Clays and Clay Minerals, Vol. 21, pp. 145–149. Pergamon Press 1973. Printed in Great Britain

INTERLAYER BONDING IN KAOLINITE, DICKITE AND NACRITE

R. F. GIESE, JR.
Department of Geological Sciences, State University of New York at Buffalo, P.O. Box U, Station B, Buffalo, New York 14207, U.S.A.

(*Received* 1 *June* 1972)

Abstract—A simple electrostatic model has been used to demonstrate that the inner surface hydroxyls in kaolinite, dickite and nacrite are responsible for the interlayer bonding in these minerals. The contribution to the interlayer bonding of an individual hydroxyl hydrogen depends on the orientation of the hydroxyl group relative to the 1 : 1 layer since this orientation determines the H—O interlayer distance. If this distance is much greater than the sum of the van der Waals radii, 2·60 Å, there is essentially no bond. As the distance becomes less than 2·60 Å, the strength of the interlayer bond increases.

INTRODUCTION

THE BONDING between atoms in layer silicate minerals can be conveniently split into two types: bonding in the layers and bonding between layers. The interlayer bonding consists of at least three identifiable kinds (Brindley, 1967): (1) an ionic-type interaction due to the net unbalanced charges on the layers; (2) van der Waals forces between layers; and (3) hydrogen bonds between oxygen atoms on the surface of one layer and hydroxyl groups on the opposing surface. In the case of neutral-charge layer structures such as kaolinite, dickite and nacrite, the bonding between layers is almost universally thought to be of the hydrogen bond type. It has been very difficult to test whether such a bonding scheme is correct because the positions of the hydrogen atoms were not known. In the refinement of the structures of nacrite (Blount *et al.*, 1969), kaolinite (Zvyagin, 1967) and dickite (Newnham, 1961) there was no direct evidence from the diffraction data as to the positions of the hydroxyl hydrogens in the structure. It has been noted by Hendricks (1938), Newnham (1961) and others that the structures of the kaolin minerals are such that all the oxygen atoms at the surface of one layer are adjacent to hydroxyls at the surface of the next layer. The strong inference is that this arrangement permits the hydroxyls and oxygens to form hydrogen bonds and that the existence of these bonds is necessary for the stability of the minerals.

A hydrogen bond, as the term is used here, involves a long range interaction between a hydrogen of an hydroxyl group coordinated to a cation and an oxygen atom coordinated to another cation. Theoretical calculations show that this interaction is predominantly electrostatic (Coulson and Danielsson, 1954); hence, an ionic bonding model is appropriate. The validity of this assumption is indicated by the success in determining hydroxyl orientations in inorganic structures (Giese, 1971; Giese *et al.*, 1972) and water molecule orientations in hydrated inorganic structures (Baur, 1965; Ladd, 1968).

Recently we have proposed models for the hydroxyl orientations in the minerals kaolinite, dickite and nacrite (Giese and Datta, 1971) based on electrostatic energy calculations. The existence of these models invites a test of the hydrogen bond hypothesis for interlayer bonding in these minerals.

BACKGROUND

A complete description of crystalline, ionic compounds involves more than just the specification of the electrostatic or Coulomb attraction between the ions (ionic bonding). Born and Landé (1918) and later Born and Mayer (1932) developed the concept of lattice energy as the amount of work necessary to disperse an array of ions in a crystal. The lattice energy consists of attraction terms due to the Coulomb and van der Waals interactions and a nonelectrostatic repulsion term. The theory has proved to be useful in simple alkali halides and has recently been applied to a more general group of structures, the alkaline earth chlorides (Busing, 1970), with good results.

The value of the Coulomb term can be readily

https://doi.org/10.1346/CCMN.1973.0210302 Published online by Cambridge University Press

calculated from the expression (Sherman, 1932)

$$U = -\frac{e^2}{2}\sum_{j=1}^{N}\sum_{i=1}^{\infty}\frac{Z_i Z_j}{r_{ij}} \qquad (1)$$

where N is the number of atoms in the unit cell
Z is the charge on the ion
r is the interionic distance
e is the charge on the electron.

There is no exact theory for the van der Waals or the repulsion terms and it is therefore difficult to compute their contributions to the lattice energy. For the alkali halides, the repulsion term is approximately 10 per cent of the Coulomb term and the value of the van der Waals term is smaller still (Evans, 1964). For the $SrCl_2$ structure, Busing (1970) computed values of −551·8, 135·8 and −101·6 kcal/mole for the Coulomb, repulsion and van der Waals respectively. A plot of these three terms and the lattice energy as a function of the isometric lattice parameter a is shown in Fig. 1. It is clear that the Coulomb energy makes a large contribution to the lattice energy over a long range of distances while the van der Waals and repulsion terms contribute over a short range of distances and will tend to cancel each other. Even though the van der Waals and repulsion contributions to the lattice energy cannot be exactly calculated, one can see from equation (1) and Fig. 1 that a stable ionic structure requires a minimum in the plot of lattice energy versus interionic distance. This requirement implies that since the Coulomb contribution is the major element in the lattice energy the slope of the Coulomb energy must be positive; i.e. the Coulomb energy becomes less negative as the distance increases.

