

EFFECT OF SWELLING ON THE INFRARED ABSORPTION SPECTRUM OF MONTMORILLONITE

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Abstract—The i.r. spectra of mixtures of different Na-montmorillonites were determined at several water contents between 2 and 22 g of water/g of montmorillonite. It was found that Si-O absorption is represented by four closely-spaced bands, one of which is pleochroic. The pleochroic band appeared only at higher water contents. All of these bands, excepting that with the highest wave number, shifted in frequency with increasing isomorphous substitution. None of them shifted in frequency with increasing water content.

The absorption coefficient for the principal Si-O absorption decreased with increasing isomorphous substitution but increased with increasing water content. Neither isomorphous substitution nor water content appeared to have any significant effect on absorption due to O-H stretching or H-O-H bending in the interlayer water.

At a critical water content for each montmorillonite, an abrupt change occurred in the absorption coefficient for the principal Si-O absorption. This change was ascribed to a sudden rearrangement of the particles.

INTRODUCTION

In an earlier study, Ravina and Low (1972) observed by means of X-ray powder diffraction that the *b*-dimension of dioctahedral montmorillonites increased with the absorption of interlayer water until maximal swelling was attained. An increase in *b*-dimension requires that the crystal lattice change from ditrigonal toward regular hexagonal symmetry. Since this observation has significant implications relative to the mineralogy and surface chemistry of clays, we felt that it deserved substantiation by another method. Therefore, we employed i.r. spectroscopy to study possible changes in Si-O vibrations resulting from changes in crystal symmetry during swelling. We were encouraged in this study by the preliminary, unpublished results of J. L. White, H. Al-Abbas and the junior author who noted that the Si-O absorption band of montmorillonite changed somewhat in character as the ratio of water to montmorillonite increased.

MATERIALS AND METHODS

Six dioctahedral montmorillonites were used in this study. Their origins and chemical compositions are described in Table 1. All of them except that from Aberdeen, MS were obtained from Ward's National Science Establishment. The Aberdeen montmorillonite was obtained from the American Colloid Co. The methods by which their <2- μ m fractions were separated, Na-saturated, dialyzed and freeze-dried have been described by Davidtz and Low (1970).

All i.r. analyses were made with a Perkin-Elmer dual-grating, double-beam spectrophotometer (Model 421). To obtain Si-O absorption bands that were not too intense to be recorded, films containing less than 0.25 mg of montmorillonite/cm² were necessary. Such films were prepared by two different methods. In the first method (Method I) 2 ml of a suspension containing 0.075% montmorillonite by weight were spread over the surface of an Irtran-2 window and allowed to evaporate to dryness within the confines of a flat aluminum ring (i.d. = 2.85 cm) which was sealed to the window with silicone grease. Then the resulting film was allowed to adsorb water vapor by holding it above boiling water. The amount of water adsorbed was calculable because the film was weighed before and after its exposure to the vapor. Subsequently, evaporation was prevented by sealing a second Irtran-2 window to the top of the ring. After the i.r. absorbance of this film was determined, a small amount of water was allowed to evaporate from it by removing the upper window temporarily. Then the system was reweighed and the Si-O absorbance was determined again. By repeating this procedure, the Si-O absorbance of a single sample of montmorillonite was determined at several water contents.

In the second method (Method II) montmorillonite-water pastes ranging in water content from 2 to 22 g/g of montmorillonite were squeezed between two Irtran-2 windows until the absorbance of the principle Si-O vibration band was about 0.7. The time between the preparation of the pastes and the recording of their spectra was approx. $\frac{1}{2}$ hr. Evidently, this equilibration period was long enough because the

Table 1. Mineralogical composition of unit cell (based on 20 oxygens)*

Clay mineral	Octahedral layer				Tetrahedral layer	
	Al ³⁺	Fe ³⁺	Fe ²⁺	Mg ²⁺	Si ⁴⁺	Al ³⁺
Aberdeen (Am. Colloid Company)	2.88	0.68		0.48	7.72	0.28
Belle Fourche (API No. 27)	3.11	0.34	0.02	0.57	7.80	0.20
Upton (API No. 25b)	3.06	0.30	0.02	0.65	7.82	0.18
Polkville (API No. 21)	2.81	0.26	0.03	0.90	7.86	0.14
Otay (API No. 24)	2.69	0.11		1.20	7.95	0.05
Bayard (API No. 30a)	2.91	0.12	0.02	0.95	8.00	

* Data for Aberdeen clay were obtained from Foster (1953). Data for other clays were obtained from Schultz (1969).

spectra were the same after 3 days as they were after $\frac{1}{2}$ hr. This procedure did not assure that the amount of clay exposed to the i.r. beam was the same for every sample.

During the investigation, it became advisable to measure the O–D stretching absorbance (2521 cm^{-1}) of mixtures containing different proportions of montmorillonite and a D_2O – H_2O solution containing 6.4% D_2O by vol. The mixtures were prepared for analysis by squeezing them between Irtran-2 windows until the windows came into intimate contact with a Teflon spacer $15\text{ }\mu\text{m}$ thick. Under these conditions, the OD absorbance of every mixture was within the range of the instrument.

RESULTS AND DISCUSSION

Effect of isomorphous substitution on Si–O vibrations

The primary purpose of the present study was to determine, by i.r. analysis, the effect of swelling on the crystal symmetry of montmorillonites. Hence, it was necessary to study an absorption band which could be identified with a fundamental lattice vibration and which was resolvable from the absorption bands of other components. The Si–O absorption band was ideally suited to our needs. It was identified earlier by Stubican and Roy (1961c) and Lerot *et al.* (1974). Also it was easily separated from the absorption band due to the librational vibration of water which occurs below 800 cm^{-1} .

