OPTICAL DENSITY OF VERTISOL CLAY SUSPENSIONS IN RELATION TO SEDIMENT VOLUMES AND DITHIONITE-CITRATE-BICARBONATE-EXTRACTABLE IRON

EYAL BEN-DOR AND ARIEH SINGER

The Seagram Center for Soil and Water Sciences, Faculty of Agriculture
The Hebrew University of Jerusalem

Abstract—Clay fractions of eight vertisols and vertisolic soils from Israel were found to consist principally of a Fe-rich beidellite. Sediment volumes of Na-clay suspensions, obtained in measuring cylinders and read every 24 hr for as long as 720 hr, ranged from 3.8 to 8.4 cm³/100 mg clay and were as much as 19 times larger than corresponding suspensions of Ca-clays. Optical density data for all clay suspensions showed absorption curves typical of smectite. The relative number of platelets per tactoid, calculated from optical density measurements, ranged between 1.4 and 5.4 for the Na-clays and between 7.4 and 14.1 for the Ca-clays. In the Ca-clays, the sediment volume decreased with an increase in the relative number of platelets per tactoid. With increase in the major dimension of particles (calculated also from optical density curves), sediment volume tended to increase for the Na-clays and decrease for the Ca-clays. These relationships can be explained on the basis of particle arrangement patterns: face-to-face arrangements dominated the Ca-clays and edge-to-edge and edge-to-face arrangements dominated the Na-clays. The amount of iron extractable in dithionite-citrate-bicarbonate (DCB) correlated positively with the relative number of plates per tactoid and with the major dimensions of the particles in the Ca-clay suspensions. This correlation suggests that DCB-extractable iron affects the tactoid dimensions of Ca-clays from vertisols and, therefore, may also affect structural properties of vertisols.

Key Words—Beidellite, Extractable Fe, Fabric, Optical density, Tactoid, Vertisol.

INTRODUCTION

Vertisols cover vast areas of the world and represent one of the few, as yet underutilized agricultural soil reserves. Their agricultural utilization is, however, severely limited by their unfavorable structural characteristics, including excessive swelling and cracking and related characteristics, such as poor drainage and severe soil erosion.

Dispersion, swelling, aggregation, and stabilization of all soils are related to the colloidal properties of their clay fractions. Shanmuganathan and Oades (1982) noted that surface reactions of colloids control swelling and flocculation-dispersion phenomena, characteristics which are of prime importance in determining soil structure and stability. Surface reactions of the clay fractions of vertisols are dependent on the nature of the clay species present and are affected by small changes in external factors, such as the amount of exchangeable cations, pH, and electrolyte composition and strength. The mineralogical composition of clay fractions from vertisols is fairly uniform, consisting predominantly of smectite minerals (Dixon, 1982). Therefore, under controlled external conditions, only slight differences in the colloidal behavior of vertisols should be expected. Sensitive methods such as swelling behavior and optical density of clay suspensions have been shown to be effective in examining this colloidal behavior (Lahav and Banin, 1968; Shainberg and Otoh, 1968). Oades (1984) showed that surface properties of clays

are strongly affected by the presence of colloidal iron oxides. Alperovitch *et al.* (1985) found that the addition of Fe and Al to clay mixtures affected their swelling and dispersion. Vertisolic clays contain variable amounts of free iron oxides (Dixon, 1982), but whether naturally occurring free iron oxides affect the colloidal properties of soil clays is not well known (Borggaard, 1983).

In the present study the optical densities of clay suspensions derived from some vertisols from Israel are examined and related to their sediment volumes and DCB-extractable iron contents.