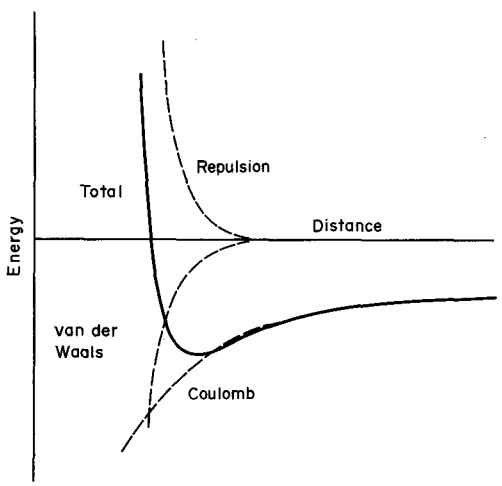


Fig. 1. A plot of the repulsion, van der Waals and Coulomb terms for $SrCl_2$ as computed by Busing (1970). The horizontal axis represents the length of the crystallographic axis of the isometric material which determines the interionic distances in the structure.

The computation of the Coulomb energy has been described by Bertaut (1952). We used the computer program of Baur (1965) for the calculations. The atomic positional parameters, unit cell parameters and space group were taken from the structure determinations of Blount *et al.* (1969) for nacrite, Newnham (1961) for dickite and Zvyagin (1967) for kaolinite. The positional parameters of hydrogen were obtained as mentioned before (Giese and Datta, 1971).

RESULTS

Initially, the Coulomb energy was calculated for dickite and nacrite with interlayer distances varying from 0·1 Å less than to 0·2 Å greater than the actual interlayer distance, while maintaining the same interionic distances and angles within the kaolin layer (Fig. 2). The slope is positive indicating a net electrostatic attraction between the kaolin layers. A measure of the strength of the attraction is given by the value of the slope at the equilibrium interlayer distance. Such values have been calculated numerically for kaolinite, dickite and nacrite (Table 1).

The contribution of the hydroxyls to the interlayer bonding can be estimated by performing similar calculations for structures of the kaolin minerals from which the hydrogen ions have been deleted. To maintain electrostatically neutral

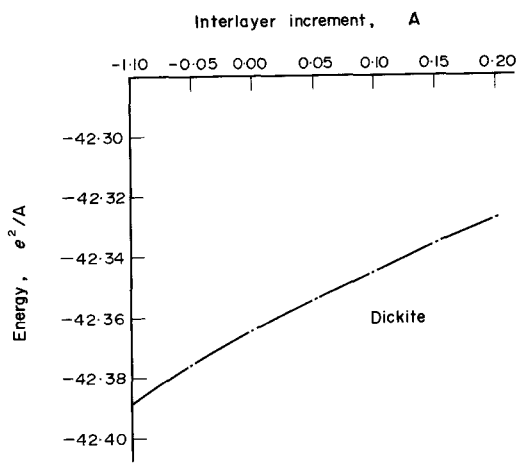


Fig. 2. The variation in the Coulomb energy of dickite as a function of the interlayer separation distance.

https://doi.org/10.1346/CCMN.1973.0210302 Published online by Cambridge University Press

Table 1. Slopes of the coulomb energy vs interlayer distance for the kaolin minerals

Mineral	With hydroxyl ($e^2/A/A$)	With fluorine ($e^2/\AA/\AA$)
Dickite	0·200	−0·012
Nacrite	0·183	−0·012
Kaolinite	0·161	−0·017

layers, the hydroxyl groups can be replaced in the computations by F^{-1} ions situated at the hydroxyl oxygen positions. The slopes calculated for these fluoride analogues are small and negative, indicating a net electrostatic repulsion between the kaolin layers. The removal of hydrogen by the exchange of fluoride for hydroxyl can be done on a selective basis to determine the contribution of an individual hydrogen to the interlayer bonding. This calculation has been performed for each of the four crystallographically unique hydrogens in each of the kaolin minerals. The resulting slopes of the plots of the Coulomb term versus the interlayer distance are listed in Table 2.

