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Abstract

Full Text

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BIREFRINGENCE OF THIN LIQUID LAYERS

There are a number of indications (^{1}) of the special structure of thin boundary layers of liquids. We measured the birefringence of thin liquid interlayers between network layers of montmorillonite during its swelling, in order to demonstrate the anisotropy of their structure.

Method. The object of the investigation was montmorillonite from Wyoming, U.S.A. It was saturated with Na ions in NaCl solutions and then freed of Cl ions by water-alcohol mixtures.

Fig. 1. Schematic of the apparatus for measuring the retardation in the direction of the axis of the clay aggregate

Fig. 2. Dependence of B on S: a —experimental data, b —results of calculation by Wiener' s formula. The values of the thicknesses d' were taken from work (^{3})

To obtain well-oriented aggregates, the clay particles were stirred up in water, which was evaporated through a cellophane membrane. By excluding evaporation from the surface of the gel, we prevented the formation and subsequent wrinkling of the crust, improved the orientation of the aggregates, and facilitated their removal from the substrate. Blocks 0.1-0.2 mm in cross section were cut from the clay film with a safety-razor blade and were studied with a polarization microscope M (Fig. 1). The clay block was oriented on a microscope slide that had a depression; the c axis lay in the plane of the glass; then liquid was added and a cover glass was carefully slid over it from above. After swelling of the block in the liquid had ceased, the retardation Δ was measured in sodium D-line light with a Sénarmont compensator, and the birefringence B was calculated.

Results

1. Water films. To present the results, one may, first, plot the values of B, observed in aqueous NaCl solutions of known concentration, as a function of the thicknesses of the liquid interlayers measured by Norrish by means of x-ray diffraction. Second, one may plot the values of B as a function of the macroswelling S, equal to the ratio of the sample thickness measured with a microscope to the initial thickness. However, the observed S always exceeds S according to Norrish' s data, since the intercrystalline layers are much thicker than the intracrystalline ones. Nevertheless, with increasing S, the dependence of B on S approaches the dependence of B on S calculated from Norrish, coinciding with it at $S > 10$.

In order, knowing B, to determine the birefringence of the intracrystalline films, it is necessary to take into account the form birefringence. According to Wiener (^{2}), for a system of parallel isotropic plates

$$\varepsilon_0 = \delta_1\varepsilon_1 + \delta_2\varepsilon_2 + \dots, \qquad \frac{1}{\varepsilon_a} = \frac{\delta_1}{\varepsilon_1} + \frac{\delta_2}{\varepsilon_2} + \dots, \tag{1}$$

where ε_0 is the mean (effective) value of the dielectric constant parallel to the layers, ε_a is perpendicular to the layers, and δ_x is the volume fraction of the fraction with dielectric constant ε_x. Wiener' s formula is applicable if each of the parallel plates has a thickness much smaller than the wavelength of the incident light, which was always satisfied.

Profilite-like layers, each 10 Å thick and separated by liquid films, have values $\varepsilon_1^{\parallel}$ and $\varepsilon_1^{\perp}$ and an intrinsic birefringence B_0 presumably of the same magnitude as profilite crystals; consequently, $B_0 \cong 0.04$. Dehydrated aggregates of montmorillonite show a somewhat smaller B_0: from 0.02 to 0.03, probably because of imperfect orientation of the crystallites of which the aggregates consist; the orientation coefficient $\frac{0.25}{0.4} = 0.6$ was used in calculating B of the aggregate from the value of B for a single crystal. The Wiener equations were used in the form:

$$n_0^2 = \delta_1 n_1^{\parallel 2} + \delta_2 n_2^2; \qquad n_a^2 = \frac{n_1^{\perp 2} n_2^2}{\delta_1 n_2^2 + \delta_2 n_1^{\perp 2}}; \qquad B = 0.6(n_a - n_0),$$

where n_0 is the effective refractive index of the aggregates parallel to the layers, n_a is perpendicular to the layers, and $n_1^{\parallel}$, $n_1^{\perp}$, and n_2 are the same indices for the silicate layers and the liquid film (assumed isotropic).

Fig. 3

Figure 3: Fig. 3

Fig. 3. Dependence of Δ on S. Open circles are experimental data obtained after establishment of apparent equilibrium over a short time, when different degrees of swelling corresponded to different salt concentrations. Filled circles are experimental data corresponding to one and the same salt concentration. S and, correspondingly, Δ varied as a function of time during prolonged swelling—up to 48 hours. The ordinate scales in both cases were chosen so that points corresponding to one and the same state ($S = 18$, swelling time 5 min.) coincided.

In Fig. 2, as a function of S, are presented the values of B calculated according to Wiener (curve b) and the directly measured equilibrium values (curve a) in solutions of various NaCl concentrations. The scatter of the points is due to the fact that each point represents a measurement on a new aggregate. In measurements on a single specimen (see Fig. 3) the scatter of the points is much smaller.

Discussion of results. From Fig. 2 it is seen that for all values of S the experimental points lie below the curve constructed according to Wiener; thus either B_0 under these conditions differs from the adopted (volume) value, or the water interlayers contribute to the optical anisotropy of the system. However, it is easy to see that the Wiener curve—at large S, a hyperbola—cannot be brought into coincidence with the experimental one for any value of B_0; consequently, without assuming birefringence of the liquid interlayers 100-200 Å thick, the results obtained cannot be explained.