Initially, we prepared oriented, air-dried specimens of all the montmorillonites by method I and determined their i.r. spectra at different orientations with respect to the incident beam. The results for the montmorillonites from Upton, WY and Otay, CA are presented in Fig. 1 A & B. Each spectrum in this figure is labelled with the corresponding angle of incidence, i.e. the angle between the incident i.r. beam and the normal to the specimen surface.

Essentially four bands compose the complex Si–O absorption pattern of the Upton clay. They occur at 1028, 1052, 1090 and 1122 cm^{-1} (Fig. 1A). The only band that changes with orientation of the specimen is that at 1090 cm^{-1} . It increases in intensity as the angle of incidence increases and must, therefore, be

associated with a perpendicular vibration, i.e. one that is parallel to the incident beam. Following Farmer and Russell (1964), we assign it to a complex vibration involving apical oxygen atoms that are shared by the tetrahedral and octahedral layers. The bands at 1028, 1052 and 1122 cm^{-1} cannot be identified with any particular Si–O vibrations at the present time. However, it is probably that they are attributable to complex cooperative vibrations within the tetrahedral layer.

An analysis of the spectra of the Otay clay shows that its Si–O absorption bands occur at 1005, 1035 and 1114 cm^{-1} (Fig. 1B). On close examination, a very weak shoulder is also discernible at 1122 cm^{-1} . The only band that is sensitive to orientation is that at 1114 cm^{-1} . Here, it is attributed, as before, to a perpendicular vibration.

As shown in Table 2, the frequencies of the four Si–O absorption bands are different for each clay. They are identified in the table, in order of increasing frequency, by the numbers 1, 2, 3, 4, respectively. This method of identification will be used hereafter.

All of the montmorillonites used in the present study have the same basic crystal structure. They differ only in the extent of isomorphous substitution that has occurred within this structure. Consequently, we conclude that the differences exhibited in Table 2 are related to differences in isomorphous substitution. This conclusion is expressed quantitatively by the following empirical equations:

$$v_2 = 1041.5 - 17.4\text{ Fe}_{\text{VI}} - 7.5\text{ Mg}_{\text{VI}} + 111.7\text{ Al}_{\text{IV}}\text{ cm}^{-1} \quad (1)$$

$$v_3 = 1080 + 45.2\text{ Fe}_{\text{VI}} + 28.3\text{ Mg}_{\text{VI}} - 132\text{ Al}_{\text{IV}}\text{ cm}^{-1} \quad (2)$$

which were obtained by multiple linear regression analysis using data from Tables 1 and 2 and a CDC 6500 computer. In these equations, v_2 is the frequency of band 2, v_3 is the frequency of band 3, Fe_{VI} and Mg_{VI} are the number of iron and magnesium atoms, respectively, in octahedral sites and Al_{IV} is the number of aluminum atoms in tetrahedral sites per unit cell (based on 20 oxygen atoms). The equations predict the observed v_2 and v_3 to within two or three

wavenumbers. However, in view of its small coefficient, the inclusion of the term for Mg_{VI} in equation (1) is of doubtful statistical significance.

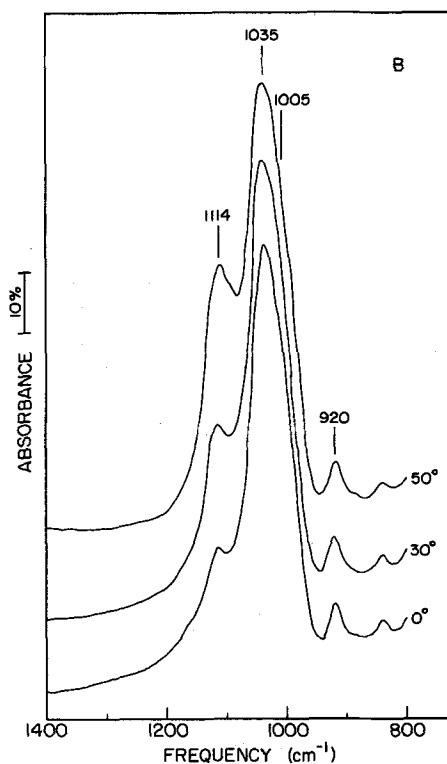
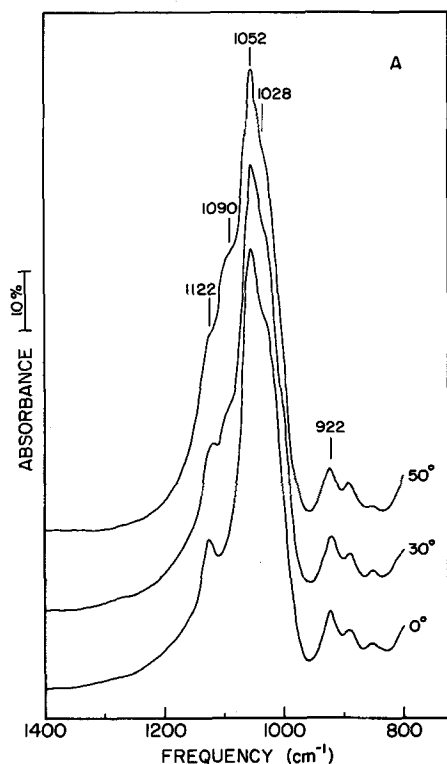


Fig. 1. I.R. spectra of dry Na-montmorillonites from Upton, WY (A) and Otay, CA (B) at different angles of incidence.

