THE INTERACTION OF POLYSACCHARIDES WITH SILVER HILL ILLITE

Baohua Gu and Harvey E. Doner

Department of Soil Science, University of California, Berkeley, California 94720

Abstract—The clay-polysaccharide interaction is of practical importance in the formation and stabilization of soil aggregates. This study examined the adsorption of three synthetic polysaccharides (PSS) and one soil PSS on Silver Hill illite. The adsorption of PSS was influenced by both the adsorbed cations on the adsorbents and the charge characteristics of the polymers. The adsorbed cations formed different surface complexes with the clay surfaces, with varying ability to screen the surface negative charge and thereby influenced the adsorption of charged polymers. Na-illite adsorbed substantially higher amounts of the cationic PSS, but lower amounts of the anionic PSS, than hydroxy-Al illite. The adsorption of the nonionic PSS was, however, little influenced by those adsorbed cations. The adsorption of the soil PSS resembled that of anionic PSS. However, it yielded linear adsorption isotherms due to the heterogeneous nature of the soil PSS. The adsorption of the three synthetic PSS on Na-illite was in the general order: cationic > nonionic > anionic, confirming that electrostatic forces played a role in the adsorption of charged polymers. pH and ionic strength influenced the adsorption of the charged PSS, because of their influences on the charge characteristics of both the polymer and the clay, and on polymer conformation. This study indicates that surface charge properties of both clays and organic polymers and the presence of polyvalent cations in the system are important factors influencing the complexation between soil clays and organic constituents.

Key Words—Adsorption, Illite, Ionic strength, pH, Polysaccharides, Polyvalent cations.

INTRODUCTION

Clay-polysaccharide interactions in soil play an important role in the formation and stabilization of desirable soil structure, although polysaccharides (PSS) generally comprise a minor fraction (5–20%) of the soil organic matter (Olness and Clapp, 1975). Numerous studies have been conducted on the interaction of synthetic PSS and polymers with montmorillonite and kaolinite (Parfitt and Greenland, 1970; Olness and Clapp, 1975; Chenu *et al.*, 1987; Gill and Herrington, 1987a, 1987b; Aly and Letey, 1988), but little information is available on the interaction of PSS with illitic minerals.

Early studies have demonstrated that the adsorption of an uncharged, flexible, linear polymer from aqueous solutions onto a clay surface generally leads to the desorption of numerous water molecules from the surface (Parfitt and Greenland, 1970; Parfitt, 1972). The entropy so gained provides the driving force for adsorption, especially of high molecular weight species. Hydrogen bonding between hydroxyls, or other polar groups in the polymers, and surface oxygens of the silicate layers further lowers the free energy of the system (Theng, 1982).

For charged polymers, the interaction is more complex than that involving nonionic species. Saini and MacLean (1966) reported that the adsorption of a soil PSS by kaolinite was influenced by adsorbed cations on clay surfaces with the effect of $Fe^{3+} > Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > Na^+$. Since many clay minerals carry a net negative charge, Parfitt (1972) and Theng (1982) have proposed that positively-charged polymers are adsorbed primarily by a cation exchange mechanism. For this reason, their overall affinity for the clay is greater than that shown by uncharged species. On the other hand, negatively-charged polymers tend to be repelled from the clay surface. Aly and Letey (1988) studied the interaction of three guar polymers with Na-montmorillonite and found that adsorption was in the general order: cationic > nonionic > anionic.

Ambient solution pH and ionic strength influence the surface charge and conformation of charged polymers, and therefore influence polymer adsorption. Parfitt (1972) reported a negative adsorption of poly(galactouronic acid) by Na- and Ca-montmorillonite at pH 5.9, whereas a positive adsorption was observed at pH 2.9. Similarly, Finch *et al.* (1967) reported that the uronic acid unit of the PSS was preferentially adsorbed by H^+-saturated montmorillonite. The influence of ionic strength on the adsorption of charged polymers was demonstrated by Aly and Letey (1988), who observed that the adsorption of an anionic polymer by Na-montmorillonite was greater from well water (EC = 0.7 dS m⁻¹) than from canal water (EC = 0.05 dS m⁻¹), whereas the opposite was true for the cationic polymer.

