

ADSORPTION OF HYDROXY-AL POLYCATIONS AND DESTABILIZATION OF ILLITE AND MONTMORILLONITE SUSPENSIONS

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Abstract—Water-infiltration characteristics of soil can be improved by preventing clay dispersion. The present study determined the adsorption properties of hydroxy-Al polycations (Al-p) and their relation to the destabilization of clay suspensions. Al-p was synthesized and fractionated into nominal molecular weights between 10^4 and 5×10^4 . The reactions of Al-p with Na-illite and Na-montmorillonite indicated a very strong affinity of Al-p to the clay surfaces. The maximum adsorptions of Al-p by Na-illite and Na-montmorillonite were found to be 0.37 and 1.7 mmole Al/g, and very close to the cation-exchange capacity of the two clays, suggesting that the adsorption was chiefly controlled by the mechanism of charge screening. Adsorption of Al-p increased the points of zero charge (PZCs) and the apparent points of zero salt effect (PZSEs) of illite and montmorillonite. PZSEs for both clays were 4.7 at their maximum Al-p adsorption, and PZCs ranged from 5.3 to 6.4, depending on solution ionic strength and the individual clay minerals. The differences in PZCs were probably due to outer-sphere complex formation between Al-p-treated illite and montmorillonite and the swamping electrolyte. Critical flocculation concentrations (CFCs) of Al-p for Na-illite and Na-montmorillonite were at 0.28 and 1.0 mmole Al/g, whereas zero electrophoretic mobilities were at about 0.36 and 1.67 mmole Al/g Al-p additions. Excessive addition of Al-p reversed this surface charge of clay colloids and restabilized the illite but not montmorillonite suspensions. This difference was probably due to the stronger and more extensive interparticle bridging of montmorillonite particles by Al-p than those of illite. The CFCs for the two clays were also found to be dependent on sodium adsorption ratio (SAR), pH, and ionic strength. Increases in SAR and pH significantly increased the CFC, whereas an increase in ionic strength decreased the CFC.

Key Words—Adsorption, Flocculation, Hydroxy-Al, Illite, Montmorillonite, Point of zero charge.

INTRODUCTION

The surface adsorption of Al hydrous oxide or hydroxy-Al polycations (Al-p) is known to cause significant changes in the chemical and physical properties of clay colloids. For example, a reduction in the cation-exchange capacity (CEC) following the treatment of Al hydrous oxide or Al-p has been observed by a number of investigators (Keren, 1979, 1980; Oades, 1984; Shen and Rich, 1962; Turner and Brydon, 1967). Hendershot and Lavkulich (1983) and Harsh *et al.* (1988) found that precipitating Al-hydroxides onto various clays and minerals altered surface-charge characteristics, such as points of zero salt effect (PZSEs) and zeta-potential. The stabilizing effect on soil structure resulting in improved water infiltration rate by Al hydrous oxide or Al-p was demonstrated by El Rayah and Rowell (1973) and Wada *et al.* (1983). Alperovitch *et al.* (1985) also found that Al-p reduced the adverse effect of Na^+ ions on the hydraulic conductivity of columns containing a montmorillonite-sand mixture.

Hydrolysis of Al^{3+} in aqueous solution results in the formation of various monomeric and polymeric hydroxy cations (Al-p) having different OH/Al ratios. At OH/Al ratios of 2–2.7, each Al-p has been suggested to carry a multi-charge ranging from 7+ to 18+ (Hsu, 1989). The separated Al-p with nominal molecular

weights between 10^4 and 5×10^4 was found to be very efficient and to destabilize clay suspensions irreversibly (Rengasamy and Oades, 1978). The reaction was thus suggested by these authors to involve chemical bonding with surface hydroxyls. McLean (1965) and Shen and Rich (1962) believed that adsorbed Al-p were non-exchangeable with neutral salts, however, their results contradict those of Bache and Sharp (1976), who found that Al-p behaved like normal exchangeable cations. Frink and Peech (1963) indicated little, if any, reduction of CEC by hydroxy-Al treatment. The adsorption-desorption characteristics of Al-p by clay colloids are, therefore, not yet clear. The stability of Al-p-treated clay suspensions is largely unknown, especially under different chemical environments of pH, sodium adsorption ratio (SAR) and ionic strength. According to Goldberg and Glaubig (1987), the critical coagulation concentrations (CCCs) of aluminum oxide, kaolinite, montmorillonite, and various mixtures of these materials were all pH-dependent. Oster *et al.* (1980) reported that CCCs of illite and montmorillonite were affected by SAR.

