sign. This conclusion was further confirmed in some preliminary investigations[16] performed at a later stage using much more homogeneous samples prepared with a supercentrifuge (60,000 g).

- *Concentration dependence*

As stated earlier, Sakmann[15] and O'Konski[11] observed negative birefringence of colloidal sols only at high concentrations, and therefore they attributed the phenomenon to interaction of the particles. The concentration dependence of negative birefringence was therefore of special interest to us.

Birefringence data for various concentrations of bentonite samples are presented in Fig. 17. Samples C-13 and D-13 (bentonite dispersion centrifuged for 15 minutes and 2 hours, respectively, and then dialyzed for 20 days) were diluted with distilled water to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{16}$ of the original concentration and then tested one day after dilution. At lowest concentration, accurate measurements were obtained with the 40 mm cell at low voltages. The figures indicate that the magnitude of the negative optical retardation decreased with decreasing concentration. Similarly, the phase reversal voltage also decreased when the concentration was reduced.

Figures 18 and 19 show the negative birefringence of the diluted suspensions on a magnified scale. The phenomenon of birefringence reversal, as well as the magnitude of the negative optical retardation, was apparently greatly affected by a decrease in the concentration of the sol. However, in the lowest concentration region (0.03%), the negative value of δ was distinctly noticeable, and the birefringence reversal voltage did not decrease appreciably after the solution was diluted to $\frac{1}{4}$ the original concentration. These results lead us to conclude that the reversal of birefringence is exhibited also in the absence of interactions.

As noted in the previous section, samples S-1 and OS-2 did not show any measurable negative birefringence below 150 v/cm. These samples contained larger particles settled in centrifuging than those suspended in dispersions C-13 and D-13. Concentration of these samples was also much higher than the diluted C-13 suspension. If interaction of the particles (or dipole-dipole interaction) was largely responsible for negative birefringence at lower voltages, samples S-1, OS-2 and OS-4 would be expected to show a more pronounced

Figure 15 **Birefringence of bentonite suspensions separated by particle classifier.**
Fine fraction, 0.5% sample centrifuged 2 hours and dialyzed for 20 days. Coarse fraction, 0.5% sample centrifuged 2 hours and dialyzed for 20 days.

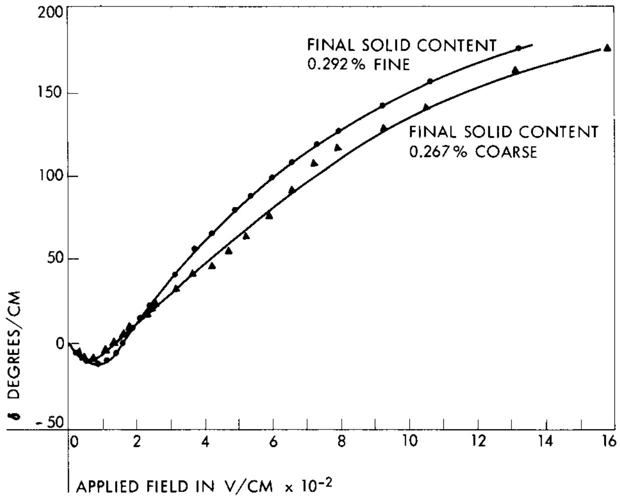
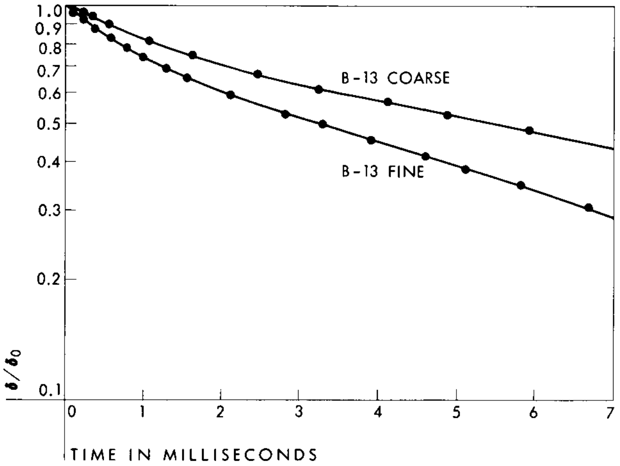


