MECHANISM CONTROLLING THE VOLUME CHANGE BEHAVIOR OF KAOLINITE

SUDHAKAR M. RAO AND A. SRIDHARAN

Soil Mechanics Laboratory, Department of Civil Engineering
Indian Institute of Science, Bangalore-560 012, India

Abstract—The possible physical and chemical forces controlling the volume change behavior of kaolinite were ascertained from the sediment volume of kaolinite in various solvents under no external load condition and from conventional oedometer measurements of kaolinite in several pore fluids. The minimum sediment volume of 14.5 cm³/10 g clay occupied by kaolinite in water where repulsive (R) forces were dominant indicated that the R contribution was insignificant for kaolinite. The maximum sediment volume of 25.0 cm³/10 g clay in benzene where coulombic attraction forces were significant suggested that electrostatic attraction between silicate sheets and midplane cations and van der Waals forces were not appreciable for kaolinite. The positive edge-negative face bonding of kaolinite particles in benzene was unlikely because the protons required to impart a positive charge to the edges were not available in the nonpolar solvent. The 3688 cm⁻¹ band in the infrared spectrum of a kaolinite-dimethylamine sample decreased by 10 cm⁻¹ on H-bond formation of the solvent molecule with the exposed structural hydroxyls of the octahedral sheet. The adsorbed solvent molecules likely H-bonded with an adjacent clay particle. That such interparticle H-bonds controlled the sediment volume and interparticle attraction in kaolinite was indicated by the decrease in sediment volume with increase in dipole moment of the solvent molecule, i.e., 25.0 cm³/10 g clay in n-heptane (dipole moment, $\mu = 0$), 23.5 cm³/10 g clay in toluene ($\mu = 0.36$), 17.0 cm³/10 g clay in ethanol ($\mu = 1.67$), and 14.5 cm³/10 g clay in water ($\mu = 1.84$).

In the oedometer tests with various pore fluids, a high void ratio (i.e., volume of voids/volume of solids) of ~1.3 was obtained for kaolinite in n-heptane, and hexane ($\mu \simeq 0$) at an external pressure of 1 kg/cm² probably because the weakly bonded kaolinite particles were randomly oriented. At the corresponding applied pressure a lower void ratio of 0.88 resulted in water ($\mu = 1.84$) where the stronger hydrogen bond between flat layer surfaces of adjacent particles favored a parallel orientation of clay particles.

The variations in void ratio-external pressure relationship indicated that kaolinite underwent lower compressibility in a solvent with low dipole moment and *vice versa*. Thus, the interparticle H-bond did not play a significant role in controlling the shear resistance and volume change behavior. The volume change behavior was essentially controlled by frictional forces and clay fabric. In nonpolar solvents the random arrangement of kaolinite particles and the frictional forces mobilized a high shear resistance on the application of a consolidation pressure, resulting in a lower compressibility. In a solvent with high dipole moment the parallel array of clay particles mobilized less shear resistance and produced a greater compression.

Key Words—Compression, Dipole moment, Hydrogen bond, Infrared spectroscopy, Kaolinite, Organic solvents, Volume change.

INTRODUCTION

Most basic studies on the volume change behavior of clays have dealt with the expanding mineral montmorillonite (see, e.g., Bolt, 1956; Mitchell, 1960; Olson and Mesri, 1970; Sridharan and Rao, 1973; Sridharan and Jayadeva, 1982). These investigations have established that electrical double layer forces play an important role in controlling the swelling and compressibility of the clay. In comparison, few studies are available on the compressibility behavior of the nonexpanding mineral kaolinite. Olson and Mesri (1970) reported that kaolinite compressibility is a function of physical factors, i.e., surface friction, geometric arrangement of particles, and particle shape. Sridharan and Rao (1973) proposed that the volume change behavior of kaolinite is governed by shearing resistance at interparticle level. They observed that, apart from the physical components, the attractive forces arising

from physiochemical mechanisms contribute to shearing resistance. These forces mainly include van der Waals forces, the coulombic attractions between negative surfaces and positive edges, particle-cation-particle linkages, and forces arising from hydrogen bonds. The factors determining the shearing resistance and volume change behavior of kaolinite hence include (1) frictional resistance, (2) clay fabric, and (3) attractive forces arising from physiochemical mechanisms. The relative importance of the various constituents is, however, not clear.