Table 2. Slopes of the coulomb attraction vs interlayer distance for the kaolin minerals with individual hydroxyl groups replaced by fluorine

Mineral	Missing hydroxyl group	Slope*
Dickite	0H(1)	0·191†
	(2)	0·112
	(3)	0·138
	(4)	0·114
Nacrite	0H(1)	0·157†
	(2)	0·151
	(3)	0·083
	(4)	0·087
Kaolinite	0H(1)	0·063
	(2)	0·069
	(3)	0·161
	(6)	0·155†

*$e^2/\AA/\AA$
†inner hydroxyl

DISCUSSION

The van der Waals radius of oxygen is 1·4 Å. A distance between one hydroxyl oxygen and another oxygen, not coordinated to the same cation, less then twice this van der Waals radius is usually taken as evidence for a long hydrogen bond. If the hydrogen position in the structure is known, then a more stringent criterion of hydrogen bonding is that the sum (2·6 Å) of the van der Waals radii of the hydrogen and the acceptor oxygen should be considerably greater than the observed H−0 distance (Hamilton and Ibers, 1968). For the kaolin minerals, the hydroxyl–oxygen interlayer distances are larger than 2·8 Å, the sum of the van der Waals radii. However, some of the H−0 distances are considerably less than 2·6 Å, the sum of their van der Waals radii (Table 3). All the inner surface hydroxyls in dickite satisfy this requirement. In nacrite H(2) falls on the border line while the other hydrogens have H−0 distances much less than 2·6 Å. In kaolinite H(3) is definitely not involved in hydrogen bonding.

These conclusions are substantiated by the slopes of the Coulomb term calculated with individual hydroxyls replaced by fluorine (Table 2). The slope decreased by approximately the same amount regardless of which inner surface hydrogen is removed from the dickite structure. The removal of H(3) has less effect on the slope than either H(1) or H(2) as would be expected from the longer H−0 distance of 2·14 Å as compared with 2·00 and 2·02 Å. For kaolinite, the inner surface hydrogen H(3), which is almost in the plane of the hydroxyl oxygens, makes essentially no contribution to the interlayer bonding and correspondingly the H−0 distance of 2·76 Å is much larger than the van der Waals radii sum. The hydrogen of the inclined hydroxyl in nacrite, H(2), makes a very small contribution to the interlayer bonding. This inclusion is supported by the H−0 distance of 2·60 Å which is equal to the van der Waals radii sum. As one would expect, the contribution of an individual hydrogen to the interlayer bonding decreases as the H−0 distance increases and distances greater than 2·60 Å result in essentially no contribution by that hydrogen. Also, the inner hydroxyl, which is shared between the tetrahedral

Table 3. Distance between hydroxyl hydrogens and the acceptor oxygens in the kaolin minerals

Mineral	Donor hydroxyl hydrogen	Acceptor oxygen	H–O distance (Å)
Dickite	H(2)	0(1)	2·00
	H(3)	0(3)	2·14
	H(4)	0(2)	2·02
Nacrite	H(2)	0(1)	2·60
	H(3)	0(2)	2·02
	H(4)	0(3)	2·02
Kaolinite	H(1)	0(8)	1·93
	H(2)	0(9)	1·95
	H(3)	0(7)	2·76

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and octahedral sheets, has little effect on the interlayer bonding.

Cruz, Jacobs and Fripiat (1972) have treated the kaolin minerals as condenser plates with surface charges due to the hydroxyl dipoles and concluded that the cohesion energy is primarily electrostatic. In fact, a linear relationship exists between their bonding energies and the slopes given in Table 1. These authors object to the use of the term "hydrogen bonding" since this term implies a covalent sharing of the hydrogen by two oxygens. However, the work of Coulson and Danielsson (1954) indicates clearly that long hydrogen bonds are largely electrostatic.

CONCLUSIONS

The model of the interlayer bonding in the kaolin minerals described here is based on Coulombic interactions between fully ionized atoms and neglects van der Waals attraction, nonelectrostatic repulsion and other interactions. The success of the model indicates that the interlayer bonding is predominantly electrostatic. Detailed consideration establishes that the inner surface hydroxyls of kaolinite, dickite and nacrite are necessary for the interlayer bonding. In dickite all these hydroxyls participate in the bonding. Two of the three hydroxyls in nacrite are strongly involved, the third weakly. In kaolinite two hydroxyls contribute while the third does not. The inner hydroxyls, common to the tetrahedral and octahedral sheets, make only a small contribution to the interlayer bonding.

Acknowledgements—I wish to thank Professors G. W. Brindley and J. J. Fripiat for commenting on the manuscript and Mr. R. Wolfe for stimulating discussions.

REFERENCES

Baur, W. H. (1965) On hydrogen bonds in crystalline hydrates: *Acta Cryst.* **19**, 909–916.

Bertaut, F. (1952) L'energie electrostatique de reseaux ioniques: *J. Phys. Radium* **13**, 499–505.

Blount, A. M., Threadgold I. M. and Bailey S. W. (1969) Refinement of the crystal structure of nacrite: *Clays and Clay Minerals* **17**, 185–194.