Figure 16 **Relaxation curves of bentonite fractions.**



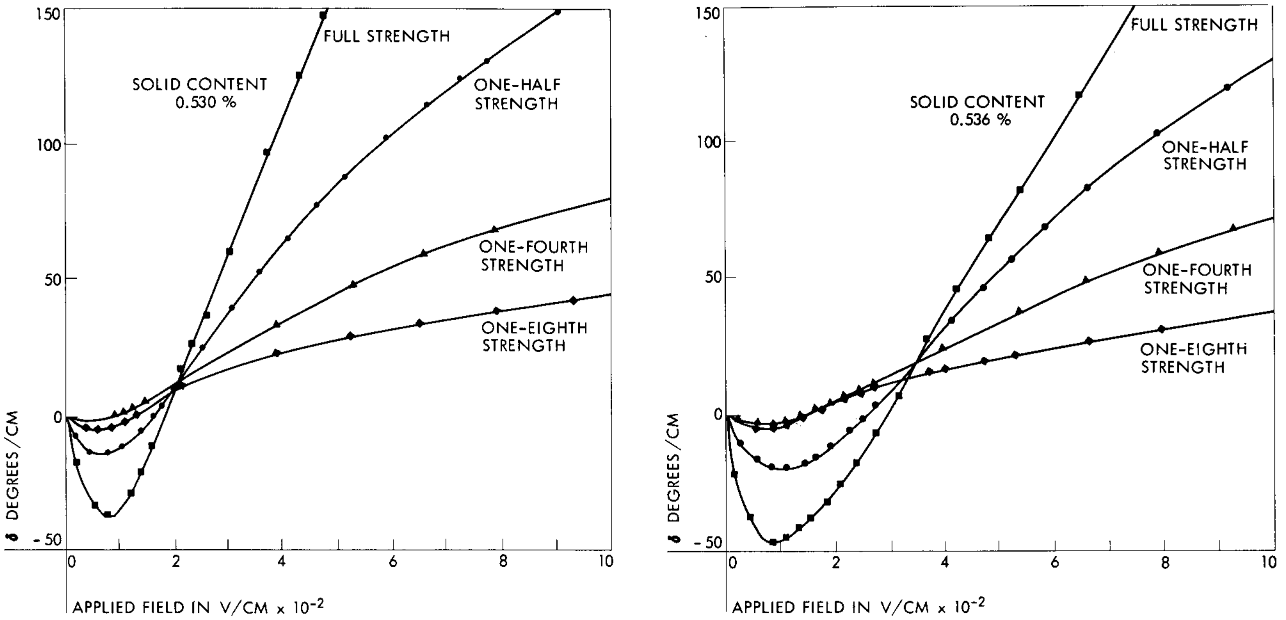


Figure 17 **Effect of dilution on the electro-optical birefringence of bentonite.** *Left: sample C-13. Right: sample D-13.*

negative birefringence than the diluted C-13 and D-13 dispersions, which is contrary to the observed results.

It is concluded then that although the negative birefringence at lower voltages is augmented at higher concentration, some inherent property of the particles is primarily responsible for the anomaly.

- *Orientation and relaxation times*

Absence of negative birefringence for high concentration sols of large bentonite particles, and the fact that very dilute suspensions (0.03 and 0.06 %) exhibit anomalous behavior, point to the possibilities that 1) the birefringence reversal is caused by different orientations of the micelles and 2) the anomaly is probably more pronounced for smaller sized particles.

Assuming that the reversal of birefringence is caused by different orientations of the bentonite micelle, negative birefringence may well result from a permanent dipole orientation at low field strengths, whereas the induced dipole alignment may contribute to the positive birefringence. Birefringence reversal may then result from a predominant induced orientation torque at high field strengths.