To date no established procedure for determining quantitatively the attractive or repulsive forces (arising from physiochemical mechanisms) operative in a clay-water system has been developed. It is, however, possible to bring about variations in these forces by changing the environment. The forces in coulombic attraction vary inversely with the dielectric constant

Table 1. Physical characteristics of kaolinite from Karnataka, India.

Property	Results
Liquid limit (%)	49
Plastic limit (%)	29
Plasticity index (%)	20
Specific gravity	2.59
Silt size fraction (%)	45
Clay size fraction (%)	54
Cation-exchange capacity (at pH 7.0) (meq/100 g)	3.21
Surface area (water vapor adsorption method) (m²/g)	21.24

of the medium and the distance between the units (Mitchell, 1976). The van der Waals force is also a function of dielectric constant (Rosenqvist, 1955; Lambe, 1958; Sridharan and Rao, 1979). In addition to cation valence and size, the double layer repulsion is also affected by the dielectric constant.

In the present investigation, variations in interparticle attraction and repulsion were brought about by using organic solvents with different bulk properties. First, the sediment volume of kaolinite under no external load was determined in various solvents and the results used to evaluate the relative importance of various attractive and repulsive forces for kaolinite. Second, conventional oedometer tests with various solvents were used to understand the mechanism controlling the pressure-volume change behavior of the material.

MATERIALS AND METHODS

Materials

Kaolinite, from Tirthahally, Karnataka state, India was used in the studies. The specific surface area as evaluated by the single-point water-vapor adsorption method was 21.24 m²/g. The aqueous cation-exchange capacity (CEC) was determined by the ammonium acetate (pH 7.0) extraction method. Na, Ca, and K were determined by flame photometry and Mg by volumetric E.D.T.A. analysis (Vogel, 1968). A CEC of 3.21 meq/100 g (Na⁺ = 0.67 meq/100 g; Ca²⁺ = 1.48 meq/ 100 g; K⁺ = 0.17 meq/100 g; Mg²⁺ = 0.89 meq/100 g) was obtained. The absence of a 3669-cm⁻¹ band in the infrared (IR) spectrum of the kaolinite specimen indicated that the clay was not well crystallized; the CEC and surface areas were also close to those reported by van Olphen and Fripiat (1979) for a less well-crystallized kaolinite from Georgia, U.S.A. Hydrometer analysis showed that about 54% of the clay sample had a particle size of <2 μm and that the remaining material ranged in size between fine and medium silt. The characteristics of the kaolinite used in this investigation are listed in Table 1.

X-ray powder diffraction (XRD) patterns of the Mg-saturated, glycerol-solvated kaolinite showed no reflection corresponding to smectite. The weak reflections at 4.46 and 3.83 Å and at 4.25 and 3.35 Å indicated the presence of traces of muscovite and quartz, respectively (Jackson, 1964; Jasmund and Mering, 1979). Selective dissolution of free hydroxides and oxides of aluminum in kaolinite by successive extractions with 5% Na_2CO_3 solution at room temperature (Schwertmann, 1979) and determination of the dissolved aluminum colorimetrically using aluminon reagent (Lindsay and Stephenson, 1959) showed 0.046% free Al_2O_3. Free iron oxide was extracted using sodium sulfate combined with $NaHCO_3$ as a buffer and sodium citrate as a complexing agent (Jackson, 1964). A colorimetric test using orthophenanthroline (Hesse, 1972) showed 0.012% free Fe_2O_3 to be present.

The reagent grade solvents used were benzene, hexane, n-heptane, toluene, dimethylamine, ethanol, methanol, and distilled water.

Methods

The sediment volumes of kaolinite in different solvents were determined as follows: oven-dried (110°C) kaolinite samples (10 g) were submerged in 40 ml of benzene, n-heptane, hexane, toluene, dimethylamine, ethanol, and water in 100-ml, previously standardized graduated cylinders. The suspensions were repeatedly stirred and allowed to equilibrate for 24 hr to ensure thorough wetting of the samples. The suspensions were then made up to the 100-ml mark with the respective solvents, with stirring. The cylinders were stoppered and left undisturbed for a further period of 24 hr at which time the volumes occupied by kaolinite particles on settling (referred to as the sediment volume) were noted.

The IR spectra of kaolinite and kaolinite-dimethylamine samples were recorded using a Perkin Elmer 599 spectrophotometer. The dimethylamine sample was prepared by pipeting 5 ml of the equilibrium suspension onto a watch glass and allowing it to dry in air. On air drying, the sample was immediately kept in Nujol. The spectra of the samples were recorded by the Nujol mull method.