Numerous studies have been conducted on the effects of synthetic polymers in controlling soil clay dispersion and aggregation (Mitchell, 1986; Wallace, 1986; Aly and Letey, 1988; Nadler and Letey, 1989). However, few studies have examined their adsorption properties under conditions of varying saturating cations, pH, and ionic strength. Specifically, no adsorption studies have been conducted on illitic minerals, al-

151

though they commonly occur in soils. This study was, therefore, intended to examine the effects of saturating cations, solution pH, and ionic strength on the adsorption of three synthetic PSS and one soil PSS by Silver Hill illite.

MATERIALS AND METHODS

Illite from Silver Hill, Montana (IMt-1) was obtained from the Source Clay Repository of The Clay Minerals Society. Na-illite and hydroxy-Al polycations (Al-p, $10^4 < MW < 5 \times 10^4$) were prepared as previously described by Gu and Doner (1990). Ca-illite was prepared by washing Na-illite three times with 500 mol/m³ Ca(ClO₄)₂, and once with deionized water. Al-p-illite was prepared by treating Na-illite with Al-p solution at a rate of 0.37 mol(Al)/kg, which was equivalent to the maximum amount of Al-p adsorption by Na-illite (Gu and Doner, 1990). Both Ca- and Al-p-illites were freeze-dried after centrifugation.

The PSSs used for this study were cationic (CP-14), nonionic (HP-8), and anionic (T-4246) guar polymers. Detailed information about these polymers has been provided by Aly and Letey (1988). These polymers are essentially galactomannans consisting of mannose and galactose units, with molecular weights between 0.2×10^6 and 2×10^6 g/mol. The cationic, nonionic, and anionic properties of the polymers were created by substituting the nonionic *cis*-hydroxyl groups with quaternary ammonium, hydroxypropyl, and carboxyl groups, respectively.

A soil PSS, isolated from a local soil (Millsholm loam), was also used. The isolation procedure was modified from Lowe (1975) and Cheshire (1979). About 5 liters of 200-mol/m³ NaOH were added to 1 kg soil. After displacing the air in the bottles with N₂, the soil slurry was sonified for 2 hr by an ultrasonic cleaner (Mettler Electronics). It was then immediately centrifuged and the alkaline extract was acidified to pH 1.5 with 6×10^3-mol/m³ HCl. An additional 3 liters of 200-mol/m³ NaOH were added to the soil residue and the extraction was repeated once. The acidified extracts were combined and centrifuged to separate the humic acid from the fulvic-acid fraction. The fulvic-acid fractions were combined and passed through a previously-washed PVP (a cross-linked polyvinyl pyrrolidone polymer) column. Most of the colored materials (polyphenolic fraction) in the fulvic acid were retained leaving the PSS fraction unadsorbed. The large volume of the PSS fraction was reduced to about 1 liter by a Rotavapor at 313 K. The PSS fraction was then mixed with twice its volume of acetone, precipitated, and then redissolved in about 0.2 liter water. This procedure was repeated three times. Finally the PSS fraction was freeze-dried and stored in a desiccator. This soil PSS contained 0.9% ash, and a solution of 1-kg/m³ PSS had a pH of 3.3. Previous studies (Lowe, 1978; Cheshire and Mundie, 1986) have shown that soil PSS is com-

posed of a variety of monosaccharides that are very similar from different soils, although the relative proportions change. After electrofocusing, Cheshire and Mundie (1986) also found that the greatest concentration of the soil PSS occurred within the pH 1.9–4.0 region, whereas the proportion of uronic acid was the greatest in the PSS fractions from the pH 3.0–4.0 region. It was assumed, therefore, that the soil PSS used here contained a significant amount of uronic acid.

