CHANGE OF *b*-DIMENSION WITH SWELLING OF MONTMORILLONITE

ISRAELA RAVINA

Faculty of Agricultural Engineering, Technion–Israel Institute of Technology, Haifa, Israel

and

PHILIP F. LOW

Department of Agronomy, Purdue University, Lafayette, Indiana 47907, U.S.A.

Abstract—The effect of swelling on the *b*-dimension of Na-saturated, Upton, Wyoming montmorillonite was re-examined using powdered silicon as an internal standard. After being corrected with reference to the internal standard, the *b*-dimension did not increase through the entire range of swelling as reported previously. It increased up to a water content of ~ 3.0 g/g montmorillonite and remained constant thereafter. However, the diffraction peak of the internal standard shifted towards lower angles at higher water contents. This shift was attributed to a relaxation of the wetter samples away from the knife edge of the diffractometer. Presumably, a similar relaxation occurred in the earlier study and was responsible for the apparent increase in *b*-dimension at water contents above ~ 3.0 g/g.

The *b*-dimension of Upton montmorillonite saturated with different cations was determined using powdered silicon and a colloidal quartz impurity as internal standards. The water content at maximal swelling decreased as the *b*-dimension increased.

INTRODUCTION

Low, Ravina and White (1970) and Ravina and Low (1972) reported that the *b*-dimension of Na-montmorillonite increases continuously as it swells from the air-dried to the maximally swollen state. However, questions have arisen about the validity of their X-ray analysis and so the present study was undertaken. In this study, the *b*-dimension of each montmorillonite was determined using colloidal quartz or powdered silicon as an internal standard. Thus, the results could be corrected for any geometrical diffractometer aberrations that might occur.

MATERIALS AND METHODS

The $<2 \mu m$ fraction of Upton, Wyoming montmorillonite was saturated with different cations by batch washing, initially in 1 N chloride solutions of the cations and finally in deionized water, by the method of centrifugation and decantation. The maximal swelling of each of the resulting homoionic montmorillonites was then determined in triplicate by placing a one-g sample of the dry montmorillonite on the wet, sintered glass filter of a Gooch crucible, setting the crucible in a tray of deionized water and allowing the montmorillonite to absorb the water. To prevent evaporation, the crucible was covered by a plastic sheet with a perforation in it. When equilibrium was attained, as indicated by constancy in the weight of the crucible, the water content of the swollen montmorillonite was determined gravimetrically.

For X-ray powder diffraction analysis, an air-dried or swollen sample of homoionic montmorillonite was confined in the "window" of a powder mount by a glass film on one side and a Mylar film on the other. Before sealing the Mylar film in place with rubber cement, the surface of the sample was made level with the flat surface of the mount by means of a razor blade. Then, after bringing this surface into coincidence with the knife-edge of a Phillips X-ray diffractometer, arranged for symmetrical reflection, the sample was scanned automatically at a speed of $1/8°$ (2θ)/min using Ni-filtered Cu Kα radiation. The slit system consisted of a $1°$ divergence slit, a $1°$ receiving slit and a 0.1 mm scatter slit.

Each sample contained natural colloidal quartz as an impurity. Initially, it was used as an internal standard to correct the results for any geometrical diffractometer aberrations. For this purpose, its diffraction peak was assumed to be at $60°$ (2θ), the location of the corresponding peak for pure crystalline quartz. Later, spectrographically standardized, powdered (<140 mesh) silicon was used as an internal standard. Small amounts of it were mixed thoroughly with the sample, either in the air-dried or swollen state, and diffractograms of the mixtures were obtained as before. The diffraction peak of the silicon was assigned a value of $56.12°$ (2θ). When the colloidal quartz was used as an internal standard, duplicate diffractograms were obtained on 5–10 samples of each montmorillonite. When the powdered silicon was used instead, triplicate diffractograms were obtained on three samples of each montmorillonite. After locating the resulting (060) diffraction peak of the montmorillonite with reference to the corresponding diffraction peak of the internal standard, the respective

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b-dimension was calculated. The average b-dimension is believed to be accurate to within ± 0.001 Å.

RESULTS AND DISCUSSION

As noted by Norrish (1954), there are two ranges of clay swelling, namely: (1) the range of water adsorption between 0 and 0.5 g water/g clay in which the interlayer spacing varies, often in stepwise fashion, from ~ 9.5 Å to ~ 20 Å and (2) the range of water adsorption above 0.5 g water/g clay in which the interlayer spacing varies continuously from ~ 40 Å upwards. Evidently, interlayer spacings between 20Å and 40 Å are forbidden. The first range, which is referred to as the range of crystalline swelling, has been studied extensively. The second range has received relatively little attention. Our study is concerned largely with the latter range.