One-dimensional consolidation tests were conducted in oedometers modified for permeability measurements. The desired pore fluid was circulated through the clay bed, and the effluent was collected after passing through the clay. Silicone grease was lightly smeared on the inner walls of the consolidation ring (7.6-cm diameter, and 1.91-cm height) to minimize errors due to side friction. The ring was placed on a 0.4-cm thick, porous carbon disc, and a Whatman No. 41 paper was positioned between the ring and the disc. The kaolinite sample, oven-dried at 110°C for 24 hr and cooled in a desiccator over P_2O_5, was compacted with a displacer plate (0.64-cm thick) to a dry density of 1.13 g/cm³ in

the consolidation ring and to a thickness of 1.27 cm. The piston containing the upper porous disc was then carefully inserted into the consolidation ring which was then mounted in a consolidation cell and positioned in a loading frame. Under a nominal pressure of 0.0625 kg/cm², the kaolinite sample was submerged in the desired solvent. Evaporation of the pore fluid from the consolidation cell was minimized by placing close-fitting metal jackets on the top of the cell. Care was also taken to replace any solvent that evaporated from the cell. Entrapped air in the clay bed was displaced by circulating the solvent through the clay sample and by applying a slight vacuum to the lower porous disc. After equilibrium had been attained, as indicated by the constant readings in the vertical deflection dial, conventional oedometer tests were carried out. A load increment ratio of one was adopted, and the load was maintained for 24 hr or until primary consolidation was complete.

RESULTS AND DISCUSSION

Forces controlling sediment volume

Table 2 presents the sediment volumes obtained for kaolinite in different solvents, the dipole moments, and dielectric constants of the respective solvents. Murray and Quirk (1982) reasoned that the physical swelling of kaolinite and illite was likely to depend on the bulk properties of the intervening solvent molecules. They viewed the physical swelling of clays as resulting from the electrostatic attractive forces between silicate sheets and midplane cations being exceeded by the cation solvation forces. Treating the intersurface region as a condensor array, the attractive electrostatic potential is given as follows:

$$V_A = 2\pi\sigma^2(\frac{1}{2}d)/\xi_s, \qquad (1)$$

where σ is the surface density of charge, ξ_s is the dielectric constant, and $\frac{1}{2}d$ is the distance between the silicate surface and an idealized two dimensional cation array. The repulsive solvation potential from Born equation is represented as follows:

$$V_R = \gamma e(\xi_s - 1)/2\pi\sigma r, \qquad (2)$$

where γ is the cation valence, e is the electronic charge, and r is the cation radius. Interparticle interaction is the net result of repulsion and attraction, R − A. According to Eq. (1), V_A is maximum in benzene (ξ_s = 2.27) and minimum in water (ξ_s = 79.4), and from Eq. (2) V_R is maximum in water and minimum in benzene. In benzene, as R is insignificant, R − A, is attraction; the strong face-to-face attraction between kaolinite plates via the midplane cations requires that the clay particles should occupy a minimum sediment volume. In water, because R is dominant, maximum swelling of clay particles should occur. The maximum sediment volume of 25.0 cm³/10 g clay in benzene and the min-

Table 2. Sediment volumes of kaolinite in solvents with different bulk properties.

Solvent	Sediment volume (cm³)[1]	Dielectric constant (20°–25°C)	Dipole moment (debye)
Benzene	25.0	2.27	0.0
n-heptane	25.0	1.92	0.0
Hexane	24.0	1.89	0.08
Toluene	23.5	2.38	0.36
Dimethylamine	17.5	5.26	1.03
Ethanol	17.0	24.3	1.69
Water	14.5	79.4	1.84

[1] Per 10 g clay.

imum volume of 14.5 cm³/10 g clay in water indicates that electrostatic attraction forces between silicate sheets and midplane cations and the repulsive cation-solvation forces were insignificant for kaolinite. The particle-cation-particle linkages and cation-solvation repulsive potential depend on the total exchangeable cations and surface area of the clay mineral available. The insignificant electrostatic attraction and cation-solvation repulsion forces noted for kaolinite must have resulted from its low CEC and surface area.

