Birefringence of Thin Liquid Films

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Birefringences of oriented aggregates of Na-montmorillonite expanded in sodium chloride solutions were measured and compared with birefringences calculated from Wiener's equation. The difference between the calculated and the observed values is nearly constant in the region of swelling values 10-20 X. It is inferred that the difference comes from the birefringence of the polymolecular water layers and that it is evidence for a specific anisotropic structure. Anisotropy is also shown in some intercalated organic polymolecular films.

Although there is some circumstantial evidence of a specific structure in thin liquid films, there is difficulty in showing it with certainty. This difficulty, associated with the small effects to be measured, can be overcome by allowing inter-lamellar sorption in oriented clay aggregates of montmorillonite and measuring the thickness of the films with X-ray diffraction. The resultant aggregate can then be used for optical studies of the birefringence of the intercalated films as these are parallel to each other, and the optical effects from retardation are coherent. We have used the method to study films of water, from 30 to over 100 Å in thickness, and films of four organic liquids.

EXPERIMENTAL

METHOD

The basic material used for these studies was montmorillonite from Wyoming, U.S.A., which was characterized at Rothamsted Experimental Station. Quartz, the chief impurity, was removed by sedimentation of a dilute sol in a Sharples Super Centrifuge, and the clay fraction less than $0.2\,\mu$ equivalent spherical diameter was collected. This material was saturated with sodium ions by washing with sodium chloride solutions and then freed from chloride ions with alcohol + water mixtures. A new method was developed to form the oriented aggregates needed for optical studies. The clay was suspended in water to form a 1-2 % sol which was allowed to evaporate through a cellophane membrane M, so that the aggregates A were formed on the stretched membrane (fig. 1a). By preventing evaporation from the surface of the gel, the formation of skins and their subsequent buckling was inhibited, thus improving the orientation of the aggregates and facilitating their removal from the substrate. Small sections were cut from the oriented aggregate and selected under a microscope. With practice, rectangular sections 0·1-0·2 mm thick could be cut and measured; these were studied using a polarizing microscope (fig. 1b).

The sections S were oriented on a cavity slide G so that the c-axis lay in the plane of the slide; after adding the immersing liquid a cover plate K was placed in position to prevent evaporation. When swelling stopped the retardation was measured in sodium-D light with a Sénarmont compensator; and from the known thickness t of the section the birefringence B could be estimated.

INTERPRETATION

To deduce the birefringence of intercalated films from the net birefringence of swollen clay aggregates, it is necessary to take account of the form birefringence.

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Wiener [1] showed that a system of parallel isotropic plates of differing dielectric permittivity is anisotropic because the effective dielectric permittivities are given by

$$\varepsilon_0 = \delta_1\varepsilon_1 + \delta_2\varepsilon_2 + \ldots + \delta_n\varepsilon_n,$$

$$1/\varepsilon_a = \delta_1/\varepsilon_1 + \delta_2/\varepsilon_2 + \ldots + \delta_n/\varepsilon_n. \tag{1}$$

where ε_0 = effective dielectric permittivity parallel to the layers, ε_a = effective dielectric permittivity perpendicular to the layers, δ_n = volume fraction of dielectric of permittivity ε_n. Wiener's formulas apply only when each of the parallel platelets is much thinner than the wavelength of the incident radiation. Hence, if the thicknesses of the intercalated films as well as of the films between adjacent crystallites are less than 300 Å, this condition is satisfied for sodium-D light. The other limitation of the applicability of Wiener's formulas is caused by the molecular
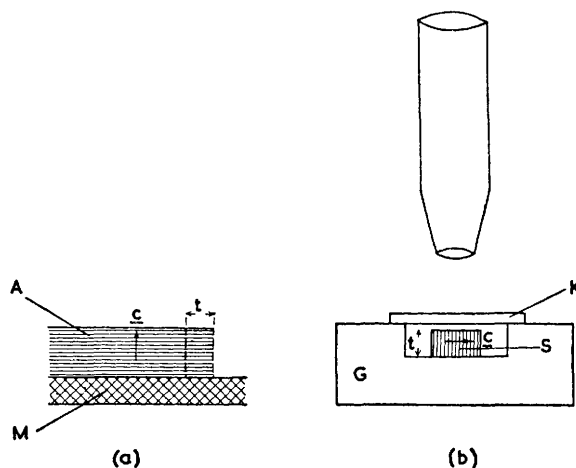

