Flocculation of Reference Clays and Arid-Zone Soil Clays

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ABSTRACT

The effect of electrolyte concentration, exchangeable sodium percentage (ESP), sodium adsorption ratio (SAR), and pH on the flocculation-dispersion behavior of reference kaolinite, reference montmorillonite, reference illite, and the clay fraction of three arid-zone soils was investigated. The clay mineralogy of the soils was dominated by either montmorillonite, kaolinite, or illite. The clavs were Na- or Ca-saturated and freeze-dried before use. Critical coagulation concentrations (CCCs) were investigated in the range of pH 5.5 to 9.5, ESP of (here equated with percent Na clay) 0, 5, 10, 20, 40, 60, 80, and 100, SAR of 0, 5, 10, 20, 40, 60, 80, and ∞, and using electrolyte concentrations of 0 to 500 mmol. L⁻¹. The CCC values increased with increasing ESP, increasing SAR, and increasing pH. The pH dependence of kaolinite and illite was greater than that of montmorillonite at all ESPs and SARs. The CCC behavior of the soil clavs resembled that of illite, especially in its pH dependence at ESP 100 and SAR ∞. The CCC values of the soil clays, kaolinite, and illite showed a sharp increase at high ESP and SAR, whereas montmorillonite showed a sharp increase in CCC at low ESP and SAR. The CCCs for all soil clays were similar in magnitude, despite their differing clay mineralogies. The CCCs for the reference clays were much lower than those for the soil clays, indicating that extrapolation from reference-clay results is not possible, and that additional factors such as organic-matter content and Al- and Fe-oxide content may influence the dispersion of soil clays.

THE MAINTENANCE of adequate soil permeability and favorable soil structure is a major concern in the irrigation of arid-zone soils. Soil structure is susceptible to the detrimental effects of low electrolyte

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concentration of the irrigation water and high Na concentration on the soil exchange complex (Shainberg and Letey, 1984). The dominant process restricting permeability of arid-zone soils is clay dispersion followed by clay migration and plugging of soil pores (Frenkel et al., 1978). Numerous factors have been related to clay dispersion.

Recent investigations have related the solution pH to clay dispersion in soils (Suarez et al., 1984; Gupta et al., 1984). Suarez et al. (1984) found that, at constant SAR and electrolyte concentration and at solution pHs of 6, 7, 8, and 9, clay dispersion increased with increasing pH for two arid-zone soils, one predominantly kaolinitic and one predominantly montmorillonitic. Gupta et al. (1984) found increasing clay dispersion with increasing pH from 6.5 to 10.5 for a Na-saturated Indian soil shaken in 0.1 M NaCl for one day.

The flocculation value or CCC is the minimum electrolyte concentration necessary to flocculate a given colloidal dispersion in a given time (van Olphen, 1977). Thus, if the electrolyte concentration is less than the CCC, dispersion occurs. The CCC values for Na montmorillonite range from 7 to 20 mmol, L⁻¹ NaCl (Arora and Coleman, 1979); CCCs for Ca montmorillonite range from 0.17 mmol, L⁻¹ (van Olphen, 1977) to 0.5 mmol, L⁻¹ of CaCl₂ (Greene et al., 1978) in neutral salt solutions. The CCC values for Na kaolinite range from 0 to 5 mmol. L⁻¹ in neutral NaCl; Ca kaolinite is stable even in distilled water (Arora and Coleman, 1979). The CCC values for Na illite range from 7 mmol. L⁻¹ (Rengasamy, 1983) to 55 mmol. L⁻¹ of NaCl (Öster et al., 1980). The CCCs for Ca illite range from 0.25 mmol, L⁻¹ (Oster et al., 1980) to 1 mmol, L⁻¹ of CaCl₂ (Greene et al., 1978). The variability exhibited by the above CCC values is prob-

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ably due to the differing methodologies used in the CCC determinations.

