

## FLOCCULATION OF ILLITE/KAOLINITE AND ILLITE/MONTMORILLONITE MIXTURES AS AFFECTED BY SODIUM ADSORPTION RATIO AND pH

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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 50/50 mixtures of reference illite with reference kaolinite or reference montmorillonite was investigated. The clays were Na- or Ca-saturated and freeze-dried before use. Critical coagulation concentrations (CCCs) were investigated in the range of pH 5.9 to 9.6, percent Na-clay 0, 10, 20, 40, 60, 80, and 100 and SAR 0, 10, 20, 40, 60, 80, and  $\infty$ . CCC values increased with increasing ESP, increasing SAR, and increasing pH. The pH dependence of illite/kaolinite was greater than that of illite/montmorillonite especially at high ESP and SAR. The presence of illite did not play a dominant role in determining flocculation-dispersion behavior of the 50/50 clay mixtures. The CCCs of illite/kaolinite resembled reference illite more than reference kaolinite for SAR 0 to SAR 60. Illite/montmorillonite exhibited CCCs more similar to reference illite than reference montmorillonite at SAR 40 and SAR 60. At the agriculturally desirable ESP and SAR values of 0 to 15, all the 2:1 clays and 2:1 clay mixtures demonstrated similar CCC values.

**Key Words**—Flocculation value, Critical coagulation concentration, Dispersion, Aggregation.

### INTRODUCTION

The maintenance of adequate soil permeability and favorable soil structure is a major concern in the cultivation of irrigated arid zone soils. In such soils, structure is susceptible to the detrimental effects of low electrolyte concentration of the irrigation water and/or high sodium concentration on the soil exchange complex (Shainberg and Letey, 1984). The dominant process reducing permeability of arid zone soils is clay dispersion followed by migration of clay and plugging of soil pores (Frenkel *et al.*, 1978). The most common measure of soil permeability in the laboratory is the determination of relative hydraulic conductivity (Shainberg and Letey, 1984). Numerous factors have been related to hydraulic conductivity and clay dispersion.

An important soil factor that has been related to hydraulic conductivity is clay mineralogy (McNeal and Coleman, 1966; Yaron and Thomas, 1968; Naghshineh-Pour *et al.*, 1970; Frenkel *et al.*, 1978; Das and Datta, 1987). McNeal and Coleman (1966) found that for seven Western soils under low salt and high sodium conditions, the hydraulic conductivity of soils with moderate amounts of montmorillonite was more stable than that of soils high in montmorillonite. The hydraulic conductivity of soils high in kaolinite was the most stable. Similarly, two Texas soils of mixed 2:1 clay mineralogy were more stable than two Texas soils of almost purely montmorillonitic mineralogy (Yaron and Thomas, 1968) and a kaolinitic California soil was less likely than a montmorillonitic California soil to suffer reductions in hydraulic conductivity at low elec-

trolyte concentration (Frenkel *et al.*, 1978). Naghshineh-Pour *et al.* (1970), applying various salt solutions to four Texas soils, concluded that the single most important soil factor affecting hydraulic conductivity in these soils was clay mineralogy.

Further evidence of the stabilizing effect of kaolinite and the destabilizing effect of montmorillonite was a significant positive correlation between hydraulic conductivity and percent kaolinite, and a significant negative correlation between hydraulic conductivity and percent montmorillonite for eight soil samples from four subtropical Indian soils (Das and Datta, 1987). These authors found no significant correlation between hydraulic conductivity and percent illite. A dispersive role for illite is suggested by the results of McIntyre (1979) who found a highly significant negative correlation between clay content and hydraulic conductivity for 41 illitic soils, but no significant correlation for seven montmorillonitic soils from Australia. Oster *et al.* (1980) found much greater dispersivity for illite than for montmorillonite clay. Australian soils dominant in illite, the red-brown earths, are susceptible to dispersion even at low sodium adsorption ratio and under weak mechanical forces (Rengasamy *et al.*, 1984). Alperovitch *et al.* (1985) studied the hydraulic conductivity of clay-sand mixtures and found more clay dispersion and clay movement for illite than for montmorillonites.

