CRYSTALLINE SWELLING OF SMECTITE SAMPLES IN CONCENTRATED NaCl SOLUTIONS IN RELATION TO LAYER CHARGE

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Abstract—The basal spacing of a set of smectites, with layer charges between 0.74 and 1.14 electrons per unit cell, have been measured while the smectites were in equilibrium with NaCl solutions having concentrations of 0.25 to 2.5 molal. Except for the most highly charged smectites, an expansion from ~15.5 to ~18.5 Å occurred as the NaCl concentrations were reduced. This expansion (or "crystalline swelling") corresponds to the transition from two to three sheets of water between the silicate layers. A random interstratification of 15.5 and 18.5 Å structure units was present during the change and gave rise to broad diffraction peaks for the 001 reflections. A balance between cation hydration forces, interlamellar electrostatic forces, and van der Waals forces was apparently the basis of the relationship between surface charge and swelling. The results can be expressed in terms of the relative vapor pressures at which the transitions were half complete; these pressures increased with surface density of charge, and over the range of surface charge studied, the P/P_0 values ranged from 0.943 to 0.974.

Key Words—Electrolyte, Layer charge, Smectite, Swelling, Vapor pressure, X-ray powder diffraction.

INTRODUCTION

The crystalline swelling of smectite and related minerals in water has been the subject of considerable interest in clay mineralogy (Suquet *et al.,* 1975) and soil physics (Alymore and Quirk, 1962). In this context smectites are defined as having 001 spacings of ~18 Å, if they are Mg-saturated and glycerol solvated. Norrish and Quirk (1954) showed that the concentration of an electrolyte in which montmorillonite was immersed could be used to control its swelling, the interlayer spacing increasing with decreasing electrolyte concentration. Posner and Quirk (1964a, 1964b) established that for the Na and Ca forms of montmorillonite from the John C. Lane Tract, Upton, Wyoming, the transition from 18.5 to 15.5 Å took place at a concentration of about 1.5 molal and that the spacing did not collapse further, even in concentrated salt solutions.

Consideration of the differences in swelling between vermiculite and smectite indicates that the layer charge effects swelling. Norrish and Tiller (1976) ascribed the non-dispersion of a soil smectite from Drayton, Queensland, to its high surface charge (mainly in tetrahedral sites) and suggested that this high charge may be the cause of the soil's sub-plasticity.

Aylmore and Quirk (1962) reported that the swelling of Ca-illite was insensitive to electrolyte concentration over the range from 4 M to distilled water. They attributed this limited intercrystalline swelling to the existence of a potential minimum between the contiguous clay crystals in an assemblage of near-parallel, aligned clay particles, described as a domain. Quirk and Aylmore (1971) regarded the domain swelling in regions of particle overlap to be similar to that in quasi-crystals

of montmorillonite. Posner and Quirk (1964a) concluded that the swelling of Ca-illite was triggered by the adsorption of two layers of water. The present study of intracrystalline swelling is thus generally relevant to intercrystalline swelling of clays (Quirk, 1968).

Kjellander *et al.* (1988), using advanced statistical mechanics, obtained a theoretical relationship between surface density of charge and the swelling of Ca-clays. They demonstrated that the amount of intercrystalline swelling decreased as surface density of charge increased. Viani *et al.* (1983) studied the interlayer spacings of variously charged, expanding Na-phyllosilicates in contact with weak (10^{-4} M) NaCl solutions. At this low salt concentration the spacings exceeded ~20 Å and, for a given swelling pressure, were independent of charge. Although surface charge may not effect swelling at spacings >20 Å, the effect on spacings less than this value has not been systematically investigated. The present work therefore is concerned with the effect of surface density of charge and the structural location of that charge on the limited crystalline swelling of a group of Na-saturated smectite samples having widely differing charges in contact with concentrated NaCl solutions. We have used salt concentrations between 0.25 and 2.5 molal and have measured the interlayer spacings, ~15 to ~19 Å, associated with the transition from two to three sheets of interlayer water.

Variation of the concentration of the equilibrium salt solutions provides a more convenient and precise way to control swelling (Posner and Quirk, 1964b) than by controlling the relative vapor pressure of water in the surrounding atmosphere. The latter method of control is experimentally difficult, especially at high vapor pressures.

Table 1. Chemical analyses for Ca-saturated, ignited[1] smectite samples[2].