The flocculation-dispersion behavior of reference clay minerals has been found to be pH dependent (El-Swaify, 1976; Swartzen-Allen and Matijevic, 1976; Arora and Coleman, 1979; Goldberg and Glaubig, 1987). The CCC values for both Na montmorillonite and Na kaolinite increased from pH 4 to 10 in NaNO₃ solution (Swartzen-Allen and Matijevic, 1976) and from pH 5.8 to 9.4 in NaCl solution (Goldberg and Glaubig, 1987); CCCs for Na illite increased from pH 2 to 12 in NaCl solution (El-Swaify, 1976). The CCC values for Ca montmorillonite and Ca kaolinite increased from pH 5.5 to 9.3 in CaCl₂ solution (Goldberg and Glaubig, 1987); pH dependence of the flocculation-dispersion behavior of Ca illite has not been investigated. The effect of pH was much greater for Na kaolinite, which was flocculated in distilled water at pH 5.8 and had a CCC of 55 mmol, L^{-1} at pH 9.1, than for Na montmorillonite, which had a CCC of 14 $mmol_c L^{-1}$ at pH 6.4 and a CCC of 28 $mmol_c L^{-1}$ at pH 9.4 (Goldberg and Glaubig, 1987). The pH dependence for Na illite in NaCl solution appears to resemble that of Na kaolinite but is known only imprecisely; the CCC at pH 4 is between 0 and 10 mmol, L^{-1} and the CCC at pH 10 is between 40 and 100 mmol_c L⁻¹ (El-Swaify, 1976). The pH dependence for Ca montmorillonite (having a CCC of $1.1 \text{ mmol}_c \text{ L}^{-1}$ at pH 6.1 and 1.3 mmol_c L^{-1} at pH 9.2) and for Ca kaolinite (flocculated in distilled water at pH 5.5 and having a CCC of 0.85 mmol_c L^{-1} at pH 9.3) was less pronounced than for the Na clays (Goldberg and Glaubig, 1987).

Arora and Coleman (1979) studied flocculation-dispersion of various reference clay minerals and the clay fractions of four California soils as a function of saturating cation, electrolyte concentration, SAR, and solution pH. The CCCs for most of the Na reference clays were higher in pH 8.3 NaHCO₃ solution than in pH 7.0 NaCl or in pH 9.5 Na₂CO₃ solutions; CCCs of all soil clays, on the other hand, consistently increased as a function of pH (Arora and Coleman, 1979). Interpretation of the above results is difficult because pH was measured only in the initial salt solutions and not in the presence of the clays. Arora and Coleman (1979) concluded that the montmorillonitic soil acted like reference montmorillonite and the micaceous soil clays behaved like reference illite and vermiculite and that, therefore, flocculation-dispersion behavior of the soil clay fractions was influenced by their clay mineralogy and could be related to the behavior of reference clays. Unfortunately, their data do not allow such a clear-cut conclusion. Not only the montmorillonitic soil, but also two of the micaceous soils, resembled the reference montmorillonites; the third micaceous soil resembled reference kaolinite as much as it resembled reference illite.

Previous investigations have evaluated the effect of SAR on flocculation-dispersion behavior of reference clavs in neutral salt solutions, as well as the effect of pH on the flocculation-dispersion behavior of Na reference and soil clays in salt solutions of SAR ∞ and Ca reference and soil clays in salt solutions of SAR 0. The interactive effect of pH and SAR on flocculationdispersion behavior is not yet quantified. The objectives of the present study were to (i) determine the effect of ESP, SAR, electrolyte concentration, and pH on the flocculation-dispersion behavior of reference montmorillonite, kaolinite, and illite and the clay fraction of three arid-zone soils in which one of these minerals is dominant, and (ii) determine if the behavior of reference clay minerals can be used to predict the effect of the above variables on the flocculation-dispersion behavior of the arid-zone soil clays.

MATERIALS AND METHODS

Samples of a well-crystallized kaolinite from Georgia (KGa-1), a Ca montmorillonite from Cheto, Arizona (SAz-1), and Silver Hill illite from Montana (IMt-1) were obtained from the Clay Minerals Society's Source Clays Repository. X-ray diffraction (XRD) analysis indicated traces of vermiculite and feldspar in the kaolinite, traces of kaolinite and vermiculite in the illite, but detected no impurities in the montmorillonite. Three soil samples whose clay mineralogy was dominantly kaolinite, montmorillonite, or illite were chosen for study. Table 1 provides soil classifications and chemical characteristics.