FIG .1.—A diagram (a) of the oriented aggregate on the stretched cellophane membrane and (b) of the apparatus with the direction of the c axis of the clay aggregate.

thickness of the silicate layers which hinders the use of bulk values of dielectric permittivity to calculate their polarizabilities. Nevertheless, we will use the values equal to the bulk values and show that the resulting uncertainty does not affect the final qualitative consequences. However, at present there is no sound experimental verification of Wiener's formulas,[2] although Ambronn and Frey [3] gave a qualitative demonstration of the predicted effect.

In a system of 10 Å pyrophyllite-type layers sandwiched between liquid films the intrinsic birefringence of the silicate layers may be taken as the same as that of crystals of pyrophyllite, i.e., about 0·042 (negative). Dehydrated montmorillonite aggregates have a slightly smaller birefringence of 0·02-0·03 (negative), probably because the crystallites composing the aggregates are imperfectly oriented; an orientation factor ϕ of 0·025/0·042 = 0·6 was therefore used to calculate the birefringence of an aggregate from that of a single crystal.[2] Wiener's equations were used in the form,

$$n_0^2 = \delta_1(n_1'')^2 + \delta_2(n_2)^2,$$

$$n_a^2 = \frac{(n_1')^2(n_2)^2}{\delta_1(n_2)^2 + \delta_2(n_1')^2}, \tag{2}$$

$$B = \phi(n_a - n_0), \tag{3}$$

where $\phi = 0.6$, and $n_0 =$ effective refractive index of the aggregate parallel to the plane of drying, $n_a =$ effective refractive index perpendicular to the plane of drying, n_1^{*}, $n_1' =$ refractive indices of the silicate layer (pyrophyllite-type) parallel (1.594) and perpendicular (1.552) to the layer respectively, $n_2 =$ refractive index (1.33) of the liquid film (assumed to be isotropic) and $B =$ birefringence of the aggregate.

Because the sections were only slightly porous, an increase in $1/\delta_1$ showed itself as macro-swelling S. This is defined as (final length)/(original length) measured in the c direction (i.e., in the plane of the slide). The measurements were made with a micrometer ocular calibrated by a stage micrometer.

RESULTS

WATER FILMS

Interlamellar swelling up to several $100 \, \text{Å}$ takes place when sodium montmorillonite is immersed in dilute sodium chloride solutions; the swelling is greater the lower the concentration of the solution.[4] This system seems an ideal one to investigate by the aforegoing methods. Two methods could be used to plot the results. The first was to plot the observed birefringence in solutions of known concentration against Norrish's values for the preferred film thicknesses; the second possibility is to measure the macro-swelling microscopically and to plot this against the birefringence. The observed macro-swelling S, however, is always greater than the values expected from Norrish's results, suggesting that intercrystalline swelling is greater than intracrystalline or interlamellar swelling; this must be allowed for when comparing the calculated and observed birefringences. A plot of birefringence against macro-swelling follows the same path as that of birefringence against $1/\delta_1$ for high values of S. In practice, this means that for swelling values more than ten times, the birefringence to S curve will follow the same path as the birefringence to $1/\delta_1$ curve.

Fig. 2 shows the birefringence (negative) B plotted against swelling both from the values calculated from Wiener's formula (the curve) and the values measured experimentally (circles). The points are scattered because each represents a measurement (usually taken after 15 min) on a new aggregate in apparent equilibrium with a sodium chloride solution of known concentration. Errors from heterogeneity of flakes and the measurement of thicknesses, become relatively large. For such studies on *one* flake (see fig. 3) the scatter of experimental points is much smaller, and possible errors are confined to uneven swelling. Fig. 2 also shows that at all swelling values the calculated curve is considerably above the observed points, suggesting that either the birefringence of the silicate layer differs from the assumed bulk value or that the water films contribute to the anisotropy of the system. Coincidence of the experimental points with the theoretical curve (which for high swelling values has a hyperbolic form) is impossible for any reasonable values of birefringence of the silicate layers. It follows that the observed results cannot be interpreted without admitting the birefringence of liquid interlayers of 100-$200 \, \text{Å}$ thickness.