The objectives of the present study were to determine the adsorption-desorption characteristics of Al-p by illite and montmorillonite, the effect of Al-p on surface charge properties and destabilization of the two clay

suspensions, and the influence of SAR, pH, and solution ionic strength on flocculation-dispersion of clay suspensions by Al-p.

MATERIALS AND METHODS

Illite, IMt-1 (Silver Hill, Montana), and montmorillonite, SWy-1 (Crook County, Wyoming), obtained from the Source Clay Repository of The Clay Mineral Society, were selected for the present study. The clay samples were Na-saturated by washing with 0.5 M NaClO₄ three times. The <2- μ m fractions were obtained by centrifugation in deionized water and further washed following the method of Sposito and LeVesque (1985) in an attempt to clean the clay surfaces. They were then washed twice with deionized water and freeze-dried after centrifugation.

The procedure adopted for the preparation of Al-p was similar to that of Oades (1984). Briefly, it involved the addition of 250 ml of 1 M NaOH to 1000 ml of 0.1 M AlCl₃ to give OH/Al ratio 2.5 over a 6-hr period. The solution was stirred until it was clear. Four days later, the solution was placed on an Amicon XM50 membrane, which allowed MW < 5 \times 10⁴ polycations of molecular weight < 5 \times 10⁴ to pass through, and washed until the effluent was free from Al. The filtrate and washings were refractionated and dialyzed on a PM10 membrane, which allowed MW < 10⁴ polycations of molecular weight < 10⁴ to pass through, until the effluent was free from Na⁺. The retainant was collected and designated as Al-p with nominal molecular weights between 10⁴ and 5 \times 10⁴. Preliminary study indicated that this fraction was more effective in blocking surface negative charge and flocculating clay colloids than the fraction having a nominal molecular weight between 10⁴ and 10⁵. The reaction of this solution with ferron reagent (Barnhisel and Bertsch, 1982) indicated that the solution was nearly free from monomeric Al. This Al-p solution was also found to be relatively stable if it was refrigerated at 3°C; it hydrolyzed further, however, and precipitated at room temperature.

The adsorption experiment was carried out by equilibrating initially wetted Na-illite (0.1–0.6 g) and Na-montmorillonite (0.05–0.4 g) with different volumes of Al-p solution in 50-ml centrifuge bottles. The pH was adjusted to 5.3 with dilute HClO₄ or NaOH, which was the pH value of the original Al-p solution, and the ionic strength adjusted at 0.01 M with NaClO₄. The final volume was made up to 30 ml by weighing the centrifuge bottles. The clay suspensions were shaken for 16 hr and then centrifuged. The amount of Al-p remaining in the supernatant after centrifugation was determined by measuring the Al content by atomic absorption with N₂O-acetylene flame.

Desorption of Al-p was studied by equilibrating Al-p-treated illite and montmorillonite (at the CFC) with either 0.5 M NaClO₄ solution or deionized water. The

suspensions were continuously shaken for 30 days at 25°C. To determine the amount of Al dissolution, 10 ml of the suspension was sampled at given time intervals, and the supernatant was analyzed for Al content by ICP (Perkin-Elmer, Plasma 40) after centrifugation.

The apparent PZSE (Charlet and Sposito, 1987) and PZC of Al-p-treated illite and montmorillonite were determined as follows: Na-illite and Na-montmorillonite were treated with Al-p at rates of 0.37 and 1.7 mmole Al/g clay, respectively, which were the amounts equivalent to their maximum Al-p adsorption capacity, as determined from curves in Figure 1. After centrifugation the Al-p-treated clays were dried at 70°C and ground to pass a 0.5-mm sieve. A 0.15-g sample was then suspended in 10 ml of 0.001, 0.01, or 0.1 M NaClO₄ solution to which various amounts of standardized HClO₄ or NaOH were added to obtain the desired pH. The amounts of acid or base added were very small so that the ionic strength of the solution was nearly constant. The total volume was brought to 15 ml in 18-ml plastic vials. The suspensions were equilibrated for 2 days before the pH was measured. All solutions were prepared in CO₂-free deionized water. Equilibrium pH values were plotted against $\sigma_{H,uv}$ in mmole/g calculated as the difference between total H⁺ or OH⁻ added and that required to bring a blank solution of the same salt concentration to the same pH. PZC was estimated from the electrophoretic mobility measurement of the suspensions after pH determination.