MATERIALS AND METHODS

Twelve horizons from eight vertisols and vertisolic soils from Israel were sampled (Table 1). Clay contents of the soils were determined by the hydrometer method (Day, 1965). Clay fractions were separated by sedimentation after dispersing the soil with 0.3 M NaHCO₃ and shaking it mechanically. Clay organic matter was removed using H₂O₂, after which the clay was saturated with Mg by three treatments with 0.5 M MgCl₂, washed free of excess salts, and dried at 60°C. The dried material was ground to pass a 100-mesh sieve and used as a stock for all examinations. Carbonates were not removed because treatments for their removal might have affected the colloidal behavior of the clay. Free iron oxides of the clay fractions were determined using the dithionite-citrate-bicarbonate (DCB) method

Table 1. Characteristics of Vertisols from Israel and their clay fraction.

Sample	Soil classification[1]	Locality	Clay content (%)	Specific surface area (m^2/g)	Cation-exchange capacity (meq/100 g)	Clay minerals[2]	Fe_2O_3[3] (%)	Smectite content (%)
1	Chromoxerert	Hermon	40.0	502	73.9	S > K > Q	2.25	67
2a	Chromoxerert	Lod	52.5	662	77.4	S $\gg$ K > Q	2.26	89
2b	Chromoxerert	Lod	52.5	635	75.5	S $\gg$ K > Q	1.88	85
3	Chromoxerert	North Kinneret	48.9	657	62.1	S $\gg$ K = I = Q = C	0.33	94
4a	Pelloxerert	Golan Heights	58.6	563	67.7	S $\gg$ K $\gg$ Q	1.22	76
4b	Pelloxerert	Golan Heights	61.8	586	67.1	S $\gg$ K $\gg$ Q	1.28	79
5a	Chromoxerert	Golan Heights	60.9	643	77.2	S $\gg$ K > Q	2.43	87
5b	Chromoxerert	Golan Heights	60.7	669	78.5	S $\gg$ K > Q	2.14	90
6	Chromoxerert	Golan Heights	51.6	442	57.2	S $\gg$ K > Q	2.66	60
7a	Chromoxerert	Yizrae'el Valley	67.5	606	79.5	S $\gg$ K > Q > C	1.05	82
7b	Chromoxerert	Yizrae'el Valley	64.1	724	88.6	S $\gg$ K > Q = C	1.40	97
8	Vertic Xeroll	Carmel	60.0	664	77.2	S $\gg$ K > C > Q	0.73	90

[1] Great Group in United States Comprehensive System (Soil Survey Staff, 1960).
[2] S = smectite; K = kaolinite; I = illite; Q = quartz; C = calcite.
[3] Determined by DCB method (Mehra and Jackson, 1960).

(Mehra and Jackson, 1960). The cation-exchange capacity (CEC) was determined by measuring the Na replaced at pH 7.0 by 1 M NH₄OAc from the Na-saturated clays (Chapman, 1965). Specific surface area was obtained using the retention of ethylene glycol-monoethyl ether (EGME) after Carter *et al.* (1965).

The kaolinite content of the clay fractions was estimated from differential thermal analysis data (Perkin-Elmer DTA Model 1700) using the area of the endothermic peak at 520°C (Barshad, 1952) and that of quartz by means of internal-standard X-ray powder diffraction analysis. The smectite content was obtained by difference. Smectite species and structure formula were determined and calculated from chemical analysis, X-ray powder diffraction analysis, and infrared spectroscopy after substracting the amount of secondary minerals. For X-ray powder diffraction (XRD) analysis a Philips Model 1010 diffractometer was used; infrared (IR) spectroscopy was carried out on a Perkin-Elmer Model 237 instrument. Elementary analyses were made using a model 2380 Perkin-Elmer atomic absorption apparatus, after HF-HClO₄ digestion of the clays. Ferrous iron was determined on samples that had not been treated with H_2O_2.