Oxide	Weight %						
	Wyoming	Hectorite	Oseaan	Beaudesert	Otay	Nibost	Drayton
SiO_2	67.78	63.83	65.61	63.07	68.01	58.70	56.52
TiO_2	0.14	0.08	0.19	0.15	0.17	0.53	0.30
ZrO_2	0.02				0.02		
Al_2O_3	22.70	0.12	22.39	19.73	19.80	20.37	19.89
Fe_2O_3	4.70	0.02	3.06	9.58	1.26	9.68	10.60
MnO	0.01		0.02	0.01	0.01	0.05	
MgO	2.49	28.40	4.99	3.81	7.50	5.57	8.99
CaO	2.86	2.63	3.66	3.58	4.05	4.04	4.03
Na_2O	0.06	0.30			0.06		
K_2O	0.03	0.05	0.09	0.06	0.03	0.49	0.02
P_2O_5	0.01				<0.01		
Li_2O		1.25					
F		6.16					
Total	100.80	102.84	100.01	99.99	100.92	99.43	100.35
O ≡ F		2.59					
		100.25					

Locality: Wyoming; John C. Lane Tract, Upton, Wyoming. Hectorite; Hector deposit in California. Oseaan; Orange Free State, Republic of South Africa. Beaudesert; Beaudesert Queensland, Australia. Otay; Otay, California. Nibost; North of Dunvegern, Vaternish, Skye, Scotland. Drayton; Queensland, Australia.

[1] Ignited to 1000°C.
[2] <0.5 μm fractions.

EXPERIMENTAL

Materials

Sodium chloride solutions in the concentration range 0.25 to 2.5 molal were made up from analytical grade salt.

Smectite samples from various localities, specified in Table 1, were selected on the basis of their changes and their visual freedom from contamination. (The hectorite sample was substantially contaminated with calcium carbonate, which was removed by gentle warming with 1 N acetic acid followed by repeated washes with distilled water.) Sub-samples were initially shaken in water and then sodium saturated by repeated treatments with 2 M sodium chloride, alternating with speed centrifugation. After washing, <2-μm and <0.5-μm fractions were obtained by gravity settling and centrifugation. The <2-μm fractions were examined by X-ray powder diffraction (XRD) and in no case found to be more than 2% contaminated, principally with quartz. A portion of the <0.5-μm fraction of each smectite was then saturated with calcium and finally washed free of excess calcium chloride with 80% (w/v) alcohol. After checking by XRD to ensure that the <0.5-μm calcium saturated fractions were free from contamination, X-ray fluorescence analyses (Norrish and Hutton, 1969) were used to obtain the results given in Table 1. The structural formulae calculated from these data with the program CLAYFORM (Bodine, 1987) are given in Table 2.

Control of swelling

Portions (~50 mg) of the <2-μm fractions of each sodium-saturated smectite were shaken at room tem-

perature at hourly intervals for 8 hr with 5 ml of the appropriate salt solution. After the suspensions had settled, the supernatants were poured off and the procedure repeated twice more to ensure that equilibrium had been reached. Finally, the clays were resuspended and small aliquots were sucked down onto unglazed ceramic tablets to produce thin, even films. The wet ceramic tablets, coated in this way, were quickly wrapped in pieces of polyethylene film to allow diffraction measurements to be made upon the clay while it was in contact with the appropriate electrolyte.

As used here, the control of swelling with salt solutions depended upon the fact that salt was excluded from the interlamellar spaces until the collapse from 19 to 15 Å. In studies of adsorption from the vapor phase, such as those of Mooney et al. (1952), it is often difficult to control the vapor pressure to the required degree of accuracy because of temperature effects near saturation. In contrast, the concentration of a solution in equilibrium with a clay can be accurately controlled and the associated XRD measurements made. In vapor phase studies, contact angle effects are sometimes encountered on external surfaces (Emerson, 1962); however, these do not seem to pertain to the adsorption of water from the vapor phase into interlamellar spaces of vermiculite (van Olphen, 1965) that are fully occupied with water; for a sample having a spacing of 14.8 Å, the adsorption was 200 mg/g.

X-ray powder diffraction investigations

The basal spacings of the montmorillonite samples in equilibrium with the various sodium chloride solutions were measured by XRD. Fe-filtered CoKα ra-

Table 2. Structural formulae of smectites calculated on a water-free basis (O = 11).

Sample	Tetrahedral		Octahedral							Interlayer			
	Si	Al	Al	Fe³⁺	Ti	Mn	Mg	Li	Σ	Ca	Na	K	Σ
Wyoming	3.964	0.036	1.529	0.207	0.006	—	0.218	—	1.960	0.179	0.007	0.002	0.188
Hectorite	3.966	0.009	—	0.001	0.002	—	2.661	0.391	3.055	0.179	0.024	0.004	0.207
Oseaan	3.881	0.119	1.441	0.136	0.008	0.001	0.440	—	2.026	0.232	—	0.007	0.239
Beaudesert	3.820	0.180	1.228	0.437	0.007	—	0.344	—	2.016	0.232	—	0.005	0.237
Otay	3.972	0.028	1.335	0.055	0.007	—	0.653	—	2.050	0.253	0.007	0.002	0.262
Nibost	3.625	0.375	1.108	0.450	0.025	0.003	0.513	—	2.099	0.267	—	0.039	0.306
Drayton	3.486	0.514	0.932	0.492	0.014	—	0.827	—	2.264	0.266	—	0.002	0.268

diation was used with a Philips model PW1050/28 diffractometer. XRD traces were obtained with a 1/12° entrance slit, a 1° exit slit, and a scanning rate of 1°/min. The polyethylene-covered, clay-coated ceramic tablets were held in a modified, spring-backed, sample holder of the type supplied by Philips for diffractometry on pressed powders. The modification consisted of small brass strips glued on the upper face of the sample holder, diagonally across the corners of the sample aperture. The upper surfaces of the clay films were thereby held at the correct specimen height for the diffractometer.