The water content of the different homoionic montmorillonites at maximal swelling is reported in Table 1. Note that the exchangeable cations have a profound effect on the water content. This effect has been observed previously by Falconer and Mattson (1933) and Winterkorn and Baver (1934).

The b-dimension of the air-dried montmorillonites was determined initially with the colloidal quartz as internal standard. However, because of the possibility that the lattice dimensions of the colloidal quartz might change with the adsorption of water, the b-dimension was determined again with powdered silicon as the internal standard. The results are reported in Table 2.

The data in Table 2 indicate that the values obtained for the b-dimension depend on the internal standard. Further, the data indicate that the b-dimension is related to the radius of the exchangeable cation when the cation is monovalent. This relation is illustrated graphically in Figure 1. A similar relation was found by Leonard and Weed (1967) for dioctahedral vermiculite dried at 350°C. Hence, it appears that the exchangeable cation perturbs the underlying crystal structure and that the degree of perturbation depends on ionic size. In keeping with the concepts of Radoslovich and Norrish (1962) and Lahav and Bresler (1973), we assume that the oxygen triads rotate until half the oxygens coordinate with the interlayer cations.

As mentioned earlier, Table 2 shows that the values obtained for the b-dimension with colloidal quartz as internal standard are different from those obtained with powdered silicon as internal standard. Figure 1 shows that the difference becomes smaller as the crystallographic radius of the exchangeable cation decreases. This difference would remain constant if it were due entirely to an error in locating the diffraction peak of one (or both) of the internal standards on an absolute scale. Therefore, either the lattice dimensions of the colloidal quartz changed with water content as affected by the exchangeable cation (Table 2); or the two sets of data were obtained under different conditions, e.g. under different relative humidities and, hence, at different water contents as affected by the exchangeable cation.

To accomplish the primary objective of the present study, we measured the b-dimension of the Na-saturated, Upton montmorillonite at different water contents using powdered silicon as an internal standard. The results, corrected with reference to this standard, are given in Table 3. They show that the b-dimension of the montmorillonite increases with water content up to a water content of 1.0–3.0 g/g and remains con-

Table 1. The water content at maximal swelling of Upton montmorillonite saturated with different cations

Cation	Water content (g H_2O/g clay)	Cation	Water content (g H_2O/g clay)
Li^+	23.3	Be^{++}	2.8
Na^+	24.4	Mg^{++}	2.6
K^+	9.3	Ca^{++}	3.8
Rb^+	2.0	Sr^{++}	2.5
Cs^+	0.8	Ba^{++}	2.4

Table 2. The water content and b-dimension of air-dried, Upton montmorillonite saturated with different cations

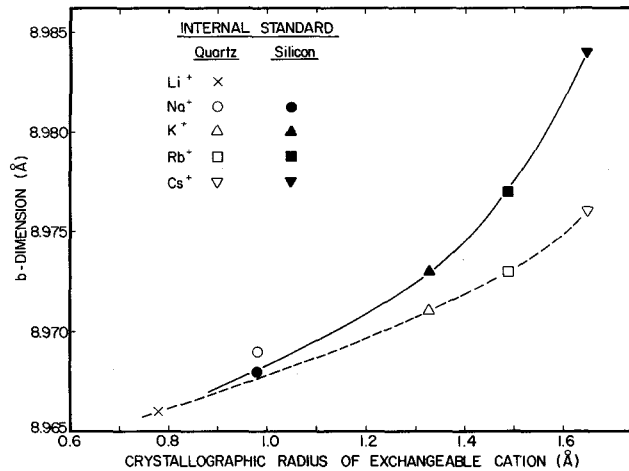| Exchangeable cation	Crystallographic radius of cation† (Å)	Water content (g/g clay)	b-dimension quartz as int. stnd. (Å)	silicon as int. stnd. (Å)
Li^+	0.78	—	8.966	—
Na^+	0.98	0.0165	8.969	8.968
K^+	1.33	0.0059	8.971	8.973
Rb^+	1.49	—	8.973	8.977
Cs^+	1.65	0.0032	8.976	8.984
Be^{++}	0.34	—	8.960	—
Mg^{++}	0.78	—	8.960	—
Ca^{++}	1.06	0.0641	8.960	8.973
Sr^{++}	1.27	0.0589	8.960	—
Ba^{++}	1.43	0.0414	8.960	—

† Data from Stillwell (1938).