The critical flocculation concentration (CFC, mmole Al/g), defined as the minimum amount of Al-p required to destabilize clay suspensions (1 g/liter) in 24 hr, was determined at room temperature following the method of Oades (1984), except that the percentage of suspended clay was estimated by comparing the optical density of the uppermost 3 cm of liquid in the tube with or without Al-p treatments by a Spectronic 100 spectrophotometer equipped with a Micro Flow-thru system at a wavelength of 615 nm. After CFC determination, the rest of the samples were used for electrophoretic mobility (EM) measurement by a Zeta-Meter 3.0. The pH and ionic strength were not adjusted for CFC and EM determinations. The pH ranged from 4.5 to 6.5, and ionic strength was near zero, inasmuch as only Al-p was added to the Na-clay suspensions.

The influence of SAR, pH, and ionic strength on CFC was studied by adjusting one of the variables while holding the other two variables constant. SAR was adjusted by initially washing the Na-illite or Na-montmorillonite three times with 0.2 M ClO₄⁻ (Na/Ca) solutions with SAR values of 0, 5, 10, 15, 30, and ∞ , and then three times with 0.001 M ClO₄⁻ solutions with the same SAR values. The CFC was then determined by holding the ClO₄⁻ at 0.001 M and pH at 6. The volume of HClO₄ or NaOH required to adjust the pH to 6 did not significantly alter the solution SAR

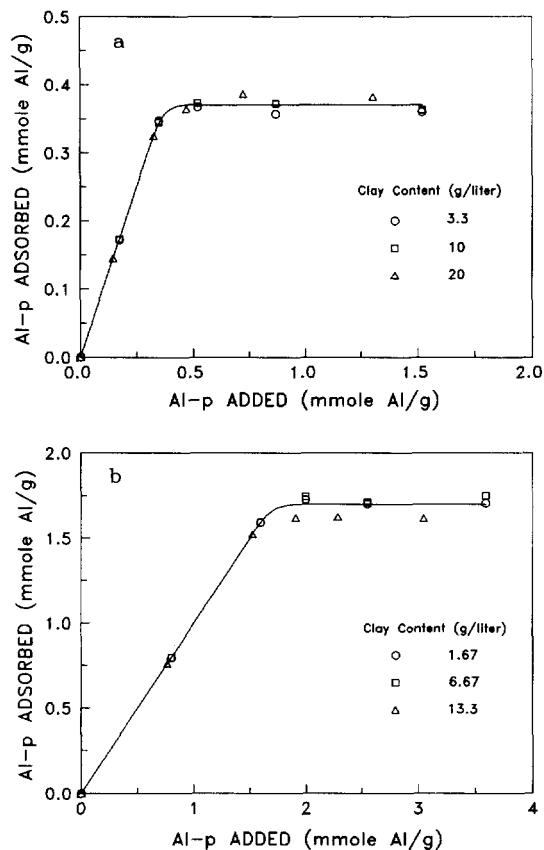


Figure 1. Hydroxy-Al polycation (Al-p) adsorption curves by (a) Na-illite and (b) Na-montmorillonite.

and ionic strength. The influence of ionic strength on CFC was studied at 0, 0.001, 0.01, 0.1, and 0.5 M NaClO_4 , while the pH was held at 6 and the SAR at ∞ . All data are averages of duplicate measurements, except the clay dispersion vs. electrophoretic mobility measurements.