When swelling reached values greater than 20 times the original volume, swelling continued after apparent equilibrium had been reached, and the birefringence slowly decreased with time. At a swelling value of 40 times the original volume the birefringence rapidly fell to an immeasurably small amount, without a corresponding increase in swelling; at the same time the swollen flake lost its cohesion and began to flow freely. At this point disorientation was taking place spontaneously. To show that the disorientation, independent of the swelling process, did not occur

BIREFRINGENCE OF LIQUID FILMS

to any great extent at lower swelling values, the effect of swelling on the birefringence was observed in two ways, first, by varying the salt concentration and observing apparent equilibrium points, and secondly, by prolonging the experiment over a
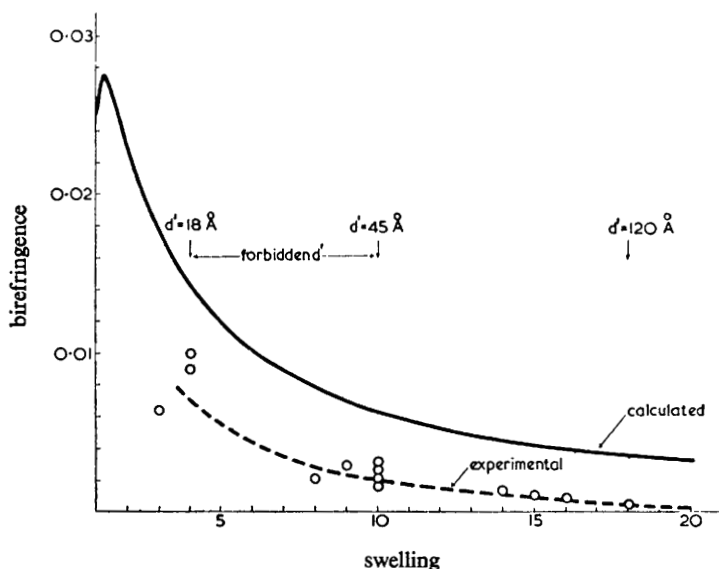

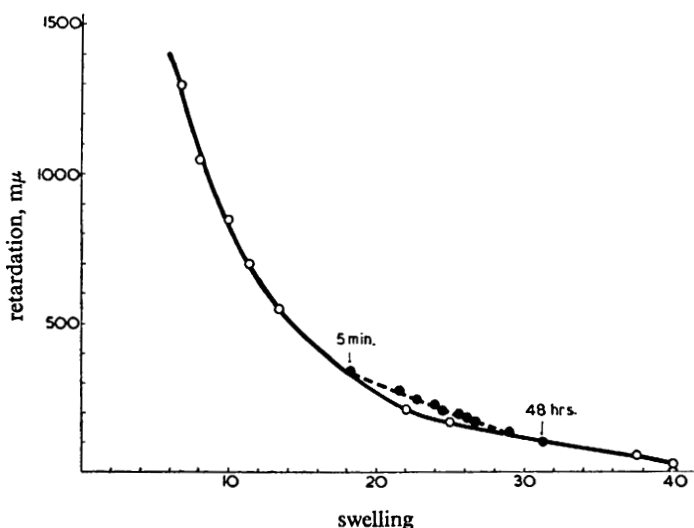FIG. 2.—The calculated and experimental (white circles) birefringence to swelling curves.

