NEW APPROACH TO THE PROBLEM OF THE INTERLAYER BONDING IN KAOLINITE

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Abstract—The possibility of recording the absorption band which is related to oscillations of free OH in a superficial plane of the octahedral sheet of kaolinite inspired the present authors to review the problem of cohesion forces in kaolinite. Structural and spectroscopic criteria as applied to kaolinite proved that the cohesion of adjacent kaolinite layers may be estimated in terms of bent hydrogen bonds. Energy calculations were performed with the aid of a Lennard-Jones function using a modified linear model of the hydrogen bonds. The entire energy is composed of four terms described by the general potential function, van der Waals repulsion and an electrostatic attraction. The energy values of the individual terms are within the limits characteristic of each of them.

INTRODUCTION

Cohesion within crystals and factors determining this cohesion are major points of interest in modern crystallography. Especially in clay studies, we must not neglect the cohesion forces between the adjacent layers in microcrystals, as they influence many important properties of clays.

Until the 1972 Clay Conference in Madrid, it was generally believed that in kaolinite, and in two other polimorphic modifications, the layers are bound together by hydrogen bonds. I.r. absorption bands at about $3700\,cm^{-1}$, $3670\,cm^{-1}$, $3650\,cm^{-1}$ were attributed by several authors to OH–O stretching vibrations (Serratosa *et al.*, 1962; Pampuch, Błaszczak, 1964; Ledoux, White, 1964; Farmer, 1964; Farmer, Russell, 1964; Pampuch, Ptak, 1970; Plusnina, Gribina, 1970) and were accepted as evidence of hydrogen bonds.

A new possibility of assigning the i.r. bands in question to a coupling phenomenon between almost identical OH (Jacobs 1971; Cruz *et al.*, 1972 after Jacobs, Rouxhet, Fripiat) gave rise to speculations on the possible character of the cohesion forces in kaolin minerals and brought Cruz *et al.* (1972) to the following final statement: "cohesion in kaolin minerals is not due to hydrogen bonding". They found "a higher contribution of electrostatic energy to interlayer bonding energy".

The second writer of the present paper tried to find further evidence (Wiewióra 1972, 1974a). The ideas presented by Cruz *et al.* to the Madrid Conference would explain both the non reactiveness of the very fine kaolinite fractions and the reactiveness of coarse particles to intercalating agents (Wiewióra and Brindley, 1969).

The authors attempted to elaborate the theoretical ideas and to find experimental means which together would enable them to calculate values of the determinants of the interlayer bonding in kaolinite.

The first question to be answered was: do the interlayer cohesion forces in kaolinite fulfill the necessary criteria of hydrogen bonds?

It is well known from structural data that oxygens and hydroxyls of adjacent layers are nearly superimposed in the c^* direction, and that X-ray- and electron diffraction-measured distances between the three pairs of OH–O are within the limits typical for long (weak) hydrogen bonds.

The forces of cohesion between the kaolinite layers should obey the general rules of hydrogen bonds applicable to other chemical compounds in which hydrogen bonds are the major cohesion forces. It should be possible to use spectroscopic criteria to prove the existence of such bonds.

According to Szczepaniak (1969) and Kęcki (1975), one should observe a decrease in the frequency of stretching vibration of OH on the order of $100\,cm^{-1}$, as well as an increase in the integral intensity of the resultant absorption band. In the case of deformational vibrations of OH, one should observe displacement of the bands toward higher frequencies with no change in intensity. According to Kęcki (1975), one of the phenomena is sufficient to prove the presence of hydrogen bonds.

In order to study hydrogen bonds by the i.r. method, one must know the frequency of vibrations of free hydroxyls. Of particular interest are those hydroxyls which form the external OH plane in the octahedral sheet, and which are not involved in H–O bonds with adjacent kaolinite layers.

In the literature, the $3750\,cm^{-1}$ band is the generally accepted frequency for the free OH. According to the authors' belief, it does not come from measurements on kaolinite but from vibration of OH^- associated with silica (McDonald, 1958).