The adsorption experiment was conducted by adding different volumes of PSS solutions (pH 7) into clay (5 kg/m³) suspensions in 40 cm³ centrifuge tubes. The pH was adjusted to 7 and ionic strength was approximately zero. The final volume was made up to 20 cm³ by weighing, taking into account the amount of clay added. The initial polysaccharide concentration ranged from 0 to 1.35 kg/m³. The mixture of clay and polysaccharide suspensions was shaken for 1 hr and then left overnight. The suspensions were centrifuged for 10 min at 27,000 RCF, and the supernatants were analyzed for organic C by photochemical oxidation using a Dohrman-C analyzer (Dohrman, Santa Clara, CA). The amount of PSS adsorbed, expressed as g PSS per kg clay, was calculated from the difference between the amount added and that found in the equilibrium solution. The effects of pH and ionic strength on PSS adsorption were studied on Na-illite. The pH was adjusted by dilute HClO₄ or NaOH, whereas the ionic strength was adjusted by NaClO₄. The initial PSS concentrations in clay suspensions were 0.9 kg/m³ for cationic, and 0.35 kg/m³ for nonionic and anionic PSS, respectively. All data in Figures 1–5 are averages of duplicate measurements.

RESULTS

Figure 1 shows the adsorption isotherms of the cationic PSS by illite saturated with different cations at about neutral pH. The Na-illite exhibited the highest adsorption capacity for the PSS. The adsorption isotherm, at equilibrium concentrations <140 g/m³, was of the "H-type" (Sposito, 1984), indicating a very high affinity of the PSS for the clay surface. However, at equilibrium concentrations >140 g/m³ the adsorption was further increased, probably resulting from multilayer adsorption. Ca-illite adsorbed slightly less than Na-illite, and the adsorption isotherm appeared to be of the "L-type." However, the presence of Al-p on illite resulted in about three-fold reduction in the PSS adsorption compared with Na-illite. The overall effect of adsorbed cations on the adsorption of cationic PSS was thus in the order, Na⁺ > Ca²⁺ > Al-p.

Only slightly different amounts of the nonionic PSS were adsorbed by the Na-, Ca-, and Al-p-illite (Figure 2), indicating that the presence of different cations on illite had little effect on the nonionic PSS adsorption. The anionic PSS was, however, adsorbed in the order, Al-p-illite > Ca-illite > Na-illite (Figure 3), which was
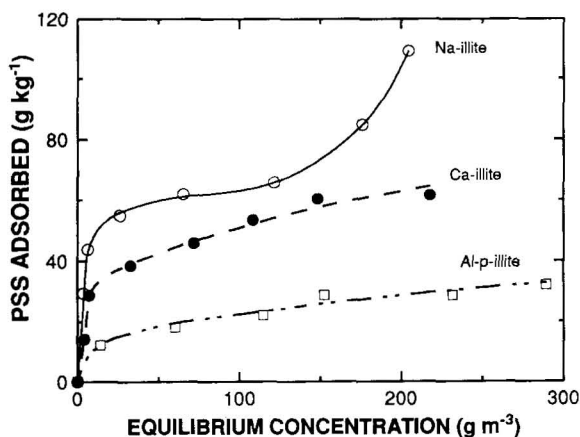
Figure 1.   Adsorption isotherms of a cationic polysaccharide by Na-, Ca- and Al-p-illite.

Figure 3.   Adsorption isotherms of an anionic polysaccharide by Na-, Ca- and Al-p-illite.

opposite to that of the cationic PSS. Also, the adsorption of the anionic PSS was much lower than that of the cationic or nonionic PSS. The adsorption on Na-illite was so low as to be hardly measurable by the difference method. This explained a relatively large variation among those data points (Figure 3, by Na-illite).

It was interesting that the adsorption isotherms of the soil PSS by Na-, Ca-, and Al-p-illites were nearly straight lines (Figure 4), although, as similar to that of the anionic PSS, Al-p-illite adsorbed more soil PSS than Ca-illite, and than Na-illite. The initial slope of the adsorption isotherm by Al-p-illite indicated a stronger affinity of the soil PSS for the Al-p-illite surface than for the Na- and Ca-illites.