The hydraulic conductivity research described so far did not maintain a constant solution pH in the soil columns and thus the effect of pH was not studied. Recent investigations have related the solution pH to

Table 1. Effect of pH on flocculation-dispersion behavior of reference clays.

Reference clay	pH	CCC value	pH	CCC value
Na-kaolinite†	5.8	flocculated	8.8	69 meq/liter NaCl
Na-montmorillonite†	6.4	15 meq/liter NaCl	9.0	32 meq/liter NaCl
Na-illite†	5.9	24 meq/liter NaCl	9.1	143 meq/liter NaCl
Ca-kaolinite‡	5.5	flocculated	9.3	0.9 meq/liter CaCl <sub>2</sub>
Ca-montmorillonite‡	6.1	1.1 meq/liter CaCl <sub>2</sub>	9.2	1.3 meq/liter CaCl <sub>2</sub>
Ca-illite†	6.8	0.8 meq/liter CaCl <sub>2</sub>	9.4	1.3 meq/liter CaCl <sub>2</sub>

† Goldberg and Forster (1990).

‡ Goldberg and Glaubig (1987).

hydraulic conductivity (Suarez *et al.*, 1984; Chiang *et al.*, 1987) and clay dispersion of soils (Suarez *et al.*, 1984; Gupta *et al.*, 1984). Suarez *et al.* (1984) found that, at constant sodium adsorption ratio (SAR) and electrolyte concentration and at solution pHs of 6, 7, 8, and 9, hydraulic conductivity decreased and clay dispersion increased with increasing pH for two arid zone soils, one predominantly kaolinitic and one predominantly montmorillonitic. In a similar experiment on three soils from Georgia, Chiang *et al.* (1987) found the hydraulic conductivity of one soil to be sensitive and that of two others to be nonsensitive to pH changes from 4.5 to 8.5. They did not relate these differences to clay mineralogy. Gupta *et al.* (1984) observed increased 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 critical coagulation concentration (CCC), is the minimum concentration of an electrolyte necessary to flocculate a given colloidal dispersion in a given time (van Olphen, 1977). Thus dispersion occurs if the electrolyte concentration is less than the CCC. The flocculation-dispersion behavior of reference clay minerals is pH dependent (Table 1).

A previous investigation evaluated the effect of exchangeable sodium percentage (ESP), sodium adsorption ratio (SAR), electrolyte concentration, and pH on the flocculation-dispersion behavior of reference montmorillonite, kaolinite, illite, and the clay fraction of three arid zone soils in which one of these minerals was dominant (Goldberg and Forster, 1990). In this study, CCC values of all three soil clays were very similar at all pHs and SARs despite their differing clay mineralogies. The results indicated that a montmorillonitic soil, a kaolinitic soil, and an illitic soil containing 17, 28, and 81% illite, respectively, all most closely resembled reference illite in their flocculation-dispersion behavior. Goldberg and Forster (1990) suggested that since the CCC values for all three soils were virtually identical, the illite component of the soil clays, even though present in small amounts, played a dominant role in determining flocculation-dispersion behavior as a function of solution pH and SAR value.

The objectives of the present study were: 1) to de-

termine the effect of ESP, SAR, and pH on the flocculation-dispersion behavior of 50/50 mixtures of reference illite with reference montmorillonite or reference kaolinite, and 2) to determine if the presence of illite dominates the flocculation-dispersion behavior of these clay mixtures.

## MATERIALS AND METHODS

Samples of a Ca-montmorillonite from Cheto, Arizona (SAZ-1), a well-crystallized kaolinite from Georgia (KGa-1), and Silver Hill illite from Montana (IMt-1) were obtained from the Source Clay Repository of the Clay Minerals Society. X-ray diffraction (XRD) analyses indicated traces of kaolinite and vermiculite in the illite, traces of vermiculite and feldspar in the kaolinite, but detected no impurities in the montmorillonite.