The R forces for a clay arise from solvation of the exchangeable cations and the double layer repulsion between surfaces of individual particles (van Olphen, 1963). As noted above, the cation-solvation forces were insignificant for kaolinite. Diffuse double layer formation is slight for kaolinite. In the absence of an appreciable R force, the net interparticle interaction, R − A, was equal to A for kaolinite, and the sediment volumes in different solvents were essentially a function of interparticle attraction.

Besides the coulombic forces due to particle-cation-particle linkages, electrostatic attraction between positive edges and negative faces were possible. A kaolinite edge develops a positive charge on the acceptance of a proton by the edge hydroxyl group from the solvent (Schofield and Samson, 1954). The reaction may be represented as:

Protons would be unavailable for reaction (3) in nonpolar solvents, but their concentration would be appreciable in water at pH <7. Positive edges favor an edge-to-face flocculation of the clay particles and a high volume of sediment (van Olphen, 1963). The minimum sediment volume of 14.5 cm³ in water found in the present study suggests that positive edge-negative face flocculation was insignificant at the experimental pH (7.2).
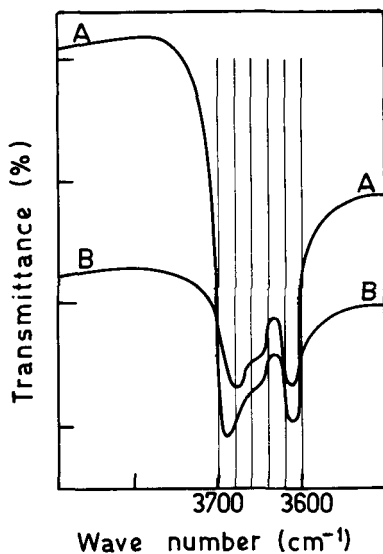
Figure 1. Infrared spectra of structural hydroxyl in kaolinite (A) and kaolinite equilibrated with dimethylamine (B).

For parallel plates separated by a distance of 2d, the van der Waals attractive energy per unit area is given by

$$V_A = A/48\pi d^2, \tag{4}$$

where A is the Hamaker constant. Sridharan and Rao (1979) showed that the value of the Hamaker constant decreases with an increase in the dielectric constant of the solvent. The other van der Waals forces contributing to interparticle attraction are those arising due to induced dipole, ion-dipole, and dipole-dipole interactions. These van der Waals forces also vary inversely with the dielectric constant of the medium and the distance between the units (Rosenqvist, 1955; Lambe, 1958). If the van der Waals forces contribute significantly to interparticle attraction, the volume occupied by kaolinite particles should increase with an increase in the dielectric constant of the solvent. The maximum sediment volume of 25.0 cm³ in benzene (ξ_s = 2.27) and the minimum volume of 14.5 cm³ in water (ξ_s = 79.4) found here, suggest that the van der Waals forces did not control the sediment volume of kaolinite suspension.

An increase in the dipole moment of the solvent was accompanied by a decrease in the volume of sediment (Table 2). This variation with the dipole moment may be explained by considering the role of hydrogen bonding in interparticle attraction as suggested by IR evidence.

The IR spectrum of kaolinite showed strong hydroxyl absorptions at 3688 and 3618 cm⁻¹ and a weak absorption at about 3650 cm⁻¹ (Figure 1). The 3618 cm⁻¹ was attributed to the inner hydroxyls located in the plane common to the octahedral and tetrahedral

sheets within a unit layer. The strong band at 3688 cm⁻¹ was assigned to the symmetrical in-phase vibrations of the surface hydroxyls of aluminum octahedral sheet, and the weak 3650-cm⁻¹ band to their out-of-phase vibrations with the degeneracy lifted (Farmer, 1964). The IR spectrum of the kaolinite-dimethylamine sample showed that the 3688-cm⁻¹ band was lowered by at least 10 cm⁻¹. The lowering of frequency likely resulted from the adsorption of the solvent molecule on the surface hydroxyls of the Al octahedral sheet by a process of hydrogen bonding. This process probably involved the interaction of a lone electron pair of the nitrogen atom in the dimethylamine molecule with the structural hydroxyls of the exposed gibbsitic surface. The adsorbed solvent molecule likely hydrogen bonded with an adjacent particle as in the following reaction:

(5)
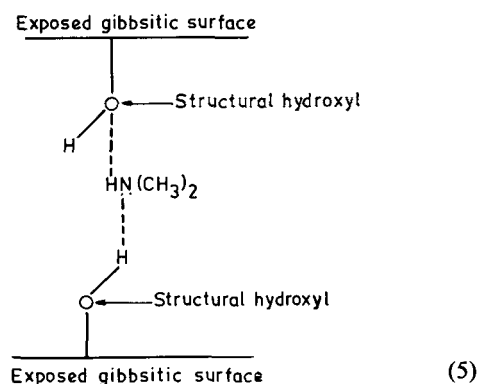
Such an interparticle bonding presumably favored a face-to-face arrangement of kaolinite particles.