The effects of pH (Figure 5a) and ionic strength (Figure 5b) on PSS adsorption were studied on Na-illite. An increase of pH decreased anionic PSS adsorption but slightly increased cationic PSS adsorption. The ad-
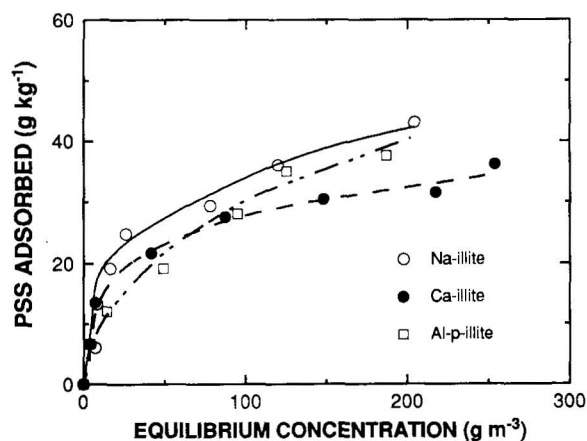
sorption of nonionic PSS was not influenced by pH. Changes in solution ionic strength had a significant effect on anionic PSS adsorption, but had little effect on cationic or nonionic PSS adsorption (Figure 5b). The most significant increase in the anionic PSS adsorption was from 0 to 50-mol/m^3 ionic strength. Further increase in ionic strength from 50 to 200 mol/m^3 had little effect on the PSS adsorption. Similar observations of the influences of pH and ionic strength on the adsorption of charged polymers were reported by Mortensen (1959) and Parfitt (1972).

DISCUSSION

Influence of adsorbed cations

A cation exchange mechanism has been suggested for the adsorption of cationic polymers by negatively-charged clay surfaces (Clapp and Emerson, 1972; Parfitt, 1972; Theng, 1979). However, the exchange re-

Figure 2.   Adsorption isotherms of a nonionic polysaccharide by Na-, Ca- and Al-p-illite.
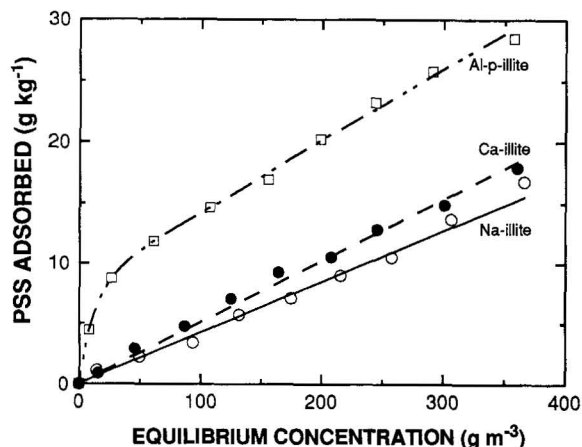

Figure 4.   Adsorption isotherms of a soil polysaccharide by Na-, Ca- and Al-p-illite.
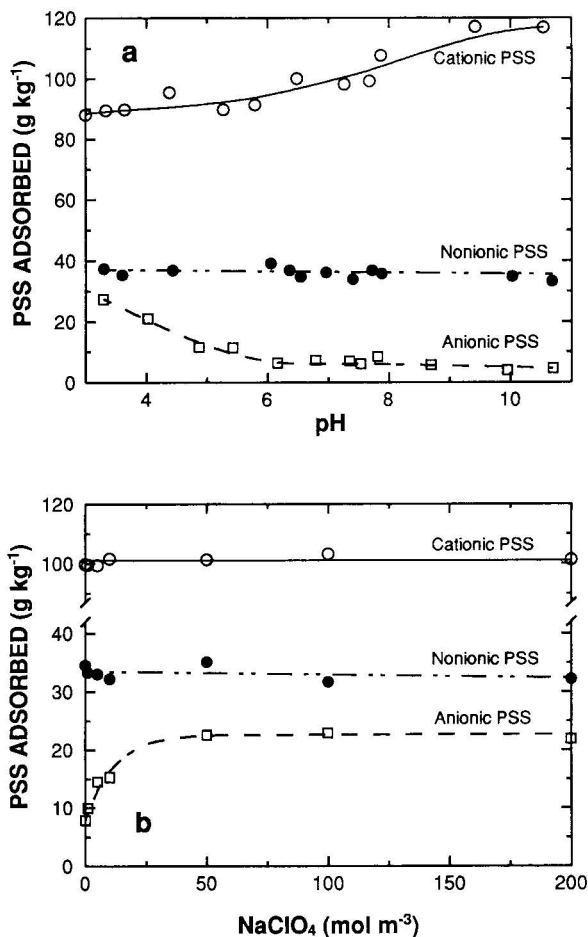
Figure 5.   Effects of pH (a) and ionic strength (b) on synthetic polysaccharide (PSS) adsorption by Na-illite.