Cation-exchange capacity (CEC) of each soil was determined using the method for arid-land soils described by Rhoades (1982). Inorganic C (IOC) and organic C (OC) analyses were performed as described by Nelson and Sommers (1982). Extraction of free Fe oxide (Fe) and free Al oxide (Al) was carried out according to the method of Coffin (1963). Aluminum and Fe concentrations were determined by ICP analysis. Clay mineralogy was determined by XRD analysis on Mg-saturated $<2-\mu m$ fractions. Estimates of kaolinite, illite, and montmorillonite were made by converting diffraction peak areas directly to clay-mineral contents using the method of Klages and Hopper (1982).

The $<2-\mu m$ fractions of reference clays and soils were collected by sedimentation. The pH of the kaolinite suspension was raised to 9.6 using NaOH to disperse the material prior to collection. Subsamples of the $<2-\mu m$ fraction of the clays were saturated with Na or Ca using 1 mol_c L⁻¹ NaCl

Table 1. Classifications and chemical characterization[†] of soils.

Soil name	Classification	Depth	CEC	IOC	OC	Fe	Al	Kaol	Ill	Mont
		cm	mmol _c kg ⁻¹ g kg ⁻¹					g kg ⁻¹ clay		
Altamont	Fine, montmorillonitic, thermic Typic Chromoxerert	25-51	160	0.04	6.5	8.2	0.64	70	170	690
Fallbrook	Fine-loamy, mixed, thermic Typic Haploxeralf	0-25	112	0.20	3.8	6.9	0.36	640	280	30
Ramona	Fine-loamy, mixed, thermic Typic Haploxeralf	25-51	29	0.25	2.1	5.9	0.40	120	810	20

† CEC = cation-exchange capacity; IOC = inorganic C; OC = organic C; Fe = free Fe oxides; AI = free Al oxides; Kaol = kaolinite; III = illite; Mont = montmorillonite.

Table 2. Critical percent transmittance for reference clays and soil clays at a range of sodium adsorption ratios (SAR).

Solid	SAR 0	SAR 5	SAR 10	SAR 20	SAR 40	SAR 60	SAR 80	SAR ∞	
<u>_</u>	%T								
Montmoril-									
lonite	52	53	57	58	63	71	75	78	
Kaolinite	39	40	46	45	51	47	56	56	
Illite	44	42	43	44	44	45	46	45	
Altamont	39	40	42	40	44	42	41	42	
Fallbrook	33	31	33	35	38	37	36	38	
Ramona	29	27	28	30	34	31	31	33	

or $CaCl_2$. The materials were washed free of Cl and freezedried.

The CCC is operationally defined as the salt concentration at which percent transmittance (%T) corresponds to 20% of the clay remaining in solution after 3 h. The CCCs were measured for the above materials in the pH range 5.5 to 9.5 and using salt concentrations ranging from 0 to 500 mmol_c L^{-1} . The SAR values of 0, 5, 10, 20, 40, 60, 80, and ∞ were matched to the percent Na clay in the system-0, 5, 10, 20, 40, 60, 80, and 100, respectively. Percent Na clay was equated to ESP. The SAR ∞ corresponds to ESP 100.

Solutions (7 mL) of different salt concentrations were pipeted into ten 10-mL spectrophotometer cuvettes. A 1.0% suspension of clay was added to a 50-mL polypropylene centrifuge tube and shaken for 5 min. The clay suspensions were obtained by combining 100 mg of clay with 10.0 mL deionized water. For the Ca saturated clays, it was necessary to sonicate the suspension for 15 s at 75 to 85 W prior to shaking. For the mixed Ca/Na clay systems, the Ca clay was sonicated before the Na clay was added and the suspension shaken. The suspensions of clays and clay mixtures were prepared just prior to use. For the Na clay and mixed Ca/ Na clay systems, the pH was adjusted by adding small volumes (<0.2 mL) of 0.1 M NaOH to the 1.0% suspensions prior to shaking. For the Ca systems, the pH was adjusted by adding $Ca(OH)_2$ to the salt solutions prior to pipeting into the cuvettes. The amounts of Na and Ca used in pH adjustment were included in the CCC calculations. A 0.50mL aliquot of the 1.0% clay or clay mixture was pipeted into each cuvette containing the salt solution. The cuvettes were sealed with Parafilm (American National Can, Greenwich, CT), agitated on a vortex mixer for 15 s, and allowed to settle. After 3 hr, the %T of each cuvette was read on a Spectronic 20 (Bausch and Lomb, Rochester, NY) at 420nm wavelength. Deionized water was used as a blank to set 100%T.