The clays were saturated with Na and Ca as follows: Na-clays were washed four times with 1 M NaCl and dialyzed against deionized water until the water solution was free of Cl. Ca-clays were washed four times with 0.5 M CaCl₂ and then washed with deionized water until excess salts were removed. The sediment volumes were measured in measuring cylinders by suspending 100 mg each of the Na- and Ca-clays into 25 ml of NaCl or 10 ml of CaCl₂, respectively, at pH 7 and at final electrolyte concentrations of 0.04 M and 0.02 M, respectively (Egashira and Matsumoto, 1981). Sediment volumes were read every 24 hr for as long as 720 hr.

Optical density (OD) of 250-ppm Na- and Ca-clay suspensions adjusted to pH 7 were obtained in the 200–800-nm wavelength range using an Uvikon 820 spectrophotometer and deionized water in the reference beam. The optical path was 1 cm; thus, the OD values could be directly converted into "absorbance index" values (K), where K is defined as the optical density per unit optical path length. The 700-nm absorbance index (K_{700}) was used to estimate relative number of platelets per tactoid, using Banin and Lahav's equation (1968):

$$\frac{n_i^3[n_j(d_c + 1) - 1]^2}{n_j^3[n_i(d_c + 1) - 1]^2} = \frac{K_i}{K_j},$$

where d is the clay specific density (taken as 2.80 g/cm³). K_i and K_j are the absorbance indexes of M-clay (M = Na^+, Ca^{2+}), and Li-clay, respectively, and n_i and n_j are number of platelets per tactoid of M-clay and Li-clay, respectively. Li-montmorillonite was used as reference clay, assuming ideal dispersion (n = 1).

Particle lengths were estimated after the absorption curve in the 350–700-nm wavelength range was used to calculate the values of b, the linear slope of the absorption curve in the 350–700-nm wavelength range in $\log \lambda$-$\log$ K scale (b = d log K/d log λ). Banin and Lahav (1970) showed b to be a function of the major dimension of average particle, measured by electron microscope observations.

RESULTS AND DISCUSSION

Characteristics of separated clay fractions

General characteristics and mineralogical composition of the separated clay fractions are given in Table 1. Smectite is the major mineral in all clays, making up nearly 100% of sample 7b and 60% of sample 6.

Table 2. Major element composition of Vertisol clay fractions and smectite chemical formula.

| | | | | | Smectite structural formula (per unit cell) | | | | | | |
| | Major element composition (%) | | | | Tetrahedral | | Octahedral | | | | Charge density |
Sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	Si	Al	Al	Fe	Mg	Σ	
1	46.00	20.28	10.62	3.93	7.04	0.96	2.71	1.00	0.58	4.30	0.71
2a	48.28	18.60	12.39	3.05	7.20	0.80	2.47	1.29	0.36	4.12	0.82
2b	50.35	18.43	11.77	2.72	7.33	0.67	2.51	1.25	0.30	4.06	0.76
3	41.83	11.67	8.92	4.93	7.53	0.47	2.01	1.22	1.03	4.26	0.69
4a	47.80	18.25	12.54	1.41	7.15	0.85	2.37	1.65	0.01	4.16	0.80
4b	42.06	18.63	13.36	1.80	6.76	1.24	2.31	1.76	0.12	4.19	0.82
5a	42.06	16.84	10.61	1.72	7.11	0.89	2.63	1.28	0.06	3.97	1.09
5b	41.60	16.64	10.15	1.70	7.23	0.77	2.66	1.23	0.06	3.95	0.98
6	39.69	21.80	14.23	1.44	6.38	1.62	2.51	1.74	0.06	4.31	0.72
7a	46.44	16.04	11.76	3.32	7.23	0.77	2.16	1.47	0.50	4.12	0.88
7b	48.70	17.40	12.21	3.73	7.17	0.83	2.19	1.42	0.52	4.13	0.94
8	48.64	9.42	12.70	4.82	8.87	0.13	1.66	1.55	0.83	4.04	0.82