RESULTS AND DISCUSSION

Al-p adsorption-desorption

The adsorption of Al-p by Na-illite and Na-montmorillonite is shown in Figure 1. No significant differences were observed in the amount of Al-p adsorption for the three clay concentrations used in the study. An adsorption maximum was found for illite at 0.37 mmole Al/g and 1.7 mmole Al/g for montmorillonite. If the addition of Al-p was less than the adsorption maximum, the adsorption of Al-p was nearly complete as indicated by the initial slopes of 1 from the adsorption curves. Figure 2 shows the desorption of Al-p from Al-p-treated illite and montmorillonite complexes. Almost no Al-p was desorbed by shaking with deionized water, and <5.5% and 8.5% of total, adsorbed Al-p were desorbed initially by 0.5 M NaClO_4 from the Al-

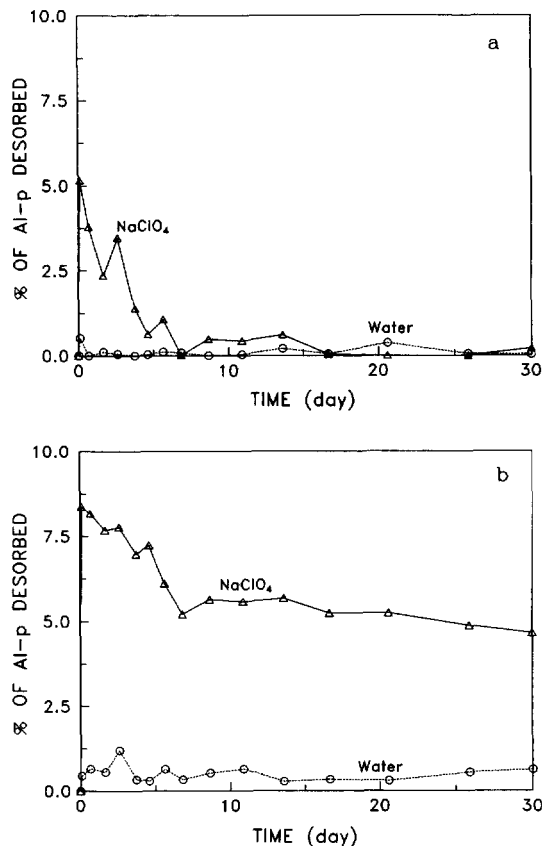


Figure 2. Desorption curves of (a) hydroxy-Al polycation Al-p-treated illite and (b) montmorillonite by 0.5 M NaClO_4 or deionized water.

p-illite and Al-p-montmorillonite complexes, respectively. After 7 days of shaking, the Al-p desorbed by NaClO_4 was reabsorbed almost completely by the illite, and <6% of Al-p remained in solution phase of Al-p-montmorillonite complexes, which may have been due to the further hydrolysis and polymerization of Al-p in the system.

Both the adsorption and desorption curves of Al-p (Figures 1 and 2) clearly indicate a high affinity or selectivity of Al-p by the illite and montmorillonite. This affinity was expected inasmuch as each Al-p molecule carried a multi-positive charge (7+ to 18+), providing a very strong electrostatic attraction between Al-p and the negatively charged clay surfaces. Multi-sites adsorption of Al-p could have occurred displacing the weaker competitor, Na^+ , from the exchange sites. The maximum Al-p adsorption values (0.37 mmole Al/g illite and 1.7 mmole Al/g montmorillonite) closely corresponded to the cation-exchange capacity (CEC) of the two clays. By the potentiometric titration, Al-p was found to carry 0.45+ residual charge per Al atom. The estimated CEC values of illite and montmorillonite were, therefore, 16.7 and 76.5 meq/100 g, respec-