action depended on the nature of the exchangeable cations (Figure 1). Na$^+$ is a monovalent cation, residing mainly in the diffuse double layer, so that it can readily be exchanged by other cations. On the other hand, Al-p forms strong surface complexes with the clay surfaces and cannot be as readily exchanged by other cations, especially by monovalent cations (Gu and Doner, 1990). Excessive addition of Al-p can even reverse the surface charge on illite. Therefore, a reduction of the active sites on the illite surface, due to surface complex formation between Al-p and the illite, largely explained that the Na-illite adsorbed about three times more cationic PSS than the Al-p-illite. Ca^{2+} was not as effective as Al-p in forming a surface complex and in screening the surface negative charge, so that Ca-illite adsorbed only slightly less than the Na-illite. The influences of adsorbed cations on the adsorption of cationic PSS can also be demonstrated by the fact that the initial slopes of the adsorption isotherms were in the order: Na-illite > Ca-illite > Al-p-illite (Figure 1). The initial slope of the adsorption isotherm may be regarded as a measure

of the affinity between solute molecules and the surface (Theng, 1979). The strong polymer-surface bonding is characterized by the "H-type" adsorption isotherm, in which a large amount of polymer can be removed from very dilute solutions. Since a coulombic force was involved in the reaction between the cationic PSS and the Na-illite, a higher energy of adsorption was expected than that involved in the Al-p-illite.

Opposite to the cationic PSS, the amount of anionic PSS adsorbed, and the initial slopes of the adsorption isotherms were in the order: Al-p-illite > Ca-illite > Na-illite (Figure 3). Only a small amount of the anionic PSS was adsorbed by the Na-illite, which may well be attributed to a strong electrostatic repulsion force between the two components. On the other hand, very little residual negative charge may be left on the Al-p-illite, since the point of zero charge (PZC) of the Al-p-illite was about 5.3 at 1 mol/m^3 ionic strength (Gu and Doner, 1990). Therefore, only a weak electrostatic force was expected between the anionic PSS and Al-p-illite. Furthermore, Al-p on illite surfaces could form complexes with carboxyls of the PSS by the ligand exchange mechanism (Parfitt, 1972), and a high energy of adsorption was thus expected as shown by a steep initial slope of the adsorption isotherm (Figure 3, on Al-p-illite). Direct infrared spectroscopic evidence for the coordination between carboxyls of a poly(galacto-uronic acid) and Al-montmorillonite has been reported by Parfitt (1972). It appeared, therefore, that the mechanism of complexation should be very important for the interaction of negatively-charged organic polymers with clay minerals. A practical implication here is that in soils containing illite, stable soil aggregation with organic substances may only be achieved when polyvalent cations such as Al, Fe, and Ca are present. In the absence of polyvalent cations, studies have shown that soil humic substances are only weakly- or negatively-adsorbed by clay minerals (Theng, 1976). This explains the poor soil structure and greater movement of HA on sodic soils.