Using the i.r. reflection method, the authors recorded the absorption band at $3742\,cm^{-1}$ related to oscillations of free OH in a superficial plane of

the octahedral sheet of kaolinite. Comparing the data from i.r. reflection and absorption spectra, we have successfully solved several problems related to the cohesion between adjacent kaolinite layers. We have established the properties of the bonding, calculated the bond length, and designed an adequate model of the bonds.

EXPERIMENTAL

Fine particle fractions of the well-known Polish sedimentary, Maria kaolin (Wiewióra, 1974b) were used in the experiments. According to our experience, the finest fractions $< 0.2 \mu$m and 0.2–0.5μm show the most distinct absorption bands.

The i.r. reflection technique requires well-polished samples. Oriented aggregates were prepared for both the reflection and transmission methods. Samples were prepared as follows: (1) sedimentation of kaolinite on a polyethylene film stretched between two metal rings for the reflection method and (2) sedimentation on to polymethacrylane methyl plate for the transmission method. Orientation of kaolinite particles in the aggregates was controlled through use of the X-ray diffractometer Dron-1.5 S.U. made. Aggregates showing only 00l X-ray reflections were chosen for the experiments. Samples were dried at 90°C *in vacuo* of 1 mm Hg to eliminate molecular water, unwanted especially in the reflection method
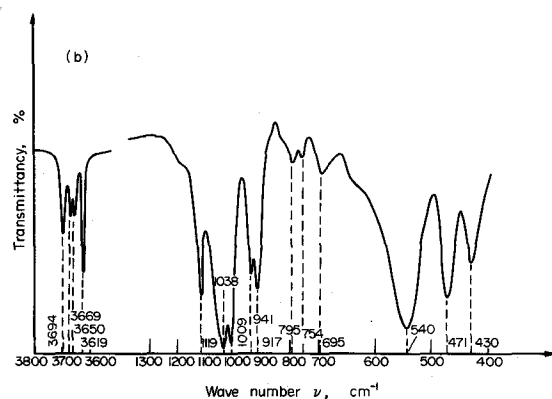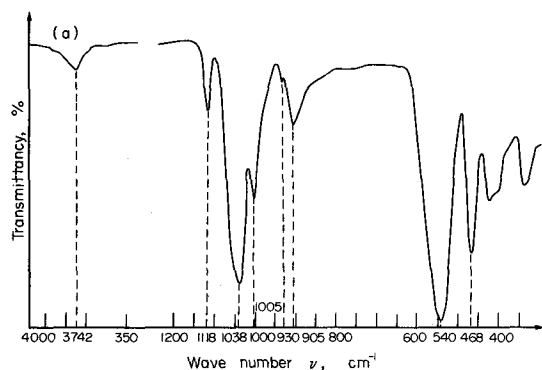
Table 1. Comparison of frequency of vibrations in the i.r. spectra of 0.2–0.5 μm fractions of Maria kaolinite recorded by reflection and transmission methods

Wave number	cm^{-1}	
Reflection method	Transmission method	Character of vibration
3742	—	ν (OH)
—	3694	ν (OH)
—	3669	ν (OH)
—	3650	ν (OH)
—	3619	ν (OH)
1118	1119	ν as (Si–O–Si)
1038	1038	ν (Si–O)
1005	1009	ν (Si–O)
930	941	δ (Al.O–H)
905	917	δ (Al.O–H)
	795	ν_s (Si–O–Si)
	754	ν_s (Si–O–Si)
	695	ν_s (Si–O–Si)
540	540	Al^{VI}–O–Si
468	471	δ (Si–O)
	430	δ (Si–O)

which is designed for recording the free OH vibration frequencies.