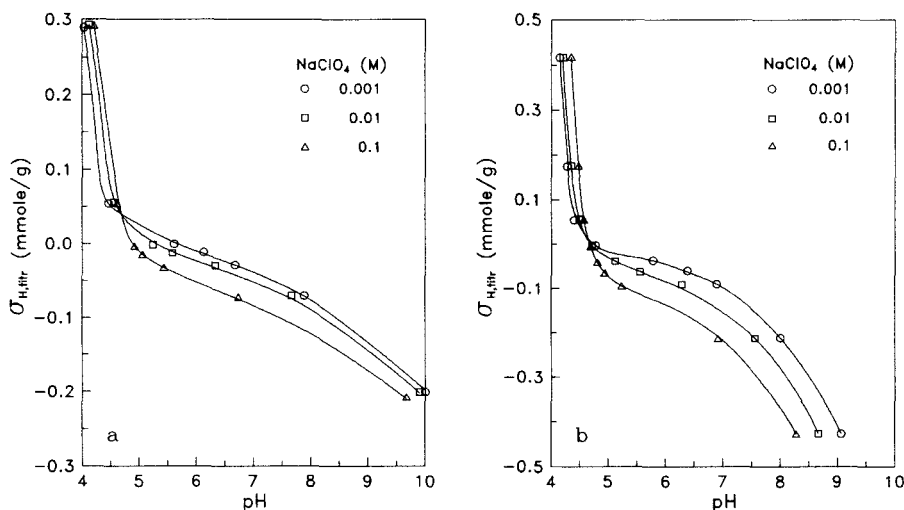


Figure 3. Potentiometric titration curves of (a) hydroxy-Al polycation-treated illite and (b) montmorillonite at three electrolyte concentrations.

tively, whereas the reported CEC values were 15 and 76.4 meq/100 g, respectively (Hower and Mowatt, 1966; van Olphen and Fripiat, 1979). These data suggest that Al-p replaced other cations from the clay colloids and that the adsorption was primarily controlled by charge screening. Rengasamy and Oades (1978) reported a much higher adsorption maximum for Al-p (0.63 mmole Al/g) having similar molecular weight for illite and a much lower adsorption maximum for montmorillonite (0.74 mmole Al/g). The discrepancies between their data and the present results may be explained by differences in the preparation of Al-p and experimental conditions, inasmuch as their experiments were conducted at pH 3.5 and the residual positive charge of their Al-p was 0.50+ per Al atom.

PZSE and PZC of Al-p-treated clays

Figure 3 is the potentiometric titration curves of Al-p-treated illite and montmorillonite at three salt concentrations. The intersection of the curves was defined as the PZSE (Parker *et al.*, 1979; Hendershot and Lavkulich, 1983). It was later termed as the apparent PZSE (Charlet and Sposito, 1987) because the true PZSE can be determined only when $\sigma_{H,titr}$ is renormalized relative to $\sigma_H \equiv 0$ at the point of zero net proton charge (PZNPC) for each curve. The apparent PZSE was determined in this experiment to be 4.7 ± 0.1 for both illite and montmorillonite treated with Al-p at their maximum adsorption capacity. The points of zero charge (PZCs), defined as the pH at which electrophoretic mobility equals to zero (Sposito, 1989), for Al-p-treated illite and montmorillonite are listed in Table 1. With an increase in the solution ionic strength, PZC increased slightly from 5.3 to 6.0 for the Al-p-illite and from 5.6 to 6.4 for the Al-p-montmorillonite complexes. All PZC

values were, however, greater than the apparent PZSEs. The desorption and dissolution of Al-p were not considered to be appreciable until pH < 4.5, inasmuch as at pH 4.5 and NaClO₄ concentration of 0.1 M < 4% Al-p was found in the solution.

Hendershot and Lavkulich (1983) reported an apparent PZSE value of 4.0 for illite (API 35) coated by Al-hydrous oxide. They pointed out that the surface charge generated at the interface of the solid and liquid phase depends not only on the charge of the minerals themselves, but also on the charge developed by the coating materials, such as Al and Fe hydrous oxides. Al-p coating seems to have been more effective in increasing PZSE (4.7), probably due to the higher positive residual charge developed on the illite surfaces by Al-p. Although the montmorillonite adsorbed about 4.6 times more Al-p than the illite, the same apparent PZSE value of 4.7 was found for both clays. If the illite and montmorillonite were assumed to have the same edge surfaces, which contributed to the determined PZSE, more residual positive charge per mole of Al-p may have been formed on the illite surfaces than on the montmorillonite surfaces. This was also evidenced by the CFC determinations of Al-p-treated illite and montmorillonite suspensions (*vide infra*). The surface charge, measured as electrophoretic mobility (EM), of Al-p-treated illite and montmorillonite changed from positive to negative with pH increase or OH⁻ uptake by the clay surfaces. Increase in solution ionic strength tended to increase the PZCs of the Al-p-treated illite and montmorillonite (Table 1). This increase cannot be explained by specific ion adsorption because NaClO₄ was used as the swamping electrolyte; however, the increase may have been the result of outer-sphere complex formation between Al-p-treated illite or mont-

Table 1. Points of zero charge of illite and montmorillonite after treatment at a rate equivalent to the maximum adsorption of hydroxy-Al polycations.