Kaolinite accompanies smectite in amounts ranging from 4% to 22%. Accessory minerals are quartz in all samples and calcite in some samples. This composition is also reflected in the CECs, which range from 57 to 89 meq/100 g clay. From the chemical analyses in Table 2 the smectites appear to be close to Fe-rich beidellite; they have charge densities of 0.69–1.09 per unit cell; all of the iron is ferric. The absence of an IR absorption band at 965 cm^{-1} (Goodman *et al.*, 1976) and no changes in the absorption curves before and after DCB treatment and UV spectroscopy (absence of absorption band at 215 nm (Karickhoff and Bailey, 1973)) indicate that most of the structural Fe in the smectites is octahedral and that tetrahedral Fe is negligible. Thus, it is unlikely that any of the Fe extracted by DCB was structural iron. In nontronite, in which a significant proportion of the Fe is commonly tetrahedral, DCB treatments have been shown to remove some structural Fe (Russell *et al.*, 1979).

Sediment volumes of clays

The sediment volumes of Na- and Ca-clays after 24- and 720-hr ageing are presented in Table 3. In all samples, the sediment volume decreased with time. The

Table 3. Sediment volumes (cm^3/100 mg) of Na-clay and Ca-clay after 24- and 720-hr sedimentation.

| | 24 hr | | 720 hr | |
Sample	Na-clay	Ca-clay	Na-clay	Ca-clay
1	14.6	1.10	6.4	0.90
2a	14.4	0.90	8.0	0.63
2b	10.0	1.10	6.6	0.90
3	13.8	1.80	7.2	1.60
4a	11.6	0.60	7.6	0.40
5a	17.0	1.20	7.4	1.00
5b	16.3	0.90	8.4	0.80
6	8.5	1.60	4.8	1.00
7a	4.5	1.10	3.8	1.00
7b	9.2	1.20	5.1	1.10
8	8.1	1.40	5.6	1.30

sediment volume of the Na-clays decreased by an average of 44% of its original volume, whereas for Ca-clays the decrease averaged only 20%.

Figure 1 shows the changes in sediment volume with time for sample 7b. For the Na-clays, decreases in sediment volume were initially rapid and became minute (0.03 cm^3/100 hr) only after about 288 hr. The Ca-clays stabilized after 48 hr. The stabilized Na-clay volumes were as much as 19 times greater than the corresponding Ca-clay volumes.

Na-saturated smectites give rise to larger sediment volumes than Ca-clays because of their dominant edge-to-face and edge-to-edge structures, i.e., the so-called "card-house" arrangement (Frenkel and Shainberg, 1981; Yariv and Cross, 1979). Ca-clays, where face-to-face arrangements dominate, form "tactoid" structures (Blackmore and Miller, 1961), and the clay volumes are much smaller that those of the Na-clays. The tactoid arrangement apparently forms more quickly than the card-house arrangements, thus the volume of the Ca-clays is stabilized much earlier than for the Na-clays (Frenkel and Shainberg, 1981).

The volumes of the Ca-clays are similar to those reported by Egashira and Matsumoto (1981) for Japanese clays separated from soils. The sediment volumes of the Na-clays, on the other hand, are considerably greater, probably because of the smaller smectite content of the Japanese clays, as reflected in their smaller specific surface areas (SSAs).