RESULTS AND DISCUSSION

Figure 1 shows the basal spacings of the sodium-saturated samples in relationship to the concentrations of the salt solutions with which they were in contact. The electrolyte concentration at which the transition to 18.5 Å is half complete (taken as 17 Å) is seen to increase with decreasing charge density.

Except for the Nibost and Drayton montmorillonites, a change in spacing from ~15.5 to ~18.5 Å occurred over a concentration range, which varied from sample to sample. This change corresponds to the transition from two to three sheets of water between the silicate layers, and, hence, the intermediate spacings represent mixtures of 15.5- and 18.5-Å structure units. Any one intermediate spacing for a given material corresponds to some fixed proportion of the two, irregularly interstratified, end-members. Furthermore, Figure 1 broadly demonstrates that for a given electrolyte concentration, the proportion of 15.5-Å structure units increased with surface density of charge. For the very highly charged Nibost and Drayton montmorillonite samples, no transition from 15.5 to 18.5 Å occurred at any of the electrolyte concentrations used. In this respect, the behavior of these two montmorillonite samples was similar to that of vermiculite.

The Drayton sample provides a useful comparison with the Otay montmorillonite, which carries a similar high surface charge density but a lower charge in its tetrahedral sites (0.6) compared with (1.02). For the Otay montmorillonite, the electric field strength associated with the silicate layers, and interacting with its interlayer cations, apparently was insufficient to overcome the hydration forces of Na⁺ ions and so the transition to 18.5 Å occurred at suitably low electrolyte concentrations.

The Oseaan and Beaudesert montmorillonite samples have identical surface charge densities, but for the Oseaan material, the transition to ~18.5 Å was half complete at 1.4 molal, whereas that for the Beaudesert material occurred at 1.0 molal. This difference in behavior may be related with the tetrahedral charge difference between the minerals. The Oseaan montmorillonite has a tetrahedral charge of 0.24; the Beaudesert montmorillonite, 0.36.

The swelling curves for Wyoming montmorillonite and the hectorite from California are within the region of the graph appropriate to materials of such low overall charge. The relative positions of the two curves, however, do not accord with the samples' slightly different charges. The reason for this is not obvious, but it may follow from the hectorite being the only trioctahedral clay in the group studied. The O–H vectors in trioctahedral phyllosilicates are more steeply inclined to the (001) plane than those in dioctahedral members. Consequently, in trioctahedral clays, hydroxyl-group protons are better positions to weaken the attraction between interlayer cations and the silicate layers than in dioctahedral clays. Therefore, for a similar distribution of charges, trioctahedral clays can be expected to swell more readily than dioctahedral clays. The effect, however, will be reduced as F− substitutes for OH−. In hectorite, where about ⅔ of the total OH− sites are unsubstituted by F−, an effect on swelling can still be expected.

Table 3 presents the half point of expansion in terms of the free energy of the water in the solution in which the clay was immersed. The free energy is expressed both in terms of relative vapor pressure and the osmotic pressure of the solutions. From these data, the expansion from two to three water sheets is half complete at relative vapor pressures of <0.988. This pressure corresponds to a suction of 15 bars (1.5 MPa) and is frequently used as a reference point in soil science.

For the Otay montmorillonite, the expansion was complete at a salt concentration of 0.4 molal, which corresponds to a P/P₀ value for the solution of 0.986
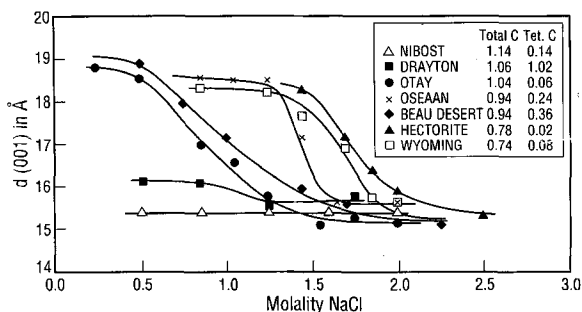
Figure 1. Relation of basal spacings of Na-saturated smectite samples and concentration of NaCl solutions. Total C = total charge; Tet. C = tetrahedral charge.