NaClO ₄	Illite	Montmorillonite
0.001	5.3 ± 0.3	5.6 ± 0.3
0.01	5.6 ± 0.3	5.6 ± 0.3
0.1	6.0 ± 0.4	6.4 ± 0.4

morillonite and the swamping electrolyte, according to the PZC theorems of Sposito (1989). Although a very low adsorption maximum for Al-p was reported for a montmorillonite (0.74 mmole Al/g), a PZC of 7–9 was observed by Rengasamy and Oades (1978). Our results do not agree with these authors, but are similar to those of Oades (1984), who reported a PZC for montmorillonite of 5.5–6. Oades (1984) also reported that excessive addition of Al-p raised the PZC towards that of gibbsite.

Destabilization of clay suspensions

Figure 4 shows the influence of Al-p on the flocculation-dispersion and EM of illite and montmorillonite suspensions. The results indicated that as the amount of Al-p added in suspension increased, the amount of dispersible clay decreased until it approached zero (CFC). CFCs of Al-p for illite and montmorillonite were found to be about 0.28 and 1.0 mmole Al/g clay, respectively. Similarly, the negative EM decreased with increased addition of Al-p until it approached zero (PZC). Zero EMs of illite and montmorillonite were at 0.36 and 1.67 mmole Al/g Al-p additions, close to the maximum Al-p adsorption for the two clays (Figure 1). These results confirmed the previous conclusion that the adsorption of Al-p was primarily controlled by the charge screening. Excessive addition of Al-p restabilized the suspension of illite, but not montmorillonite. Also, the surface charge became positive for both clays. The positive EM for montmorillonite particles, however, was very difficult to detect. The coagulated montmorillonite particles appeared as a large floc under the microscope of the electrophoresis equipment, and only a slight movement towards the cathode could be seen when an electrical field was applied. It was also noted from Figure 4a that a continuous increase in positive EM and dispersion of illite with increased addition of Al-p could not be attributed to increased adsorption of Al-p (based on Figure 1a), but was probably due to the decreased pH of illite suspensions from 6.5 to 4.5. The PZC of the Al-p-treated illite was 5.3 at ionic strength of 0.001 M (Table 1).

From the measurements of PZSE and PZC, more residual positive charge per mole of Al-p may have developed on the illite particles than on the montmorillonite particles if the addition of Al-p exceeded the PZC. In addition, a stronger and more extensive

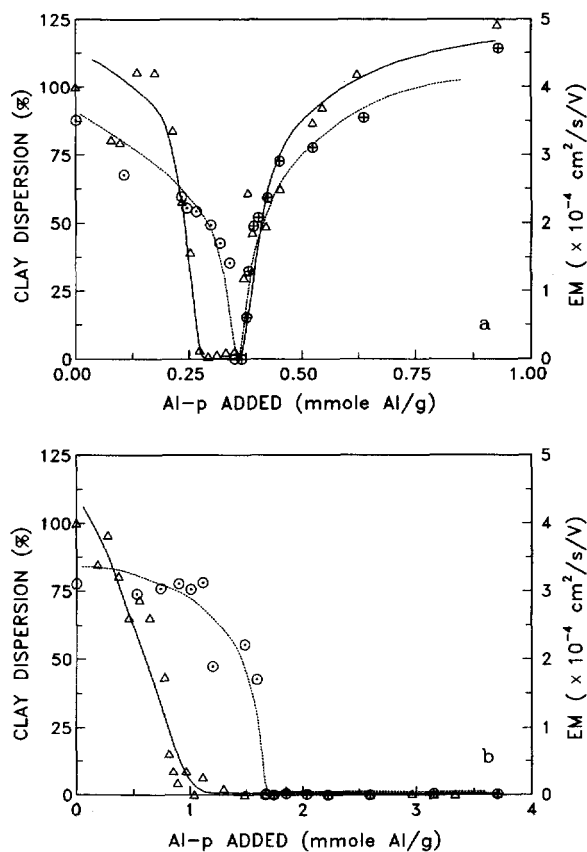


Figure 4. Effect of hydroxy-Al polycations on the flocculation-dispersion (solid line) and electrophoretic mobility (EM) (dashed line) of (a) illite and (b) montmorillonite. O = negative and O+ = positive EM.

