

BIREFRINGENCE OF CLAY MINERAL COMPLEXES¹

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ABSTRACT

The birefringence of complexes of montmorillonite with aromatic liquids depends on the type of liquid, and this fact was used to determine the proportion of expanding layers in some partly expanding minerals. A simple method of assessing samples for the presence of expanding minerals probably could be devised on the same lines.

INTRODUCTION

The refractive indices of clay mineral aggregates have long been known to be influenced by the medium in which the measurements are made (Larsen and Wherry, 1917; Correns and Mehmel, 1936). Van Baren (1936) investigated the effects of many immersion media and found that whereas the indices of kaolinites were independent of the medium, those of montmorillonites differed greatly, and that liquids which contained molecules with amino-groups caused the greatest change. There seems to be general agreement that montmorillonite minerals are thus affected because they quickly sorb water and polar organic liquids to form interlamellar complexes.

The birefringence of a crystal is more directly related to its structure than are its refractive indices (Hartshorne and Stuart, 1960, pp. 145–172). Therefore, in investigation of the change in optical properties of a clay mineral on complex formation, the birefringence changes can be expected to be sensitive to the structure, especially when the complexing molecules are highly anisotropic and are mutually oriented. Simple aromatic molecules fit this role well (Stuart, 1934; Greene-Kelly, 1955). Also, corrections for form birefringence are not needed because the refractive indices of simple aromatic liquids are usually near those of the clay mineral (Ambronn and Frey, 1926; Grim, 1953, p. 291).

EXPERIMENTAL METHOD

Measurement of Birefringence

The birefringence usually is found from the refractive indices, but with clay sections heterogeneities either inherent or introduced make the indices too inaccurate for anything but a crude estimate of the birefringence.

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Additionally, the procedure is too difficult and lengthy to use in routine work. Therefore an attempt was made to measure the retardation of sections of oriented aggregates of known thickness. The retardation of reasonably transparent sections can be measured easily but it is difficult to produce sections of known thickness. However, tolerable sections could be cut, using a microtome, after embedding the clay film in Ester Wax (obtained from the British Drug Houses, Poole, Dorset, England). Some sections showed splitting parallel to the plane of film, caused by vibrations set up while the knife passes through the aggregate with the edge parallel to the plane of the film. Splitting is lessened by cutting at 20° to the plane of the flake. It is very important that the knife is sharp and no part of the edge is used more than five times before resharping. After cutting, the sections are selected and the wax dissolved—usually by the chosen immersion liquid, because Ester Wax is soluble in a wide range of solvents. Although embedding is preferable, sections can be cut from films waxed to a firm support which is permanently attached to the center column of a hand microtome. The column is raised and lowered by a precision screw and the knife slides on a flat (usually glass) surface perpendicular to the column. This technique is useful when rapid work is necessary; sections can be cut of natural oriented aggregates or X-ray specimens in a few minutes and inspected in different media.

Any of the conventional methods can be used to measure retardation but the Sénarmont compensator is particularly useful with sections thinner than 25μ . Sections should be measured at a representative point which can be found again. Thus when making comparative measurements of the same section in different solvents the accuracy of any observed change in birefringence depends only on the section's thickness at that point and is independent of any variability over the section. Sections usually sorb organic liquids of low viscosity in a few minutes although sometimes they take a day to reach equilibrium. If the immersion liquid is volatile, evaporation can be prevented by using a cavity slide sealed with a well-fitting cover slip.

Preparation of Oriented Aggregates

The clay fraction is separated by sedimentation and the resultant suspension is evaporated on a cellophane membrane stretched across one end of a tube. The other end is closed with an ungreased ground glass stopper through which sufficient air can leak to avoid creating a suction in the tube as evaporation takes place through the cellophane. This avoids a skin forming on the clay gel which would later distort during the drying process. The drying process is hastened by placing the tube in a desiccator with calcium chloride or silica and leaving it on an oven. The dimensions of the tube are dictated by the area of clay film required and the concentration of the clay suspension. The film should be about 0.2 mm thick and, for example, if the area of the base is 1 cm^2 , the weight of clay needed would be about 50 mg. In practice the thickness of the resultant film would be a little less than 0.2 mm because of surface tension on the sides of the tube. Also when the clay suspension has a

wide range of particle sizes, heterogeneities will occur from differential settling.

