Relation between Swelling, Water Properties and *b*-Dimension in Montmorillonite-Water Systems*

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* Journal Paper No. 4348, Purdue University Agriculture Experiment Station.

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Abstract: The *b*-dimensions of the unit cells of six different Na-saturated montmorillonites were determined by X-ray diffraction at water contents ranging from 0 to 20 g per g of montmorillonite. In every case, the *b*-dimension increased progressively with water content from its initial value, which was characteristic of each dry montmorillonite, to a final value of ~9.0 Å, which was common to all montmorillonites. The latter value was reached when the water contents of the respective montmorillonites were equal to those at maximal swelling. When these water contents were plotted against the corresponding changes in *b*-dimension, a straight line that passed through the origin was obtained.

Different structure-sensitive properties of the water in montmorillonite-water systems (i.e. the partial specific volume, the amount remaining unfrozen at −5 ° C and the activation energy required for ions to move through it) were available, as functions of the species of exchangeable cation, from previous studies. Relevant *b*-dimensions were determined in the present study. It was found that all of these water properties were correlated with the *b*-dimension of the associated montmorillonite.

Our results indicate that epitaxy exists between the crystal lattices of montmorillonite and adsorbed water and that these lattices undergo mutual adjustment with each increment of water. The resulting loss of free energy causes water adsorption, i.e. swelling, to occur spontaneously. Swelling stops when no further adjustment takes place. This does not happen until the adsorbed water is several hundred angstroms thick and has achieved a preferred configuration.

Clays and Clay Minerals; June 1972 v. 20; no. 3; p. 109-123; DOI: 10.1346/CCMN.1972.0200302

Clay Minerals Society (www.clays.org)