interparticle bonding may have formed by the Al-p between montmorillonite particles than between illite particles, thereby explaining the observed flocculation-dispersion pattern of illite and montmorillonite suspensions. A consideration of the shape and surface area of Na-illite and Na-montmorillonite particles supports this hypothesis. Electron micrographs have shown that illite particles are poorly defined flakes commonly grouped together in irregular aggregates (Grim, 1968) and have very irregular surfaces (Greene *et al.*, 1978) that are commonly terraced (Grim, 1968; Quirk, 1978). On addition of Al-p, adjacent illite particles probably came in contact at only a few points with relatively small areas of particle overlap; therefore, interparticle bonding by Al-p was relatively weak. Because each Al-p carried multiple charges, more residual positive charge of Al-p should have been left on the edges and surfaces of the particles if the addition of Al-p exceeded the CEC of the particles. The overall effect should have been to restabilize the illite suspension. On the other hand, electromicrographs have shown that montmorillonite particles are very thin flakes (Brown *et al.*,

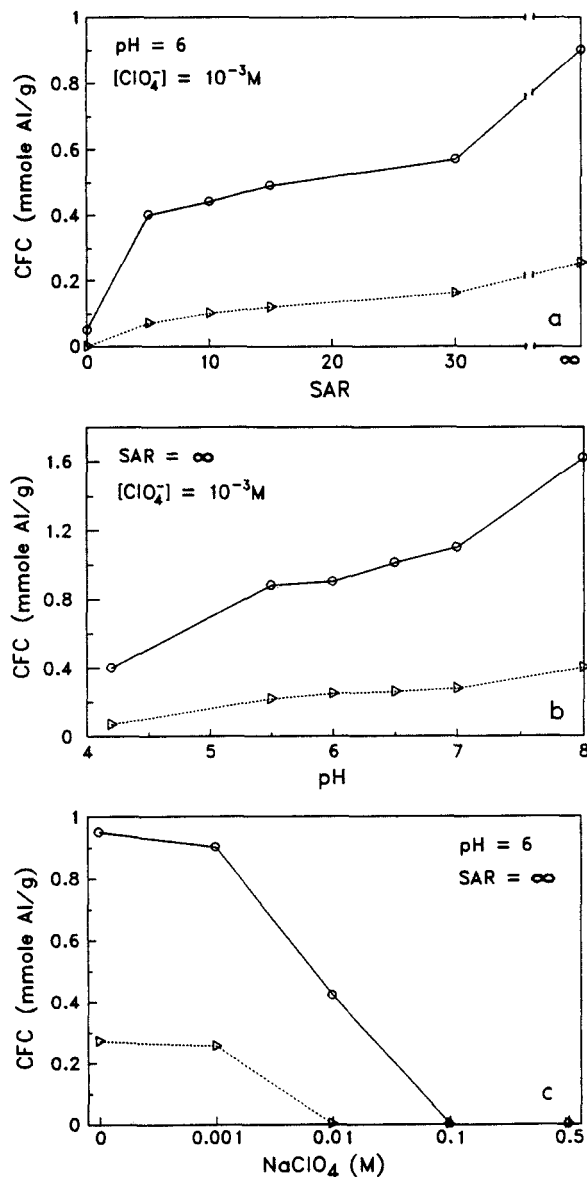


Figure 5. Critical flocculation concentration (CFC) of hydroxy-Al polycation as affected by (a) sodium adsorption ratio (SAR), (b) pH, and (c) ionic strength for illite (dashed line) and montmorillonite (solid line).

1978). Montmorillonite has a much higher specific surface area, although its charge density is similar to that of illite. In the presence of Al-p adjacent montmorillonite particles should have formed face-to-face aggregates due to surface charge neutralization. A relatively large area of particle overlap, therefore, contributed to much stronger and more extensive interparticle bonding by Al-p and made redispersion more difficult. McAtee and Wells (1967) observed microscopically that Al-hydrous oxide was adsorbed on the basal surfaces of montmorillonite.