Before determining the CCC for each system, the %T corresponding to 20% of the clay remaining in solution was established. This "critical %T" was determined for each clay and clay mixture (Table 2). The pHs of the suspensions near the critical %T were measured immediately after reading of the %T values. For calculating the CCC and the corresponding pH for each clay system, a linear relationship was assumed between the two data points bracketing the critical %T. All clays were found to obey Beer-Lambert's law in the concentration ranges investigated.

RESULTS AND DISCUSSION

The effect of pH and SAR on the flocculation of reference kaolinite, montmorillonite, and illite is indicated in Fig. 1. The CCC values for illite were similar in magnitude to those of montmorillonite at low SAR; at SAR 40 to 100, CCC values for illite were much greater than for montmorillonite. Increased dispersibility for Na illite over Na montmorillonite has been observed previously (Oster et al., 1980). The CCC values of all three clay minerals increased with increasing pH and SAR value. The CCCs for kaolinite and illite are much more pH dependent than those for montmorillonite at all SARs. That is, the slopes of the CCC vs. pH plots are greater for kaolinite and illite at all SARs. The slopes for kaolinite and illite are very similar in magnitude at all SARs, except SAR ∞ , where the slope is about 25% greater for illite. The difference in pH dependence of CCC, previously observed by Swartzen-Allen and Matijevic (1976) for reference Na montmorillonite and Na kaolinite (SAR ∞) and by Goldberg and Glaubig (1987) for reference montmorillonite and kaolinite at SAR 0 and SAR ∞ , is attributed to the greater proportion of pH-dependent charge of kaolinite. Because of the nonswelling nature of illite and its smaller cation-exchange capacity, it would also have a greater proportion of pHdependent charge than montmorillonite. Arora and Coleman (1979) found a sharp increase for CCC of Na illite from 9 mmol_c L⁻¹ at pH 7 to 185 mmol_c L⁻¹ at pH 8.3.

The CCC values for kaolinite and illite are more dependent on SAR than those for montmorillonite, especially at high pH. For montmorillonite, the greatest incremental change in CCC occurs when SAR and ESP change from 0 to 20. This pronounced effect has been attributed to demixing of Na and Ca ions on the tactoid surfaces. Until ESP reaches approximately 20, Na is the predominant cation on the external surfaces of the clay particles and Ca ions dominate in the interlayers (Oster et al., 1980). For kaolinite and illite, in contrast, the greatest incremental change in CCC occurs when SAR changes from 80 to ∞ , approximately corresponding to an ESP change from 80 to 100. Similar results were obtained by Arora and Coleman (1979), who found sharp increases in CCC values for two reference kaolinite minerals and one reference illite mineral (at an unspecified pH value) when SAR was changed from 60 to ∞. Kaolinite does not contain interlayer cations, while illite contains no exchangeable interlayer cations; thus, for both minerals, all exchangeable cations are adsorbed on the exterior surfaces of the particles (van Olphen, 1977). Since demixing does not occur, a much higher ESP is required to increase the CCC than for montmorillonite.

The effect of pH and SAR on the flocculation of the three soil clays is indicated in Fig. 2. The CCCs for all three soil clays are pH and SAR dependent and are very similar at all pHs and SARs, despite their differing clay mineralogies. These results contradict those of Arora and Coleman (1979), who found CCC values differing by more than an order of magnitude for four arid-zone soil clays of differing clay mineralogies. The soil clays are consistently more dispersive than the reference clays, requiring greater salt additions at all SARs and all pH values. Rengasamy (1983) found CCCs for homoionic reference illites in neutral Na and Ca salt solutions to be much lower than CCCs for two homoionic soils dominant in illite.