FIG. 3.—The retardation as a function of swellings S, where it is determined by salt concentration (white circles) and where it is a function of time (black circles). Each curve refers to an experiment with a single flake; proportional adjustment of the ordinates was made to enable the common points, $S = 18$ (time 5 min) to coincide on the two curves in order to allow more exact comparison. Note the point of spontaneous disorientation at $S = 40$.

much longer period (up to 48 h) but at constant salt concentration in the region where time dependent slow swelling was observed. When the measurements were referred to the same thickness, substantially the same result was obtained by the two

methods over the same swelling values (fig. 3). It was concluded that disorientation independent of the swelling process did not seriously alter the measured birefringence at swelling values of less than 30 times.

Uncertainty must remain as to the disorienting effect of the swelling process, about which little is known. Three reasons can, however, be put forward in support of the idea that disorientation is small. The theory of the diffuse double layer suggests that the silicate layers are in their position of least potential energy when they are parallel, and furthermore, observation of the aggregates shows that the swelling up to 30 times is confined predominantly along the c-axis, with the optical extinction remaining well defined. Experiments on sections with c vertical showed that the increase in thickness of the section was usually less than 10 % of the original thickness. This is within the experimental error from the non-uniformity of the swollen flake. Attempts were made to contract swollen flakes to see whether hysteresis existed in the birefringence to swelling curve, but without success because the flakes broke up.

If the difference curve (i.e. obs. $B-$ calc. B) is drawn in the significant region $S = 10\text{-}18$ times, it will be seen that ΔB only changes from 0·004 to 0·003 (positive). If the whole difference ΔB is attributed to a real birefringence of the liquid interlayers, it follows that it decreases by about 25 % as the most probable thickness of the layers increases from 45 to 120 Å [4] as the salt solution concentration decreases.*

The birefringence of the silicate layers is probably less than the assumed value, so this will have the effect of lowering the calculated curve although its hyperbolic trend at high S values will be conserved. The lowest possible position is determined by the condition that ΔB does not rise with increasing S. This reasonable limit corresponds to $\Delta B = 0\cdot002$ (although it requires a rather unrealistic value of the intrinsic birefringence). This minimum value may be compared with 1·3104-1·3090 = 0·0014 the maximum birefringence observed for ice.[5] With the qualifications noted earlier the result suggests a specific anisotropic structure of thin films of water as predicted by Derjaguin et al.[6] from other evidence. The birefringence of a montmorillonite aggregate never changes its optical sign in water as it does when it swells in some organic liquids (see below).

Application of the Kerr constant [5] for water $4\cdot03 \times 10^{-7}$ c.g.s.e. to the observed minimum birefringence $\Delta B = +0\cdot002$ leads to an effective (mean squared) field strength $\sqrt{\overline{E^2}}$ of $9\cdot2 \times 10^3$ e.s.u., directed perpendicularly to the plane of the silicate layers. This is interesting because the field direction is what would be expected for parallel negatively charged silicate layers separated by diffuse double layers of positive ions. Hence the sign of ΔB can be explained. But the magnitude of ΔB is too high.

From the theory of the double layers [8] for low potentials it follows

$$\sqrt{\overline{E^2}} = \sqrt{\frac{1}{d}\int_0^d E^2 \mathrm{d}x} = \frac{\sqrt{8\pi\sigma}}{\varepsilon}\left(\frac{\coth xd}{xd} - \frac{1}{\sinh^2 xd}\right)$$

or, at
$$xd \to 0,$$

$$\sqrt{\overline{E^2}} = 4\pi\sigma/\sqrt{3\varepsilon},$$

where E is the field strength at distance x from the phase interface, σ is the charge density per cm², ε is the dielectric permittivity, d is the half-film thickness. The resultant minimum value of 1×10^5 e.s.u./cm² for the charge density † is much higher than the experimental value of $3\cdot8 \times 10^4$ e.s.u./cm².[7]

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* These results have been confirmed for the batch of montmorillonite which was used.
† The same value (for $xd \to 0$) is valid for any high potentials.

FILMS OF ORGANIC SUBSTANCES

Jordan [9] showed that montmorillonite saturated with long chain amines (as cations) swells in some solvents. X-ray diffraction measurements were not made but the swelling measurements suggest that interlamellar expansion must have been extensive. Therefore X-ray scattering and birefringence of these systems were studied.