The adsorption of soil PSS was similar to that of anionic PSS and in the order: Al-p-illite > Ca-illite > Na-illite (Figure 4). This was probably because the soil PSS contained a large proportion of uronic acid units or was negatively charged. However, all adsorption isotherms of soil PSS (at equilibrium concentrations >25 g/m^3) were nearly linear (or C-type; Sposito, 1984). This may be partially explained by the polydispersity theory of Cohen Stuart *et al.* (1980). Since the soil PSS is a mixture of polymers that range from disaccharides to polymers that can have molecular mass of more than a million (Cheshire, 1979), some of these are expected to be more strongly adsorbed than others (Finch *et al.*, 1967; Parfitt and Greenland, 1970). With increasing amount of polymer addition those polymers with higher affinities for the clay surfaces would compete with or displace those with lower affinities, and

thus result in the "L-type" or "C-type" adsorption isotherms instead of the "H-type" isotherms. The linear adsorption isotherms may also be explained by Theng's hypothesis (Theng, 1976) that the adsorption of the low molecular weight components induced intradomain expansion. This means that more sites become available thereby giving rise to linear adsorption isotherms. Theng (1976) found that the adsorptions of a fulvic acid by montmorillonites saturated with different polyvalent cations all yielded linear adsorption isotherms. Each reaction was a cation-bridge type in which the affinity of the fulvic acid for the clay surface was related to the ionic potential of the respective cation. The linear adsorption isotherms of a soil PSS by the montmorillonite at equilibrium concentrations <400 g/m³ was also reported by Parfitt and Greenland (1970), although at higher equilibrium concentrations the adsorption tended toward a maximum.

It could be expected that only slightly different amounts of the nonionic PSS were adsorbed by the Na-, Ca-, and Al-p-illite (Figure 2). This may well be due to the fact that the adsorption was not affected by the surface charge and surface complex formation. The entropy gained during the adsorption was the principal driving force, as indicated by a number of investigators (Parfitt and Greenland, 1970; Parfitt, 1972; Theng, 1982). This result was, however, different from that on montmorillonite. Gu (1991) found that the adsorbed cations on montmorillonite had a drastic effect on the adsorption of nonionic PSS because the size of the montmorillonite quasicrystals changed with the presence of Na, Ca, or Al-p. The influence of exchangeable cations on the adsorption of neutral polymers was also demonstrated by several investigators (Parfitt and Greenland, 1970; Chenu *et al.*, 1987). Chenu *et al.* (1987) found that the polymers were adsorbed primarily on the external surfaces of the montmorillonite quasicrystals.

Influences of pH and ionic strength on PSS adsorption

It was not surprising to find that the solution ionic strength had no effect on the adsorption of nonionic PSS since there were no surface charge and conformation changes of the PSS (Figure 5). However, an increase in pH decreased the adsorption of anionic PSS, whereas the opposite was true for the adsorption of cationic PSS. A low pH may be associated with an increase in positive edge sites on illite surfaces. More importantly, perhaps, a low pH may result in the appearance of Al^{3+} or hydroxy-Al ions released from the clay structure, which acted as bridges between the PSS and the clay surfaces as discussed previously. In addition, the anionic PSS may become uncharged due to deionization of hydroxyl groups so that there was a reduced electrostatic repulsion force between the two components. All of these factors should lead to an increased anionic PSS adsorption at low pH values. On the other hand, an increase of solution pH increases the negative edge sites on illite surfaces, leading to a slightly increased cationic PSS adsorption with pH (Figure 5a).