To analyze the birefringence of bentonite under such a hypothesis, one could attempt to separate the two orientation mechanisms by using a high frequency ac field or conducting a birefringence study at various temperatures. Unfortunately, in colloidal systems ionic polarization may cause additional complications due to temperature effects on ionic mobilities. The study of birefringence of bentonite under ac and other types of fields is the subject of a subsequent paper.[16] However, some observations on the rise and decay of the birefringence curves, as well as the variation of the diffusion coefficients with voltage (especially in the vicinity of the birefringence reversal voltage), lead to some interesting conclusions about the peculiar behavior of the bentonite particles under electric fields.

Photomultiplier response of a dilute suspension is shown in Fig. 20 at various voltages. The photographs are arranged in the sequence of increasing field strength. Also, the graphs of $\log \delta/\delta_0$ versus time for these solutions, calculated from the relaxation curves are shown in Fig. 21. The relaxation curves follow the simple exponential relationship, Eq. (3), rather well, and furthermore the diffusion coefficient in the negative birefringence region appears to be six times the value in the positive region. In other words, the decay appears to be faster in the negative region, especially in the vicinity of the reversal voltage. In view of the relationship of D to the particle dimensions, the discrepancy in the diffusion coefficients implies two different axes of rotation in the positive and negative birefringence regions.

An examination of Fig. 20 supports the above statement. Once the value of δ reaches a maximum in the negative region, the light output pulse changes shape as the voltage is increased. The field-free decay becomes faster as the reversal voltage is approached, and near the point of minimum light output, two peaks are observed. The first peak, which appears at the instant the field is applied (see Figs. 20f and 20g), is caused by negative value of δ, the second peak, which appears when the field is brought to zero, is caused by a positive value of δ. As the field strength is increased

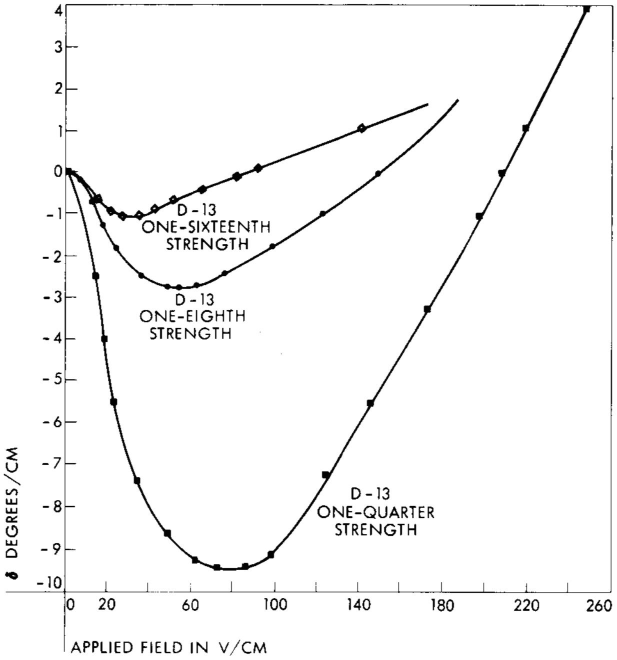


Figure 18 **Comparison of magnitude of δ and birefringence reversal voltage at various concentrations of bentonite suspensions.**