As the hydrogen bond is largely electrostatic in nature (Pauling, 1960), the strength of the interparticle hydrogen bond should depend on the dipole moment of the adsorbed solvent molecule. For solvents, with zero dipole moment the interparticle bond is mainly dispersive in nature (Kiselev and Lygin, 1966). In a solvent with zero or low dipole moment, kaolinite particles, due to their weak binding, were randomly arranged on setting and occupied a high volume of sediment. An increase in the dipole moment of the solvent resulted in a stronger hydrogen bonding of adjacent clay particles via the adsorbed solvent molecule. The kaolinite particles were more regularly arranged on settling, and, hence, occupied a lesser volume of sediment. Thus, the interparticle hydrogen bond was a major determinant of the sediment volume and of the interparticle attraction. The coulombic and van der Waals forces were less significant than the H-bonding force in determining interparticle attraction.

Forces controlling volume change behavior

Figure 2 presents the void ratio-applied pressure relationships obtained using a conventional oedometer

with different pore fluids (Sridharan and Rao, 1973). At a consolidation pressure of 1 kg/cm² a void ratio of ~1.3 was observed for kaolinite in benzene, n-heptane, and hexane ($\mu \simeq 0$), whereas, at the corresponding applied pressure the void ratio values in ethanol ($\mu = 1.69$), methanol ($\mu = 1.7$), and water ($\mu = 1.84$) were 1.12, 1.09, and 0.88, respectively. In nonpolar solvents, the particles were presumably randomly oriented due to their weak binding as mentioned above, with large void spaces in between. In a solvent with higher dipole moment, the stronger hydrogen bonding between flat layer surfaces of adjacent clay particles via the adsorbed solvent molecule favored a face-to-face orientation of the kaolinite particles, resulting in a lower void ratio.

A void ratio of ~1.36 was observed for kaolinite in benzene, n-heptane, and hexane ($\mu \simeq 0$) at a seating pressure of 0.0625 kg/cm². A void ratio of ~1.1 was observed at a maximum applied pressure of 8 kg/cm². At these same pressures, the void ratios in water ($\mu = 1.84$) were 1.22 and 0.66, respectively. These results indicate that kaolinite underwent a lesser compressibility in a solvent with low dipole moment and *vice versa,* contrary to the expected reaction if the interparticle hydrogen bond controlled the compressibility of kaolinite. In addition to the hydrogen bonding force, the coulombic and van der Waals forces could also have contributed to the shear resistance. As these forces were less significant than the H-bonding force in controlling the sediment volume and, hence, in interparticle attraction, their contribution to shear resistance is considered not to have been significant.

Mitchell (1960) observed that for clays containing particles with size >1 μm diameter, the initial particle arrangement is of overriding importance in determining the compressibility of the clay. This relation also appears to be true for the kaolinite mineral used in the present study (>1-μm fraction = 80%). The application of consolidation pressure tended to cause adjacent particles to move towards a parallel array. The relative resistance to such a reorientation for kaolinite was mainly a function of the physical components. For clay minerals with random or flocculated fabric, considerable energy must be expended to reorient the particles (Gillot, 1968). In such systems besides friction, the physical entanglement and elastic bending of the clay particles mobilize a high shear resistance on external loading. Hence, in solvents such as benzene, n-heptane, and hexane ($\mu \simeq 0$), the disorderly clay fabric exhibited lower compressibility.

In a solvent with higher dipole moment, the kaolinite particle arrangement presumably tended towards a parallel orientation. For a fabric with preferred orientation, the contribution from physical entanglement and elastic bending to shear resistance was considerably less, resulting in a higher compressibility.