The increase in the anionic PSS adsorption with increasing ionic strength (up to 50 mol/m³) may be explained as follows. Increasing ionic strength depressed the negative diffuse double layer that made the anionic PSS much easier to access and to interact with the illite surfaces. According to Sposito (1989), the thickness of the diffuse double layer on montmorillonite decreases from 30 to 3 nm when the ionic strength increases from 0.1 to 10.3 mol/m³. Ruehrwein and Ward (1952) and Mortensen (1959) also suggested that electrolyte was necessary to reduce the electrostatic repulsion between the anionic polymer and the clay particles. Furthermore, studies have shown that solution ionic strength affects the charge and configuration of polymer coil (Markovitz and Kimball, 1950). High electrolyte concentration may lead to a decreased charge and size of the polymer coils (Mortensen, 1959), and therefore, result in an increased adsorption. An increase in ionic strength from 50 to 200 ml/m³, however, resulted in a small increase in the anionic PSS adsorption (Figure 5b), probably because of the lower influence of ionic strength on the diffuse double layer and polymer conformation. These results were also consistent with those of Mortensen (1959), who found that the most significant increase in the adsorption of a hydrolyzed polyacrylonitrile on kaolinite was from 0 to 20-mol/m³ ionic strength. It is interesting to note, however, that the adsorption of the cationic PSS was relatively insensitive to changes in solution ionic strength. This may be tentatively explained by the fact that surface charge on illite does not change with the ionic strength ($NaClO_4$), while the adsorption of the cationic PSS on Na-illite is primarily by surface charge neutralization.

CONCLUDING REMARKS

The adsorption of PSS on illite was shown to be influenced by the charge characteristics of polymers themselves, and by the adsorbed cations on illite. The adsorbed cations form different surface complexes with the clay surfaces, varying in ability to screen the surface negative charge and thereby influencing the adsorption of charged polymers. Polyvalent cations acted as bridges between the anionic PSS and negatively-charged clay surfaces, leading to an increased adsorption of the anionic PSS, compared with that on Na-illite. The adsorbed cations, however, had little effect on the adsorption of nonionic PSS. This was in contrast to that on montmorillonite (Gu, 1991), where the adsorbed cations were found to have a drastic effect on the nonionic PSS adsorption because different montmorillonite quasicrystals were formed in the presence of Na, Ca, or Al-p.

The present study provides evidence for specific interactions between clay surfaces and the PSS, which probably take place when soil PSS binds soil particles into stable aggregates. These results are relevant to findings that pH values, ionic strength, and exchangeable cations influence soil aggregation and soil clay dispersion (Reid *et al.*, 1982; Chaney and Swift, 1986; Bartoli *et al.*, 1988). The results suggest that, for stable soil aggregation, soil organic polymers must first be strongly adsorbed to form anchor points for particle bridging. The presence of polyvalent cations is important when anionic polymers are involved in the aggregation.

ACKNOWLEDGMENTS

REFERENCES

Aly, S. M. and Letey, J. (1988) Polymer and water quality effects on flocculation of montmorillonite: *Soil Sci. Soc. Am. J.* **52,** 1453–1458.

Bartoli, F., Philippy, R., and Burtin, G. (1988) Aggregation in soils with small amounts of swelling clays. I. Aggregate stability: *J. Soil Sci.* **39,** 593–616.

Chaney, K. and Swift, R. S. (1986) Studies on aggregate stability. I. Techniques for reforming soil aggregates: *J. Soil Sci.* **37,** 329–335.

Chenu, C., Pons, C. H., and Robert, M. (1987) Interaction of kaolinite and montmorillonite with neutral polysaccharides: *Proc. Intl. Clay Conf., Denver 1985,* L. G. Schultz, H. van Olphen, and F. A. Mumpton, eds., The Clay Minerals Society, Bloomington, Indiana, 375–381.

Cheshire, M. V. (1979) *Nature and Origin of Carbohydrates in Soils:* Academic Press, London, 68–124.

Cheshire, M. V. and Mundie, C. M. (1986) The fractionation of soil polysaccharide by electrofocusing: *J. Soil Sci.* **37,** 567–575.

Clapp, C. E. and Emerson, W. W. (1972) Reactions between Ca-montmorillonite and polysaccharides: *Soil Sci.* **114,** 210–216.

Cohen Stuart, M. A., Scheutjens, J. M. H. M., and Fleer, G. J. (1980) Polydispersity effects and the interpretation of polymer adsorption isotherms: *J. Polymer Sci.* **18,** 559–573.

Finch, P., Hayes, M. H. B., and Stacey, M. (1967) Studies on soil polysaccharides and their interactions with clay preparations: *Intl. Soil Sci. Soc. Trans. Commissions: II and IV,* Aberdeen, Scotland, 19–32.