Optical density and tactoid dimensions vs. sediment volumes

OD data of all samples give rise to adsorption curves typical of smectite (Figure 2). A typical curve shows a gradual decrease in OD from the ultraviolet to the visible range and exhibits a distinct inflection at 245 nm, due to O^{2-} → Fe^{3+} charge transfer (Karickhoff and Bailey, 1973). The absence of a distinct inflection at 260 nm is additional evidence that the clays are not nontronitic (Chen *et al.*, 1979).
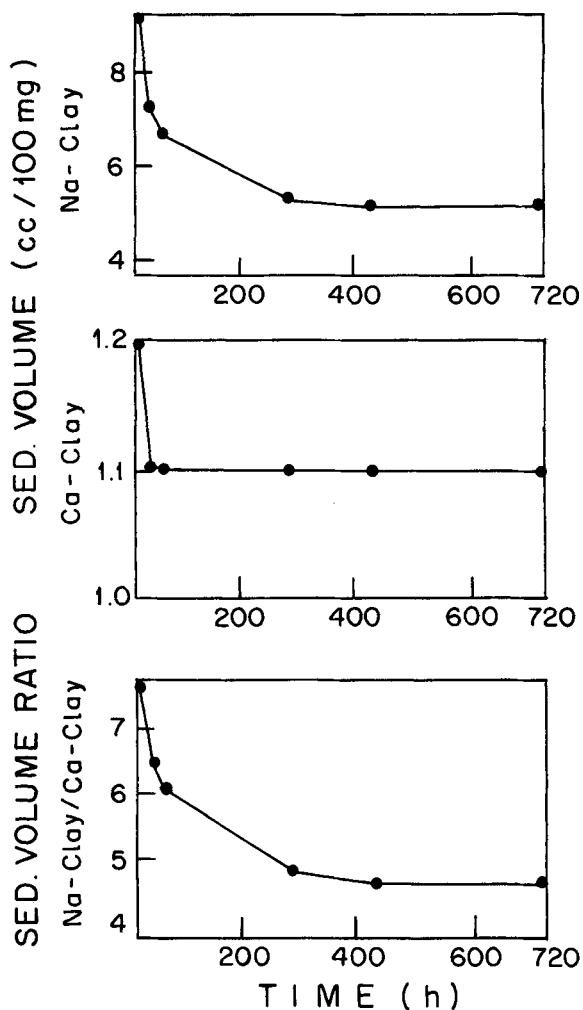
Figure 1. Sediment volume of Na- and Ca-clay (in cm³/100 mg) and the ratio of volume vs. time after the last shaking for sample 7b.

Figure 2. Ultraviolet-visible absorption spectra of two Na- and Ca-clay suspensions of samples 2b and 3.

The number of platelets obtained by the method of Banin and Lahav (1968) for the Na- and Ca-clay suspensions from the vertisols ranged from 1.4 to 5.4 and 7.4 to 14.1, respectively. The 24-hr sediment volumes of the Na- and Ca-clay suspensions are plotted against the number of platelets in their respective tactoids in Figure 3. For the Ca-clays, the sediment volume decreases with an increase in the relative number of platelets per tactoid, probably because of the structural organization of the platelets in the tactoids, i.e., the structure is probably dominated by face-to-face arrangements. As the number of platelets per tactoid decreases and the number of tactoids per volume increases, more surface area becomes exposed and the contribution of pore volumes becomes larger.

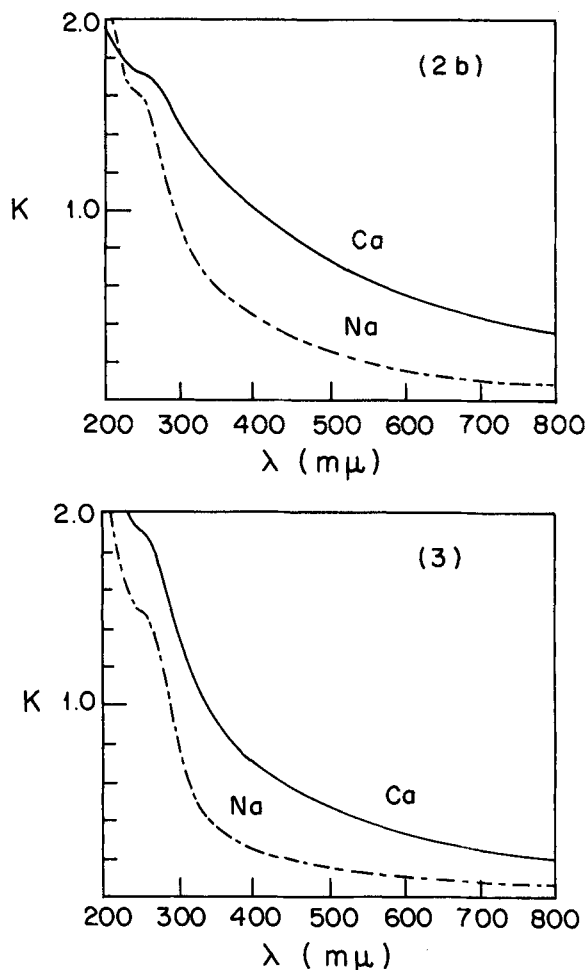In Na-clays no relationship was observed between the relative number of platelets per tactoid and sediment volume. The number of possible edge-to-face or edge-to-edge configurations in the Na-clays was large, and, hence, the number of platelets per tactoid was much less likely to have affected sediment volume.