Isomorphous substitution in a clay crystal alters the angle α through which the tetrahedra must rotate about their vertical axes to reduce the dimensions of the tetrahedral layer to fit those of the octahedral layer (Radoslovich and Norrish, 1962; Radoslovich, 1962). It probably alters the $O_{\text{apical}}\text{-Si-O}_{\text{basal}}$ angle, τ , and other structural parameters as well. According to Pampuch and Ptak (1969), the frequencies of the different vibrational modes of the tetrahedral layer in layer-lattice silicates depend mainly on two factors, namely, the angles α and τ . As these angles change, a shift occurs in the frequency of each mode of vibration. The magnitude and direction of the shift differ for different modes of vibration. The shift is toward higher frequencies in some cases and toward lower frequencies in others. Thus it is not surprising that ν_2 and ν_3 shifted by different amounts and in opposite directions with an increase in isomorphous substitution. Nor is it surprising that no general relation between lattice vibrations and isomorphous substitution can be established for all silicates by combining our data with those of others (e.g. Lyon and Tuddenham, 1960; Milkey, 1960; Stubican and Roy, 1961a,b; Farmer and Russell, 1964; Flanigen *et al.*, 1971). All that can be said definitely at present is that the vibrations within a silicate crystal are cooperative and are, therefore, affected by the replacement of one ion by another in any part of the crystal.

Effect of swelling on Si-O vibrations

A change in the b -dimension of montmorillonite would be accompanied by a change in the angle α and, perhaps, by a change in the angle τ as well. Therefore, if swelling produces a change in b -dimension, it should affect the frequencies of the Si-O absorption bands. Figures 2A and B present the i.r. spectra of the Belle Fourche and Otay montmorillonites, respectively, in the 800–1400 cm^{-1} range at different water contents, expressed as the ratio of the mass of water, n_2 , to the mass of montmorillonite, n_1 . The sample used to obtain the spectrum in Fig. 2A was prepared by method I, whereas, that used to obtain the spectrum in Fig. 2B was prepared by method II. Observe from these figures that, although their intensities change, there is no displacement of any of the Si-O bands with increasing water content. Similar observations were made with the other clays.

Table 2. Frequencies of the i.r. bands composing the complex Si-O absorption

Clay mineral	Frequency (cm^{-1})			
	(1)	(2)	(3)*	(4)
Aberdeen		1057	1088	1122
Belle Fourche	1020	1052	1086	1122
Upton	1028	1052	1090	1122
Polkville		1047	1097	1122
Otay	1005	1035	1114	1122
Bayard		1032	1113	

* Perpendicular vibration.

Consequently, we conclude that, in the range of water contents of this experiment (2–22 g/g), swelling produced no change in *b*-dimension. This conclusion is not consistent with the original X-ray data of Ravina and Low (1972). However, it is consistent with their more recent X-ray data, and with the X-ray data of Margheim and the junior author, all of which will be published soon.

From Fig. 2 it is evident that an increase in water content causes the appearance and development of the band associated with the perpendicular vibration (band 3). We interpret this to mean that, as the layers move apart, they tend to become disoriented and an increasing proportion of them intercept the i.r. beam with angles of incidence other than zero. Also, an increase in water content causes the principal Si–O band (band 2) to narrow and increase in intensity. For example, in Fig. 2A this band narrowed from 77 to 50 cm⁻¹ at half-height and increased in intensity

by 28% as the water content increased from air-dry to 15 g/g. In order to interpret the latter observation, it will be instructive to derive an equation for the transmittance of radiant energy by clay particles dispersed in water. Although satisfactory equations are available for the transmittance of radiant energy by dispersions of spheres and cubes (Otvos *et al.*, 1957; Duyckaerts, 1959), they are not strictly applicable to dispersions of planar clay particles. Our derivation follows that of Otvos *et al.* (1957). It is subject to the following conditions: (1) the ratio of the diameter of the particles to the wavelength of the light is small enough for scattering to be negligible, (2) the water is non-absorbing at this wavelength, (3) the particles are oriented with their planar surfaces perpendicular to the incident light but are randomly dispersed otherwise, and (4) the particles are uniform in size.

Consider an arbitrarily chosen light ray passing through the sample as illustrated in Fig. 3. It will strike any particle with a dia., *d*, whose center is within the cylinder of radius, *d*/2, and length, *l*, i.e. any particle whose center is within the volume $v = \pi d^2 l / 4$ of the cylinder having the ray as its axis. The probability, *P_r*, of finding *r* particles with their