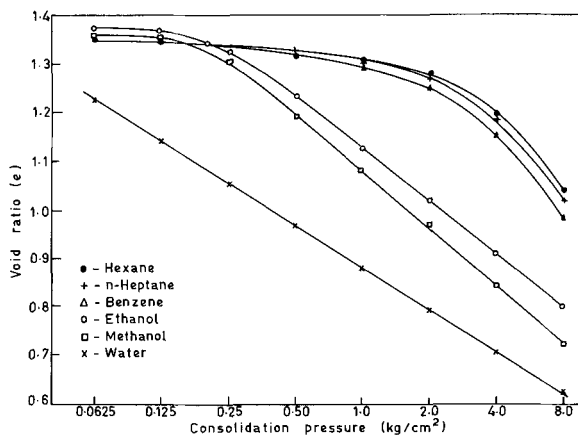It follows from the above discussion that (1) the

Figure 2.   One-dimensional consolidation curves for kaolinite with different pore fluids: compression.

dipole moment of the pore fluid was responsible for the geometric arrangement of the clay particles, and (2) the shear resistance at particle level which governs the volume change behavior was a function of the clay fabric. In a nonpolar solvent, the randomly oriented particles exhibited maximum shear strength. In a solvent with high dipole moment, the parallel arrayed clay particles possessed less shear strength.

Figure 3 plots the shear strength against normal pressure for kaolinite samples compacted with various pore liquids and determined using a conventional box-type shear apparatus (Sridharan and Rao, 1979). Kaolinite samples exhibited maximum shear strength under any normal pressure in the presence of nonpolar solvents and a minimum in water (high dipole moment). In nonpolar solvents, the random clay fabric and frictional forces mobilized a high shear resistance under any normal pressure. In a solvent with high dipole moment, the parallel arrayed clay particles mobilized less shear resistance, resulting in a minimum shear strength of the clay.

CONCLUSIONS

In the absence of an appreciable R force, the net interaction, R − A, was equal to A for kaolinite, and its sediment volumes in different solvents was a function of interparticle attraction. The interparticle hydrogen bond formed via the adsorbed solvent molecule between exposed gibbsitic surfaces of adjacent clay particles controlled the sediment volume. The dipole moment of the adsorbed solvent molecule was a major determinant of the strength of such bonds. The coulombic and van der Waals forces were less significant than the hydrogen bonding force in controlling the sediment volume.

In nonpolar solvents, the kaolinite particles due to their weak binding were presumably randomly oriented with large void spaces in between. In a solvent with
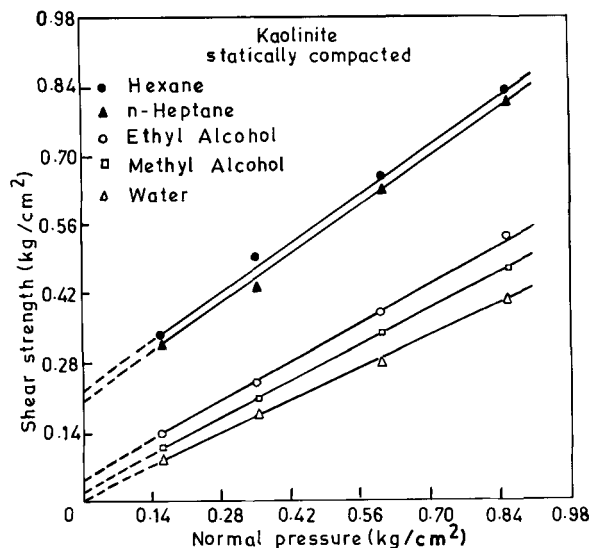
Figure 3. Shear strength vs. normal pressures for kaolinite with different pore fluids.

higher dipole moment, due to stronger hydrogen bonding between flat layer surfaces of adjacent clay particles via the adsorbed solvent molecule, the particle arrangement was closer to a parallel orientation and resulted in a lower void ratio.

The attractive forces arising from physiochemical mechanisms did not play a dominant role in controlling the volume change behavior of kaolinite. The interparticle hydrogen bond, however, determined the kaolinite fabric, the latter being a major constituent of shear resistance.

In nonpolar solvents, the random clay fabric and frictional force mobilized a high shear resistance on external loading, resulting in a lower compressibility. In a solvent with high dipole moment, the parallel orientation of the clay particles mobilized a lesser shear resistance, leading to a larger volume change.

The proposal that the shear resistance of kaolinite is a function of clay fabric and surface friction was confirmed.