The <2- $\mu$ m fractions of the clays were collected by sedimentation following dispersion. The pH of the kaolinite suspension was raised to 9.6 using NaOH to effect dispersion of the clay prior to collection. Subsamples of the <2- $\mu$ m fractions were saturated with Na or Ca using 1 N NaCl or CaCl<sub>2</sub>. The clays were washed free of Cl<sup>-</sup> and freeze dried.

In this study, the CCC was operationally defined as the salt concentration at which percent transmittance (%T) corresponds to 20% of the clay or clay mixture remaining in solution after 3 hr. CCCs were measured for the above clays and clay mixtures in the pH range 5.5 to 9.5. SAR values of 0, 10, 20, 40, 60, 80, and  $\infty$  were matched to the percent Na-clay in the system, 0, 10, 20, 40, 60, 80, and 100, respectively. Percent Na-clay was matched to SAR and SAR  $\infty$  corresponds to ESP 100.

Suspension of clay or clay mixture was added to a 50-ml polypropylene centrifuge tube and shaken for 5 min. Clay suspensions (1% by weight) were prepared just prior to use by combining 100 mg of clay(s) with 10.0 ml of deionized water. For the Ca-saturated clays or clay mixtures, it was necessary to sonicate the suspension for 15 sec at 75–85 watts prior to shaking. For the mixed Ca/Na clays or clay mixtures, the Ca-clay was sonicated before the Na-clay was added and the suspension shaken. The clay portion of the mixtures

Table 2. Critical %T for reference clays and clay mixtures.

SAR	Illite/ Kaolinite	Illite/ Montmoril- lonite	Kaolinite†	Montmoril- lonite†	Illite†
%T					
0	34	51	39	52	44
10	35	50	46	57	43
20	35	52	45	58	44
40	39	54	51	63	44
60	38	53	47	71	45
80	39	58	56	75	46
∞	44	61	56	78	45

† Goldberg and Forster (1990).

consisted of 50% illite and 50% kaolinite or montmorillonite (by weight of clay). For the Na-clay and mixed Ca/Na clay or clay mixture, the pH was adjusted by adding small volumes (<0.2 ml) of 0.1 N NaOH to the 1.0% clay suspensions prior to shaking. For the Ca systems, the pH was adjusted by addition of Ca(OH)<sub>2</sub> to the salt solutions prior to pipeting into the cuvettes. The amounts of Na and Ca used for pH adjustment were included in the CCC calculations.

Solutions (7 ml) of different salt concentrations and SARs were pipeted into ten 10-ml spectrophotometer cuvettes. A 0.50-ml aliquot of the 1.0% clay or clay mixture was pipeted into each cuvette containing salt solution. The cuvettes were sealed with Parafilm, agitated on a vortex mixer for 15 sec, and left to settle. After 3 hr, the %T of each cuvette was read on a Spectronic 20 at 420 nm wavelength using deionized water as a blank to set 100%T.

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

To verify the validity of light transmittance measurements for the study of illite clay mixtures, the clay mineralogy of the resultant flocs was analyzed directly. Proportions of illite/kaolinite and illite/montmorillonite in the flocs at the CCCs were determined by quantitative XRD analysis using peak areas. These proportions were compared with those obtained from XRD peak areas of equivalent mechanical mixtures of the two reference clay minerals. The XRD analysis of each clay mixture was carried out in triplicate. The percentages of illite in the flocs are: Na-illite/kaolinite 48.9 ± 4.1, Ca-illite/kaolinite 46.0 ± 1.8, Na-illite/mont-