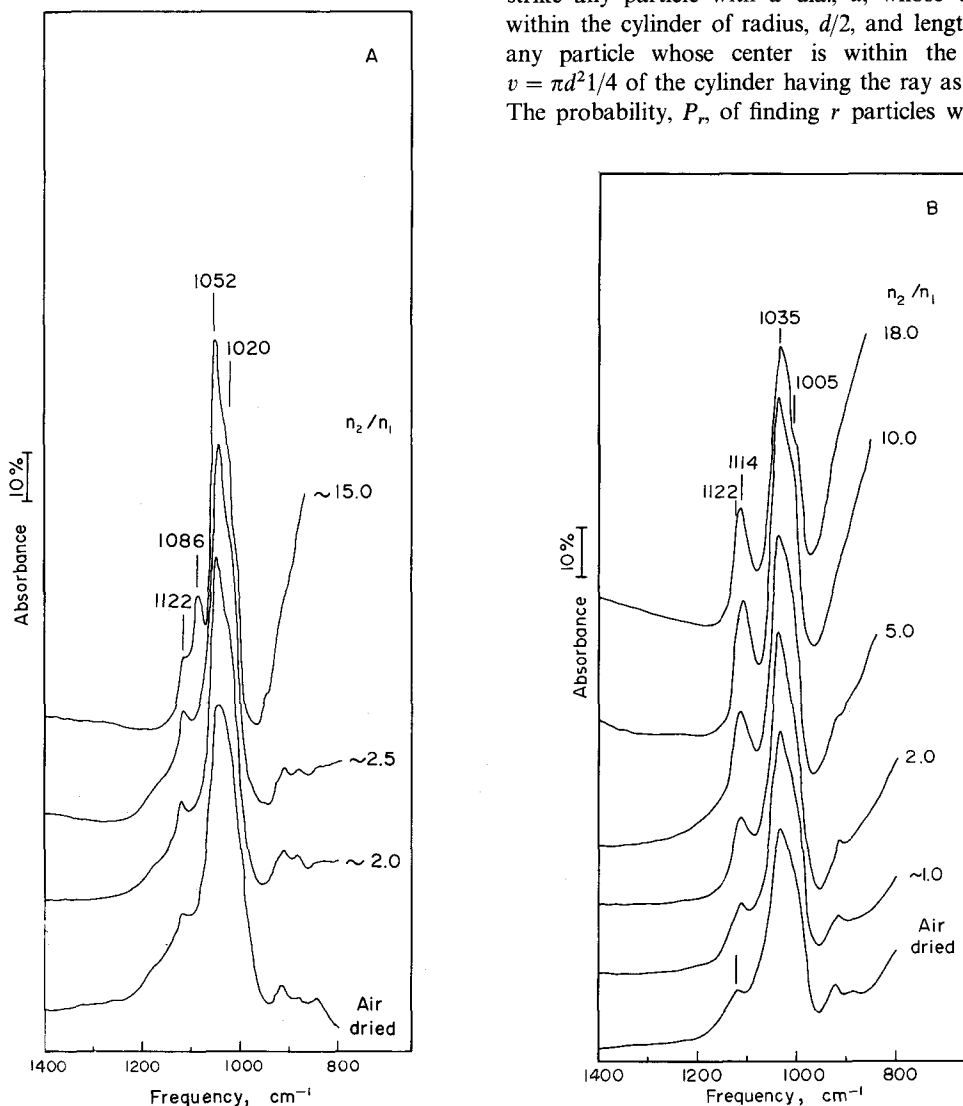


Fig. 2. I.R. spectra of Na-montmorillonites from Belle Fourche, SD (A) and Otay, CA (B) at different values of the weight ratio, n_2/n_1 , of water to Na-montmorillonite

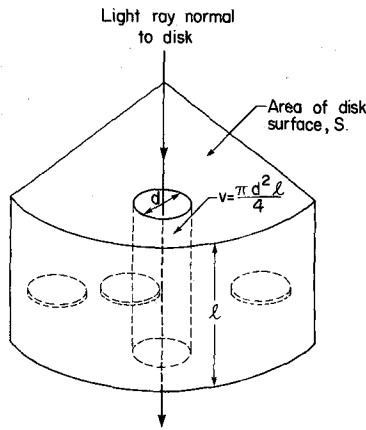


Fig. 3. Light-ray passing through a disk-shaped sample of montmorillonite in water.

centers in this cylinder is obtainable from the Poisson formula of probability theory, viz.

$$P_r = \frac{e^{-a} a^r}{r!}, \tag{3}$$

where a is the number of particles that, on the average, would be expected to be in the cylinder. Hence, the fraction of the radiation that encounters 0, 1, 2, etc. particles is $P_0 = e^{-a}$, $P_1 = ae^{-a}$, $P_2 = (a^2/2)e^{-a}$, etc. Now, if the transmittance of one particle is θ , the transmittance of r particles encountered in succession is θ^r . As a result, the total transmittance, I/I_0 , is

$$\begin{aligned} I/I_0 &= P_0 + \theta P_1 + \theta^2 P_2 + \dots \\ &= \sum_{r=0}^{\infty} \frac{\theta^r e^{-a} a^r}{r!} = e^{-a} \sum_{r=0}^{\infty} \frac{(a\theta)^r}{r!} \\ &= e^{-a} e^{a\theta} = e^{-a(1-\theta)} \end{aligned} \tag{4}$$

or

$$\ln I_0/I = a(1 - \theta). \tag{5}$$

The number of particles expected, on the average, to be in the cylinder is given by

$$a = \frac{nv}{Vm} = \frac{n}{S\rho\delta} = \frac{c1}{\rho\delta}, \tag{6}$$

where n is the total mass of particles and c is the concentration of particles (g/cm^3) in the sample, V is the volume of the sample, S is its cross-sectional area, and m , ρ and δ are the mass, density, and thickness, respectively, of a single particle. In addition, for the flat clay particle, $\theta = e^{-k\delta}$ where k is the true linear absorption coefficient. Therefore, after converting to the common logarithm, we can write

$$A = \log I_0/I = \epsilon n/S = \epsilon cl \tag{7}$$

in which A is the absorbance and

$$\epsilon = (1 - e^{-k\delta})/2.3\rho\delta. \tag{8}$$

Note that equation (7) has the same form as the Beer-Lambert equation. Analogous expressions for dispersions of spheres and cubes have been found to describe the experimental results very well (Otvos *et al.*, 1957; Duyckaerts, 1959).