Figure 1. Relation between the *b*-dimension of air-dried Upton montmorillonite and the crystallographic radius of the exchangeable cation.

stant thereafter. The total increase amounts to 0.012 Å. Ravina and Low (1972) observed that the *b*-dimension of the same montmorillonite increased through the entire range of swelling, i.e. up to a water content of 20 g/g, and that the total increase amounted to 0.062 Å. Therefore, it appears that their results are in error, at least at the higher water contents. The error can not be attributed to the effect of water content on the transparency of the sample because this effect requires a correction of only 0.008 Å at the highest water content attained. Since we observed that the diffraction peak of the powdered silicon shifted toward lower angles at water contents above 7.0 g/g of clay, displacement of the sample from the knife edge must have occurred at those water contents. We suspect that a similar displacement occurred in the work of Ravina and Low (1972) but that they were unaware of the error introduced thereby because they did not refer all of their results to an internal standard. Such a displacement could have been caused by relaxation of the wet sample or by its shrinkage as water evaporated from it. It is noteworthy that they observed a rapid increase in *b*-dimension at the water content at which a sudden rearrangement of the clay particles is now known to occur (Lerot and Low, 1976). Undoubtedly, this rearrangement affects the consistency of the sample.

Attention is called to the fact that the *d*-spacing of the colloidal quartz, corrected with reference to the silicon peak, increased 0.001 Å as the water content of the montmorillonite increased from its value in the air-dried state to 1.0 g/g clay. This increase is close to the experimental error but, if it is real, the necessary conclusion is that water adsorption affects the lattice dimensions of colloidal quartz.

In Figure 2, the water contents of the different homoionic montmorillonites at maximal swelling are plotted against the corresponding *b*-dimensions of these montmorillonites in the air-dried state. The relevant data were taken from Tables 1 and 2, respectively. Observe that the water content at maximal swelling decreases with increasing *b*-dimension. The same is true when the *b*-dimension depends on isomorphous substitution instead of the nature of the exchangeable cation (Davidtz and Low, 1970; Ravina and Low, 1972). Therefore, it appears that, for montmorillonites saturated with monovalent cations, it is primarily the *b*-dimension (and not the cation per se) that governs swelling. The same conclusion was reached earlier (Ravina and Low, 1972).

Table 1 shows that all the montmorillonites saturated with divalent cations had essentially the same water content at maximal swelling. Table 2 shows that they also had the same *b*-dimension, namely, 8.96 °A. Consequently, their behavior does not violate the concept that swelling depends on *b*-dimension. However, on the basis of the curves in Figure 2, they should have swelled to a much higher water content at the specified *b*-dimension. It is probable that the relation between maximal swelling and *b*-dimension is not the same for montmorillonites saturated with monovalent cations as for those saturated with divalent cations because, in the former, the layers are

Table 3. The corrected lattice spacings of Na-montmorillonite and its natural quartz impurity at different water contents

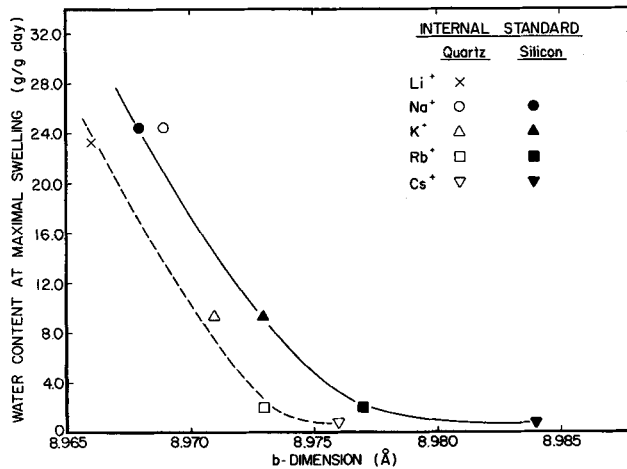| Water content (g/g clay)	*b*-dimension of montmorillonite (Å)	*d*-spacing of quartz (Å)
air-dried	8.968	1.540
1.0	8.974	1.541
3.0	8.980	1.541
5.0	8.980	1.541
7.0	8.980	1.541
9.0	8.980	1.541
24.0	8.980	1.541

Figure 2. Relation between the water content of Upton montmorillonite at maximal swelling and its b-dimension (as affected by the exchangeable cation).

capable of full expansion whereas, in the latter, they remain partially collapsed.

The dependence of swelling on b-dimension, regardless of whether the b-dimension is controlled by ionic substitution within the crystal structure or by ionic adsorption on the crystal surface, suggests that the configuration of this surface is involved in some way. Therefore, we postulate, as we did earlier (Ravina and Low, 1972) that epitaxy exists between the montmorillonite and water structures. As a result, the relative partial molar free energy of the water (and, hence, the tendency of the montmorillonite to swell) depends on the configuration of the underlying surface as reflected by the b-dimension.

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