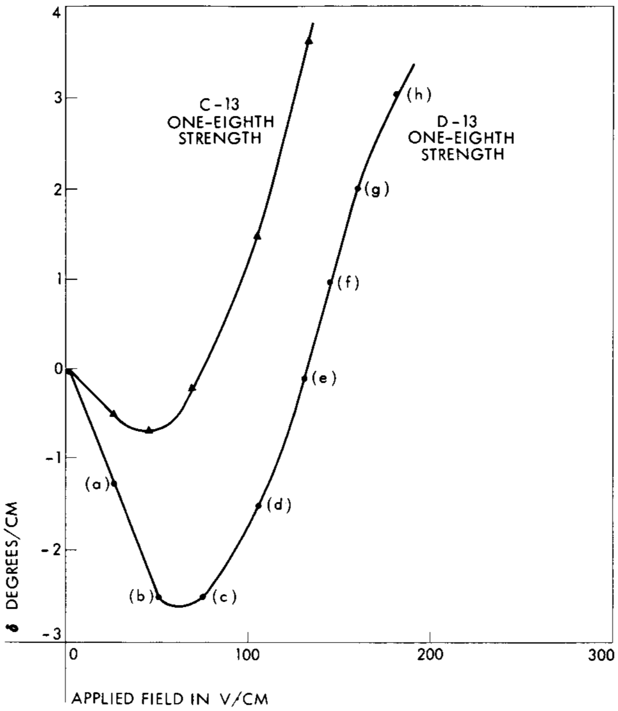
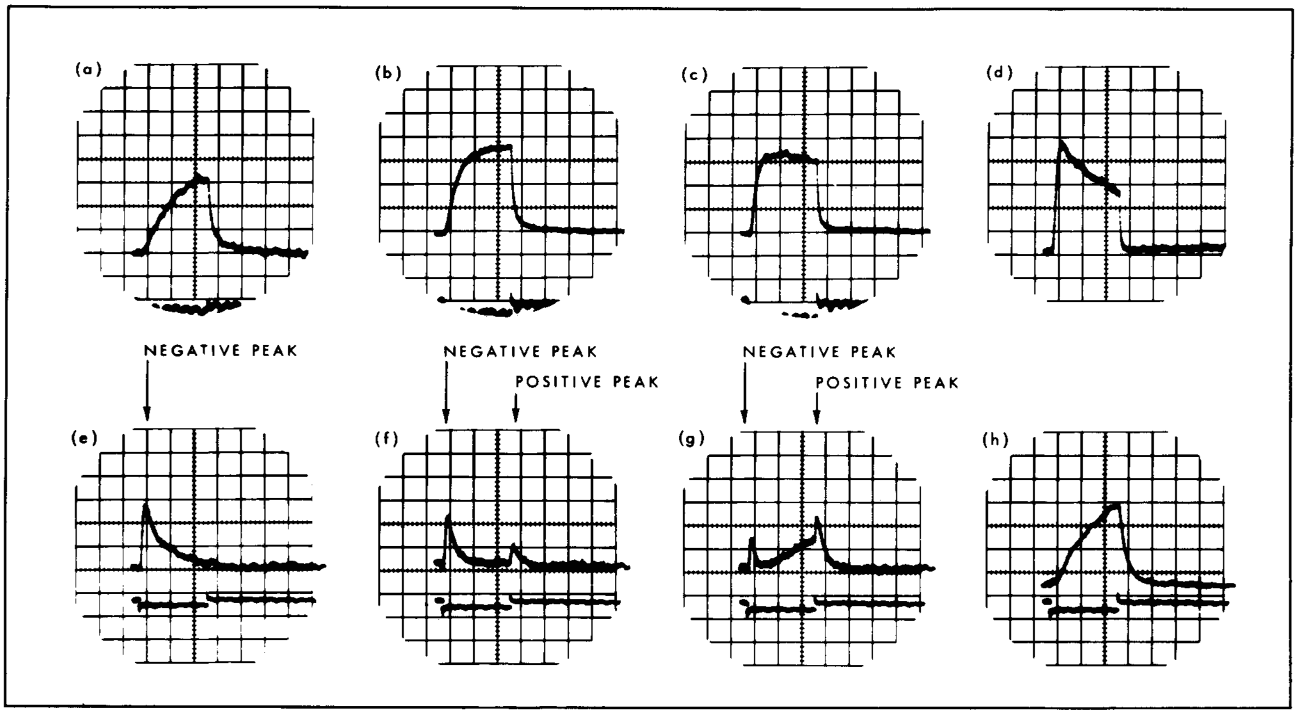


Figure 19 **Birefringence of very dilute bentonite suspensions.**
Solid content for both solutions: 0.066%.