A principal assumption in the derivation of equation (7) is that the Poisson formula holds. According to Otvos *et al.* (1957), this formula is applicable as long as: (1) v/V is small compared to 1, (2) the total number of particles, t , in the sample is large enough that $t(t - 1) \approx t^2$, and (3) the particles do not interfere sterically with each other. It is easy to verify that the first two requirements are fulfilled in the systems under investigation. For the third one to be fulfilled, the probability of finding no particles within two radii of a given particle (which is calculable by the Poisson formula) must be close to 1. Our calculations show that the probability of this event is greater than 0.9 if c is less than 0.074 g/cm^3 .

The spectra in Fig. 2A were obtained with a constant value of n/S . Since A increased with increasing water content, we conclude that ϵ in equation (7) must have increased. Reference to equation (8) suggests that the increase in ϵ is due to either an increase in k or a decrease in δ . An increase in k could arise from the decoupling of the dipoles of adjacent layers as they move apart. A decrease in δ would be expected as the stacks of non-expanded superimposed layers in the dry quasi-crystal separate into discrete unit layers.

If we assume that the absorption of radiant energy by water obeys the Beer-Lambert equation, we can use this equation for the water and equation (7) for the clay to form the ratio

$$\frac{A_1}{A_2} = \frac{\epsilon_1 c_1}{\epsilon_2 c_2} = \frac{\epsilon_1 n_1}{\epsilon_2 n_2} \tag{9}$$

in which A , ϵ , c and n represent, as before, the absorbance, absorption coefficient, mass concentration and total mass, respectively, and the subscripts 1 and 2 signify the montmorillonite and water, respectively. Thus, we see that, as long as a plot of A_1/A_2 versus n_1/n_2 yields a straight line, the slope of the line equals ϵ_1/ϵ_2 .

In order to further examine the effect of swelling on the intensity of Si-O absorption, we determined by method II both the principal Si-O absorbance of the montmorillonite and the H-O-H (bending) absorbance of the interlayer water at several water contents for each montmorillonite. The H-O-H absorbance occurs at 1648 cm^{-1} . Then, in keeping with equation (9), we plotted the ratio of these absorbances against the ratio of the corresponding masses of montmorillonite and water. Our results are presented in Fig. 4.

From Fig. 4 it is evident that the curves of A_1/A_2 vs n_1/n_2 are linear up to a characteristic inflection point and curvilinear thereafter. The inflection points are pronounced for the Otay and Polkville montmorillonites but relatively weak for the Belle Fourche and

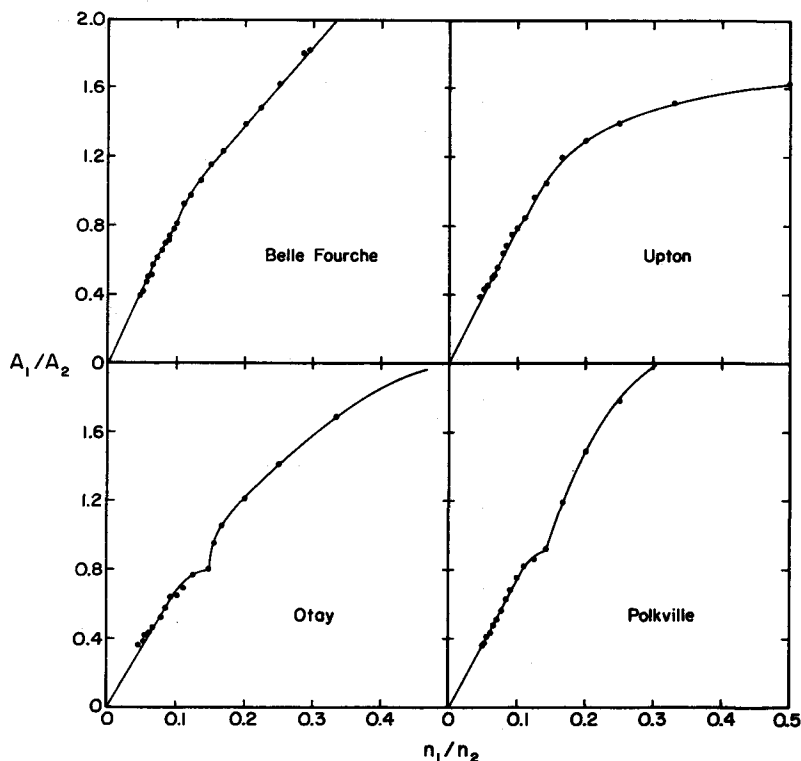


Fig. 4. Relation between the absorbance ratio, A_1/A_2 , and the weight ratio, n_1/n_2 , of Na-montmorillonite to water for four Na-montmorillonites.