In Figure 4, the 24-hr sediment volumes of Ca- and Na-clay suspensions are plotted against the respective b in absolute values |b| (b observed is always negative). For the Na-clays, the |b| value tends to decrease with an increase in sediment volume, although this relationship is weak (r = −0.43). Samples 2a and 2b are from two horizons of the only soil profile that had been intensively cultivated for a lengthy period. This cultivation may have affected the structural properties of this soil. If samples 2a and 2b are eliminated from the statistical analysis, the correlation is much more significant (r = −.81). Because |b| is inversely related to the major dimensions of the clay particles, Figure 4 suggests that with an increase in the major length dimension of Na-clay particles, their sediment volume also increases. Assuming edge-to-edge or edge-to-face particle arrangement for the Na-clays, larger maximum
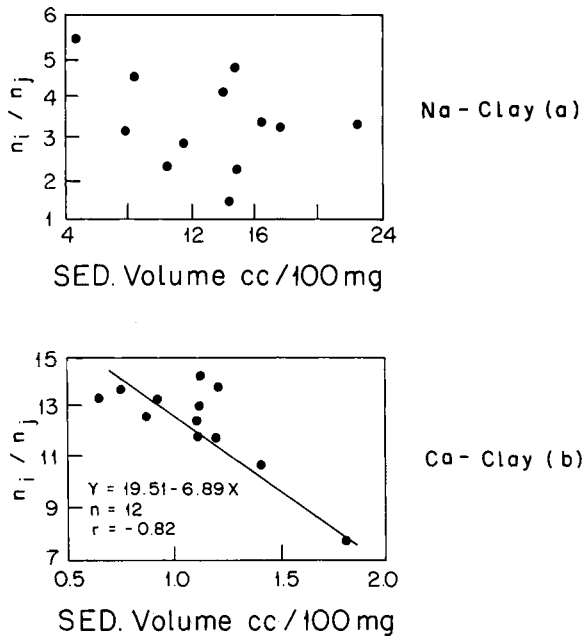
Figure 3. Sediment volume of (a) Na- and (b) Ca-clay suspensions after 24 hr from the last shaking vs. relative number of platelets per tactoid.
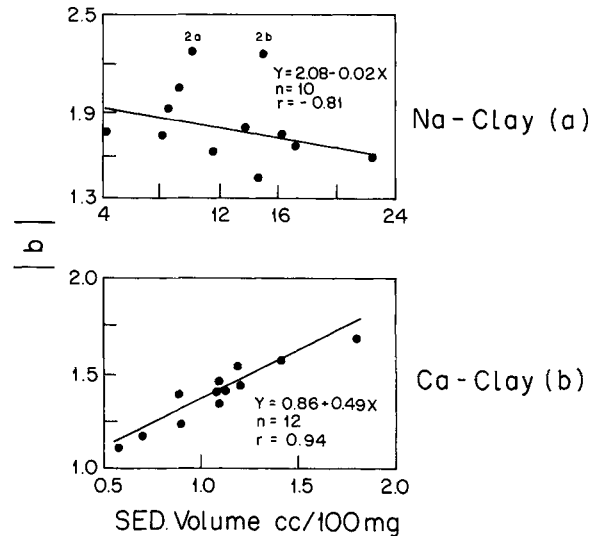