For the first part of this work a fraction smaller than 0.2μ was obtained from Wyoming bentonite which was then washed with a sodium chloride solution followed by alcohol-water mixtures to remove the excess salt. Oriented aggregates were then prepared by redispersing and evaporation through cellophane. Pyridinium-montmorillonite was prepared by washing the oriented aggregates with pyridinium hydrochloride followed by alcohol-water mixtures.

For the second part, the crude material was purified by sedimentation when necessary and an oriented aggregate prepared by evaporation through cellophane. As a matter of convenience all the montmorillonites were sodium saturated, but the same effects were found when they were calcium saturated.

RESULTS

A Comparison of Methods

Dry aggregates (dried at 290°C) of Na-montmorillonite (Wyoming) were used for the following determinations of birefringence:

1. Sections were cut and the refractive indices, parallel, N_o ,¹ and perpendicular, N_a , to the plane of the film, were determined by the usual method of comparison with mixtures of α chloro-naphthalene and kerosene (see Results 1).

The values were $N_o = 1.549 (\pm 0.003)$; $N_a = 1.520 (\pm 0.003)$. The films viewed along N_a gave a poor biaxial interference figure with $2V$ small. Hence the refractive indices in the plane of the flake were for all practical purposes the same. The birefringence is therefore $-0.029 (\pm 0.006)$.

2. Sections 25μ thick were cut and their retardation (viewed along N_o) determined in *p*-xylene. This medium is non-polar and therefore does not penetrate dry montmorillonite. The retardation was $700\text{--}800 \text{ m}\mu$ (negative) giving an average birefringence of $-0.03 (\pm 20 \text{ percent})$.

3. The method used in (1) was repeated with quinoline-decahydronaphthalene mixtures. The results were $N_o = 1.581$; $N_a = 1.598 (\pm 0.003)$, giving a birefringence of $+0.017 (\pm 0.006)$.

4. The method used in (2) was repeated using quinoline instead of *p*-xylene. The birefringence was $+0.024 (\pm 20 \text{ percent})$.

The results indicate that there is satisfactory agreement between the comparison and retardation methods when using the same type of immersion liquid. They also illustrate the great effect that the immersion liquid may have on the birefringence of a clay film.

Complexes of Montmorillonite

Table 1 shows the birefringences of some complexes of montmorillonite (Wyoming) with aromatic molecules. All the complexes were investigated by X-ray diffraction (Greene-Kelly, 1955) and all, except the benzene complex,

¹ It seems preferable to denote the indices of an oriented aggregate as N_o and N_a after Ambronn and Frey (1926) to distinguish them from values obtained from single crystals.

TABLE 1.—BIREFRINGENCE OF VARIOUS COMPLEXES OF MONTMORILLONITE TOGETHER WITH THEIR "MOLECULAR ANISOTROPIES"

Complex	Birefringence	Anisotropy, Å ³ /molecule
Uncomplexed	-0.029	---
Pyridine (15 Å)	isotropic	+4.7
Quinoline	+0.024	+9.5
4-Methyl pyridine	-0.010	---
Benzonitrile	-0.010	---
4-Tolunitrile	-0.02 to 0.03	---
2-Tolunitrile	-0.005	---
Benzene	very small	+4.3

were formed from Na-montmorillonite. The benzene complex was formed from pyridinium-montmorillonite and thus was a mixed complex, one-third pyridine and two-thirds benzene (Greene-Kelly, 1956). The birefringence of the complexes shows that the interlayer molecules have a profound effect which should be related to their structure, composition and their orientation with respect to the silicate layers. An attempt, therefore, was made to calculate the effective "anisotropy" of a molecule from polarizability data (Stuart, 1934; Le Fèvre *et al.*, 1959). The molecule was assumed to be in the expected orientation (from X-ray data) and assigned orthogonal axes b_1 , b_2 and b_3 (see Fig. 1). To express that the silicate layers were randomly arranged in the clay film, the molecules were rotated perpendicular to the silicate layers (along b_2) and the average polarizability (ρ) calculated from the values of b_1 and b_3 by using an equation of an ellipse with semi-axes of b_1 and b_3 . The average value (ρ) is then found where $\theta = 45^\circ$; that is

$$\frac{\rho^2 \cos^2 \theta}{b_1^2} + \frac{\rho^2 \sin^2 \theta}{b_3^2} = 1$$

The difference between b_2 and ρ is the anisotropy and is tabulated in Table 1. The anisotropy of benzene is near that of pyridine, which explains why benzene substitutes for pyridine with so little change in birefringence. The larger anisotropy of quinoline also explains why the birefringence of the quinoline complex is much greater than the pyridine complex.