There is also additional evidence. Thus, if S was greater than 20, B decreased more slowly, while S increased with time. At $S > 40$, B rapidly fell to zero without a corresponding increase in S, and the swollen specimen began to spread out as a result of spontaneous disorientation.

To prove that at smaller values of S no disorientation occurs independently of the swelling process, observations of the influence of S on B were carried out in two ways. First, by measuring B after equilibrium had been established at each new value of the salt concentration, and, second, by carrying out measurements at constant concentration over 48 h. In the region where S changes slowly with time, the results of both methods essentially coincide (Fig. 3); consequently, disorientation independent of the swelling process does not substantially change the value of B for $S < 30$-fold.

Fig. 4. Microphotograms of photographs of the diffraction pattern of dodecylammonium-montmorillonite: a—in nitrobenzene, b—in pyridine, v—in quinoline.

One may suppose an influence of the swelling process on disorientation; however,

Figure 4: Microphotograms of photographs of the diffraction pattern of dodecylammonium-montmorillonite: *a*—in nitrobenzene, *b*—in pyridine, *v*—in quinoline. The vertical axis is "Darkening" ; the horizontal axis is $1.25\,\mathrm{tg}\,2\theta$, with markings corresponding to 40, 33 Å, and $\lambda/(2\sin\theta)$.

Figure 4: Figure 4: Microphotograms of photographs of the diffraction pattern of dodecylammonium-montmorillonite: *a*—in nitrobenzene, *b*—in pyridine, *v*—in quinoline. The vertical axis is "Darkening" ; the horizontal axis is $1.25\,\mathrm{tg}\,2\theta$, with markings corresponding to 40, 33 Å, and $\lambda/(2\sin\theta)$.

the theory of the interaction of diffuse double layers shows that the minimum of the potential energy corresponds to parallelism of the silicate layers. Secondly, observation of aggregates reveals that swelling at $S < 30$ is limited mainly to the c axis (in the perpendicular direction it is less than 10%), and the optical absorption of the aggregates remains well defined and constant.

If we plot $\Delta B \equiv B_{\text{obs.}} - B_{\text{calc.}}$ as a function of S in the interval $10 \div 18$, then ΔB changes only from 0.004 to 0.003. If the entire difference ΔB is ascribed to the birefringence B_1 of the liquid interlayers, we arrive at the conclusion that it decreases by 25% as their thickness increases from 45 Å to 120 Å. If we assume that B_0 does not coincide with the accepted value, then the curve calculated by Wiener will shift while retaining the form of a hyperbola for large S. The lowest possible position of the curve will be found by requiring that the values of ΔB do not increase with increasing S. The corresponding ΔB is +0.002; for comparison, the maximum birefringence of ice (^{4}) is

$$1.3104 - 1.3090 = +0.0014.$$

It may be supposed that the birefringence of aqueous interlayers is explained by the Kerr effect of the electric field in the double electric layers. However, calculations show that the maximum possible value of the charge density of the double layers at the silicate-layer-water-film boundary, of the order of $1 \cdot 10^4$ abs. units, can explain only 1/10 of the observed birefringence. This result indicates an anisotropic structure of the thin layers of water.

2. Films of inorganic substances

Jordan (^{6}) showed that montmorillonite saturated with long-chain amines (as cations) swells in certain organic solvents.

Dodecylamine-montmorillonite was obtained by us by washing montmorillonite flakes with an amine dissolved in water with a small excess of diluted HCl. The excess salt was removed by washing with ethyl -

by this. The X-ray diffraction pattern (in water) revealed a basal interplanar spacing of 17.4 Å. This indicates that most of the sodium ions had been exchanged for organic cations. After drying, the oriented aggregates were cut into blocks, and Δ and B were measured in several selected solvents. Some blocks were placed in capillaries and treated with the same solvents. After orientation under a polarizing microscope, the swollen flakes were placed in a chamber for investigation of diffraction at small angles, and photographs were taken with filtered radiation from a copper anticathode excited by a potential of 30 kV. Fig. 4 shows the results of microphotometry of the photographs obtained. These data were interpreted, following Norrish, by applying the method of one-dimensional Fourier transformation. It was found that the diffraction patterns indicated the formation of polymolecular solvent layers, possibly linked with the hydrocarbon chains of the organic cations. Table 1 gives the birefringence of these complexes.

Table 1

Birefringence, swelling, and position of diffraction maxima of dodecylamine-montmorillonite aggregates in various solvents

Solvent	Birefringence B	Swelling (linear) S	Diffraction maximum $2\frac{\lambda}{\sin\alpha}$, Å	Gel volume, ml, by (7)
Water	−0.02	1×	17.4	2.0
Decalin	−0.01 (5)	1×	–	–
Quinoline	+0.02	1.5×	33	–
Pyridine	+0.002	2.5×	40	28.0
Nitrobenzene	+0.002	4.0×	very small angle	88.0

In comparison with the corresponding Na-montmorillonite complexes belonging to the monolayer type, the pyridine and nitrobenzene dodecylamine-montmorillonites have substantially different birefringence. Thus, pyridine gave zero birefringence in the monolayer complex, but +0.002 for the multilayer type. Nitrobenzene gave −0.004 and +0.002, respectively, for the same two types of complexes. It should also be noted that the sign of the path difference is reversed during swelling, in contrast to the case of Na-montmorillonite in water. All this is strict evidence of the anisotropic structure of the polymolecular layers, different from the structure of monolayers.

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Note: Figure translations are in progress. See original paper for figures.