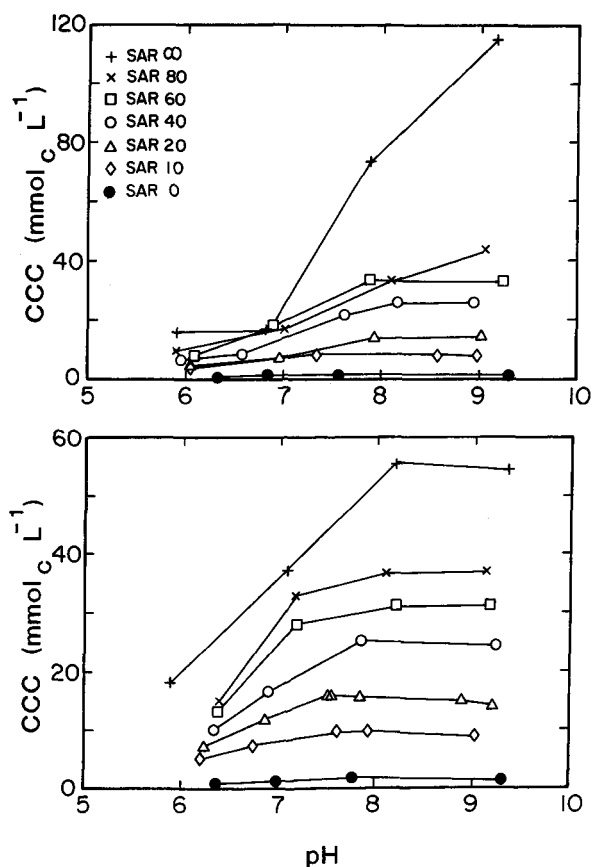


Figure 1. Critical coagulation concentrations of reference clay mixtures as a function of pH and SAR: (a) illite/kaolinite (b) illite/montmorillonite.

morillonite 57.1 ± 1.1, Ca-illite/montmorillonite 45.0 ± 2.6. These direct measurements show that the mineral proportions in the flocs are very similar to those in the initial solutions, clearly indicating that the clays are interacting and flocculating as mixtures.

## RESULTS AND DISCUSSION

The effect of pH and SAR on the flocculation of 50/50 mixtures of reference illite with reference kaolinite or reference montmorillonite is indicated in Figure 1. The CCC values for illite/kaolinite (Figure 1a) are similar in magnitude to those of illite/montmorillonite (Figure 1b) at low SAR; at SAR 40 to SAR ∞ CCC values for illite/kaolinite are greater than for illite/montmorillonite. Sodium-illite exhibits greater dispersibility than Na-montmorillonite (Oster *et al.*, 1980; Goldberg and Forster, 1990). The CCC values of both clay mixtures increase with increasing pH and SAR value. CCCs for illite/kaolinite are more pH dependent than for illite/montmorillonite, especially above SAR 20. That is, the slopes of the CCC versus pH plots are greater for illite/kaolinite than for illite/montmorillonite. The difference in pH dependence of CCC has been

previously observed by Goldberg and Forster (1990) for pure reference montmorillonite, kaolinite, and illite and is attributed to the greater proportion of pH-dependent charge of kaolinite and illite over montmorillonite.

The CCC values for illite/kaolinite are more dependent on SAR than those of illite/montmorillonite, especially at high pH. For both illite/kaolinite and illite/montmorillonite, the greatest incremental change in CCC occurs when SAR changes from 80 to  $\infty$ . Similar results had been obtained previously for pure reference illite and kaolinite (Goldberg and Forster, 1990). For pure reference montmorillonite, in contrast, the greatest incremental change in CCC occurs when SAR changes from 0 to 20 (Goldberg and Forster, 1990). This pronounced effect is due 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 montmorillonite particles and Ca ions dominate in the interlayers (Oster *et al.*, 1980). Near ESP 20 montmorillonite tactoids separate and act as single particles. This causes a large increase in CCC. For kaolinite and illite all exchangeable cations are adsorbed on the exterior surfaces of the particles (van Olphen, 1977). Since demixing does not occur in these minerals, a much higher ESP is required to increase the CCC of illite, kaolinite, or illite/kaolinite than that of montmorillonite. The effect of demixing from the montmorillonite component is seen in the CCCs of the illite/montmorillonite system. The incremental increase in CCC when SAR changes from 0 to 20 is almost equal to that occurring when SAR changes from 80 to  $\infty$ .