The i.r. reflection spectra were obtained with a Perkin-Elmer model 577 spectrophotometer. IR transmission spectra were obtained with the UR-10 spectrophotometer made in GDR. These spectra are presented in Fig. 1(a) and (b) respectively. In Table 1, frequencies of vibrations obtained by the two methods are compared and the character of the oscillations is shown.

BOND LENGTH CALCULATIONS

The most precise semi-empirical relation describing the decrease of stretching frequency vibrations in comparison to vibration of free OH was proposed by Bellamy and Owen (1969). According to these authors the decrease of frequency in cm^{-1} can be calculated from the Lennard-Jones 12-6 potential function:

$$\Delta = 50 \left[\left(\frac{d}{R} \right)^{12} - \left(\frac{d}{R} \right)^{6} \right]$$

where:

  d = a value close to the sum of collision radii of atoms X and Y in the $X - H \ldots Y$ bonding,
  R = hydrogen bond length.

This formula was used for the calculation of hydrogen bond lengths in kaolinite (Table 2), according to the structural scheme of interlayer bonding adopted from Giese and Datta (1973) and presented in Fig. 2.

Comparison of interatomic distances calculated from the i.r. data and from the diffraction data showed that the former values are greater than the latter. It seems proper then to apply a model of bent

Fig. 1. I.r. absorption spectra of kaolinite; (a) spectrum obtained by reflection method, (b) spectrum obtained by transmission method.

Table 2. Comparison of the hydrogen bond lengths and interlayer distances O–O in kaolite

Pairs of oxygen similar like in Fig. 2	$\Delta\,[\text{cm}^{-1}]$ frequency shift free OH–OH in hydrogen bond	Hydrogen bonds length R from i.r. data [Å]	Interlayer O–O distance from diffraction data after Giese and Datta (1973) according to Zyyagin's data [Å]
$O_{(2)}-O_{(9)}$	3742–3650 = 92	3.00	2.89
$O_{(1)}-O_{(8)}$	3742–3669 = 73	3.04	2.90
$O_{(3)}-O_{(7)}$	3742–3694 = 48	3.10	3.02

Fig. 3. The model of the possible bent hydrogen bond $X-H \ldots Y$, where $(r) = X-H$; $r' = (r) \cos \theta$; $(r^*) = H-Y$; $r^{*\prime} = (r^*) \cos \theta^*$.

hydrogen bonds instead of the linear ones (Schroeder and Lippincott, 1957). Such a model (Fig. 3) has been used to estimate the energy of cohesion forces in kaolinite.

It may be seen from Fig. 3 that the $X-H$ and $H-Y$ distances projected on to the $X-Y$ axis enable consideration of the bonding in a linear system. Applying the method of Schroeder and Lippincott (1957), one may write two equations describing the properties of the bonding in terms of energy:

$$V_1 = D_0\left[1 - \exp\left(\frac{-n(\Delta r')^2}{2\,r'\cos\theta}\right)\right]$$

$$V_2 = -D_0^*\exp\left(\frac{-n^*(\Delta r^{*\prime})^2}{2\,r^{*\prime}\cos\theta^*}\right).$$

Taking

$$\frac{n(\Delta r')^2}{2\,r'\cos\theta} = \alpha_i \quad \frac{n^*(\Delta r^{*\prime})^2}{2\,r^{*\prime}\cos\theta^*} = \beta$$

$$D_0^* = \frac{k_0^*\,r_0^*}{n^*},$$

where:

$r' = r' - r_0'$ is a stretch of the bond I in Fig. 3,
$r^{*\prime} = r^{*\prime} - r_0^{*\prime}$ is a stretch of the bond II in Fig. 3,
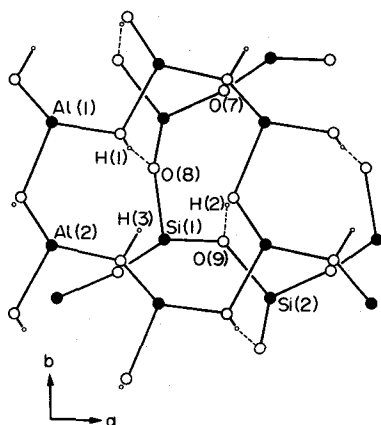