Born, M. and Landé, A. (1918) Ueber die Berechnung der Kompressibilität regulärer Kristalle aus der Gittertheorie: *Verh. der Deutsch. Phys. Ges.* **20**, 210–216.

Born, M. and Mayer, J. E. (1932) Zur Gittertheorie der Ionenkristalle: *Z. Phys.* **75**, 1–18.

Brindley, G. W. (1967) AGI Short Course Lecture Notes—Layer Silicates, Section A.

Busing, W. R. (1970) An interpretation of the structures of alkaline earth chlorides in terms of interionic forces: *Trans. Amer. Crystall. Assoc.* **6**, 57–72.

Coulson, C. A. and Danielsson, W. (1954) Ionic and covalent contributions to the hydrogen bond: *Arkiv Fysik Bd* **8**, 239–244.

Cruz. M., Jacobs, H. and Fripiat, J. J. (1972) The nature of the cohesion energy in kaolin minerals: *Internat. Clay Conf.*, Madrid, Preprints, Vol. 1, 59–70.

Evans, R. C. (1964) *An Introduction to Crystal Chemistry*: Cambridge University Press, Cambridge.

Giese, R. F. (1971) Hydroxyl orientation in muscovite as indicated by electrostatic energy calculations: *Science* **172**, 263–264.

Giese, R. F. and Datta, P. (1971) The orientation of hydroxyl groups in kaolinite, dickite and nacrite: *20th Annual Clay Conf.*, Rapid City (abs).

Giese, R. F., Weller, S. and Datta, P. (1972) Electrostatic energy calculations of diaspore (alpha AlOOH), goethite (alpha FeOOH) and groutite (alpha MnOOH): *Z. Krist.* **134**, 275–284.

Hamilton, W. C. and Ibers, J. A. (1968) *Hydrogen Bonding in Solids*: Benjamin Inc., New York.

Hendricks, S. B. (1938) The crystal structure of nacrite $Al_2O_3 . 2SiO_2 . 2H_2O$ and the polymorphism of the kaolin minerals: *Z. Krist.* **100**, 509–518.

Ladd, M. F. C. (1968) The location of hydrogen atoms in crystalline ionic hydrates: *Z. Krist.* **126**, 147–152.

Newnham, R. E. (1961) A refinement of the dickite structure and some remarks on polymorphism in kaolin minerals: *Mineral. Mag.* **32**, 683–704.

Sherman, J. (1932) Crystal energies of ionic compounds and thermo-chemical applications: *Chem. Rev.* **11**, 93–170.

Zvyagin, B. B. (1967) *Electron-Diffraction Analysis of Clay Mineral Structures*: Plenum Press, New York.

Résumé—Un modèle électrostatique simple a été utilisé pour démontrer que les hydroxyles de la surface interne de la kaolinite, de la dickite et de la nacrite sont responsables de la liaison entre les feuillets de ces minéraux. La contribution à la liaison interfeuillet de l'hydrogène d'un hydroxyle pris individuellement dépend de l'orientation du groupe hydroxyle par rapport à la couche 1:1, puisque cette orientation détermine la distance H—0 entre deux feuillets consécutifs. Si cette distance est beaucoup plus grande que la somme des rayons de van der Waals, 2,60 Å, il n'y a par définition aucune liaison. Lorsque cette distance devient inférieure à 2,60 Å, l'intensité de la liaison interfeuillet augmente.

Kurzreferat—Um zu zeigen, daß Hydroxylgruppen der inneren Oberflächen in Kaolinit, Dickit und Nakrit für die Zwischenschichtbindung in diesen Mineralen verantwortlich sind, wurde ein einfaches elektrostatisches Modell benutzt. Der Beitrag eines einzelnen Hydroxyl-Wasserstoffs zur Zwischenschichtbindung hängt von der Orientierung der Hydroxylgruppe zur 1:1-Schicht ab, da diese den H—0-Zwischenschichtabstand bestimmt. Ist dieser Abstand sehr viel größer als die Summe der van der Waals-Radien, 2,60 Å, so tritt keine wesentliche Bindung auf. Unterschreitet der Abstand den Wert von 2,60 Å, so steigt die Stärke der Zwischenschichtbindung an.

https://doi.org/10.1346/CCMN.1973.0210302 Published online by Cambridge University Press

Резюме — Простая электростатическая модель применяется для доказательства того, что внутренние поверхностные гидроксилы каолинита, диккита и накрита ответственны за межслойную связь этих минералов. Способность индивидуального гидрокислого водорода содействовать межслойной связи зависит от ориентации гидроксильной группы относительно слоя 1 : 1, т. к. ориентация определяет расстояние H . . . 0 между слоями. Если это расстояние намного превышает сумму радиусов Ван-дер-Ваальса, 2,60 А, то, по существу, связи не имеется. По мере того как расстояние становится менее 2,60 А, повышается прочность связи между слоями.

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