Dodecylammonium-montmorillonite was formed by washing Na-montmorillonite flakes with the amine dissolved in a slight excess of dilute hydrochloric acid and the excess of salt was removed by washing with alcohol. X-ray diffraction patterns of a portion of the resultant flake in water showed a 17·4 Å basal spacing.
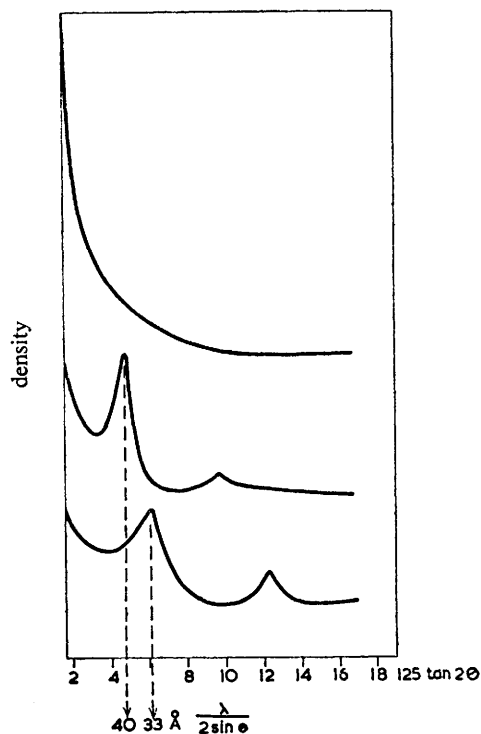

FIG. 4.—Microphotometer traces of the X-ray scattering patterns from dodecylammonium-montmorillonite in (*a*) nitrobenzene, (*b*) pyridine, (*c*) quinoline.

This indicated that there had been a high proportion of sodium ions exchanged by organic cations. After drying, the oriented aggregates were cut and their retardation and swelling measured in a few selected solvents. Some of the sections were put in capillaries and treated with the same solvents. After orienting under a polarizing microscope the swollen flakes were put in a low-angle diffraction camera and exposures taken with filtered copper radiation excited by 30 kV potential. The camera was so adjusted that for the same exposure times the background scatter without a specimen was negligible. Fig. 4 shows microphotometer traces of the photographs obtained. The interpretation of these scattering patterns would follow Norrish [4] who used a one-dimensional Fourier transform method. For our purposes, we note that the scattering patterns indicate that polymolecular solvent films, possibly enmeshed in hydrocarbon chains of the organic cation, are formed. Table 1

gives the birefringence of these complexes. Compared with the corresponding Na-montmorillonite complexes, which are of the monolayer type, pyridine and nitrobenzene-dodecylammonium montmorillonites had significantly different bi-refringences. Thus, pyridine gave zero birefringence in the monolayer complex * but gave 0·002 (positive) for the multilayer type. Nitrobenzene * gave 0·004 (negative) and 0·002 (positive) in the same two types of complex. These results show that pyridine and nitrobenzene polymolecular films have an anisotropic structure.

TABLE 1.—SHOWING THE BIREFRINGENCE, SWELLING AND POSITION OF SCATTERING MAXIMUM OF DODECYLAMMONIUM-MONTMORILLONITE AGGREGATES IN VARIOUS SOLVENTS

solvent	birefringence sign		swelling (linear)	scattering maximum $\lambda/2 \sin \theta$, Å	gel volume * (ml)
water	0·02	neg.	1	17·4	2·0
decalin	0 01(5)	neg.	1	—	—
quinoline	0·02	pos.	1·5	33	—
pyridine	0·002	pos.	2·5	40	28·0
nitrobenzene	0·002	pos.	4·0	none	88·0

* gel volumes given by Jordan.[9]

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* A monolayer complex with the aromatic rings perpendicular to the silicate layers.

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[7] Greene-Kelly, *Clay Min. Bull.*, 1962, **5**, 1.
[8] Derjaguin, *Trans. Faraday Soc.*, 1940, **36**, 203. Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, 1948, formulas (99) and (100)).
[9] Jordan, *Min. Mag.*, 1949, **28**, 598.