Figure 4. Sediment volume of (a) Na- and (b) Ca-clay suspensions after 24 hr from the last shaking vs. absolute values of the linear slope (b) of 350–700-nm absorption curve in log K-log λ scale (b = d log K/d log λ).

dimensions suggests a predominance of edge-to-edge arrangements, fewer tactoids, and, thus, more accessibility for water in more and larger pores.

Particles of Ca-clays are thought to be arranged in face-to-face tactoids. The decrease in major dimension of the particles for an assumed equal thickness of tactoids, suggests an increase in the number of tactoids and thus an increase in the probability of pore formation and a concomitant increase in sediment volume.

Optical density and tactoid dimensions vs. DCB-extractable iron oxides

Egashira and Matsumoto (1981) found a positive linear or exponential correlation between sediment volumes of Gray Lowland Soil clays and specific surface area. The mineralogy of their clay samples was heterogeneous, and many contained kaolinite as a major component. Hence, the relationship of sediment volume to specific surface area was as expected. For clays from the Red and Yellow Soils, for which this relationship was less significant, they concluded that particle size and shape probably controlled sediment volume. Egashira and Ohtsubo (1983) supported Foster (1955) by attributing the poor swelling characteristics of some soil smectites to the substitution of octahedral Al by Fe^{2+}.

No Fe^{2+} was detected in the vertisol clay fractions in the present study; therefore, the oxidation state of the Fe in the clay could not have been responsible for the range of sediment volumes. Moreover, no direct

relationship was noted between swelling volume and some surface characteristics such as specific surface area, CEC, charge density, and tetrahedral charge, which have been proposed as controlling factors for clay swelling (Verwey and Overbeek, 1948; Odom and Low, 1978; Low, 1981; Viani et al., 1983). All these characteristics may have an effect on sediment volume, but with so many variables the impact of one single factor is difficult to isolate and demonstrate.

Studies of the interaction of aluminum and iron hydroxides with clays have shown that even if relatively small amounts of oxide are added to the clay, the surface properties of the clay are dominated by the oxides. Oades (1984) found that water uptake and swelling of montmorillonite decreased with the addition of Fe polycations. Al and Fe polycations were shown by Alperovitch et al. (1985) to prevent clay swelling of clay-sand mixtures. This effect was attributed to the cementing of clay platelets. Shanmunganathan and Oades (1982) modified the physical properties of soil by the addition of Fe polycations. Basically, all these changes have been attributed to the effect of iron oxides on the charge characteristics of soil clays (Herbillon, 1985).

The DCB-extractable iron oxides of the vertisol clays are plotted against the relative number of platelets per tactoid in the Na- and Ca-clay suspensions in Figure 5. A positive correlation was found for the Ca-clays only. The DCB-extractable iron oxide content correlates positively with the major length dimensions of the particles in the Ca-clay suspensions only, suggesting that DCB-extractable iron oxides have an effect on the tactoid size dimensions of Ca-clays from vertisols, but not the Na-clays (Figure 6).
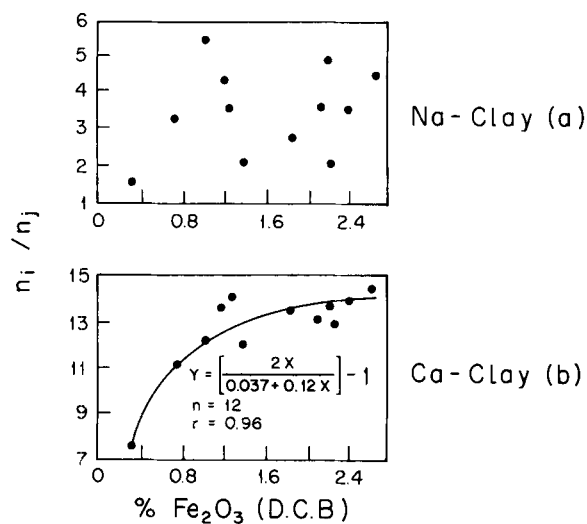
Figure 5. Dithionite-citrate-bicarbonate-extractable iron oxides vs. relative number of platelets per tactoid in (a) Na- and (b) Ca-clay suspensions.