Effect of SAR, ionic strength, and pH on CFC

Figure 5 shows the influence of SAR, ionic strength, and pH on the CFC of Al-p. In general, CFC increased with increased SAR and pH and decreased with increased ionic strength. At SAR = 0, the $5 \times 10^{-4} \text{ M}$ $\text{Ca}(\text{ClO}_4)_2$ background solution was sufficient to destabilize the illite suspensions (CFC = 0, Figure 5a). CCC values of 3×10^{-4} and $2 \times 10^{-4} \text{ M}$ were determined by Arora and Coleman (1979) and Rengasamy (1983), respectively, for Ca-illite in CaCl_2 . For the montmorillonite suspension the CFC was equal to 0.05 mmole Al/g (Figure 5a). The increase of CFC with an increase of SAR was most significant from SAR 0 to SAR 5, especially for montmorillonite. Between SAR values of 5 and 30 the increase of CFC was relatively small. These observations may be partially explained by the "demixing" model (Bar On *et al.*, 1970) in which Na^+ was the predominant cation on the external surfaces of the clay particles if $0\% < \text{exchangeable } \text{Na}^+ (E_{\text{Na}}) < 20\%$. This model results in a greater expression of the diffuse double layer on the external surface and a more stable suspension than if the Na^+ was distributed evenly over all surfaces. If CFC could be achieved by displacing Na^+ on external positions, less Al-p would be needed proportionally at higher SAR values to fulfill that condition. As shown in Figure 5a, at SAR 5 (about 5% E_{Na}) a CFC value of 0.4 mmole Al/g for montmorillonite would cover about 24% of the exchange sites (based on the maximum Al-p adsorption). An SAR value of 30 (about 30% E_{Na}) and ∞ (100% E_{Na}), however, required an amount of Al-p equivalent to only about 33% and 55%, respectively, of the exchange sites. The relatively high proportion of Al-p required at SAR 5 may also have been due to the steric and multi-charge effect of Al-p that displaced both Na^+ and Ca^{2+} on external positions.

The increase of CFC with increased pH was most apparent at $5.5 > \text{pH} > 7$, whereas at pH 5.5–7, the curve was relatively flat (Figure 5b). At low pH, Al-p may hydrolyze into Al-monomers thereby increasing the residual positive charge per Al atom and decreasing the CFC. At pH > 7 , however, Al-p might have further polymerized and hydrolyzed into gibbsite, resulting in little or no residual positive charge on each Al-p molecule and an increase in the CFC. The complexes between Al-p and illite or montmorillonite seemed relatively stable within the pH range 5.5–7. Ionic strength had little effect on CFC for $< 0.001 \text{ M}$ NaClO_4 (Figure 5c). The CFC decreased significantly at ionic strengths of $> 0.001 \text{ M}$ NaClO_4 because of the suppression of the diffuse double layer of the clay colloids by increased swamping electrolyte. CFC was zero at ionic strengths of > 0.01 and $> 0.1 \text{ M}$ NaClO_4 for the illite and montmorillonite suspensions, respectively. Reported CCC values for Na-illite range from 0.0072 to 0.01 M (Arora and Coleman, 1979; Rengasamy, 1983), whereas Oster

et al. (1980) reported a CCC value of 0.055 M. For Na-montmorillonite CCCs range from 0.007 to 0.02 M (Arora and Coleman, 1979; Oster *et al.*, 1980).

SUMMARY AND CONCLUSIONS

Both illite and montmorillonite exhibited a strong affinity to Al-p ($10^4 < MW < 5 \times 10^4$). The adsorption was irreversible in water, and very little adsorbed Al-p was desorbed by Na⁺. The adsorption of Al-p effectively blocked negative charge on clay surfaces, resulting in an increased PZSE and PZC for Na-illite and Na-montmorillonite and destabilized the colloidal suspensions. At the maximum Al-p adsorption, surface charge was reversed from negative to positive, which caused restabilization of the illite but not the montmorillonite suspensions. This difference was probably due to the stronger and more extensive interparticle bridging of montmorillonite particles by Al-p than of illite particles. The CFC of Al-p for both clays was found to be dependent on SAR, ionic strength, and pH. In general, the CFC increased with increase of SAR and pH, and decreased with increase of ionic strength.

This research indicates that small amounts of Al-p can effectively prevent soil clay dispersion. As reported by Wada *et al.* (1983), Al-p may be used on soil to improve its aggregation and water infiltration characteristics. Al-p should have little adverse effect to plants due to its strong affinity to clay minerals. Variation of SAR, EC, and pH over a relatively wide range of values can be tolerated for the Al-p-treated clays, especially illite, before dispersion occurs.

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