To evaluate whether the presence of illite has a dominant effect on the flocculation-dispersion behavior of clay mixtures, the CCCs of the mixed systems must be compared to those for the pure clay end members. CCC values for the pure clay end members were obtained by Goldberg and Forster (1990) and are presented with CCCs for the mixed clays in Figure 2 to facilitate interpretation. CCC values are presented as a function of pH for each SAR value. Examination of each SAR separately allows the resolution of small differences not noticeable in Figure 1, especially at low SAR values. Similarly, the study of Goldberg and Forster (1990) focused on the interactive effect of pH and SAR on the flocculation of reference clays and arid zone soil clays. Thus, the evaluation of flocculation-dispersion behavior of pure reference clays by SAR value will be presented here.

The Ca-clay systems (Figure 2a) and SAR 10 systems (Figure 2b) exhibit relatively small stability differences for the 2:1 clay minerals and mixtures containing at least one 2:1 mineral. CCC values for kaolinite are significantly lower than those for the 2:1 clay systems. CCCs for montmorillonite are a little higher than CCCs for illite, especially at low pH. The effect of illite com-

pletely dominates the flocculation-dispersion behavior of illite/kaolinite. CCCs for the mixtures are equal to or slightly greater than those for pure illite. CCCs for illite/montmorillonite are intermediate between illite and montmorillonite at low pH and slightly higher than montmorillonite at high pH.

The SAR 20 clays (Figure 2c) exhibit very similar stability for the 2:1 clay minerals and mixture. CCC values for kaolinite are significantly lower than for 2:1 clay systems. The illite/kaolinite systems have CCCs intermediate between illite and kaolinite at low pH and CCCs similar to illite at high pH.

For the SAR 40 (Figure 2d) and SAR 60 (Figure 2e) systems, CCC values for illite, montmorillonite, and illite/montmorillonite are similar at low pH. At high pH value, however, CCCs for illite and illite/montmorillonite are significantly higher than those for montmorillonite. Kaolinite is significantly more stable than the 2:1 mineral systems except for the SAR 60 system at high pH where its CCC equals that of montmorillonite. CCC values for illite/kaolinite are more similar to illite than to kaolinite at all pHs.

The SAR 80 systems (Figure 2f) and the Na-clay systems (Figure 2g) show illite to be significantly more dispersive than montmorillonite, kaolinite, and the clay mixtures. Na-kaolinite is more dispersive than Na-montmorillonite at high pH values. The CCC values of the clay mixtures are intermediate between the pure reference clays.

The stability of Ca-illite and Ca-montmorillonite was very similar, with CCCs for illite being slightly lower than those for montmorillonite especially at low pH value. The stability of Na-illite was less than that of Na-montmorillonite. This difference became increasingly pronounced with increasing pH value. At pH 9 the CCC of Na-illite was four times that of Na-montmorillonite. Kaolinite was the most stable of the reference clays over most of the pH and SAR ranges. Na-kaolinite, however, was less stable than Na-montmorillonite at pH 9.

The increase in pH dependence of CCC for reference kaolinite over reference montmorillonite is attributed to the greater proportion of pH-dependent charge of kaolinite. Illite, because of its nonswelling nature and smaller cation exchange capacity, would also have a greater proportion of pH-dependent charge than montmorillonite and thus greater pH dependence of CCC. Although kaolinite has the larger percentage of pH-dependent charge than illite, the total amount of pH-dependent charge is greater for illite leading to increased pH dependence of CCC of illite over kaolinite.

## CONCLUSIONS

Critical coagulation concentration (CCC) values of illite/kaolinite and illite/montmorillonite increased with increasing pH and increasing sodium absorption ratio (SAR). The 50/50 illite/kaolinite mixture showed