Table 3. Osmotic pressure and relative water vapor pressure for the 18.5-to-15-Å transition in relation to charge characteristics.

| Material | Solution characteristics at half-transition (d(001) = 17Å) | | Charge (electrons) per unit cell | |
	Osmotic pressure (MPa)	Relative vapor pressure (P/P₀)	Total	Tetrahedral
Wyoming	8.2	0.943	0.74	0.08
Oseaan	6.7	0.953	0.94	0.24
Beaudesert	4.7	0.967	0.94	0.36
Otay	3.7	0.974	1.04	0.06

or an osmotic pressure of 1.8 MPa. The osmotic pressures given to Table 3 may also be regarded as the isotropically imposed mechanical load or suction that would have to be applied to half-collapse the spacings from about 19 to 15 Å.

The distribution of water between the salt solutions and the clay can be explained in the following way. Both the interlayer cations and the cations in the external solution compete for water molecules. The interlayer cation concentration is fixed by the charge on the clay and is very high, ~4 molal. If no forces other than cation hydration forces are involved, very high electrolyte concentrations would be required to limit swelling. Moreover, inasmuch as interlayer cation concentration increases with clay charge, swelling should increase with charge. For a given electrolyte concentration, the reverse was observed. The interlayer forces were a balance between cation hydration, electrostatic, and van der Waals forces; the van der Waals forces, however, did not vary with cation or surface charge.

The tendency of the interlayer cations to hydrate is accompanied by an interlayer expansion that is opposed by electrostatic attention between the cations and the clay surfaces (Norrish, 1954). Whereas the tendency to take up water increases linearly with interlayer cation concentration, i.e., clay charge, the opposing electrostatic force increases with (charge)^p. For point charges adjacent to planar silicate layers, p = 1, or, alternatively, if the silicate layers are considered as condenser plates, p = 2. In practice, p has an intermediate value (Norrish, 1954) so that the electrostatic forces opposing swelling increase more rapidly than the forces causing swelling; consequently, swelling becomes less with increasing charge.

If the clay charge is generated in tetrahedral positions, the electrostatic attractive force between the interlayer cations and the surface will be greater than if the clay charge is generated in the more deeply buried octahedral positions. Tetrahedrally developed charge therefore plays an important role in controlling the relative swelling of smectites. This interpretation is

consistent with the behavior of vermiculites, which have very high tetrahedral charges (Norrish, 1973).

The literature on the swelling of montmorillonite, e.g., MacEwan and Wilson (1980) suggests that all Na-saturated montmorillonite and hectorite samples will initially swell to ~19 Å in low concentration electrolytes, but as the concentration falls further, the spacing jumps to ~40 Å and then increases continuously to very high values. Commercial montmorillonite materials, especially Wyoming bentonite, have frequently been used in swelling studies. Analyses of many pure smectites suggest that common, commercial montmorillonite materials, are at the low charge end of the smectite series. Perhaps this gives them the properties that make them commercially desirable; however, such materials are not representative of the smectite group in general, and conclusions regarding smectite behavior cannot be obtained by considering them alone.

This study shows that the higher charged smectite samples behave in a dramatically different way from those of lower charge. At a surface charge density of 1.14 electrons per unit cell, with 0.74 arising in the tetrahedral sites, the Na-Nibost montmorillonite did not expand, even in distilled water. The Drayton montmorillonite (Norrish and Tiller, 1976) has a total surface charge density of 1.06 electrons per cell with 1.02 arising from tetrahedral substitutions. The behavior of the Drayton montmorillonite was similar to that of the Nibost material, in that it did not exhibit extensive swelling or dispersion in dilute solutions when saturated with sodium. If the sample was saturated with lithium, however, and in accord with this cation's greater hydration energy, the Drayton montmorillonite swelled and dispersed readily. Similarly, highly charged montmorillonite materials in soils may significantly diminish the effects of sodium ions (Quirk and Schofield, 1955; Quirk, 1986).

Estimation of charge

Soil mineralogists commonly estimate the montmorillonite content of soils by assuming that the exchangeable cations are derived from montmorillonite

materials having a ration-exchange capacity of 100 meq/100 g on an ignited basis. Such an assumption is not necessarily correct, and ideally the charge should be known.

Because the basal spacings of Na-saturated montmorillonites samples in equilibrium with a given concentration of sodium chloride are governed by charge, swelling curves can be used to approximate the charge of a montmorillonite from several measured spacings. To use this method, the sample of unknown charge should be sodium saturated and three separate portions taken for equilibrium with sodium chloride solutions of, e.g., 1.75, 1.5, and 0.75 molal. The basal spacings of the unknown at these three salt concentrations can be referred to Figure 1 to obtain an approximate charge. The technique could prove especially valuable in estimating the charge of smectite materials admixed with other clays.

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