This approach is at present very limited because of lack of data, and it is necessary to be satisfied with comparing complexes of similar molecules in similar orientations. Thus the difference between the birefringence of the pyridine and of the 4-methyl pyridine complexes shows that the 4-methyl pyridine is less anisotropic than pyridine; 4-tolunitrile is also less anisotropic than benzonitrile. This suggests that a 4-methyl group exerts a considerable effect on the polarizability of the molecule in the b_1 direction. If this is correct, 2-tolunitrile which is intercalated with b_2 perpendicular to the silicate layers

should show greater anisotropy than benzonitrile because the 2-methyl group exerts its influence predominantly along the b_2 direction. This is borne out by the observed birefringence. These three examples illustrate the large

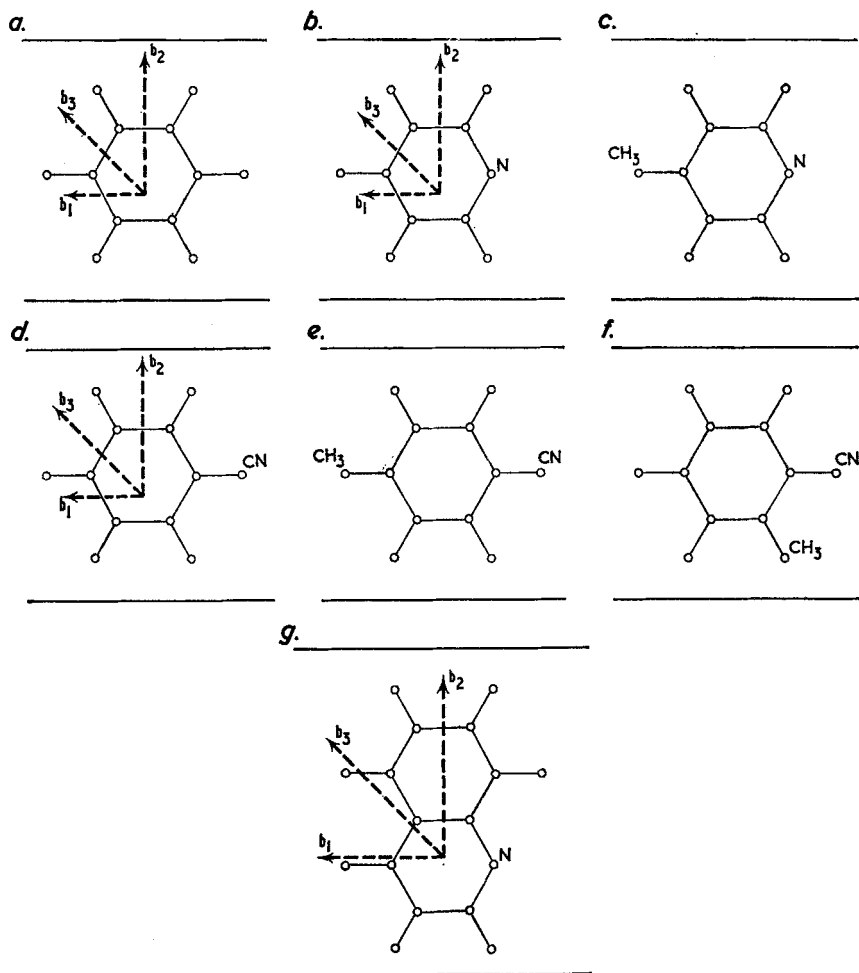


FIGURE 1.—The orientation of the complexing molecules in the complexes shown in Table 1 with their axes b_1 , b_2 and b_3 : (a) benzene; (b) pyridine; (c) 4-methylpyridine; (d) benzonitrile; (e) 4-tolunitrile; (f) 2-tolunitrile; (g) quinoline.

directional effect of a methyl group attached to an aromatic ring; it is substantiated by the measured polarizabilities of benzene and toluene (Stuart, 1934). The examples also show that the inferred orientations of the molecules in the complexes are probably correct.