Upton montmorillonites. When values of ϵ_1/ϵ_2 , determined from the *linear portions* of the curves, are plotted against the corresponding b -dimensions of the wet montmorillonites, which were measured by J. Margheim, Fig. 5 is obtained. Now, the values of ϵ_1/ϵ_2 in this figure are valid between $n_1/n_2 = 0$ and $n_1/n_2 \approx 0.1$, i.e. between $n_2/n_1 = \infty$ and $n_2/n_1 \approx 10$. In this range of water contents, all of the montmorillonite layers should be separated by interlayer water and δ should equal the layer thickness ($\approx 10^{-7}$ cm). For such a small value of δ , $k\delta \ll 1$ and equation (8), after expanding $e^{-k\delta}$ in series and dropping terms of higher order, reduces to $\epsilon = \epsilon_1 = k/2.3\rho$. Further, the absorbance due to H-O-H bending is quite insensitive to structural perturbations in water (Falk and Ford, 1966), and so ϵ_2 is presumed to be constant. Therefore, we conclude that k decreases linearly with increasing b -dimension or, since the b -dimension is a linear function of isomorphous substitution (Radoslovich and Norrish, 1962; Radoslovich, 1962), with increasing isomorphous substitution.

The inflections in the curves of Fig. 4 are of interest. Reference to equation (9) suggests that, since ϵ_2 is supposed to be constant, they represent an abrupt change in ϵ_1 . We propose that this change is produced by a sudden rearrangement of particles which affects δ and perhaps, because of interactions between dipoles in adjacent layers, k as well.

The foregoing proposal is supported by the data in Fig. 6 and 7. The data in Fig. 6 were obtained

from Low (1974). Those in Fig. 7 were calculated by means of a modified Stokes-Einstein equation. For diffusion in a porous medium, this equation can be written (Low, 1968)

$$D_i = \beta b_i T / \eta, \quad (10)$$

where D_i is the diffusion coefficient of species i , β is a factor that is governed by the geometry (tortuo-

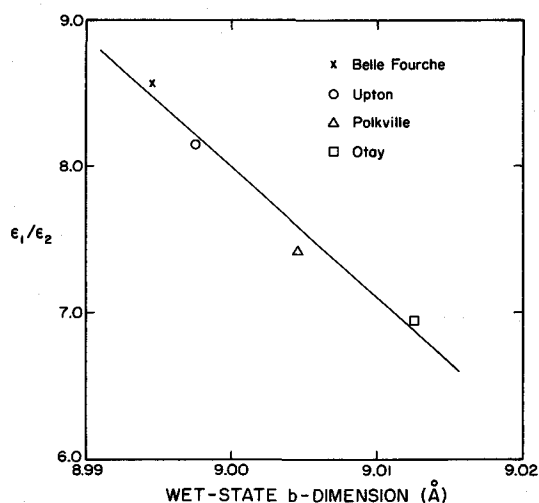


Fig. 5. Relation between the absorption coefficient ratio, ϵ_1/ϵ_2 , of Na-montmorillonite to water and the b -dimension of Na-montmorillonite (determined in the wet state at $n_1/n_2 < 1.0$).

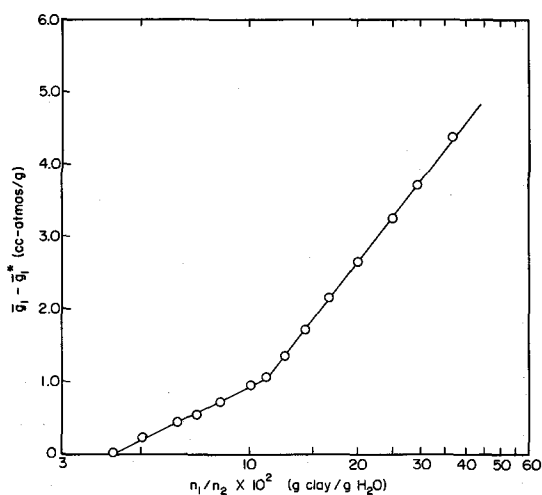


Fig. 6. Relation between $\bar{g}_1 - \bar{g}_1^*$, the relative partial specific free energy of Na-montmorillonite (Upton), and n_1/n_2 , the weight ratio of Na-montmorillonite to water.

sity, porosity, etc.) of the medium, b_i is a constant that is characteristic of the species, T is the absolute temperature and η is the viscosity of the water in the pores. Values of D_i for the self-diffusion of Na⁺ in Na-montmorillonite were obtained from the papers of Lai and Mortland (1962, 1968), van Schaik *et al.* (1966) and Mokady and Low (1968). Values of η in Na-montmorillonite at the same water contents were determined from a curve of η vs water content reported by Low (1976). The value of b_i for Na⁺ is 3.94×10^{-10} dyn/deg (Low, 1968). Attention is called to the pronounced breaks in the curves of both figures. Since $\bar{g}_1 - \bar{g}_1^*$ depends on the degree of dispersion of the particles and how they interact with each other, and since β depends on how the particles are interconnected in space, the most plausible explanation for these breaks is that they are caused by a sudden rearrangement of the particles. Note that the inflection in the curve for the Upton clay in Fig. 4 and the breaks in the curves of Figs. 6 and 7, which refer to the same clay, all occur at the same n_1/n_2 (or corresponding n_2/n_1). Hence, credence is given to our proposal that the inflections in the curves of Fig. 4 are due to particle rearrangements. It is surprising that such rearrangements occur when the average interlayer distances are so large.

Values of $(n_1/n_2)^\ddagger$, the ratio of the mass of montmorillonite to the mass of water at the inflection point, were obtained from Fig. 4 and plotted against the wet-state b -dimensions of the respective montmorillonites as shown in Fig. 8. Observe that $(n_1/n_2)^\ddagger$ is related to the b -dimension. Now if, in keeping with our prior conclusion, $(n_1/n_2)^\ddagger$ represents the critical clay content at which the particles rearrange, it must depend on the magnitudes of the interparticle forces. For example, as the attractive forces become stronger, the critical clay concentration required for layer condensation or particle agglomeration would decrease.