The CCC values for all Na soil clays show a very strong pH dependence. That is, the slopes of the CCC vs. pH curves are even steeper than the slope for reference Na illite. Similar results were obtained by Arora and Coleman (1979), who found sharp increases in the CCC value for Ramona and three other aridzone soil clays at SAR ∞ when the pH of the salt solution was changed from 7 to 9.5. The pH dependence of the CCC values at SAR 0 to 80 for all soil clays is much less pronounced. The overall CCC behavior of the soils as a function of pH and SAR most closely resembles reference illite, showing a steep slope at SAR ∞ combined with greatly reduced CCC values and slopes at SAR 0 to 80. Suarez et al. (1984) observed little difference in the pH dependence of clay dispersion at SAR 20 and SAR 40 for Fallbrook soil and a montmorillonitic arid-zone soil. The CCC values for all three soil clays are more dependent on SAR than those of the reference clays, especially at high pH. At pH 9, CCC for reference kaolinite changes from 0.85 mmol_c L⁻¹ at SAR 0 to 69 mmol_c L⁻¹ at SAR 100, CCC for reference montmorillonite changes from 1.3 mmol_c L⁻¹ at SAR 0 to 32 mmol_c L⁻¹ at SAR 100, CCC for reference illite changes from 1.3 mmol_c L⁻¹ at SAR 0 to 143 mmol_c L⁻¹ at SAR 100, and CCC for soil clays changes from less than 2 mmol_c L⁻¹ at SAR 0 to greater than 230 mmol_c L⁻¹ at SAR 100. Again, the behavior of the soil



Fig. 1. Critical coagulation concentrations (CCC) of reference clays as a function of pH and sodium adsorption ratio (SAR): (a) kaolinite (b) montmorillonite (c) illite.



Fig. 2. Critical coagulation concentrations (CCC) of soil clays as a function of pH and sodium adsorption ratio (SAR): (a) Altamont (b) Fallbrook (c) Ramona.

clays most closely resembles that of reference illite. For the soil clays, as for reference kaolinite and illite. the greatest change in CCC over the pH range tested occurs when SAR changes from 80 to ∞ , approximately corresponding to an ESP change from 80 to 100. Similar results were obtained by Arora and Coleman (1979), who found sharp increases in the CCC value for Ramona soil clay, reference kaolinite, and reference illite (at an unspecified pH value) when SAR was changed from 60 to ∞ . In contrast, Arora and Coleman (1979) found that, as for reference montmorillonite, the greatest change in CCC for one montmorillonitic and two mixed-mineralogy soil clays occurred when SAR and ESP changed from 0 to 30.

The CCC values of all three soil clavs were very similar at all pHs and SARs, despite their differing mineralogies; CCCs of soil clays were much higher than those of reference clays. These two results refute the conclusion of Arora and Coleman (1979) and indicate that extrapolation from reference-clay results to predict the flocculation-dispersion behavior of soil clays dominant in those clay minerals is not valid. Additional factors such as organic-matter content, organic-anion content, and AI- and Fe-oxide content may have to be considered. Organic matter has been shown to increase clay dispersion (Gupta et al., 1984; Durgin and Chaney, 1984). Adsorption of organic anions increased the clay dispersion of an illitic Australian soil (Shanmuganathan and Oades, 1983). Addition of excess Al and Fe polycations increased the dispersion of soil clays (Oades, 1984).

From the point of view of prediction, it is, however, encouraging that the flocculation-dispersion behavior of soil clays of vastly different clay mineralogies is effectively identical. The red-brown earths, Australian soils dominant in illite, are susceptible to dispersion even at low SAR and under weak mechanical forces (Rengasamy et al., 1984). Our results indicate that a montmorillonitic soil, a kaolinitic soil, and an illitic soil containing 17, 28, and 81% illite, respectively, all most closely resemble reference illite in their flocculation-dispersion behavior. Since the CCC values for all three soils are virtually identical, our results suggest that, even though present in minor amounts, the illite component of our soil clays plays a dominant role in determining their flocculation-dispersion behavior as a function of solution pH and SAR value.

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All references to sodium adsorption ratio, SAR, 100 should be SAR ∞ .