Figure 20 **Traces of photomultiplier response for 0.066% bentonite (D-13 diluted) at various voltages.** *Photo identifications correspond to points on the D-13 curve of Fig. 19. Time base: 20 ms/division. Upper trace: cell output. Lower trace: applied pulse current. In all cases, δ was measured at the end of the applied pulse. Note that relative magnitude of response is not indicated. See Fig. 19 for magnitude.*



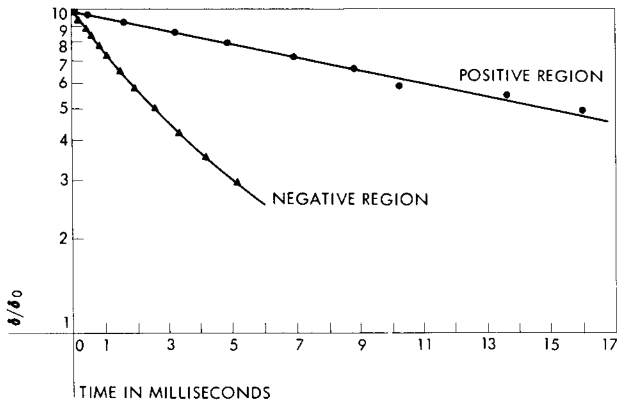


Figure 21 **Relaxation curves for dilute bentonite suspensions (D-13 diluted to 0.066%) in the regions of positive and negative birefringence.**

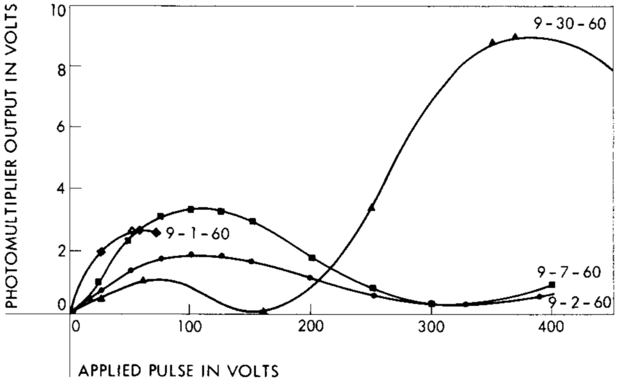


Figure 22 **Birefringence response of bentonite after electrodialysis.**

past the phase reversal point, the first peak remains as a part of the light pulse, until at very high voltages when it disappears. Apparently in the positive region, bentonite micelles undergo two different rotations, especially at field strengths close to the birefringence reversal point. Also, the two rotations contribute to optical retardations of opposite sign.

Optical micrographs of the dry bentonite sample (Fig. 4) show that the particles are flake-shaped. Thus the positive birefringence may result from an orientation along an axis parallel to the large surface; and when the orientation is such that the electric field is perpendicular to the flake surface, a negative birefringence can result. Whether or not the permanent dipole is responsible for the orientation along the thickness of the flake remains to be determined.

- *Effect of ion concentration*

As stated earlier, the montmorillonite lattice has bound charges with free ions of opposite polarity around the particle. Any change in the nature of these free ions is certain to bring about some effect on birefringence behavior of bentonite, because ionic polarization in a colloidal system contributes heavily to the induced orientation mechanism.[11]

We pointed out earlier that the removal of soluble ions in the suspension by dialysis caused a substantial shift in the birefringence reversal voltage. This was much more noticeable in the electrodialyzed samples (see Fig. 22). The figure shows that birefringence of these dispersions also depends upon the time lapse between the completion of electrodialysis and the measurement of optical retardation.

Also, Fig. 23 shows the results for three identical suspensions which were dialyzed in three different cylinders for 20 days. Although the original suspensions were identical, their birefringence characteristics differed appreciably in the low-voltage region.