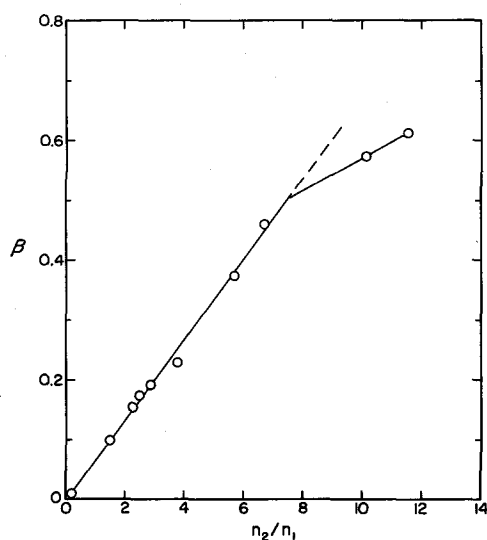


Fig. 7. Relation between β , the geometry factor for diffusion in Na-montmorillonite (Upton) and n_2/n_1 , the weight ratio of water to Na-montmorillonite.

Hence, the interparticle forces must be related directly or indirectly to the b -dimension. This is not surprising since swelling, which is governed by the same forces, has been shown to be related to the b -dimension (Davidtz and Low, 1970; Ravina and Low, 1972).

The O-H stretching frequency of interlayer water

A high proportion of water molecules in liquid water and ice are involved in intermolecular H-bonding. Such bonding shifts the O-H stretching band to lower wave numbers (Coggeshall, 1950; Lippincott and Schroeder, 1954; Ford and Falk, 1968). Hence, Jørgensen (1968) used this band as an indicator of

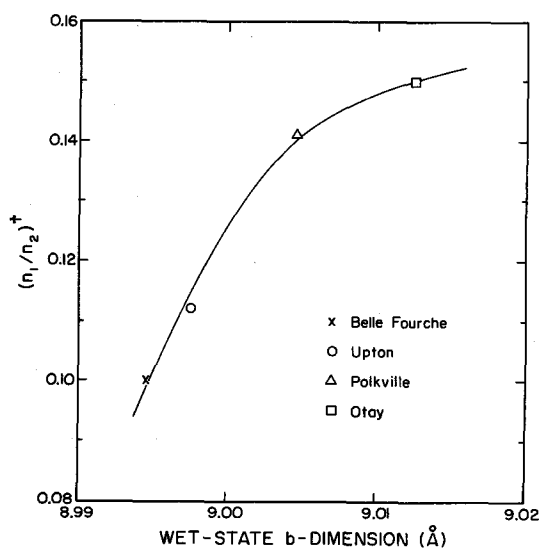


Fig. 8. Relation between $(n_1/n_2)^\ddagger$, the weight ratio of Na-montmorillonite to water at the inflection point in the curve of A_1/A_2 vs n_1/n_2 , and the b -dimension of Na-montmorillonite (determined in the wet state at $n_1/n_2 < 1.0$).

H-bonding in the interlayer water in montmorillonite. He found that, at water contents below about 4 g/g, there was less H-bonding in the interlayer water than in bulk water. We wanted to extend Jørgensen's study to higher water contents but were unable to do so because, at the water contents of interest, the intensity of the O-H stretching band was too high to be recorded. Therefore, we mixed the Upton montmorillonite in different proportions with a D₂O-H₂O solution containing 6.4% D₂O by vol and used the resulting O-D stretching band instead.

We observed that the O-D stretching band remained at $2521.5 \pm 1.0 \text{ cm}^{-1}$ at all water contents in the range of 2–22 g H₂O/g clay. Consequently, there was no indication that the structure of the water changed with swelling. It should be recognized, however, that there can be a change in structure without a change in bond length and, hence, in vibrational frequency. For example, there are ice polymorphs with different structures but essentially the same H-bond length and O-D stretching frequency (Kamb, 1968). In all of them, a tetrahedral network of H-bonded water molecules is the basic feature.

In general, the intensity of the O-D stretching band is more sensitive than the frequency to a change in the environment, especially to a change in dipole moment, of the water (Swenson, 1965; Wall and Hornig, 1965). Consequently, we measured the intensity of the O-D stretching band in mixtures prepared as described above. Every mixture was kept at the same thickness by a Teflon spacer. The concentration of HDO in g/cm³ of mixture was calculable from the equilibrium constant for the reaction



and the proportions of H₂O, D₂O and montmorillonite in the mixture. According to Swenson (1965), the value of the equilibrium constant is 3.96. Consequently, we were able to calculate the absorption coefficient by means of the Beer-Lambert law. A statistical analysis of the results indicated that the absorption coefficient increased by about 10% as the water content increased from 2 to 22 g H₂O/g montmorillonite. This indicates that there was an accompanying change in the water structure. However, the results showed considerable scatter, presumably because all the samples did not have a constant thickness. It was difficult to press the Irtran-2 windows against the flexible Teflon spacer and always achieve the same degree of contact because the intervening montmorillonite-water samples had different water contents and, therefore, different consistencies. Consequently, no definite conclusions about structural changes in the water are possible.

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ing the statistical analysis on which equations (1 and 2) are based.