Fig. 2. The projection of the two atomic planes in the octahedral and similarly in the tetrahedral sheets of the adjacent layers onto (001), after Giese and Datta (1973). The (O) are oxygen ions, the (●) are cations and the (○) are hydrogen ions. The (---) represents the possible hydrogen bonds.
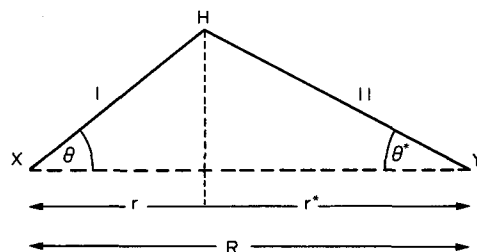
and all the other values are the same as those in Schroeder and Lippincott's (1957) work, the energy related to the potential value is as follows:

$$V_1 + V_2 = D_0[1 - \exp(-\alpha)] - D_0^*\exp(-\beta).$$

In addition, van der Waals' repulsion and electrostatic attraction may be expressed as follows:

$$V_3 = Ae^{-bR} \quad \text{and} \quad V_4 = -A(\tfrac{1}{2})\left(\frac{R_0}{R}\right)^m e^{-bR_0},$$

respectively and through application of the four equilibrium conditions characteristic for the linear model of the hydrogen bond:

$$A = \frac{\left[\dfrac{D_0^*\,n^*}{2\cos\theta^*}\right]\left[1 - \left(\dfrac{r_0^{*\prime}}{r^{*\prime}}\right)^2\right][\exp(-\beta)]}{[\exp(-b\,R_0)]\left[b - \left(\dfrac{1}{2R_0}\right)\right]}.$$

Finally, the formula used for the entire energy calculation can be written:

$$V = D_0[1 - \exp(-\alpha)] - D_0^*\exp(-\beta) + A\left[e^{-bR} + \right.$$

$$\left. -(\tfrac{1}{2})\left(\frac{R_0}{R}\right)^m e^{-bR_0}\right].$$

The following formula was designed for estimating the force constant of the hydrogen bonding, which is characteristic for a given 0–0 interlayer distance:

$$k_x\ldots y = \left[\frac{D_0^*\,n^*}{(r^{*\prime})^3\cos\theta^*}\right][\exp(-\beta)]\left[(r_0^{*\prime})^2 + \right.$$

$$\left. -\frac{\beta}{2}(r^{*\prime} + r_0^{*\prime})^2\right] + A\left[\frac{R_0^2 b^2 - 1}{R_0^2}\right][\exp(-bR_0)].$$

Results of computation of a bulk energy of the hydrogen bonds and of their components V_3 and V_4 as well as of the O–O force constant are presented in Table 3.

DISCUSSION AND CONCLUSIONS

The results presented in Fig. 1 and in Tables 1–3 supply sufficient data to prove that the cohesion between the kaolinite layers may be considered as hydrogen bonding. They show that all the spectroscopic criteria of hydrogen bonding are fulfilled. No

Table 3. Values of the entire energy V of the hydrogen bonds, values of van der Waals' repulsion V_3, electrostatic attraction V_4 and force constant k_{0-0} characteristic for the interlayer cohesion in kaolinite

Oxygen involved in hydrogen bonds	Interlayer distance O–O (Å)	Frequency of vibration (cm^{-1})	V kcal/mole	V_3 kcal/mole	V_4 kcal/mole	k_{0-0} newton/ metre
$O_{(2)}$–$O_{(9)}$	2.89	3650	4.692	0.049	−2.823	18.1
$O_{(1)}$–$O_{(8)}$	2.90	3669	3.993	0.044	−1.479	17.8
$O_{(3)}$–$O_{(7)}$	3.02	3694	0.634	0.040	−0.609	2.7

coupling phenomena between the hydroxyl groups as described by Jacobs (1971) have been observed.