Figure 6. Dithionite-citrate-bicarbonate-extractable iron oxide vs. absolute values of the slope of 350–700-nm absorption curve in log K-log λ scale (b = d log K/d log λ) in (a) Na- and (b) Ca-clay suspensions.

Interactions between clay minerals and Fe (and Al) affect aggregate stability; for example, McNeal *et al.* (1968) concluded that the cementing action of iron oxides in a group of Hawaiian soils prevented swelling and dispersion of clays having a range of exchangeable Na percentages. El Rayah and Rowell (1973) found that relatively small amounts of Al and Fe sesquioxides effectively controlled swelling of Na-montmorillonite, but they attributed this effect to the formation of interlayers. The formation of large tactoids in Al- and Fe-montmorillonite suspensions titrated with NaOH was attributed to the cementing effect of hydroxy Al and Fe polymers (Frenkel and Shainberg, 1980).

According to Oades (1984), if iron or aluminum oxides are added to the clay, the surface properties of the clay are dominated by the oxides. The "point of zero charge" (PZC) is raised considerably, and even small amounts of oxide are sufficient to produce flocculation. Even charge reversal with resuspension can be achieved (Oades, 1984). Evidently, adsorption of Fe affects the forces and interactions between particles by creating positive charges on the clay particle surfaces; as Oades pointed out, because of their spherical configuration (30–100 Å in diameter), Fe polycations have only a limited ability to block negative sites on the clay surfaces; thus, the CEC remains high. The presence of the Fe polycations thus may diminish but not prevent the formation of the double layer. Fe polycation fractions of molecular weight >50,000 were identified as goethite, a common mineral in natural sesquioxides (Oades, 1984). Therefore, the effect of the iron sesquioxides on the vertisol clay-mineral surfaces may be similar to that of the polycations added to artificial systems.

In the Ca-clay suspensions the double layer apparently contracted, and clay particles were able to ap-
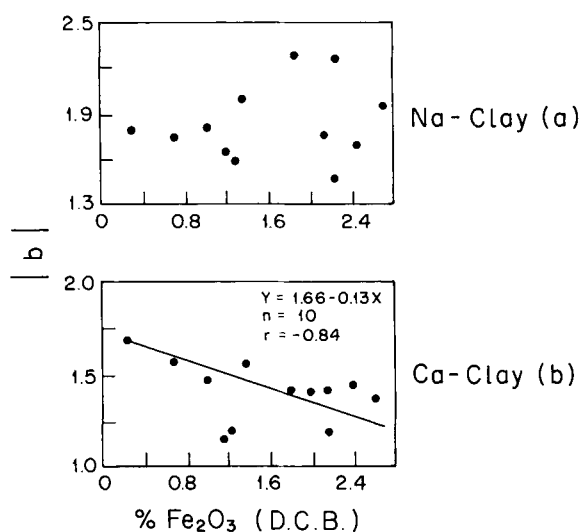
proach each other sufficiently for the bridging mechanism of the iron oxide to become effective. Thus, larger tactoids were formed. The thicker double layers in the Na-clays did not permit such close contacts between the particles and the "cementing" action of the iron oxides was not effective. Also, the (positive) surface charge density of the iron oxide probably increased with the valence of the counter ion present. Thus, the larger (positive) surface charge density obtained in the Ca-clay system may also have contributed to a more effective bridging mechanism.

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