REFERENCES

- Coggeshall, N. D. (1950) Electrostatic interaction in hydrogen bonding: *J. Chem. Phys.* **18**, 978–983.
- Davidtz, J. C. and Low, P. F. (1970) Relation between crystal-lattice configuration and swelling of montmorillonites: *Clays and Clay Minerals* **18**, 325–332.
- Duyckaerts, G. (1959) The infra-red analysis of solid substances: *Analyst* **84**, 201–214.
- Falk, M. and Ford, T. A. (1966) Infrared spectrum and structure of liquid water: *Can. J. Chem.* **44**, 1699–1707.
- Farmer, V. C. and Russell, J. D. (1964) The infra-red spectra of layer silicates: *Spectrochim. Acta* **20**, 1149–1173.
- Flanigen, E. M., Szymoinski, H. A. and Khatami, H. (1971) Infrared structural studies of zeolite frameworks: *Adv. Chem. Series*, No. 101. *Molecular Sieve Zeolites I*, 201–229.
- Ford, T. A. and Falk, M. (1968) Hydrogen bonding in water and ice: *Can. J. Chem.* **46**, 3579–3586.
- Foster, M. D. (1953) Geochemical studies of clay minerals: II Relation between ionic substitution and swelling in montmorillonites: *Am. Mineral.* **38**, 994–1006.
- Jørgensen, P. (1968) I. R. study of water adsorbed on Wyoming bentonite: *Geologiska Fören. Stockholm Förh.* **90**, 213–220.
- Kamb, B. (1968) Ice polymorphism and the structure of water: In *Structural Chemistry and Molecular Biology* (Edited by Rich, A. and Davidson, N.) Freeman, San Francisco.
- Lai, T. M. and Mortland, M. M. (1962) Self-diffusion of exchangeable cations in bentonite: *Clays and Clay Minerals* **9**, 229–247.
- Lai, T. M. and Mortland, M. M. (1968) Cationic diffusion in clay minerals: I. Homogeneous and heterogeneous systems: *Soil Sci. Soc. Am. Proc.* **32**, 56–61.
- Lerot, L., Poncelet, G. and Fripiat, J. J. (1974) Synthesis, structural characterization and stability of a germanic (Al-Ge) near faujasite zeolite: *Mat. Res. Bull.* **9**, 979–988.
- Lippincott, E. R. and Schroeder, R. (1954) One-dimensional model of the hydrogen bond: *J. Chem. Phys.* **23**, 1099–1106.
- Low, P. F. (1968) Observations on activity and diffusion coefficients in Na-montmorillonites: *Israel J. Chem.* **6**, 325–336.
- Low, P. F. (1974) Application of the Gibbs-Duhem equation to a clay-water system: *Trans. 10th Internat. Congress Soil Sci.* **1**, 42–46.
- Low, P. F. (1976) Viscosity of interlayer water in montmorillonite: *Soil Sci. Soc. Am. J.* In press.
- Lyon, R. J. P. and Tuddenham, W. M. (1960) Determination of tetrahedral aluminum in mica by infra-red absorption analysis: *Nature* **185**, 374–375.
- Milkey, R. G. (1960) Infrared spectra of some tectosilicates: *Am. Mineral.* **45**, 990–1007.
- Mokady, R. S. and Low, P. F. (1968) Simultaneous transport of water and salt through clays: I. Transport mechanisms: *Soil Sci.* **105**, 112–131.
- Otvos, J. W., Stone, H. and Harp, W. R., Jr. (1957) Theory of radiant-energy absorption by randomly dispersed discrete particles: *Spectrochim. Acta* **9**, 148–156.
- Pampuch, R. and Ptak, W. (1969) Infrared spectra and structure of 1:1 layer lattice silicates. Part 1. The vibrations of the tetrahedral layer: *Polska Akad. Nauk. Komisja Nauk. Mineral.* **15**, 6–39.
- Radoslovich, E. W. and Norrish, K. (1962) The cell dimensions and symmetry of layer lattice silicates. I. Some structural considerations: *Am. Mineral.* **47**, 599–616.
- Radoslovich, E. W. (1962) The cell dimensions and symmetry of layer lattice silicates. II. Regression relations: *Am. Mineral.* **47**, 617–636.

- Ravina, I. and Low, P. F. (1972) Relation between swelling, water properties and *b*-dimension in montmorillonite-water systems: *Clays and Clay Minerals* **20**, 109–123.
- Schultz, L. G. (1969) Lithium and potassium absorption, dehydroxylation temperature, and structural water content of aluminous smectites: *Clays and Clay Minerals* **17**, 115–149.
- Stubican, V. and Roy R. (1961a) Isomorphous substitution and infra-red spectra of the layer lattice silicates: *Am. Mineral.* **46**, 32–51.
- Stubican, V. and Roy, R. (1961b) Infrared spectra of layer structure silicates: *J. Am. Ceram. Soc.* **44**, 625–627.
- Stubican, V. and Roy, R. (1961c) A new approach to assignment of infra-red absorption bands in layer-structure silicates: *Z. Kristallogr.* **115**, 200–214.
- Swenson, C. A. (1965) Absolute infrared intensities of HDO in aqueous solution: *Spectrochim. Acta* **21**, 987–993.
- van Schaik, J. C., Kemper, W. D. and Olsen, S. R. (1966) Contribution of adsorbed cations to diffusion in clay-water systems: *Soil Sci. Soc. Am. Proc.* **30**, 17–22.
- Wall, T. T. and Hornig, D. F. (1965) Raman intensities of HDO and structure in liquid water: *J. Chem. Phys.* **43**, 2079–2087.