Gill, R. I. S. and Herrington, T. M. (1987a) The effect of surface charge on the flocculation of kaolin suspensions with cationic polyacrylamides of varying molar mass but similar cationic character: *Coll. Surf.* **25,** 297–310.

Gill, R. I. S. and Herrington, T. M. (1987b) The flocculation of kaolin suspensions using polyethylenimine and cationic polyacrylamides of the same molar mass but different charge density: *Coll. Surf.* **28,** 41–52.

Gu, B. (1991) Interactive effects of hydroxy-Al polycations, polysaccharides and humic acid on soil/clay suspension and aggregate stability: Doctoral dissertation, University of California, Berkeley, California, 38–61.

Gu, B. and Doner, H. E. (1990) Adsorption of hydroxy-Al polycations and destabilization of illite and montmorillonite suspensions: *Clays & Clay Minerals* **38,** 493–500.

Lowe, L. E. (1975) Fractionation of acid-soluble components of soil organic matter using PVP: *Can. J. Soil Sci.* **55,** 109–126.

Lowe, L. E. (1978). Monosaccharide distribution in selected coniferous forest humus layers in British Columbia and its relationship to vegetation and degree of decomposition: *Can. J. Soil Sci.* **58,** 19–25.

Markovitz, H. and Kimball, G. E. (1950) The effect of salts on the viscosity of solutions of polyacrylic acid: *J. Coll. Sci.* **5,** 115–139.

Mitchell, A. R. (1986) Polyacrylamide application in irrigation water to increase infiltration: *Soil Sci.* **141,** 353–358.

Mortensen, J. L. (1959) Adsorption of hydrolyzed polysaccharide on kaolinite: II. Effect of solution electrolytes: *Soil Sci. Soc. Amer. Proc.* **23,** 199–202.

Nadler, A. and Letey, J. (1989) Organic polyanions' effect on aggregation of structurally disrupted soil: *Soil Sci.* **148,** 346–354.

Olness, A. and Clapp, C. E. (1975) Influence of polysaccharide structure on dextran adsorption by montmorillonite: *Soil Biol. Biochem.* **7,** 113–118.

Parfitt, R. L. (1972) Adsorption of charged sugars by montmorillonite: *Soil Sci.* **113,** 417–421.

Parfitt, R. L. and Greenland, D. J. (1970) Adsorption of polysaccharide by montmorillonite: *Soil Sci. Soc. Amer. Proc.* **34,** 862–866.

Reid, J. B., Goss, M. J., and Robertson, P. D. (1982) Relationship between the decreases in soil stability affected by the growth of maize roots and changes in organically bound iron and aluminum: *J. Soil Sci.* **33,** 397–410.

Ruehrwein, R. A. and Ward, D. W. (1952) Mechanism of clay aggregation by polyelectrolytes: *Soil Sci.* **73,** 485–492.

Saini, G. R. and MacLean, A. A. (1966) Adsorption-flocculation reactions of soil polysaccharides with kaolinite: *Soil Sci. Soc. Amer. Proc.* **30,** 697–699.

Sposito, G. (1984) *The Surface Chemistry of Soils:* Oxford Univ. Press, New York, 113–122.

Sposito, G. (1989) The diffuse-ion swarm near smectite particles suspended in 1:1 electrolyte solutions: in *Rheology of Clay/Water Systems,* Workshop Notes, N. Güven, ed., Clay Minerals Society, Sacramento, California, 1–30.

Theng, B. K. G. (1976) Interactions between montmorillonite and fulvic acid: *Geoderma* **15,** 243–251.

Theng, B. K. G. (1979) *Formation and Properties of Clay-Polymer Complexes:* Elsevier, Amsterdam, 243–273.

Theng, B. K. G. (1982) Clay-polymer interactions: Summary and perspectives: *Clays & Clay Minerals* **30,** 1–10.

Wallace, A. (1986) A polysaccharide (guar) as a soil conditioner: *Soil Sci.* **141,** 371–373.