ACKNOWLEDGMENT

REFERENCES

Bolt, G. H. (1956) Physico-chemical analysis of the compressibility of pure clays: *Geotechnique* **6**, 86–93.

Farmer, V. C. (1964) Infrared absorption of hydroxyl group in kaolinite: *Science* **145**, 1189–1190.

Gillot, J. E. (1968) *Clay in Engineering Geology:* Elsevier, New York, 296 pp.

Hesse, P. R. (1972) *A Text-book of Soil Chemical Analysis:* Chemical Publishing Co., New York, 520 pp.

Jackson, M. L. (1964) Soil clay mineralogical analysis: in *Symposium on Soil Clay Mineralogy, Virginia Polytechnic Institute, 1962,* C. I. Rich and G. W. Kumze, eds., University North Carolina Press, Durham, North Carolina, 245–294.

Jasmund, K. and Mering, J. (1979) X-ray diffraction: in *Data Hand-book for Clay Materials and Other Non-metallic Minerals,* H. Van Olphen and J. J. Fripiat, eds., Pergamon Press, New York, 177–194.

Kiselev, A. V. and Lygin, V. I. (1966) Surface hydroxyl group and their perturbance by adsorbed molecules: in *Infrared Spectra of Adsorbed Species,* L. H. Little, ed., Academic Press, New York, 428 pp.

Lambe, T. W. (1958) The structure of a compacted clay: *J. Soil Mech. Found. Div., Amer. Soc. Civil Eng.* **84**, 1–34.

Lindsay, W. L. and Stephenson, H. F. (1959) Reactions of MCP with the soil; solution that reacts with the soil: *Soil Sci. Soc. Amer. Proc.* **23**, 12–18.

Mitchell, J. K. (1960) The application of colloidal theory to the compressibility of clays: in *Seminar on Interparticle Forces in Clay Water-Electrolyte Systems, Melbourne, 1959,* R. H. G. Parry, ed., Commonwealth Scientific and Industrial Research Organization, Melbourne, 2.92–2.97.

Mitchell, J. K. (1976) *Fundamentals of Soil Behavior:* Wiley, New York, 422 pp.

Murray, R. S. and Quirk, J. P. (1982) The physical swelling of clays in solvents: *Soil Sci. Soc. Amer. J.* **46**, 865–868.

Olson, R. E. and Mesri, G. (1970) Mechanism controlling compressibility of clays: *J. Soil Mech. Found. Div., Amer. Soc. Civil Eng.* **96**, 1863–1878.

Pauling, L. (1960) *The Nature of Chemical Bond:* Oxford and IBH Publishing Co., Bombay, 449–451.

Riddick, J. A. and Bunger, W. B. (1970) *Techniques of Chemistry. Volume II. Organic Solvents:* Wiley, New York, 1041 pp.

Rosenqvist, I. Th. (1955) Some fundamental conception: in *Investigations in the Clay-Electrolyte-Water System,* Nor. Geotech. Inst. Publ. **9**, 3–9.

Schofield, R. K. and Samson, R. H. (1954) Flocculation of kaolinite due to attraction of oppositely charged faces: *Disc. Faraday Soc.* **18**, 135–145.

Schwertmann, U. (1979) Dissolution methods: in *Data Hand-book for Clay Materials and Other Non-metallic Minerals,* H. van Olphen and J. J. Fripiat, eds., Pergamon Press, New York, 346 pp.

Sridharan, A. and Jayadeva, M. S. (1982) Double layer theory and compressibility of clays: *Geotechnique* **32**, 133–144.

Sridharan, A. and Rao, G. V. (1973) Mechanisms controlling volume change of saturated clays and the role of effective stress concept: *Geotechnique* **23**, 359–382.

Sridharan, A. and Rao, G. V. (1979) Shear strength behavior of saturated clays and the role of effective stress concept: *Geotechnique* **29**, 177–193.

van Olphen, H. (1963) *An Introduction to Clay Colloid Chemistry:* Wiley, New York, 301 pp.

van Olphen, H. and Fripiat, J. J., eds. (1979) *Data Hand-book for Clay Materials and Other Non-metallic Minerals:* Pergamon Press, New York, 346 pp.

Vogel, A. I. (1968) *A Text-book of Quantitative Inorganic Analysis:* Longmans, London, 1216 pp.

Weast, R. C., ed. (1968) *Handbook of Chemistry and Physics:* Chemical Rubber Co., Columbus, Ohio, 1923 pp.