In general, the process of dialysis brings about only the removal of soluble ions, and one would expect no change in the lattice structure of bentonite during dialysis. It appears then that the concentration of the soluble ions in the dispersion strongly influences the birefringence property of bentonite; therefore, the ionic polarization must also play a significant role in birefringence reversal. Unfortunately, the results presented here are insufficient to form any conclusions about the role of ionic polarization in the negative birefringence of bentonite.

Summary

Summarizing our results, we find that

1) Wyoming bentonite suspensions exhibit a negative birefringence at low voltages, even in low concentrations.

2) This behavior is more pronounced for smaller particles. It appears unlikely, however, that the polydispersity of the suspension brings about the anomalous behavior since we failed to discover particles showing only negative birefringence.

3) The magnitude of the negative birefringence as well as the reversal voltage decreases with dilution of the suspension. However, even sols of 0.03 percent by weight of bentonite exhibit negative birefringence at low voltages. On the other hand, large particles do not exhibit birefringence reversal even at much higher concentrations. It is concluded, therefore, that although particle-particle interaction augments the negative birefringence, the anomalous behavior of bentonite is the result of an intrinsic property of the micelle.

4) The large variation in diffusion coefficients in negative and positive regions of δ suggests that the particles orient along their axis of symmetry at low voltages and perpendicular to this axis at high voltages. Whether or not a permanent dipole along this axis brings about the initial orientation remains to be determined.

5) The experimental results also indicate that the

phenomenon of ion polarization plays an important part in affecting negative birefringence. Results of electrodialyzed suspensions and an examination of conductivity of the sols seem to support this conclusion.

Acknowledgments

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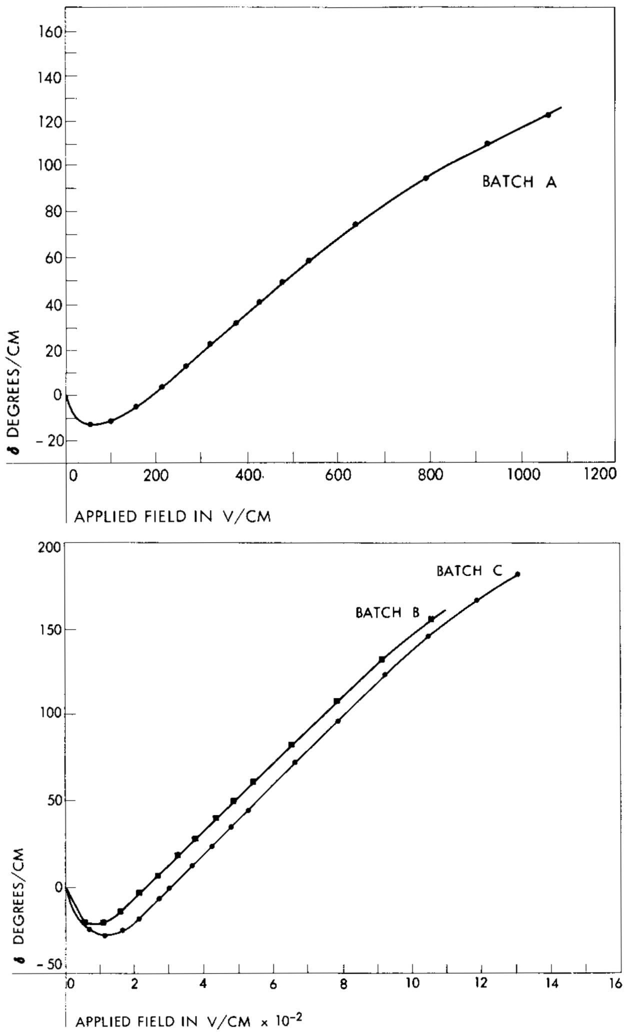

Figure 23 **Birefringence of 0.5% bentonite samples centrifuged for 2 hours.**

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