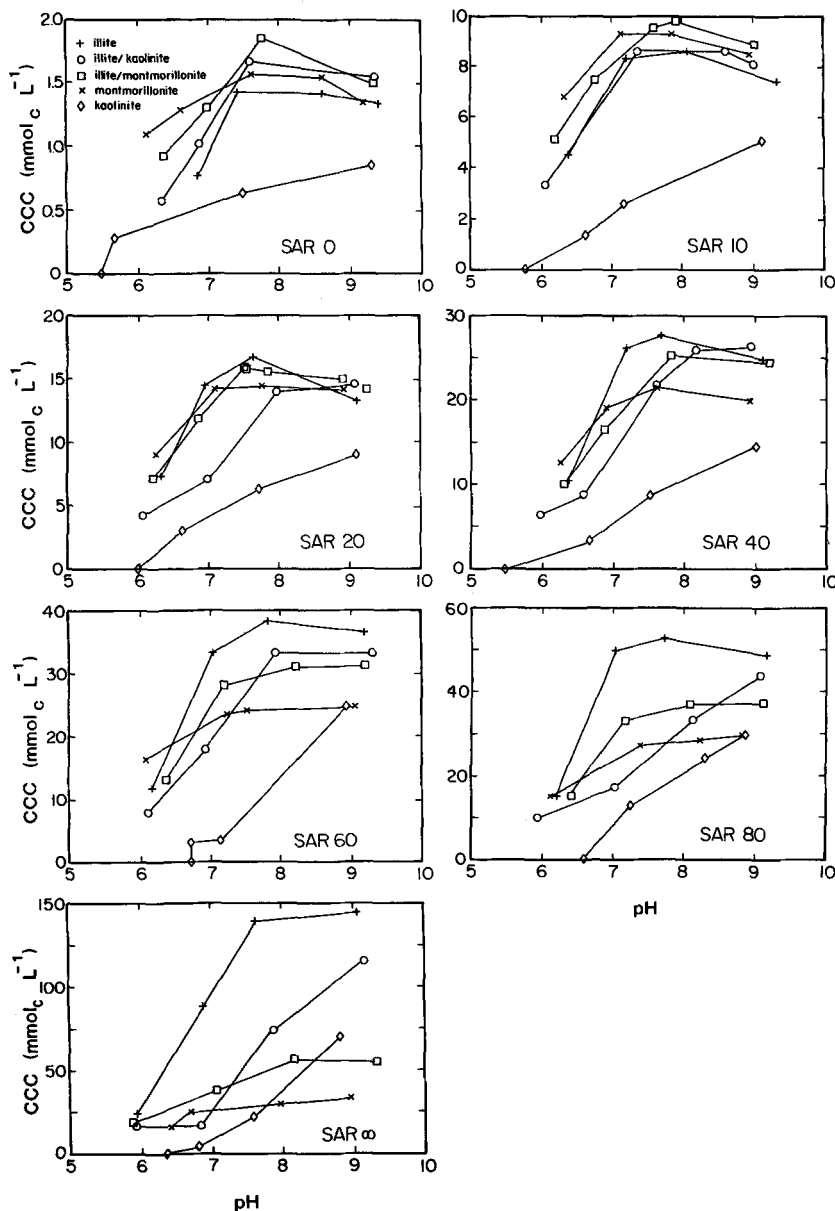


Figure 2. Critical coagulation concentrations of reference clays and clay mixtures as a function of pH: (a) SAR 0 (Ca-clay) (b) SAR 10 (c) SAR 20 (d) SAR 40 (e) SAR 60 (f) SAR 80 (g) SAR  $\infty$  (Na-clay). Reference kaolinite, montmorillonite, and illite data from Goldberg and Forster (1990).

greater pH dependence than the 50/50 illite/montmorillonite mixture especially at high SAR. As a general conclusion for the entire ranges of SAR and pH, illite did not play a dominant role in determining flocculation-dispersion behavior of 50/50 clay mixtures. However, the illite/kaolinite system behaved more like reference illite than reference kaolinite for SAR 0 to SAR 60. The illite/montmorillonite system, reference illite, and reference montmorillonite exhibited very similar CCCs for SAR 0 to SAR 20. Illite/montmorillonite more closely resembled reference illite at SAR

40 and SAR 60. At agriculturally desirable exchangeable sodium percentage and SAR values of 0 to 15, the dispersibility of all 2:1 clays and 2:1 clay mixtures in this study was similar.

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