The frequencies of the stretching vibrations (OH) of the three hydroxyls involved in the interlayer cohesion in kaolinite are lower than those of the "free" superficial hydroxyls occupying positions in the external plane of the octahedral sheet and not involved in the hydrogen bonds (Table 1).

Relative intensity of the absorption band of a free OH as recorded in the reflection spectrum (Fig. 1a) is smaller than that of the transmission spectrum of the hydroxyl groups involved in the interlayer bonding (Fig. 1b).

Additional evidence of hydrogen bonds is supplied by the bending vibrations (A1–OH). They are recorded as absorption bands at 941 cm^{-1} and 917 cm^{-1} in a transmission spectrum, and at 930 cm^{-1} and 905 cm^{-1} in a reflection spectrum. The very distinct shift of 11 cm^{-1} and 12 cm^{-1} related to the changes in status of a hydroxyl group either free or when involved in the interlayer bonding has prompted this report.

Precise data on the intensity changes of the bands in question are not available due to uncontrollable factors. This may cause diversification of the applied i.r. reflection and transmission methods but should not be taken as a disadvantage of the present proposal. It seems that the intensities of the (A1 ... OH) bands obtained by the two methods do not differ markedly.

Decrease of frequency is roughly on the order of 50–100 cm^{-1} (Table 2). A large difference in a frequency decrease is reflected in the values of total bonding energy and in the values of its components (Table 3). It is quite clear that the entire energy and all its components as well as the force constant values decrease along with an increase of the interlayer bond length.

Table 4. Comparison of the energies of hydrogen bonds in kaolinite calculated from the i.r. data with the energy of hydrogen bonds as given by various authors (kcal/mole)

This work		Coulson (1963)	Kecki (1975)	Novak (1974)
$O_{(2)}$–H ... $O_{(9)}$	4.692			
$O_{(1)}$–H ... $O_{(8)}$	3.993	3–7	2–10	2.7–8
$O_{(3)}$–H ... $O_{(7)}$	0.634			

The energies, 4.692 kcal/mole and 3.993 kcal/mole, attributed to the two shorter bonds are within the limits of hydrogen bond energies as given by various authors (Table 4). The third value, 0.634 kcal/mole, indicates that the longest bond 3.10 Å (or 3.02 when the interlayer distance 0–0 is taken into account) cannot be classified as a normal but rather as a declining hydrogen bond.

The total energy of cohesion calculated on the basis of six OH in a unit cell of kaolinite equals 18.638 kcal per unit cell. It is smaller than the values $37 < E < 56$ kcal per unit cell calculated by Cruz et al. (1972).

From our results it appears that the cohesion between adjacent kaolinite layers may be evaluated coherently in terms of the energy due to hydrogen bonds by applying a modified linear model of bonds (Schroeder and Lippincott, 1957).

The energy is composed of four terms:

$$V = V_1 + V_2 + V_3 + V_4$$

where:

V_1 and V_2 related to: I—an indifferently stretched, typically covalent bond, II—a weak, highly stretched bond (Fig. 3) are described by the general potential function $V = D[1-\exp(-n\Delta r^2)/2r]$; V_3 is a van der Waals' repulsion; V_4 is an electrostatic attraction.

The energy values of the individual terms (Table 3) are within the limits characteristic for each of them. Electrostatic energy accounts for approx. 50% of the entire energy of the hydrogen bond, which is in agreement with the theoretical presumption (Coulson 1963, after Cruz et al.). Van der Waals energy values fit well into the limits of 0.02–2 kcal/mole, limits which are wellknown from the physico–chemical literature. The correct proportions of the energy terms provides further support for the linear hydrogen bond model as applied to kaolinite. It may be concluded then that the hydrogen bond is the only structurally composed determinant of the interlayer cohesion in kaolinite.

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