Complexes of Various Minerals

Table 2 shows the changes of birefringence (ΔB) of various minerals when placed in *p*-xylene and then in quinoline. The three montmorillonites, despite differences in composition, particle size, shape, and orientation in the aggregate, show similar changes in birefringence. It therefore will be assumed

TABLE 2.—THE CHANGE OF BIREFRINGENCE OF VARIOUS MINERALS IN *p*-XYLENE AND THEN IN QUINOLINE

Mineral	Birefringence in		ΔB	<i>p</i>
	<i>p</i> -Xylene	Quinoline		
Montmorillonite (Unterrupstroth)	-0.030	+0.018	0.048	1.0
Montmorillonite (Wyoming)	-0.029	+0.019	0.056	1.0
	-0.032	+0.024	0.048	
Montmorillonite (Redhill)	-0.030	+0.021	0.051	1.0
Mica (Woodbury)	-0.023	-0.004	0.019	0.3(8)
Mica (Woolhope)	-0.022	-0.008	0.014	0.2(8)
Mica (Fithian)	-0.024	-0.012	0.012	0.2(4)
Heated Li-Montmorillonite (Wyoming)	-0.029	± 0.001 (variable)	0.030 0.028	0.6(0) 0.5(6)

that the average value of ΔB , equal to 0.05, represents a fully expanding structure with the proportion of expanding layers, *p*, equal to unity.

Wyoming montmorillonite saturated with lithium ions and heated to 200°C does not expand in water although it slowly sorbs glycerol and other organic compounds to about half the possible amount (Brown and Greene-Kelly, 1954). The change in birefringence, ΔB , of the treated montmorillonite is much less than that of the original mineral, indicating that the proportion of expanding layers governs the birefringence change. It is a reasonable assumption that ΔB is proportional to *p*, from which it follows that the value of *p* is between 0.56 and 0.60, which is in fair agreement with the X-ray results of Brown and Greene-Kelly (1954).

The same procedure was followed with three hydrous micas, and the results are in Table 2. The Woodbury material was previously investigated by an X-ray method by MacEwan (1956), who obtained *p* = 0.28, which is somewhat smaller than the optical value of 0.38. Considering the assumptions in both methods, the agreement must be considered satisfactory at present. The Woolhope and Fithian minerals show a diffuse and complex X-ray scattering and consequently have not been investigated. The optical method showed that *p* = 0.28 and 0.24 respectively.

An interesting inference from the results for the hydrous micas is that when they partly expand with quinoline they do so like a montmorillonite.

CONCLUSIONS

The changes of birefringences of clays in different solvents can provide a rapid method of assessing them for expanding minerals, or if they are entirely composed of hydrous micas they can be assessed for the proportion of expanding layers. Finally the study of the optical properties of montmorillonite complexes can provide information about the orientation and possibly about the polarizability of the sorbed molecules.

REFERENCES

- Ambrohn, H. and Frey, A. (1926) *Das Polarizations-Mikroskop*: Leipzig.
- Brown, G. and Greene-Kelly, R. (1954) X-ray diffraction by randomly interstratified clay mineral: *Acta Cryst.*, v. 7, pp. 101-103.
- Correns, C. W. and Mehmel, M. (1936) Über den optischen und röntgenographischen Nachweis von Kaolinit, Halloysit und Montmorillonit: *Z. Krist.*, v. 94, pp. 337-348.
- Greene-Kelly, R. (1955) Sorption of aromatic organic compounds by montmorillonite. Part I: *Trans. Faraday Soc.*, v. 51, pp. 412-424.
- Greene-Kelly, R. (1956) The swelling of organophilic montmorillonites in liquids: *J. Colloid Sci.*, v. 11, pp. 77-79.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill, New York, p. 291.
- Hartshorne, N. H. and Stuart, A. (1960) *Crystals and the Polarising Microscope*: Arnold.
- Larsen, E. S. and Wherry, E. T. (1917) Leverrierite from Colorado: *J. Wash. Acad. Sci.*, v. 7, pp. 208-217.
- Le Fèvre, C. G., Le Fèvre, R. T. W., Purnachandra Rao, B. and Smith, M. R. (1959) Molecular polarisability. Ellipsoids of polarisability for certain fundamental heterocycles: *J. Chem. Soc.*, pp. 1188-1192.
- MacEwan, D. M. C. (1956) A study of an interstratified illite-montmorillonite clay from Worcestershire, England: in *Clays and Clay Minerals*, Nat. Acad. Sci.-Nat. Res. Council, pub. 456 (4th Conf.), pp. 166-172.
- Stuart, H. A. (1934) *Molekülstruktur*: Springer, Berlin.
- Van Baren, F. A. (1936) Über den Einflus verschiedener Flüssigkeiten auf den Brechungsindex von Tonmineralien: *Z. Krist.*, v. 95, pp. 464-469.